1-28-1952

A study of the exchange between p-nitrobenzyl iodide and iodide ion in alcoholic solutions.

E. Lee Purlee

Purlee — Exchange Between p-Nitrobenzyl Iodide and Iodide Ion

A STUDY OF THE EXCHANGE BETWEEN p-NITROBENZYL IODIDE AND IODIDE ION IN ALCOHOLIC SOLUTIONS

By

E. Lee Purlee

A Thesis

In partial fulfillment of the
Requirements for the Degree of
Master of Science in Chemistry

The University of New Mexico
1952

This thesis, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

E F Castetter
DEAN

1/28/52
DATE

A STUDY OF THE EXCHANGE BETWEEN p-NITROBENZYL IODIDE AND IODIDE ION IN ALCOHOLIC SOLUTIONS

Thesis committee

Milton Kahn and J. L. Riebsomer
CHAIRMAN

G H Daub

C. E. Buell

A STUDY OF THE EXCHANGE BETWEEN p-NITROBENZYL IODIDE AND IODIDE ION IN ALCOHOLIC SOLUTIONS

Acknowledgment

The writer desires to express his appreciation to Dr. Milton Kahn and Dr. Jesse Riebsomer for their assistance and helpful counsel during the pursuit of this study.

The work was performed under contract SC-5 with the University of California. The cooperation of Dr. Robert W. Spence, Mr. James Sattizahn, and Mr. Gordon Knobelock of the Los Alamos Scientific Laboratories in the performance of the irradiation of the tellurium is gratefully acknowledged.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

PART I

Introduction

The recent work of Stillson[1] concerning the kinetics of exchange between benzyl iodide and iodide ion in various solvents has given impetus to the investigation of similar exchanges with substituted benzyl iodides.

The realm of this study embraces observation of the exchange of iodine atoms between p-nitrobenzyl iodide and potassium iodide in absolute methanol, absolute ethanol and absolute n-propanol at temperatures of 30.9°, 20.3° and 0.0° centigrade. The primary aims were to observe the effects of the p-nitro group upon the exchange rates in the various solvents and to compare the results with those obtained for the benzyl iodide - iodide ion exchange.

The Nucleophilic Substitution Reaction

The simple isotopic exchange reaction belongs to an important class of chemical reactions referred to as "nucleophilic substitutions". The substitution reaction of the ion-molecule type may be represented symbolically by the expression:

$$(I\text{-}1) \qquad Y^- + RX \longrightarrow YR + X^-$$

Y^- represents an anionic species; R, an organic radical saturated at the reaction center; and X^- represents an anionic species capable of being replaced by Y^-.

Two operative mechanisms are generally recognized for nucleophilic substitution reactions.[2,3,4,5] These mechanisms are classified as "S_n1" or "S_n2" types. The symbol "Sn" refers to nucleophilic substitution character and the Arabic numeral denotes the molecularity of the reaction.

The S_n1 mechanism is a two-stage process in which a rate-determining ionization step is followed by a fast reaction between the carbonium ion and the substituting anion:

$$\text{R-X} \longrightarrow \underset{\text{transition state}}{\overset{\delta+}{\text{R}}\text{----}\overset{\delta-}{\text{X}}} \longrightarrow \text{R}^- - \text{X}^- \quad \text{(slow, rate determining)} \qquad \text{(I-2)}$$

$$\text{R}^- - \text{Y}^- \longrightarrow \text{RY} \qquad \text{(fast)}$$

The S_n1 reaction is considered to be unimolecular in spite of the fact that solvolytic action, involving an attack on the anionic species X by molecules of the solvent, is operating in the ionic dissociation. The S_n1 mechanism results in first-order kinetics. The rate equation for a reaction proceeding by this mechanism may

be represented by:

$$\text{(I-3)} \quad R = k_1(R\text{-}X)$$

R represents the reaction-rate, k_1 represents the first-order specific rate constant and (R-X) represents the concentration of the species R-X.

The S_n2 mechanism is a single stage process involving an initial attack by the anionic species Y^- on the neutral molecule R-X resulting in the formation of an addition or transition state complex which upon decomposition yields RY and X^-.

$$\text{(I-4)} \quad Y^- + RX \longrightarrow \underset{\text{transition state}}{\overset{\delta- \quad \delta+ \quad \delta-}{Y\text{----}R\text{----}X}} \xrightarrow[\text{rate determining step}]{} YR + X^-$$

Since both reactants are involved in the rate determining step, the mechanism is bimolecular and gives rise to second order kinetics. The rate equation for a reaction proceeding by the S_n2 mechanism may be expressed by:

$$\text{(I-5)} \quad R = k_2(R\text{-}X)\,(Y^-)$$

R is again the reaction-rate, k_2 is the second order specific rate constant and (R-X) and (Y^-) the concentrations of the respective species.

Numerous observations have not only confirmed both orders of kinetics, but have given rise to the principle of duality of mechanism.[2,4,5,6,7] In the study of the hydrolysis of alkyl bromides of the series methyl, ethyl, isopropyl and tertiary butyl;[7] second order kinetics were observed in the series methyl, ethyl, and isopropyl in which the rates decreased in the order of mention. Variation in the conditions of hydrolysis showed that the kinetics of the isopropyl bromide hydrolysis could be made first order, second order or a combination of both. The hydrolysis of the tertiary butyl bromide was observed to follow first order kinetics. This suggested a shift in mechanism from S_n2 to S_n1 in the region of the isopropyl group. The principle of duality of mechanism has been strengthened by experimental evidence which manifests the rational dependence of the S_n1 and S_n2 mechanisms upon structural effects in the reactants and upon the environmental characteristics of the reacting medium.[2] In the ion-molecule type of reaction the mechanism appears to be dependent upon:

(a) Polar effects within the R- group.

(b) Steric effects within the R- group.

(c) The nature of X and Y.

Numerous observations have not only confirmed both orders of kinetics, but have given rise to the principle of duality of mechanism.[3,4,5,6,7] In the study of the hydrolysis of alkyl bromides of the series methyl, ethyl, isopropyl and tertiary butyl;[7] second order kinetics were observed in the series methyl, ethyl, and isopropyl in which the rates decreased in the order of mention. Variation in the conditions of hydrolysis showed that the kinetics of the isopropyl bromide hydrolysis could be made first order, second order or a combination of both. The hydrolysis of the tertiary butyl bromide was observed to follow first order kinetics. This suggested a shift in mechanism from S_N2 to S_N1 in the region of the isopropyl group. The principle of duality of mechanism has been strengthened by experimental evidence which manifests the rational dependence of the S_N1 and S_N2 mechanisms upon structural effects in the reactants and upon the environmental characteristics of the reacting medium.[8] In the ion-molecule type of reaction the mechanism appears to be dependent upon:

(a) Polar effects within the R- group.

(b) Steric effects within the R- group.

(c) The nature of X and Y.

(d) The nature of the solvent.

Solvent Effects

One influence of the solvent is evaluated by observing the magnitude and distribution of charge in the activated complex or transition state.[11] An increase in the ionizing power of the solvent tends to increase the magnitude of charges involved and tends to decrease the distribution of charge in the transition state. In the S_n1 mechanism an increase in solvent ionizing power strongly accelerates the reaction rate since the rate-determining step involves an ionization. In the S_n2 mechanism an increase in solvent ionizing power exerts a mild deceleration in the reaction rate. Hughes and Ingold[11] predicted that changes in solvents might cause shifts in mechanism. Such changes have been observed. The S_n2 reaction of benzhydril halide-halide ions in acetone shifts to a modified S_n1 reaction mechanism in liquid SO_2[12].

It is evident that the effects of dielectric constant will operate oppositely in the two mechanisms. A decrease in dielectric constant will decelerate the S_n1 rate and will accelerate the S_n2 rate.

The Laidler-Eyring theory of dielectric constant influence[13] predicts that a plot of ln k versus 1/D, where k represents the specific rate constant and D represents dielectric constant, should result in a straight line, generally of positive slope, for reactions of the ion-neutral molecule type. This has been verified in various types of bimolecular reactions.[1,14,15,16,17,18] According to the Laidler-Eyring theory then, a decrease in dielectric constant results in an increase in S_n2 reaction rate.

Solvation effects in this type reaction may exert an influence upon the energy of activation.[19] If in a given solvent, I, none of the reactants nor the activated complex are solvated and if in a given solvent, II, the activated complex is solvated but the reactants are not; the potential energy of the activated complex is reduced in solvent II by a factor equivalent to its enthalpy of solvation. This results in a decrease in activation energy and an increase in reaction rate provided no other factors are operating which affect the activation energy.

On the other hand, if the reactants are solvated by solvent II and the activated complex is not, the potential energies of the reactants are reduced by their enthalpies

The Laidler-Eyring theory of dielectric constant influence[13] predicts that a plot of ln k versus 1/D, where k represents the specific rate constant and D represents dielectric constant, should result in a straight line, generally of positive slope, for reactions of the ion-neutral molecule type. This has been verified in various types of bimolecular reactions.[1,14,15,16,17,18] According to the Laidler-Eyring theory then, a decrease in dielectric constant results in an increase in S_N2 reaction rate.

Solvation effects in this type reaction may exert an influence upon the energy of activation.[19] If in a given solvent, I, none of the reactants nor the activated complex are solvated and if in a given solvent, II, the activated complex is solvated but the reactants are not; the potential energy of the activated complex is reduced in solvent II by a factor equivalent to its enthalpy of solvation. This results in a decrease in activation energy and an increase in reaction rate provided no other factors are operating which affect the activation energy.

On the other hand, if the reactants are solvated by solvent II and the activated complex is not, the potential energies of the reactants are reduced by their enthalpies

of solvation. An increase in activation energy and a decrease in reaction rate would follow. If the activated complex as well as the reactants is solvated, little can be said about the effects on the activation energy and reaction rate other than that they will probably be small. Solvation of the reaction products produces no effect on the activation energy or reaction rate.

It seems reasonable to assume that all species of the ion-molecule type reaction are solvated by different solvents to varying and indeterminable extents. The overall effects of solvation on activation energies and reaction velocities would amount to a combination of the several influences of the solvent upon the different species. The resolution of these specific effects and their singular significances presents an intriguing and complex problem.

In the p-nitrobenzyl iodide-iodide exchange, all the reactions have been observed to be bimolecular and the effects of dielectric constant have been found to conform to those predicted by the Laidler-Eyring theory.[13]

Thermodynamical Quantities

From the statistical treatment of reaction rates and

subsequent thermodynamical analysis,[20] the specific rate constant may be expressed in the form:

$$\text{(I-6)} \qquad k = e.\mathrm{k}T/h \, .e^{\Delta S^{*}/R} \, .e^{-\Delta E_{x}/RT}$$

for reactions in ideal solutions. In which:

k = the Boltzmann constant

T = absolute temperature

h = Planck's constant

ΔS^{*} = standard entropy of activation

ΔE_{x} = experimental activation energy

R = universal gas constant

In the expression (I-6), the quantity $e.\mathrm{k}T/h \, . \, e^{\Delta S^{*}/R}$ corresponds to the Arrhenius frequency factor, A, in the expression:

$$\text{(I-7)} \qquad k = A.e^{-\Delta E_{x}/RT}$$

The appearance of the "entropy factor", $e^{\Delta S^{*}/R}$, in equation (I-6) emphasizes the consideration of the entropy of activation as well as the energy of activation in a study of reaction rates.

PART II

The Isotopic Exchange Reaction

A chemical reaction in which the atoms of a given element interchange between at least two species of the element is referred to as an isotopic exchange reaction.[21] The p-nitrobenzyl iodide - iodide ion exchange is a reaction of this nature in which an interchange of iodine atoms between iodide ions and p-nitrobenzyl iodide proceeds. In experimentation the isotopic composition of the potassium iodide was modified by the incorporation of radioactive I^{131} therein. It was then possible to follow the course of the reaction by detecting the appearance of radioactivity in the p-nitrobenzyl iodide.

The Isotope Effect

Quantum theory has predicted differences in chemical behaviour due to changes in isotopic mass. Experimentation has revealed that these effects are appreciable only in the cases of the lighter elements and that the effects with the heavier elements are negligible. Bigeleisen[22] has calculated the <u>maximum</u> isotope effect between I^{127} and I^{131} to be about 2% in the determination of specific rate constants. Discrepancies of this magnitude should seldom, if ever, be

PART II

The Original Exchange Experiment

A chemical reaction in which atoms of a given element interchange between at least two species of the element is referred to as [illegible]. The p-nitrobenzyl iodide - iodide ion exchange is a reaction of this nature in which an interchange of iodine atoms between iodide ions and p-nitrobenzyl iodide occurs. For experimentation the isotopic composition of the iodine in iodide was modified by the incorporation of radioactive I^{131} therein. It was then possible to follow the progress of the reaction by detecting the amount of radioactive iodine in the p-nitrobenzyl iodide.

The Isotope Effect

Quantum theory has predicted differences in chemical behaviour due to changes in isotopic masses. Experimentation has revealed that these effects are appreciable in the cases of the lighter elements, and that the effects with the heavier elements are negligible. [illegible] the maximum isotope effect [illegible] I^{131} [illegible] in the determination of specific rate constants. Discrepancies of this magnitude would [illegible]

observed since this maximum effect postulates the free atom as the transition state. Urey[23] calculated the isotope effect between I^{127} and I^{129} to be about 0.5%. For all practical purposes it may be assumed that the characteristics of radioactive and non-radioactive atoms of iodine are identical in chemical reactions.

The Exponential Exchange Law for Simple Reactions

The general expression for a simple isotopic exchange reaction occurring in a homogeneous, stable system may be written:

$$\text{(II-1)} \quad AX + BX^{*} \longrightarrow AX^{*} + BX$$

in which X^{*} represents a radioactive isotope of X.

The advantages of a simple isotopic exchange reaction in a homogeneous, stable system are in its simplifying features over ordinary chemical reactions:

(a) The enthalpy change is zero since there are no pressure and volume changes and since the energies of the reactants and products are, for all practical purposes, identical. It follows that the free energy decrease depends only on the temperature and the entropy change of redistribution of the interchanging species.

(b) Since the reactants and products are identical,

observed after [illegible] for the Szilard-Chalmers [illegible]
as the translation states [illegible]. The largest
effect between 10^{-7} and 10^{-3} [illegible]. For all
practical purposes it [illegible] and [illegible] characteristics of [illegible] are identical to standard reactions.

The Exponential Exchange Law for Simple Reactions

The general exchange reaction [illegible] reaction occurring in a homogeneous, static system may be written:

$$(II-1) \qquad AX + BX^* \longrightarrow AX^* + BX$$

in which X^* represents a radioactive isotope of X.

The advantages of a simple isotopic exchange reaction in a homogeneous, static system for studying [illegible] lying features over ordinary chemical reactions:

(a) The enthalpy change is [illegible] there are no pressure and volume changes [illegible] reactants and products are, for all practical purposes, identical. It follows that the free energy change depends only on the [illegible] redistribution of the [illegible].

(b) Since the reactants and products are identical,

the bonds formed are the same as the bonds ruptured.

The exchange law was first derived by H. McKay[24] for the simple case. Duffield and Calvin,[25] Friedlander and Kennedy[26] and Prestwood and Meyers[27] have also given derivations.

The appearance of radioactivity in AX parallels the growth of a short-lived radioactive daughter from a long-lived parent. The fraction exchanged, F, or the fraction not exchanged, (1-F), may be expressed as exponential functions involving concentrations, the rate of exchange, R, and time. The logarithmic form of (1-F) may be written:

$$\text{(II-2)} \quad \ln(1-F) = -Rt\left[(A)+(B)\right]/(A)(B)$$

in which:

R = constant rate of exchange of X atoms between AX and BX (gram-atoms per liter per unit-time)

(A)= concentration of AX in gram-atoms of X per liter

(B)= concentration of BX in gram-atoms of X per liter

F = fraction of total exchange*

*See Part V for a more complete discussion of the fraction of exchange.

t = time

If $t_{1/2}$ is defined as the time required for one-half of the total exchange to occur, then R may be expressed in the following form:

$$\text{(II-3)} \qquad R = +0.69315(A)(B) \ / \ \left[(A)+(B)\right] t_{1/2}$$

The general procedure in the determination of R is to establish F as a function of time. This is accomplished by removing aliquots of the reacting mixture at various time intervals, separating the reactants and measuring the activity present in each. F and (1-F) are calculated for each aliquot and ln(1-F) or log(1-F) plotted as ordinate versus time. The result (see equation II-2) is a straight line from which $t_{1/2}$ can be determined. R values can be calculated by equation (II-3).

In order to determine the values of specific rate constants, the reaction mechanisms discussed in Part I are considered. If the reaction proceeds by an S_n1 mechanism:

$$\text{(II-4)} \qquad R = k_1(A)$$

in which k_1 represents the first-order specific rate constant. If the reaction proceeds by an S_n2 mechanism:

t = time

If $t_{1/2}$ is defined as the time [illegible] for one-half [illegible] total exchange to occur, then R may be expressed [illegible] following form:

(II-5) R = [illegible]

The general procedure [illegible] to establish F as a function of time. [illegible] by removing aliquots of [illegible] at various time intervals, separating the [illegible] activity present in each. F and [illegible] each aliquot and ln(1-F) [illegible] plotted [illegible] versus time. The result (see equation II-4) [illegible] line from which $t_{1/2}$ can be [illegible]. [illegible] calculated by equation (II-5).

In order to determine the values of [illegible] constants, the reaction [illegible] are considered. If the reaction [illegible] mechanism:

(II-6) R = [illegible]

in which k_1 represents the first-order [illegible] constant. If the reaction [illegible]

(II-5) $$R = k_2(A)(B)$$

in which k_2 represents the second-order specific rate constant. Should the reaction proceed by a combination of S_n1 and S_n2 mechanisms:

(II-6) $$R = k_2(A)(B) + k_1(A)$$

Examination of equations (II-4), (II-5) and (II-6) shows that a plot of R/(A) as ordinate versus (B) as abscissa for a given solvent at a given temperature would yield a straight line:

(1) parallel to the abscissa with an ordinate intercept of k_1 if the reaction mechanism were S_n1.

(2) passing through the origin with positive slope k_2 if the reaction mechanism were S_n2.

(3) of positive slope k_2 with an ordinate intercept of k_1 if the reaction mechanism were a combination of S_n1 and S_n2.

Any non-linear characteristics of R/(A) versus (B) would indicate reaction mechanisms other than S_n1 or S_n2.

The reaction mechanism, once established, permits the calculation of the specific rate constants, k. Series of reactions performed at different temperatures permits the calculation of the experimental activation energy,

E_x, from equation (I-7) put into logarithmic form:

$$\ln k = -\Delta E_x / RT + \ln A \qquad \text{(II-7)}$$

The constant lnA is readily calculable and from equation (I-6):

$$A = e.\bar{k}T/h \, .e^{\Delta S^*/R} \qquad \text{(II-8)}$$

therefore:

$$\ln A + 1 + \ln(\bar{k}T/h) + \Delta S^*/R \qquad \text{(II-9)}$$

The entropy of activation can be computed by equation (II-9). Other calculable quantities of interest are:

(a) The entropy factor, $e^{\Delta S^*/R}$, which can be calculated from equation (II-8).

(b) The activation energy factor, $e^{-\Delta E_x/RT}$, which can be obtained from equation (I-7).

PART III

The Preparation of Chemical Reagents

Radioactive Iodine

Eight-day I^{131} was utilized as a tracer in this exchange study. This isotope is indirectly produced by the irradiation of naturally occurring tellurium with thermal neutrons. Consideration of the stable isotopes of tellurium, their respective thermal neutron cross-sections and their (n,γ) reaction products reveals that radioactive isotopes I^{129} and I^{131} are produced.[28] Since the I^{129} is a very long-lived beta emitter, practically all the iodine activity arises from the I^{131}. The I^{131} descends from the stable Te^{130} isotope, which has an isotopic abundance of 34.46%, through the course of the following nuclear reactions:

$$
\begin{array}{llll}
 & Te^{130} & (n,\gamma) & Te^{\underline{131}} \\
 & Te^{130} & (n,\gamma) & Te^{131} \\
 & Te^{\underline{131}} & \xrightarrow[I.T.]{30 h.} & Te^{131} \\
(III\text{-}1) & Te^{131} & \xrightarrow[\beta^-]{25 m.} & I^{131} \\
 & I^{131} & \xrightarrow[\beta^-,\gamma]{8.0 d.} & Xe^{131} \text{ (stable)}
\end{array}
$$

Ten-gram samples of powdered tellurium contained in quartz vials packed in aluminum cylinders were irradiated

at the Los Alamos Scientific Laboratory with thermal neutrons to the extent of 500-800 kWh.

The radioactive iodine was extracted by the method of Kenney and Sprague.[29] The extraction process was carried out in an all-glass apparatus and consisted of the following stages:

Stage I - Conversion of the Te to the Te(VI) state and I_2 to the I(V) state.

(a) 40.00 grams of potassium dichromate was added to the reaction flask.

(b) 10.00 grams of irradiated tellurium was added.

(c) 200 ml. of c.p. 50% sulfuric acid was added.

(d) The reaction mixture was cautiously heated to about 80° C. and kept under reflux for 2-3 hours.

Stage II - Reduction of the excess Cr(VI) to Cr(III), I(V) to I_2 and about one-third of the Te(VI) to Te(V).

(a) The reaction mixture of stage I was cooled to room temperature and 23.30 grams of oxalic acid dihydrate was cautiously added.

(b) The mixture was slowly heated and kept under reflux for 2-3 hours in order to assure complete reduction.

Stage III - Distillation of the I^{131}.

(a) The I^{131} was distilled into 15 ml. of 0.1 M sodium carbonate which contained a trace of sodium sulfite. When the total volume of the distillate reached 30-35 ml., practically all of the available activity was collected.

At this point about 0.5 ml. of 0.1 M potassium iodide was added to the carrier-free radioactive iodine solution to give an iodide concentration of 3-4 x 10^{-5}M. This solution was stored in a 60 ml. glass-stoppered bottle. From this point on, this radioactive iodine solution will be referred to as "RAI" solution.

The Preparation of p-Nitrobenzyl Iodide

The p-nitrobenzyl iodide was prepared by a method similar to that described by H. Finkelstein.[30]

Equivalent quantities of Eastman Kodak p-nitrobenzyl bromide and sodium iodide were dissolved in separate, minimum quantities of warm acetone. The solutions

were then mixed and the nearly quantitatively-precipitated sodium bromide was removed by filtration. Yellow, needle-like crystals of p-nitrobenzyl iodide were separated from the mother-liquor after a crystallization period of eight hours at a temperature slightly below room temperature. A second fraction of crystals was obtained by dissolving the first fraction in boiling acetone and recrystallizing over a six hour period at 10°C. A third, fourth, fifth and sixth fraction were similarly obtained by recrystallization from absolute ethanol. After air-drying for 24-36 hours the melting points of these same fractions were checked. The melting points of the fourth, fifth and sixth fractions were identical, 126.5-127° C. This is somewhat higher than the melting point of 124° C. reported by Finkelstein.[31] The melting point of the first-fraction crystals agreed with this value, however.

The resultant product of the sixth fraction represented an over-all yield of about 35%. Qualitative tests for trace amounts of bromine[32] were negative. Analysis of the product by the Volhard method of iodide determination[33] rendered an iodide content of 48.18% versus a theoretical of 48.28%. Carbon-hydrogen

were then mixed and the nearly quantitative [illegible] sodium bromide was removed by filtration. [illegible] like crystals of p-nitrobenzyl iodide were [illegible] the mother-liquor after a crystallization period [illegible] hours at a temperature slightly below [illegible] second fraction of crystals was [illegible] first fraction in boiling acetone and [illegible] a six hour period at 10°C. A third, [illegible] fraction were similarly obtained from [illegible] absolute ethanol. After air-drying for [illegible] melting points of these many fractions were [illegible] melting points of the fourth, fifth and [illegible] were identical, 126.5-127° C. This [illegible] than the melting point of 124° C. [illegible] The melting point of the first-fraction [illegible] with this value, however.

The resultant product of [illegible] presented an over-all yield of about [illegible] tests for trace amounts of bromine [illegible] Analysis of the product by the Volhard [illegible] determination[25] rendered an iodide [illegible] versus a theoretical of 48.28%. [illegible]

determinations were found to be within experimental error of their theoretical values.

The p-nitrobenzyl iodide was stored in a glass-stoppered amber bottle. From this point on in general discussion and tables the p-nitrobenzyl iodide will be referred to as "PNBI".

Absolute Solvents

Absolute methanol, absolute ethanol and absolute n-propanol were prepared from "absolute" c.p. grade reagents by methods similar to those of Lund and Bjerrum.[34] This consisted of a refluxing of the alcohols with their respective magnesium alkoxides and subsequent distillation therefrom in an all-glass, moisture-free apparatus.

Absolute acetone was obtained by distilling c.p. acetone which had been dried over "drierite" for 48 hours. The distillation was carried out in an all-glass, moisture-free apparatus.

All absolute solvents were stored in glass-stoppered bottles with covers. No moisture was detected in any of the solvents immediately after preparation or after 6-8 weeks of storage. The Henle-calcium carbide test was

determinations were found to be within experimental error of their theoretical values.

The p-nitrobenzyl iodide was stored in a glass-stoppered amber bottle. From this point on in general discussion and tables the p-nitrobenzyl iodide will be referred to as "PNBI".

Absolute Solvents

Absolute methanol, absolute ethanol and absolute n-propanol were prepared from "absolute" c.p. grade reagents by methods similar to those of Lund and Bjerrum.[34] This consisted of a refluxing of the alcohols with their respective magnesium alkoxides and subsequent distillation therefrom in an all-glass, moisture-free apparatus.

Absolute acetone was obtained by distilling c.p. acetone which had been dried over "Drierite" for 48 hours. The distillation was carried out in an all-glass, moisture-free apparatus.

All absolute solvents were stored in glass-stoppered bottles with covers. No moisture was detected in any of the solvents immediately after preparation or after 6-8 weeks of storage. The Karl-Fischer reagent test was

used as a means of detecting water. This consisted of adding fresh calcium carbide to the solvents and observing whether any traces of acetylene were liberated.

Analytical Reagents

Standard solutions of silver nitrate and potassium thiocyanate were prepared according to the methods of Kolthoff and Sandell.[35] The potassium thiocyanate was standardized against the silver nitrate.

The indicator for the Volhard titration consisted of a saturated solution (40%) of ferric ammonium alum in distilled water slightly acidified with nitric acid.

All analytical reagents were stored in amber, glass-stoppered bottles with covers.

PART IV

Experimental

Preliminary Experiments

During the preparation of the PNBI it was observed that some decomposition occurred with solutions of the compound. It was found that the extent of the decomposition could be reduced by minimizing the oxygen content of the solvents. This was accomplished by bubbling nitrogen through the solvents for thirty-minute periods prior to the preparation of all solutions.

In order to minimize photochemical decomposition, the reaction vessels were kept in the dark. Control experiments performed with alcholic potassium iodide - PNBI solution mixtures showed no evidence of decomposition during a thirty-six hour period. Solutions exposed to normal lighting conditions of the laboratory decomposed slightly after 30 to 60 minutes. The benzene method of free iodine detection was used as a means of detecting decomposition.

It appeared that the oxygen-content reduction in the solvents and the light protective measures were necessary and sufficient to minimize the effects of decomposition.

PART IV

Experimental

Preliminary Experiments

During the preparation of the PMBI it was observed that some decomposition occurred with solutions of the compound. It was found that the extent of the decomposition could be reduced by minimizing the oxygen content of the solvents. This was accomplished by bubbling nitrogen through the solvents for thirty-minute periods prior to the preparation of all solutions.

In order to minimize photochemical decomposition, the reaction vessels were kept in the dark. Control experiments performed with alcoholic potassium iodide - PMBI solution mixtures showed no evidence of decomposition during a thirty-six hour period. Solutions exposed to normal lighting conditions of the laboratory decomposed slightly after 30 to 60 minutes. The benzene method of free iodine detection was used as a means of detecting decomposition.

It appeared that the oxygen-content reduction in the solvents and the light protective measures were necessary and sufficient to minimize the effects of decomposition.

General Procedure

The general procedure utilized in all of the experiments consisted of the following:

(a) The preparation of PNBI and radioactive potassium iodide solutions.

(b) Thermostating of the prepared solutions.

(c) Mixing of equivalent volumes of the solutions.

(d) Removal of aliquots from the reaction mixture.

(e) Separation of the reactants.

(f) Determination of the activity in each reactant.

(g) Analysis of the solutions.

Preparation of the Solutions

(1) PNBI

Samples of PNBI were weighed in 25 ml. glass-stoppered volumetric flasks (50 ml. and 100 ml. volumetric flasks were employed for the more dilute solutions) and the flasks filled to the dilution mark with the desired solvent at room temperature.

(2) Radioactive Potassium Iodide

Radioactive potassium iodide solutions were prepared by the methods used by Stillson.[36] This consisted of treating one to five ml. of RAI solution with 2 ml. of 0.17 M potassium dichromate, 4 ml. of 3 M sulfuric acid and 2 ml. of benzene in a reaction vessel described by Stillson and shaking the mixture for 15 - 30 minutes. The iodine liberated by the oxidation process was extracted by the benzene. After centrifugation the aqueous acid layer was separated by employing a capillary separation tube which consisted of a piece of 8 mm. glass tubing fashioned to a capillary on one end and fitted with a medicine-dropper bulb on the opposite end. The benzene phase was retained and washed three times with 2 ml. portions of distilled water.

The activity of the benzene phase was transferred to an aqueous solution of potassium iodide by taking advantage of the almost instantaneous iodide-iodine exchange.[37] One half to 2.5 ml. of 0.100 M potassium iodide was added to the benzene in the reaction vessel and shaken intermittently for about 10 minutes. The aqueous portion was then separated and evaporated to dryness under an infra-red

heat lamp. The dry, white residue was dissolved in 25.0 ml. of the desired solvent. The activity-recovery from the benzene phase varied with the iodine concentration of the benzene and ranged from 70 to 95%.

Thermostating of the Solutions

For the temperatures of 20.3°C. and 30.9°C. a constant temperature water bath with Aminco thermoregulators was employed. For the temperature of 0.0° C., the water bath was packed with cracked ice. At all times temperatures within 0.1° of those stated were maintained.

The prepared solutions were placed in the constant-temperature bath for 45 to 90 minutes prior to mixing. At the time desired, 10.0 ml. portions of the solutions were mixed in a glass-stoppered, 50 ml. volumetric flask which was suspended in the temperature bath. The reaction vessel was manually agitated for three minutes after mixing in order to assure uniform distribution of the solutes.

Aliquot Removal and Reactant Separation

Three-ml. aliquots were removed from the reaction

heat lamp. [illegible] [illegible] [illegible] [illegible] [illegible] of the [illegible] [illegible] [illegible] [illegible] benzene [illegible] [illegible] [illegible] [illegible] [illegible] benzene [illegible] [illegible] [illegible].

[illegible] [illegible] [illegible]

For the [illegible] [illegible] [illegible] [illegible] constant temperature [illegible] [illegible] [illegible] thermo-regulators [illegible]. [illegible] the [illegible] [illegible] [illegible], the water bath [illegible] [illegible] [illegible] [illegible] temperatures within [illegible] [illegible] [illegible] maintained.

The prepared solutions [illegible] [illegible] [illegible] water-temperature [illegible] [illegible] [illegible] [illegible]. At the time [illegible] [illegible] [illegible] [illegible] were placed in a glass-stoppered [illegible] [illegible] which was [illegible] to the [illegible] [illegible] [illegible] vessel [illegible] [illegible] [illegible] mixing [illegible] [illegible] [illegible] solutes.

Aliquot Removal and Analysis [illegible]

Three [illegible] aliquots were removed [illegible] [illegible]

mixture at appropriate time intervals. Each aliquot was delivered into a separation vessel which contained a mixture of 2 ml. of distilled water and 2 ml. of benzene. After shaking and centrifugation, the aqueous and benzene phases were separated by the capillary tube method, placed in counting tubes, properly diluted, mixed and counted. The separation vessel was constructed of 16 mm. pyrex tubing. One end was pulled to a point in order to facilitate efficient phase separation. The opposite end was fitted with a 12/18 standard-taper glass joint. The capacity was about 10 ml.

In order to determine whether any exchange had been induced during the separation, an aliquot was removed as soon as possible after mixing in the case of each solvent at each temperature and treated in the usual manner. In no instance was any evidence of induced exchange found.

Operating Blank and Separation Efficiency

In order to correct for the potassium iodide retained in the benzene phase, it was necessary to determine an operating blank in all experiments. This was accomplished by treating a 3-ml. aliquot of potassium

mixture of [illegible] were [illegible] was

delivered into a [illegible] [illegible] mixture of

mixture of [illegible] [illegible] [illegible]

After shaking, [illegible] [illegible]

phases were [illegible] [illegible] [illegible]

in counting tubes, [illegible] [illegible]

The [illegible] [illegible] [illegible]

tubing. [illegible] [illegible]

facilitate [illegible] [illegible]

was [illegible] [illegible]

capacity was about [illegible]

In order [illegible] [illegible]

induced during the [illegible] [illegible]

soon as possible [illegible] [illegible]

at each [illegible] [illegible]

no instance [illegible] [illegible]

Operating [illegible] [illegible]

In order [illegible] [illegible]

retained in the [illegible] [illegible]

determine an [illegible] [illegible]

was accomplished by [illegible] [illegible]

iodide solution in the same manner that reaction-mixture aliquots were treated and ascertaining the percent of potassium iodide activity retained by the benzene phase. The operating blanks were found to vary slightly with temperature but appeared to be independent of concentration. The blanks were found to be reproducible to within 0.1 to 0.5%.

Alcoholic solutions of PNBI were treated in a similar manner in order to find out whether any PNBI was retained by the aqueous layer. Since no precipitation was detectable when 0.1 M silver nitrate was added to the aqueous phase, it was assumed that no PNBI was retained by the aqueous phase.

Quantitative verifications of the separation techniques were obtained by carrying out separations with non-radioactive materials and analyzing the respective phases by the Volhard[38] method. Material balances were obtained which agreed to within 0.5% of the known iodide content.

Determination of Activity in the Reactants

The radioactivity was detected with a standard

type scintillation counter employing a #5819 phototube and a thallium activated sodium iodide crystal.* Ordinary 18 mm. x 150 mm. pyrex test tubes were calibrated by filling them to a standard height with a standard solution of iodine activity; placing them in a standard, reproducible position in the counter holder and counting their contents. Only those tubes which gave reproducible counting rates within less than 1.0% of the counting rate of one tube designated as a standard were selected as sample holders.

Reactant aliquots, once placed in the sample holders, were diluted to the standard height with the appropriate alcohol and then uniformly mixed by bubbling a stream of air through the solution.

With few exceptions, the samples were counted long enough so that the standard deviation of the counting rate was within 1.0%. Excepting samples of low counting rates, each sample was counted twice and the average value computed. The purpose of this counting procedure was to maintain a

*The work of Dr. A. J. Freedman of the University of New Mexico in setting up the counting equipment is gratefully acknowledged.

type solu[illegible] [illegible] [illegible]

and a the [illegible] [illegible] [illegible]

15 mm. x 150 [illegible] [illegible]

filling [illegible] [illegible] [illegible]

of iodine solution [illegible] [illegible]

able position in the chamber [illegible]

contents [illegible] [illegible] [illegible]

tubes within [illegible] [illegible]

tube designated [illegible] [illegible]

holders.

Reactant extracting [illegible] [illegible]

were diluted [illegible] [illegible]

alcohol and [illegible] [illegible]

air through the [illegible].

[illegible] [illegible] [illegible]

enough so [illegible] [illegible]

was [illegible] [illegible]

each sample [illegible] [illegible]

The purpose of [illegible] [illegible]

[illegible] [illegible]
New Mexico [illegible] [illegible]
fully acknowledged.

check on the performance of the counting equipment.

Analysis of the Solutions

The Volhard method of analysis[39] was employed to determine the concentrations of the iodide solutions. Preliminary experimentation with potassium iodide and PNBI solutions was performed in order to establish the validity of the method in the various solvents. Numerous experiments were carried out in order to determine the optimum concentrations of standard solutions and the nature of volumetric ware to be employed relative to the magnitude of the iodide determinations to be encountered. Particular attention was given to the sensitivity of the indicator.

For all analyses standard solutions of 0.0250 M silver nitrate and 0.0050 M potassium thiocyanate were employed. Numerous experiments involving iodide determinations of tared potassium iodide and PNBI samples in the various solvents rendered determinations within 0.3% of the theoretical iodide contents.

In determining the concentration of a given solution in the experiments, two 5.00-ml. aliquots were

check on the [illegible].

Analysis of the [illegible]

The [illegible] method of analysis [illegible] to determine the [illegible]. Preliminary experimentation [illegible] pure [illegible] solutions was [illegible] the validity of the method [illegible] our experiments were [illegible] the optimum [illegible] nature of [illegible] magnitude of the [illegible]. Particular attention was [illegible] indicator.

For all [illegible] silver nitrate and [illegible] employed. [illegible] minations of [illegible] the various [illegible] of the [illegible].

[illegible] solution [illegible]

analyzed and the average result taken. For the first twelve runs the concentrations of both the potassium iodide and PNBI solutions were determined volumetrically. It was decided that volumetric analysis of the PNBI was unnecessary since the solutions were prepared from tared samples in volumetric ware and since the iodide determinations by the Volhard method had given results within 0.0 - 0.3% of the theoretical iodide content in all cases.

Errors

The main sources of errors are considered to be the uncertainty in the statistical fluctuation of counting, ($\pm$1.0%); the uncertainty in the concentrations of the solutions, ($\pm$1.0%) and the uncertainty in the operating blank, ($\pm$1%). It is thought that the error in the specific rate constants is not greater than 3%.

anal_ized and the [illegible] [illegible]. [illegible]
twelve [illegible] [illegible]
iodide and [illegible] [illegible]
It was decided [illegible]
unnecessary [illegible]
samples in [illegible]
minations [illegible]
0.0 - 0.[illegible] [illegible]

[illegible]

The [illegible] to [illegible]
the uncertainty [illegible]
(±1.0%); the [illegible]
solutions, [illegible]
blank, (±[illegible]). [illegible]
le rate [illegible]

PART V

Results and Calculations

The Experimental data for the exchange runs are recorded in tables I through XXVIII. The concentrations of PNBI ranged from 0.000500 M to 0.003042 M and the concentrations of KI ranged from 0.000470 M to 0.003078 M. For each temperature and concentration, log (1-F) was plotted versus time and the respective half-times determined. In all cases straight lines directed through the origin were obtained as predicted by equation (II-2). These graphs appear in figures 1 through 9.

The fraction of exchange, F, was calculated as the ratio of the net activity present in the PNBI at time t to the activity that would be present at infinite time:[40]

$$F = A_t/A_{oo} \qquad \text{(V-I)}$$

in which A_t is the net activity in the PNBI at time t and A_{oo} is the activity that would be present in the PNBI at infinite time. Since the relative fraction of PNBI molecules present determine the activity attainable at infinite time, A_{oo} was calculated for each aliquot by the following equation:

$$A_{oo} = \frac{(\text{PNBI})}{(\text{PNBI})+(\text{KI})} \times \text{(total activity in the aliquot)} \qquad \text{(V-II)}$$

in which the quantities (PNBI) and (KI) refer to the molar concentrations of the respective substances.

Rates of Exchange, R

Three runs were made with each solvent at each temperature. The exchange rates were calculated from equation (II-3) put into the form:

$$\text{(V-3)} \qquad R = 0.69315(\text{PNBI})(\text{KI}) / \left[(\text{PNBI}) + (\text{KI})\right] t_{1/2}$$

The units of R are "moles per liter per minute".

Order of the Reaction

The orders of the reactions were determined by plotting the quantity R/(PNBI) as ordinate versus the quantity (KI) as abscissa for each solvent at each temperature. These graphs appear in figures 3-a, 6-a and 9-a. In all cases straight lines directed into the origin were obtained indicating, as discussed in Part II, that the reaction was bimolecular under all conditions studied.

Specific Rate Constants

With the rates of exchange calculated and the

order of the reaction established, the specific rate constants, k, could be calculated. From equation II-5:

$$(V\text{-}4) \qquad R = k(PNBI)(KI)$$

$$(V\text{-}5) \qquad k = R/(PNBI)(KI)$$

Substitution into equation (V-5) from equation (V-3) gives:

$$(V\text{-}6) \qquad k = 0.69315/\left[(PNBI)+(KI)\right] t_{1/2}$$

The units of k are "liters per mole per minute". The values of the specific rate constants obtained from equation (V-6) were essentially constant for given solvents at given temperatures.

Corrections Applicable to R-values and k-values

It must be emphasized that correction factors need be applied to the calculated values of R and k in order to take into account the effects due to the thermal expansion and contraction of the solutions. All concentrations were determined at approximately 20°C. The concentration changes due to the thermal properties of the solvents become significant at the temperatures 30.9°C. and 0.0°C. These variations are reflected in the R and k values to the extent of about 1.0% to 2.5%. Correction factors were

order of the [illegible]

constants, K, should be [illegible] (1-6):

(V-5) [illegible]

(V-6) [illegible]

Substitution into equation (V-4) [illegible]

(V-7) [illegible]

The units of K are [illegible]

of the specific [illegible] (V-6)

were essentially [illegible] temperatures.

Correlations [illegible]

It must [illegible]

be applied to the [illegible] to

take into account [illegible]

and contraction of the [illegible]

determined [illegible]

due to the thermal [illegible]

different [illegible]

variations [illegible]

extent of [illegible]

obtained from a consideration of the thermal cubical-expansion coefficients of the respective solvents and the concentration dependencies of R and k. The correction factors were applied under the assumption that the thermal characteristics of the solutions were the same as those of the respective solvents. No corrections were applied to the experiments carried out at 20.3°C.

The following expressions for the cubical coefficients of expansion for the solvents were used:[41]

Table (V-7)

$$V_t = V_o(1+1.04139\times10^{-3}t + 0.7836\times10^{-6}t^2 + 1.7618\times10^{-8}t^3)$$
(ethanol)

$$V_t = V_o(1+1.18557\times10^{-3}t + 1.56493\times10^{-6}t^2 + 0.91113\times10^{-8}t^3)$$
(methanol)

$$V_t = V_o(1+0.7743\times10^{-3}t + 4.9689\times10^{-6}t^2 - 1.4069\times10^{-8}t^3)$$
(n-propanol)

In table (V-7):

V_t = volume of the solvent at t° C.

V_o = volume of the solvent at 0.0° C.

t = temperature in degrees centigrade.

The values of the rates of exchange and specific rate constants determined are tabulated in tables XXIX, XXX, and XXXI. All values of R and k have been corrected for thermal expansion and contraction of the solvents

obtained from a crystallographic [illegible] and the volumetric [illegible] expansion coefficients [illegible]

the concentration dependence [illegible]

factors were applied [illegible]

characteristic [illegible]

the respective [illegible]

the experimental [illegible]

The following expressions for the [illegible] of expansion [illegible] used: 1

$V_t = V_0(1+1.[illegible]$ [illegible]

$V_t = V_0(1+[illegible]$ [illegible]

$V_t = V_0(1+[illegible]$ [illegible]

In table (V-7):

V_t = volume [illegible]

V_0 = volume of the [illegible]

t = temperature [illegible]

The values [illegible]

rate [illegible]

XX, and XXXI [illegible]

for thermal expansion [illegible]

when necessary.

Dielectric Constant Effects

The dielectric constants of the solvents at the temperatures maintained in the experiments are tabulated in table (V-9). The values at 0.0° were obtained from the International Critical Tables.[42] The values at 20.3°C. and 30.9°C. were obtained by interpolations of the measurements performed by G. Ackerlöf.[43] Ackerlöf showed that the dielectric constants of these solvents would be accurately described by the general expression:

$$\text{(V-9)} \qquad D = ae^{-bT}$$

in which D represents the dielectric constant and a and b are constants peculiar to each solvent. He derived empirical equations suitable for interpolation purposes. His equations for the various solvents, appearing in table (V-8) were employed.

Table (V-8)

$$\log D = 1.5099 - 0.00234(t-20) \qquad \text{(methanol)}$$

$$\log D = 1.3979 - 0.00264(t-20) \qquad \text{(ethanol)}$$

$$\log D = 1.3183 - 0.00293(t-20) \qquad \text{(n-propanol)}$$

In the expressions of Table (V-8), t represents the temperature in ^{o}C.

Table (V-9)

Dielectric Constants at Different Temperatures

SOLVENT	0.0^{o}	20.3^{o}	30.9^{o}
Methanol	37.5	32.30	30.51
Ethanol	28.9	24.55	23.39
n-Propanol	24.5	20.00	19.34

The logarithms of the specific rate constants were plotted versus the reciprocals of dielectric constant, 1/D in figure 13, page 83. Straight lines of positive slope were obtained in all cases as predicted by the Laidler-Eyring theory of dielectric constant effects for the ion-molecule reaction.[44]

Calculation of the Energies of Activation

In figures 10, 11 and 12 plots of the logarithms of the specific rate constants versus the reciprocals of absolute temperature yield virtually straight lines in agreement with equation (I-7) when put into logarithmic form:

$$\text{(V-10)} \qquad \log k = -\Delta E_x/2.303RT + \log A$$

Equations of the lines were obtained by the method of least squares expressed in determinant form:[45]

$$\text{(V-11)} \quad \begin{vmatrix} 1/T & \log k & 1 \\ \sum_{i=1}^{3}(1/T_i) & \sum_{i=1}^{3}\log k_i & 3 \\ \sum_{i=1}^{3}(1/T_i)^2 & \sum_{i=1}^{3}(1/T_i)\log k_i & \sum_{i=1}^{3}(1/T_i) \end{vmatrix} = 0$$

The respective determinants were solved for the energies of activation. The results are tabulated in table XXXII.

Calculation of the Arrhenius Frequency Factors

The logarithms of the Arrhenius frequency factors were obtained by solution of the determinants (V-11). The Arrhenius frequency factors are tabulated in table XXXII.

Calculation of the Entropies of Activation

From equations (I-6) and (I-7), the Arrhenius frequency factor, may be expressed as:

$$\text{(V-12)} \qquad A = e.\mathbf{k}T/h.e^{\Delta S^{*}/R}$$

and the entropy of activation may be expressed by:

$$\text{(V-13)} \qquad \Delta S^{*} = R\left[2.303 \log \frac{A}{RT/h} - 1\right]$$

Entropies of activation were calculated by equation (V-12). The values obtained are tabulated in table XXXIII. As expected, the entropies of activation change little with temperature.

Entropy Factors and Activation Energy Factors

The entropy factors, $e^{\Delta S^{*}/R}$, and the activation energy factors, $e^{-\Delta E_x/RT}$, were evaluated and are tabulated in table XXXIV.

Table I

Experimental Data for Run #1

(PNBI) = 0.00106 M (KI) = 0.001050 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	18	728	33	0.0856
2	36	681	62	0.165
3	63	608	93	0.262
4	96	570	135	0.378
5	157	502	191	0.544
6	244	453	250	0.702

*Corrected for operating blank of 0.7%

$t_{1/2} = 140$ minutes

Solvent - Methanol

Table II

Experimental Data for Run #2

(PNBI) = 0.00306 M (KI) = 0.00288 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	15	1080	122	0.191
2	36	954	263	0.417
3	51	911	339	0.524
4	90	746	443	0.720
5	135	678	534	0.851

*Corrected for operating blank of 0.5%

$t_{1/2}$ = 49 minutes

Solvent - Methanol

Table III

Experimental Data for Run #3

(PNBI) = 0.00050 M (KI) = 0.00050 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	20	614	14	0.0443
2	73	557	49	0.161
3	122	560	83	0.257
4	270	476	149	0.474
5	480	401	206	0.675

*Corrected for operating blank of 0.5%

$t_{1/2}$ = 290 minutes

Solvent - Methanol

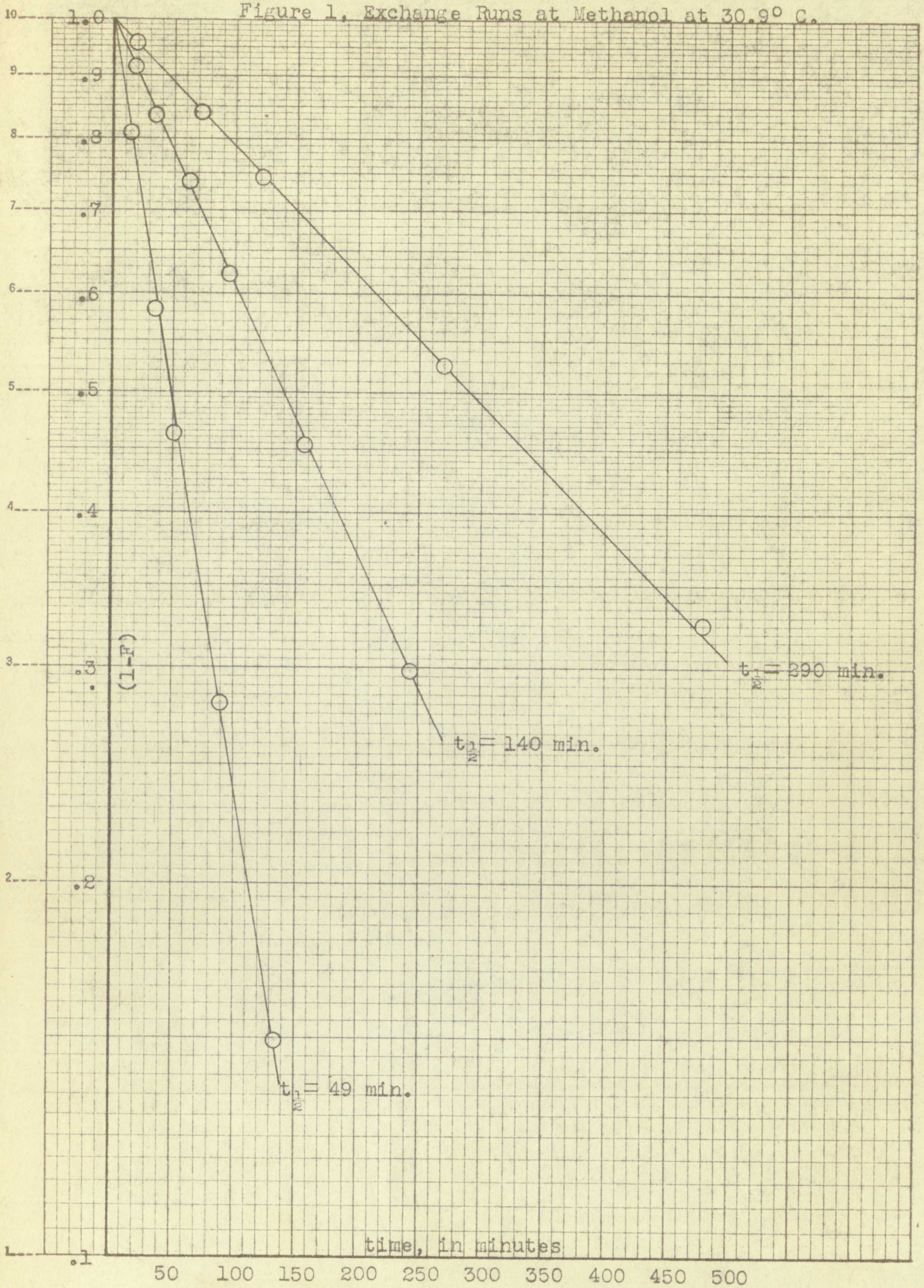


Figure 1. Exchange Runs at Methanol at 30.9° C.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
(1-F)
$t_{\frac{1}{2}}$ = 290 min.
$t_{\frac{1}{2}}$ = 140 min.
$t_{\frac{1}{2}}$ = 49 min.
time, in minutes
50 100 150 200 250 300 350 400 450 500

Table IV

Experimental Data for Run #4

(PNBI) = 0.000524 M (KI) = 0.000470 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	31	4152	554	0.223
2	70	3687	1064	0.424
3	120	3124	1474	0.607
4	255	2542	2114	0.859

*Corrected for operating blank of 0.3%

$t_{1/2} = 89$ minutes

Solvent - Ethanol

Table V

Experimental Data for Run #5

(PNBI) = 0.00100 M (KI) = 0.00105 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI counts/min.	Fraction exchanged F
1	22	6108	1006	0.284
2	53	5144	1952	0.553
3	93	4435	2692	0.759
4	130	4037	3070	0.868
5	160	3880	3239	0.915

*Corrected for operating blank of 0.3%

$t_{1/2} = 45$ minutes

Solvent - Ethanol

Table VI

Experimental Data for Run #6

(PNBI) = 0.002913 M (KI) = 0.003078 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	6	3768	493	0.237
2	11	3562	845	0.393
3	25	2937	1462	0.682
4	42	2590	1850	0.855

*Corrected for operating blank of 0.3%

$t_{1/2}$ = 15 minutes

Solvent - Ethanol

Figure 2, Exchange Runs in Ethanol at 30.9° C.

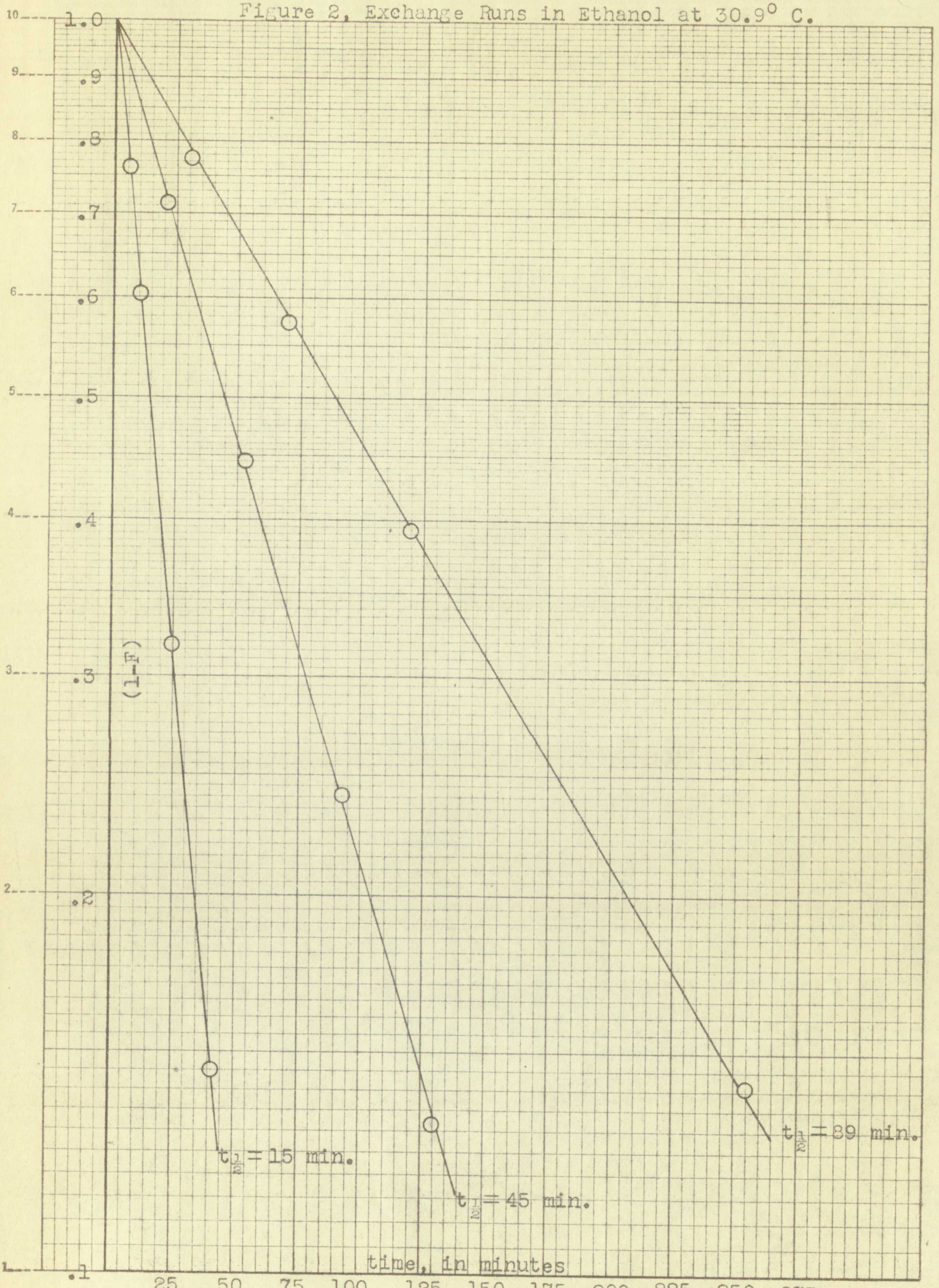


Table VII

Experimental Data for Run #7

(PNBI) = 0.000500 M (KI) = 0.000550 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	35	7706	1950	0.403
2	51	6824	2718	0.572
3	80	6306	3320	0.695
4	114	5983	4120	0.825

*Corrected for operating blank of 6.5%

$t_{1/2} = 46$ minutes

Solvent - n-Propanol

Table VIII

Experimental Data for Run #8

(PNBI) = 0.001088 M (KI) = 0.001063 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	7	8822	1006	0.199
2	16	8037	2097	0.387
3	37	6507	3686	0.684
4	58	5473	4230	0.829

*Corrected for operating blank of 7.1%

$t_{1/2} = 22.5$ minutes

Solvent - n-Propanol

Table IX

Experimental Data for Run #9

(PNBI) = 0.000675 M (KI) = 0.000570 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	12	6019	783	0.200
2	34	4948	1741	0.457
3	50	4462	2265	0.594
4	69	4117	2875	0.729

*Corrected for operating blank of 6.9%

$t_{1/2} = 38$ minutes

Solvent - n-Propanol

Figure 3, Exchange Runs in n-Propanol at 30.9° C.

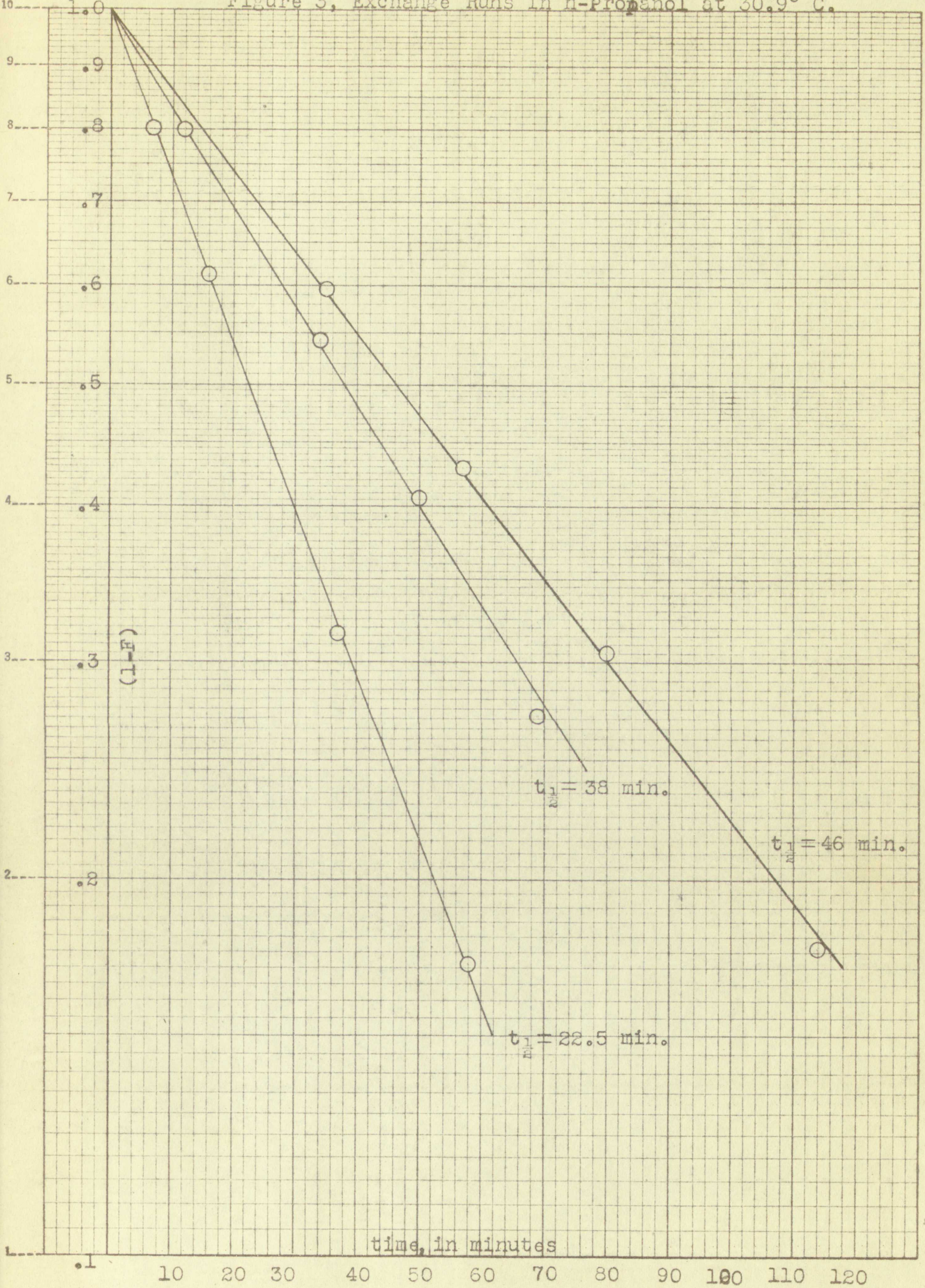


Figure 3-a. R/(PNBI) vs. (KI) for Exchange Reactions at 30.9° C.

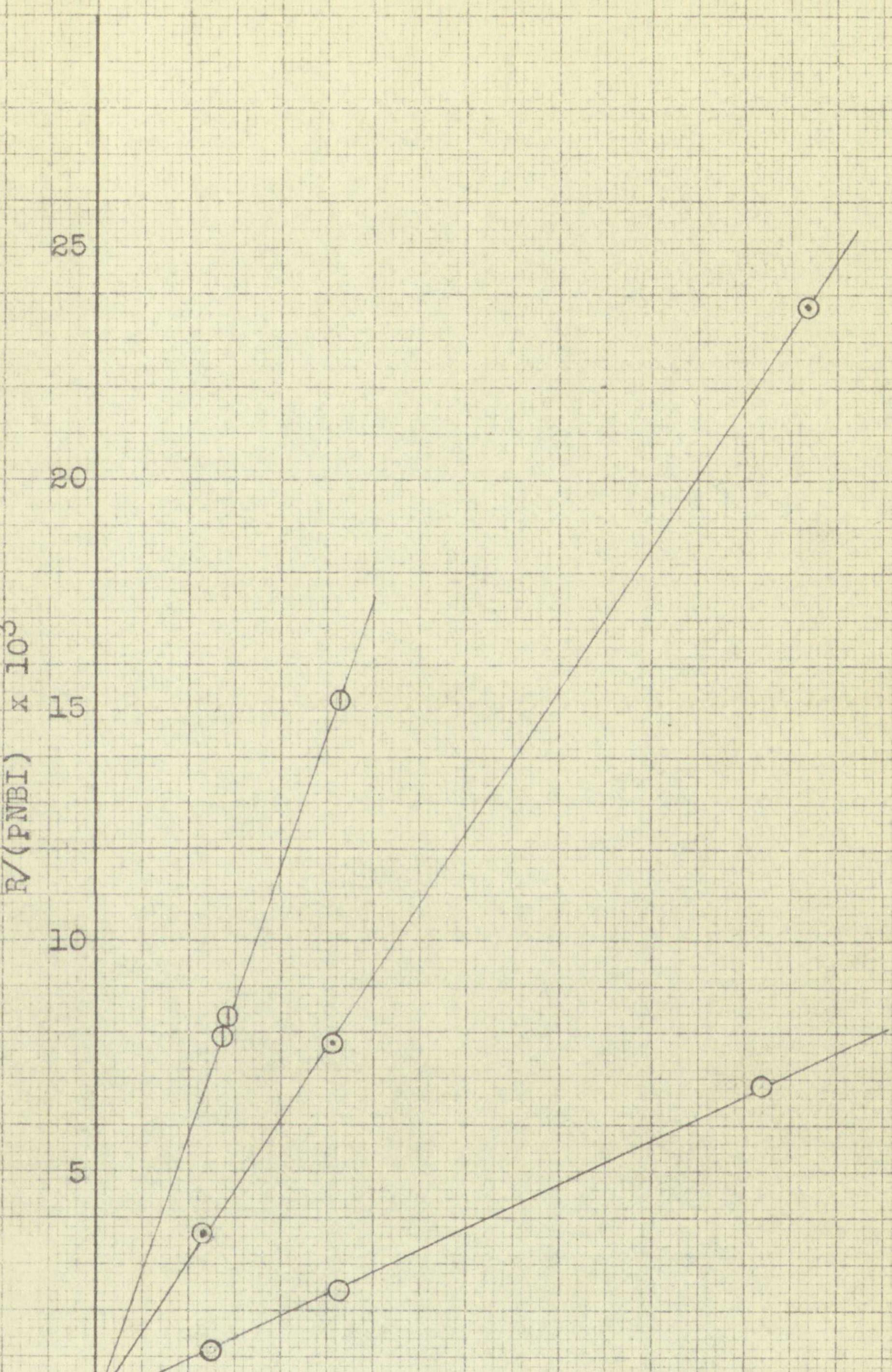


Table X

Experimental Data for Run #11

(PNBI) = 0.001604 M (KI) = 0.001650 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	300	3589	243	0.127
2	661	3065	527	0.295
3	1700	2481	928	0.548
4	2898	2255	1225	0.709

*Corrected for operating blank of 1.1%

$t_{1/2} = 1540$ minutes

Solvent - Methanol

Table XI

Experimental Data for Run #12

(PNBI) = 0.001992 M (KI) = 0.001975 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	244	3496	222	0.118
2	684	3136	513	0.285
3	1501	2594	926	0.523
4	2119	2284	1121	0.651
5	2659	1952	1151	0.734

*Corrected for operating blank of 1.1%

$t_{1/2} = 1365$ minutes

Solvent - Methanol

Table XII

Experimental Data for Run #13

(PNBI) = 0.002585 M (KI) = 0.002550 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	136	3218	163	0.0956
2	254	2995	260	0.157
3	669	2494	559	0.360
4	1296	2144	920	0.592

*Corrected for operating blank of 1.1%

$t_{1/2}$ = 1010 minutes

Solvent - Methanol

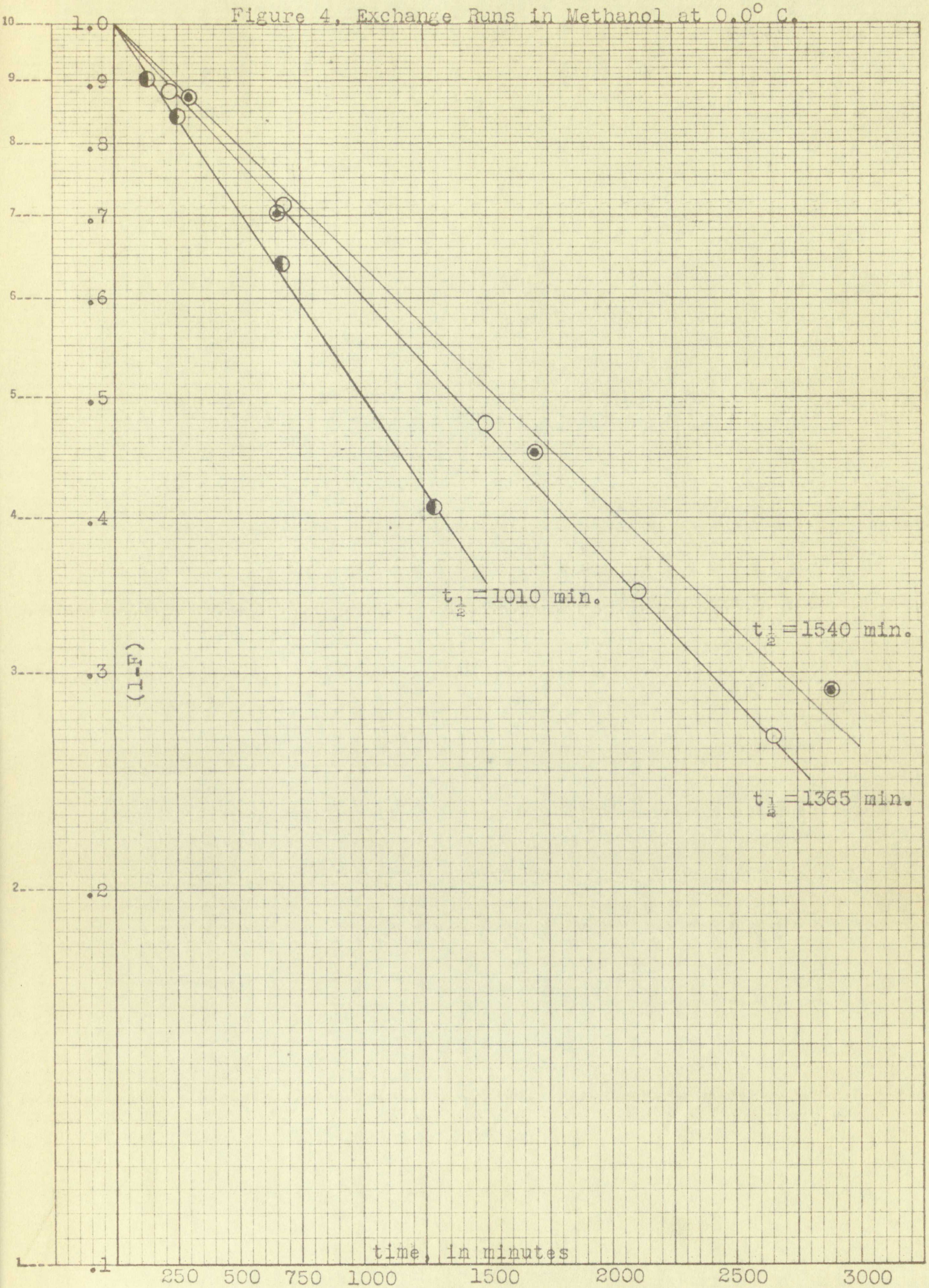


Figure 4, Exchange Runs in Methanol at 0.0° C.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
(1-F)
t½ =1010 min.
t½ =1540 min.
t½ =1365 min.
time, in minutes
250
500
750
1000
1500
2000
2500
3000

Table XIII

Experimental Data for Run #14

(PNBI) = 0.001242 M　　　　(KI) = 0.001255 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	172	2575	213	0.152
2	401	2329	432	0.312
3	741	1952	646	0.496
4	1589	1596	1005	0.772

*Corrected for operating blank of 1.1%

$t_{1/2} = 740$ minutes

Solvent - Ethanol

Table XIV

Experimental data for Run #15

(PNBI) = 0.002099 M　　　　(KI) = 0.001545 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	163	5783	774	0.203
2	240	5265	1037	0.277
3	386	4871	1493	0.404
4	940	3677	2567	0.709

*Corrected for operating blank of 0.6%

$t_{1/2} = 517$ minutes

Solvent - Ethanol

Table XV

Experimental Data for Run #16

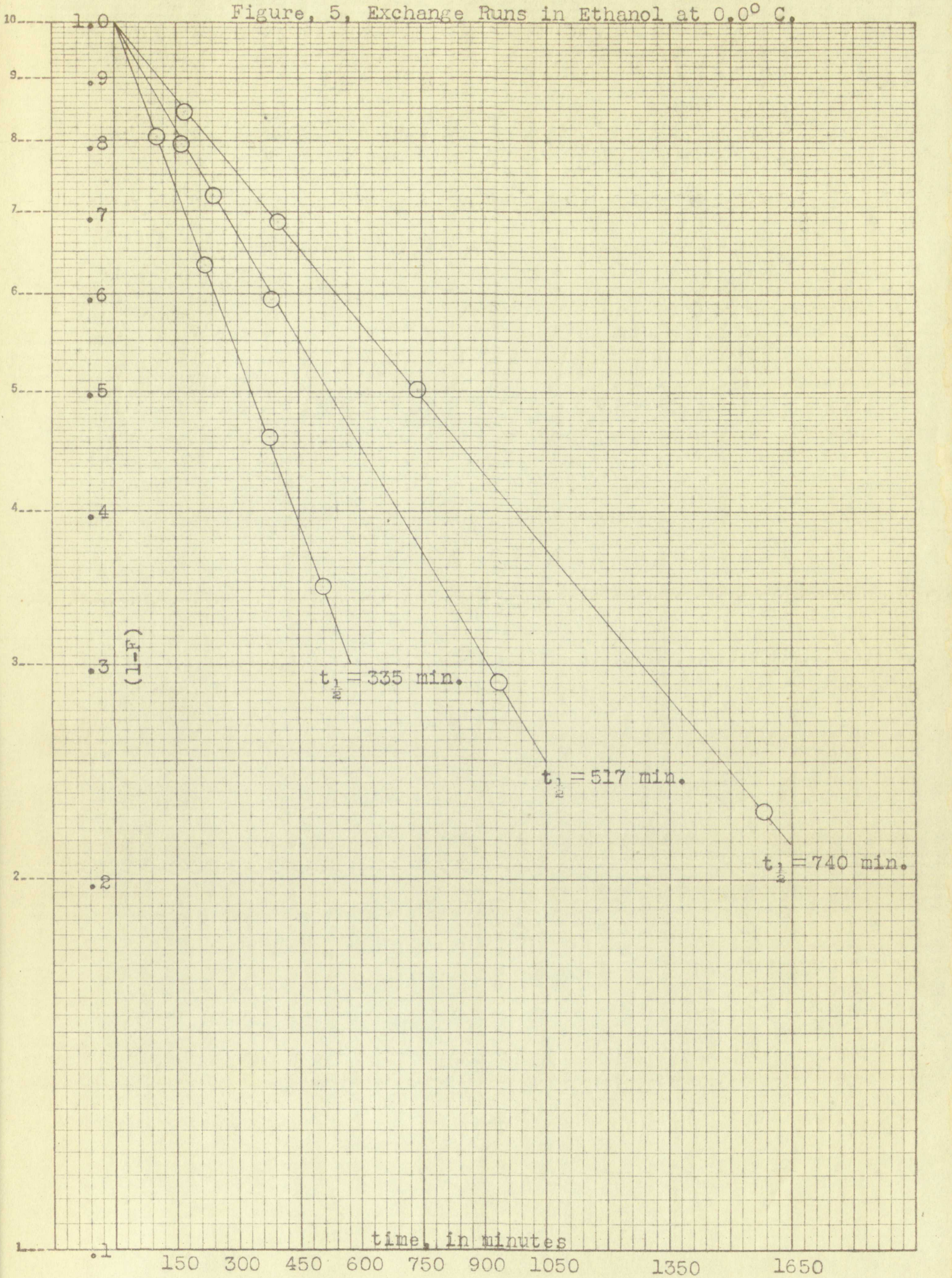
(PNBI) = 0.003042 M (KI) = 0.002513 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	102	5938	706	0.193
2	222	5258	1346	0.369
3	381	4525	1962	0.541
4	510	4201	2355	0.652

*Corrected for operating blank of 0.8%

$t_{1/2} = 335$ minutes

Solvent - Ethanol



Figure, 5, Exchange Runs in Ethanol at 0.0° C.
(1-F)
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
time, in minutes
150
300
450
600
750
900
1050
1350
1650
t½ = 335 min.
t½ = 517 min.
t½ = 740 min.

Table XVI

Experimental Data for Run #17

(PNBI) = 0.000517 M (KI) = 0.000515 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	110	4021	168	0.0753
2	500	3535	619	0.281
3	980	2972	1018	0.485
4	1530	2628	1288	0.641

*Corrected for operating blank of 6.7%

$t_{1/2} = 1030$ minutes

Solvent - n-Propanol

Table XVII

Experimental Data for Run #18

(PNBI) = 0.000958 M (KI) = 0.001005 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	190	4143	555	0.229
2	640	3309	1319	0.558
3	790	3140	1469	0.626
4	1046	2913	1693	0.724

*Corrected for operating blank of 6.4%

$t_{1/2}$ = 548 minutes

Solvent - n-Propanol

Table XVIII

Experimental Data for Run #19

(PNBI) = 0.002137 M (KI) = 0.002075 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	47	3689	241	0.113
2	181	3061	800	0.389
3	317	2738	1211	0.579
4	382	2570	1329	0.645

*Corrected for operating blank of 6.5%

$t_{1/2} = 254$ minutes

Solvent - n-Propanol

Figure 6, Exchange Runs in n-Propanol at 0.0° C.

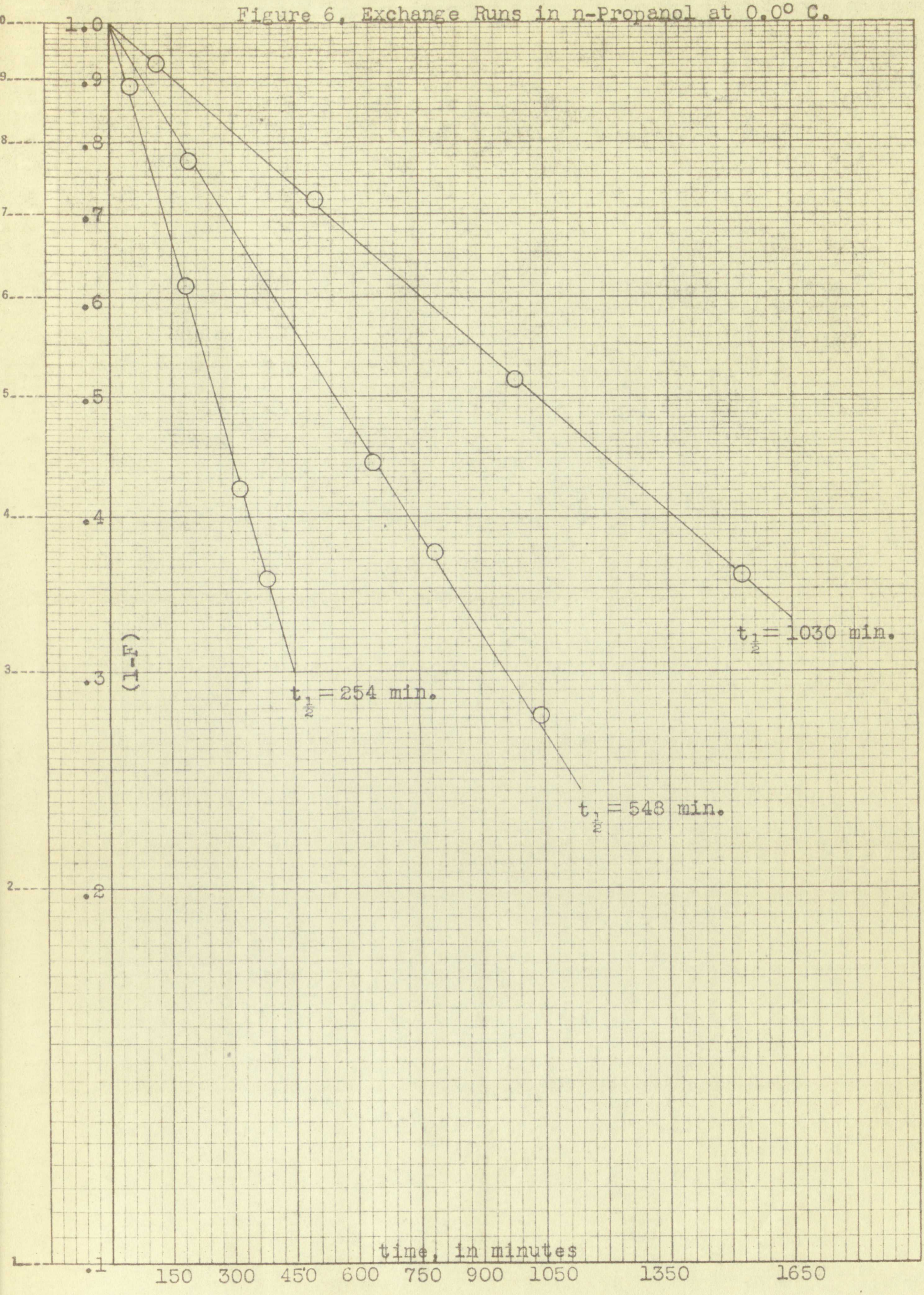


Figure 6-a, R/(PNBI) vs. (KI) for Exchange Reactions at 0.0° C.

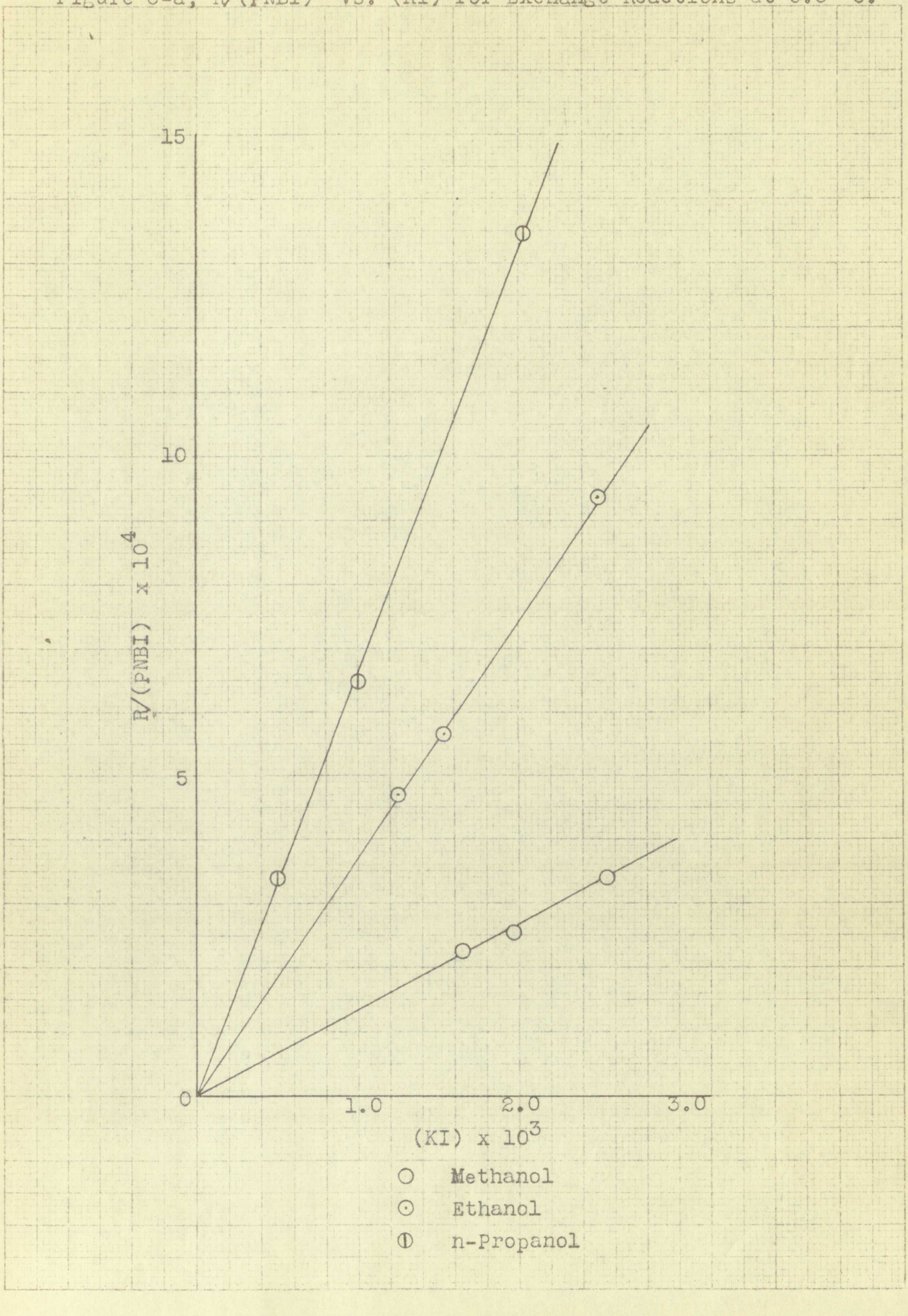


Table XIX

Experimental Data for Run #20

(PNBI) = 0.000996 M (KI) = 0.00107 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	60	6196	335	0.105
2	160	5530	800	0.260
3	285	5289	1312	0.409
4	495	4518	1767	0.593

*Corrected for operating blank of 1.0%

$t_{1/2}$ = 375 minutes

Solvent - Methanol

Table XX

Experimental Data for Run #21

(PNBI) = 0.002033 M (KI) = 0.001970 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	57	2428	265	0.192
2	149	2131	549	0.400
3	269	1809	841	0.621
4	429	1713	1161	0.791

*Corrected for operating blank of 1.0%

$t_{1/2}$ = 190 minutes

Solvent - Methanol

Table XXI

Experimental Data for Run #22

(PNBI) = 0.003110 M (KI) = 0.002980 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	30	4138	359	0.155
2	95	3551	936	0.410
3	135	3248	1192	0.532
4	190	2882	1480	0.646

*Corrected for operating blank of 1.0%

$t_{1/2}$ = 129 minutes

Solvent - Methanol

Figure 7, Exchange Runs in Methanol at 20.3° C.

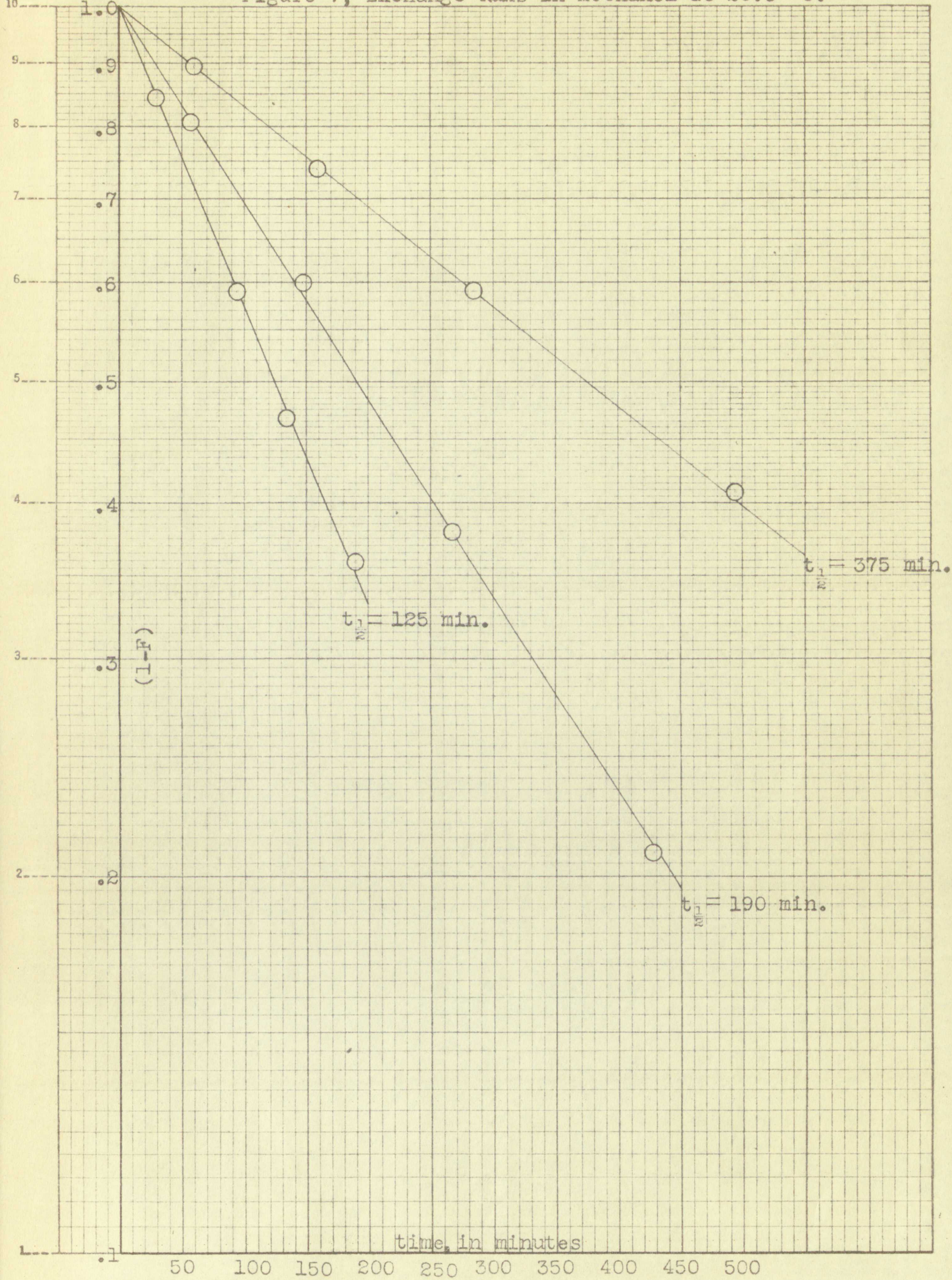


Table XXII

Experimental Data for Run #23

(PNBI)= 0.001011 M (KI)= 0.000965 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	35	3778	398	0.184
2	96	3316	940	0.428
3	148	2994	1303	0.587
4	210	2759	1588	0.708

*Corrected for operating blank of 0.6%

$t_{1/2}$ = 116 minutes

Solvent - Ethanol

Table XXIII

Experimental Data for Run #24

(PNBI) = 0.001977 M (KI) = 0.001965 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	15	9298	922	0.179
2	47	7986	2281	0.442
3	74	7212	3104	0.597
4	119	6359	3927	0.758

*Corrected for operating blank of 0.7%

$t_{1/2}$ = 57 minutes

Solvent - Ethanol

Table XXIV

Experimental Data for Run #25

(PNBI) = 0.003030 M (KI) = 0.002963 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	6	10890	673	0.114
2	26	9527	2275	0.378
3	60	7990	4078	0.664
4	80	7203	4569	0.763

*Corrected for operating blank of 1.0%

$t_{1/2}$ = 38 minutes

Solvent - Ethanol

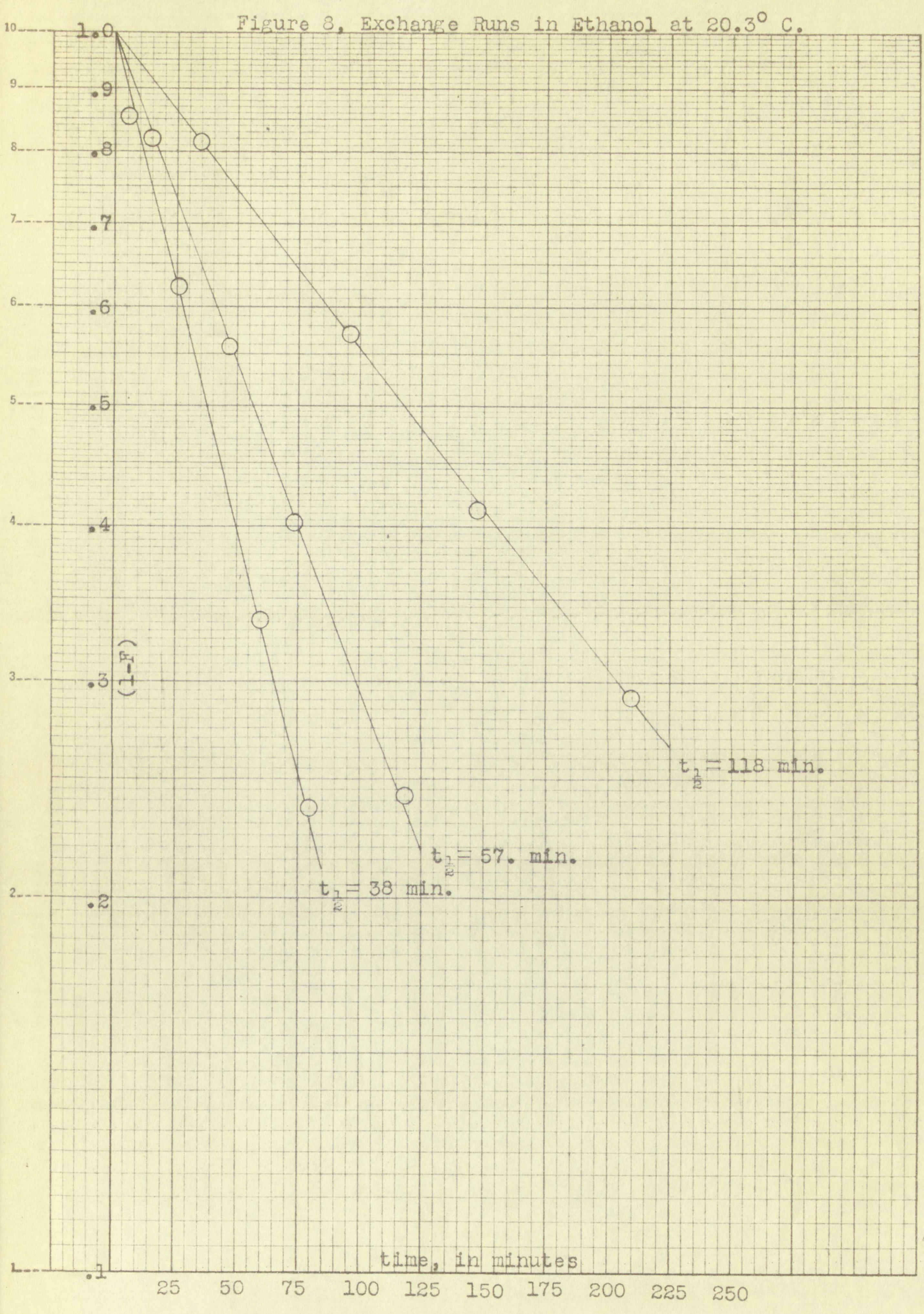


Figure 8, Exchange Runs in Ethanol at 20.3° C.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
(1-F)
$t_{\frac{1}{2}}$ = 118 min.
$t_{\frac{1}{2}}$ = 57. min.
$t_{\frac{1}{2}}$ = 38 min.
time, in minutes
25
50
75
100
125
150
175
200
225
250

Table XXV

Experimental Data for Run #26

(PNBI) = 0.001011 M (KI) = 0.000920 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	16	3595	345	0.159
2	40	3088	655	0.319
3	70	2732	1049	0.508
4	170	2131	1632	0.802

*Corrected for operating blank of 6.0%

$t_{1/2} = 71$ minutes

Solvent - n-Propanol

Table XXVI

Experimental Data for Run #27

(PNBI) = 0.002083 M (KI) = 0.001865 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	10	4816	554	0.190
2	26	4157	1216	0.419
3	50	3507	1866	0.635
4	72	3108	2271	0.775

*Corrected for operating blank of 6.0%

$t_{1/2} = 34.5$ minutes

Solvent - n-Propanol

Table XXVII

Experimental Data for Run #28

(PNBI) = 0.002798 M (KI) = 0.002950 M

Aliquot	Time, min.	Activity in KI counts/min.	Activity in PNBI* counts/min.	Fraction exchanged F
1	6	4157	369	0.161
2	14.5	3797	757	0.327
3	38	3127	1532	0.661
4	58	2734	1866	0.807

*Corrected for operating blank of 5.8%

$t_{1/2} = 24$ minutes

Solvent - n-Propanol

Figure 9, Exchange Runs in n-Propanol at 20.3° C.

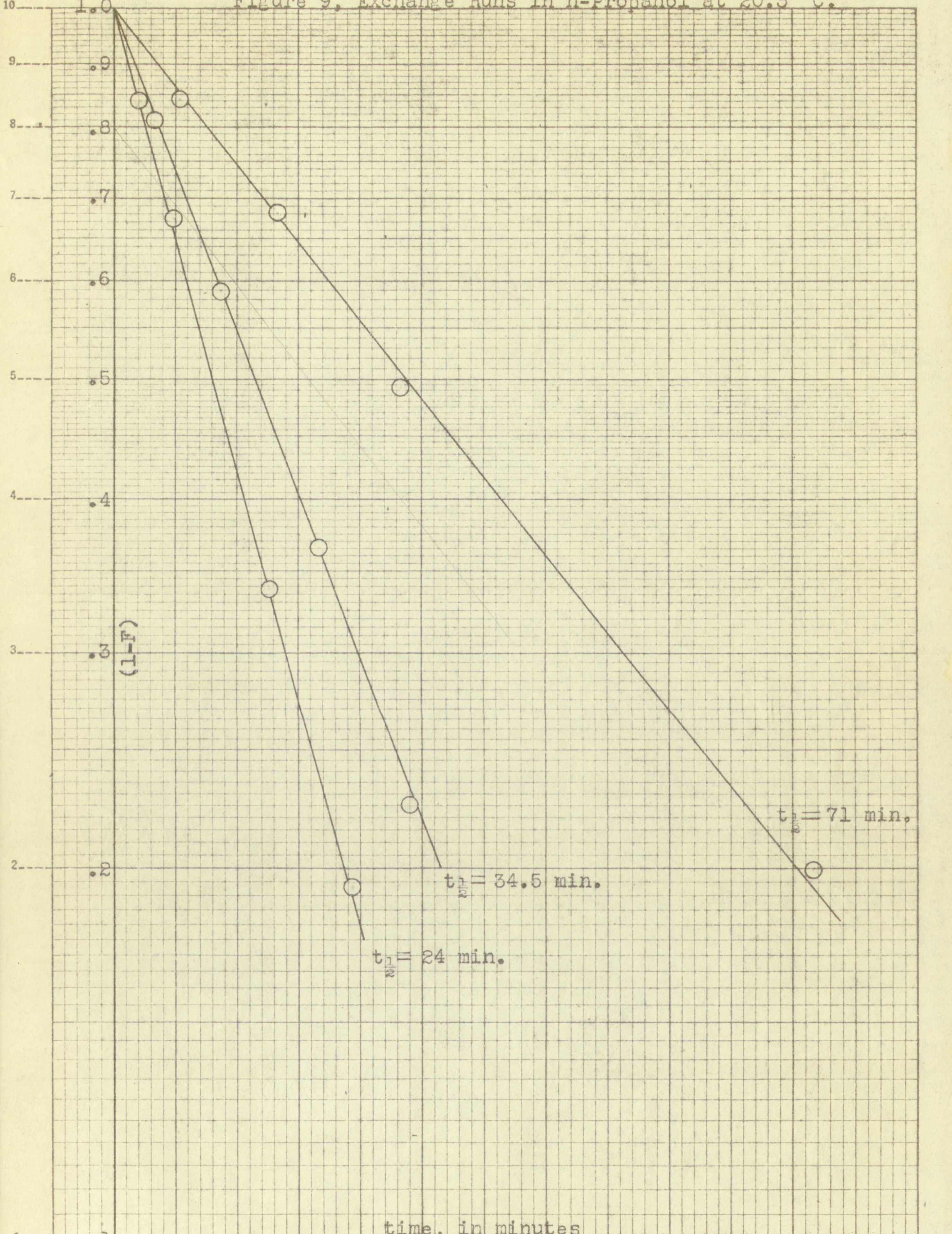


Figure 9-a, R/(PNBI) vs. (KI) for Exchange Reactions at 20.3° C.

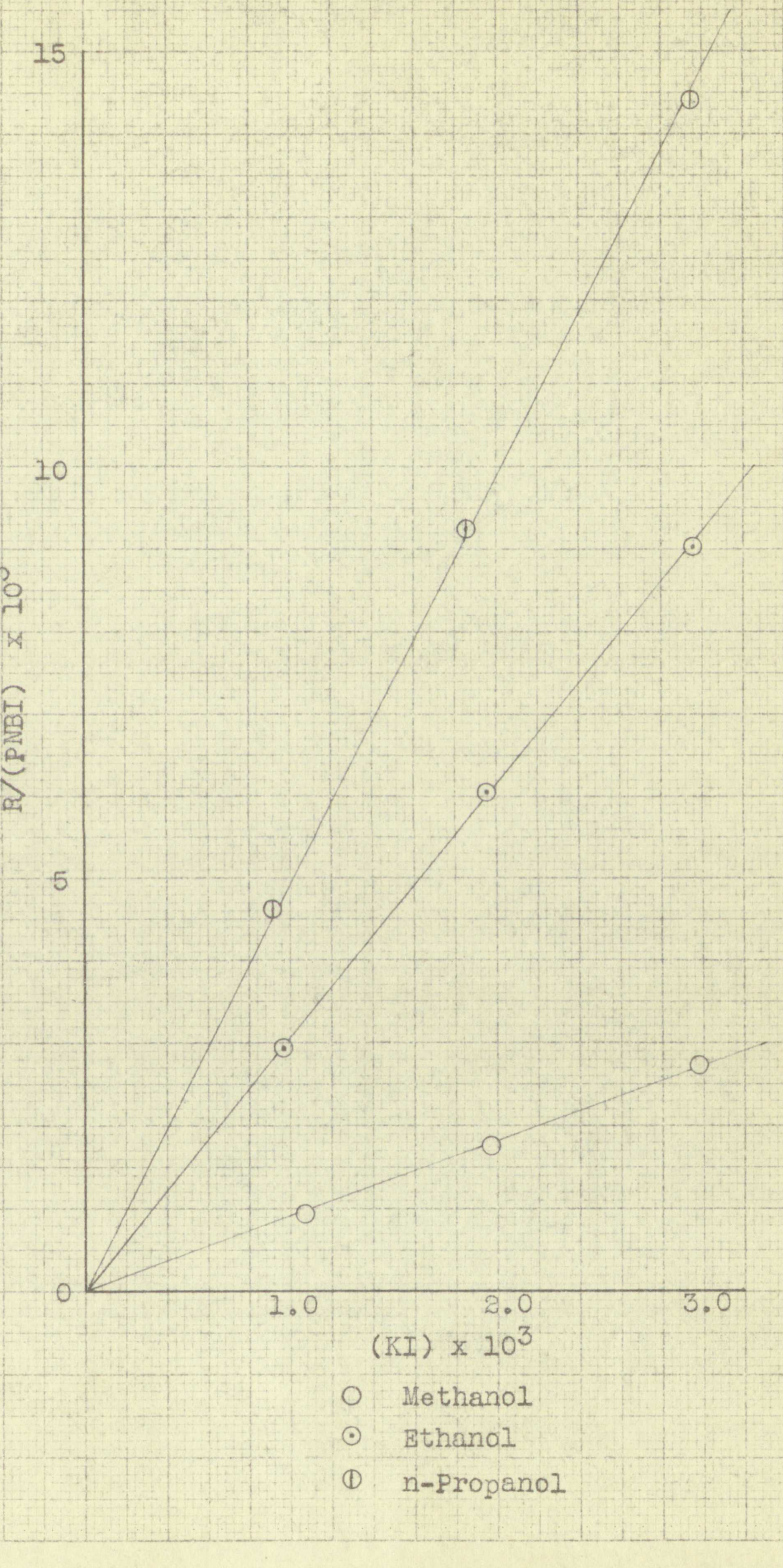


Table XXIX

Experimental Data for Exchange Runs in Methanol

Run no.	Temp. °C	PNBI conc. Molar	KI conc. Molar	$t_{1/2}$ min.	$R \times 10^6$ mol.l^{-1}min.$^{-1}$	k l.mol.$^{-1}$min.$^{-1}$	$k_{ave.}$ l.mol.$^{-1}$min.$^{-1}$
11	0.0	0.001604	0.001650	1540	0.3750	0.1350	
12	0.0	0.001992	0.001975	1365	0.5154	0.1250	0.1300
13	0.0	0.002585	0.002550	1010	0.9002	0.1301	
20	20.3	0.000996	0.001070	375	0.9535	0.8947	
21	20.3	0.002033	0.001970	190	3.650	0.9114	0.9055
22	20.3	0.003110	0.002980	129	8.939	0.9105	
1	30.9	0.001063	0.001050	140	2.585	2.370	
2	30.9	0.003060	0.002880	49	20.73	2.411	2.400
3	30.9	0.00050	0.00050	290	0.5906	2.418	

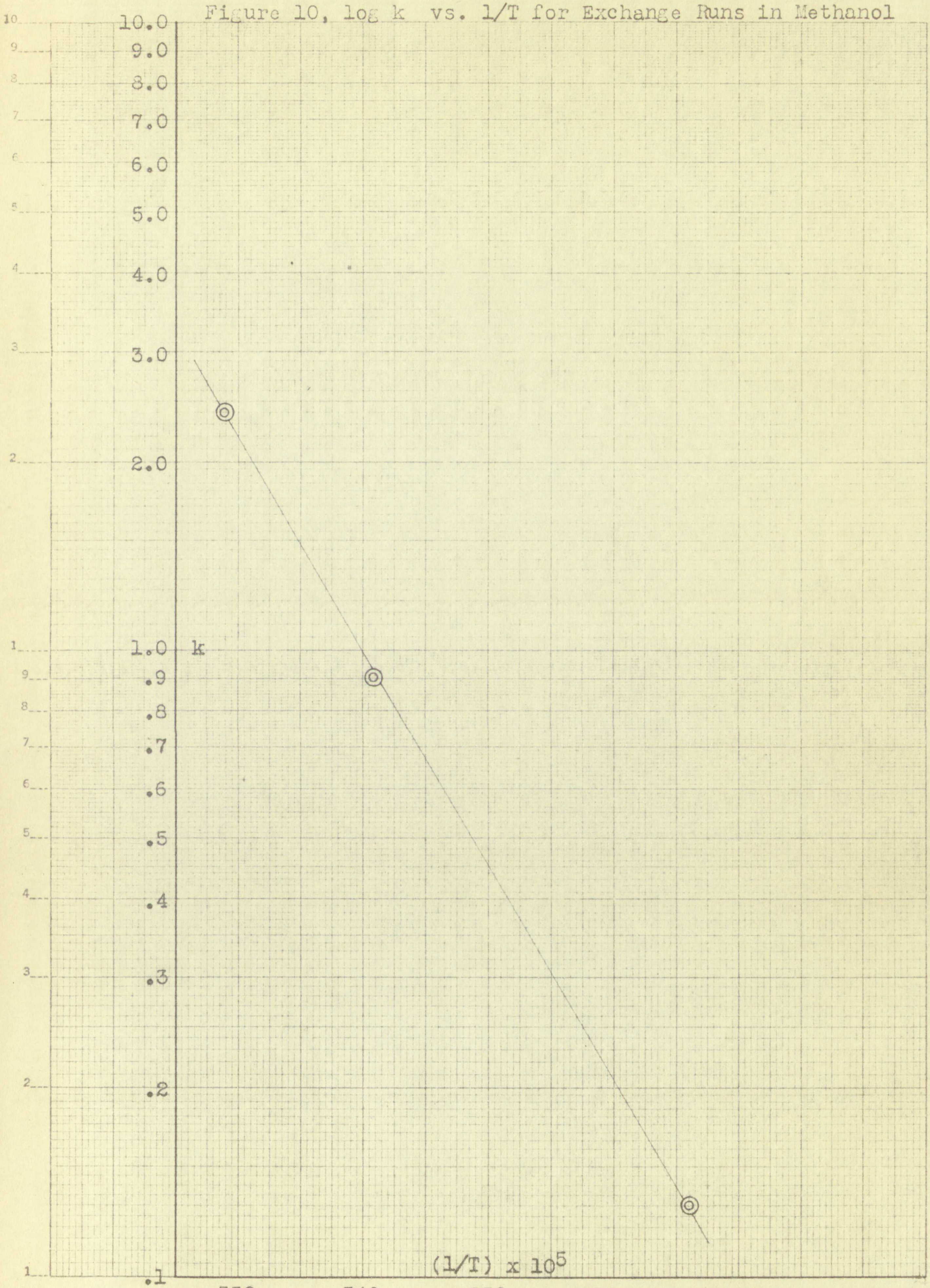


Figure 10, log k vs. 1/T for Exchange Runs in Methanol
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
k
.9
.8
.7
.6
.5
.4
.3
.2
.1
(1/T) x 10^5
330
340
350
360
370

Table XXX

Experimental Data for Exchange Runs in Ethanol

Run no.	Temp. ^{o}C	PNBI conc. Molar	KI conc. Molar	$t_{1/2}$ min.	$R \times 10^{6}$ $mol.l.^{-1}min.^{-1}$	k $l.mol.^{-1}min.^{-1}$	$k_{ave.}$ $l.mol.^{-1}min.^{-1}$
14	0.0	0.001242	0.001255	740	0.5972	0.3673	
15	0.0	0.002099	0.001545	517	1.219	0.3603	0.3642
16	0.0	0.003042	0.002513	335	2.911	0.3650	
23	20.3	0.001011	0.000965	116	2.965	3.039	
24	20.3	0.001977	0.001965	57	11.98	3.085	3.056
25	20.3	0.003030	0.002963	38	27.33	3.044	
4	30.9	0.000524	0.000470	89	1.907	7.928	
5	30.9	0.001000	0.001015	45	7.668	7.735	7.823
6	30.9	0.002913	0.003078	15	68.34	7.805	

Figure 11, log k vs. 1/T for Exchange Runs in Ethanol

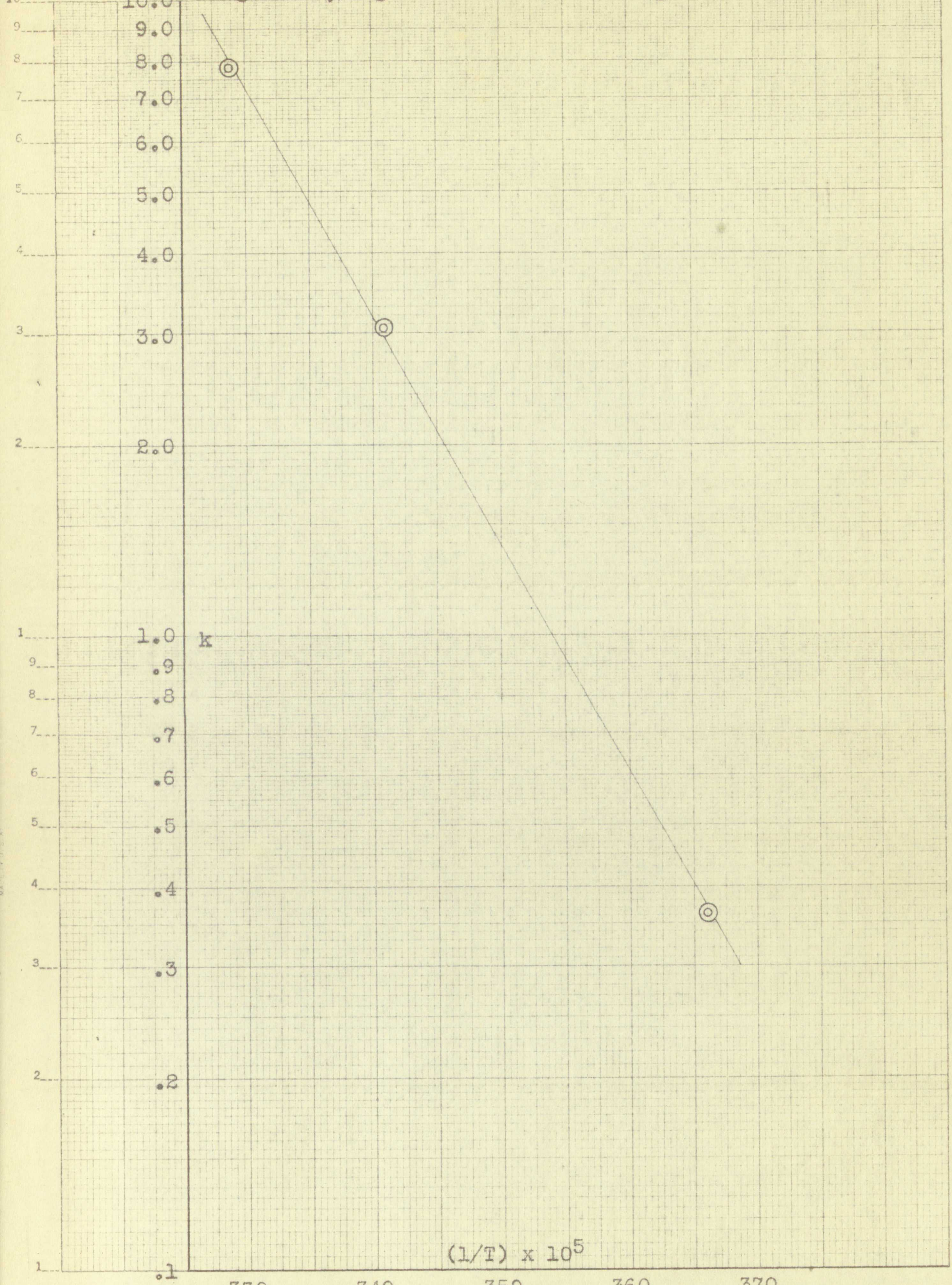


Table XXXI

Experimental Data for Exchange Runs in n-Propanol

Run no.	Temp. ^{o}C	PNBI conc. Molar	KI conc. Molar	$t_{1/2}$ min.	$R \times 10^6$ $mol.l.^{-1}min.^{-1}$	k $l.mol.^{-1}min.^{-1}$	$k_{ave.}$ $l.mol.^{-1}min.^{-1}$
17	0.0	0.000517	0.000515	1030	0.1766	0.6409	
18	0.0	0.000958	0.001005	548	0.6312	0.6333	0.6370
19	0.0	0.002137	0.002075	254	2.922	0.6369	
26	20.3	0.001011	0.000920	71	4.703	5.056	
27	20.3	0.002083	0.001865	34.5	19.32	5.089	5.057
28	20.3	0.002798	0.002950	24	41.47	5.025	
7	30.9	0.000500	0.000550	46	3.905	14.46	
8	30.9	0.001088	0.001063	22.5	16.39	14.42	14.55
9	30.9	0.000675	0.000570	38	5.579	14.77	

Figure 12, log k vs. 1/T for Exchange Runs in n-Propanol

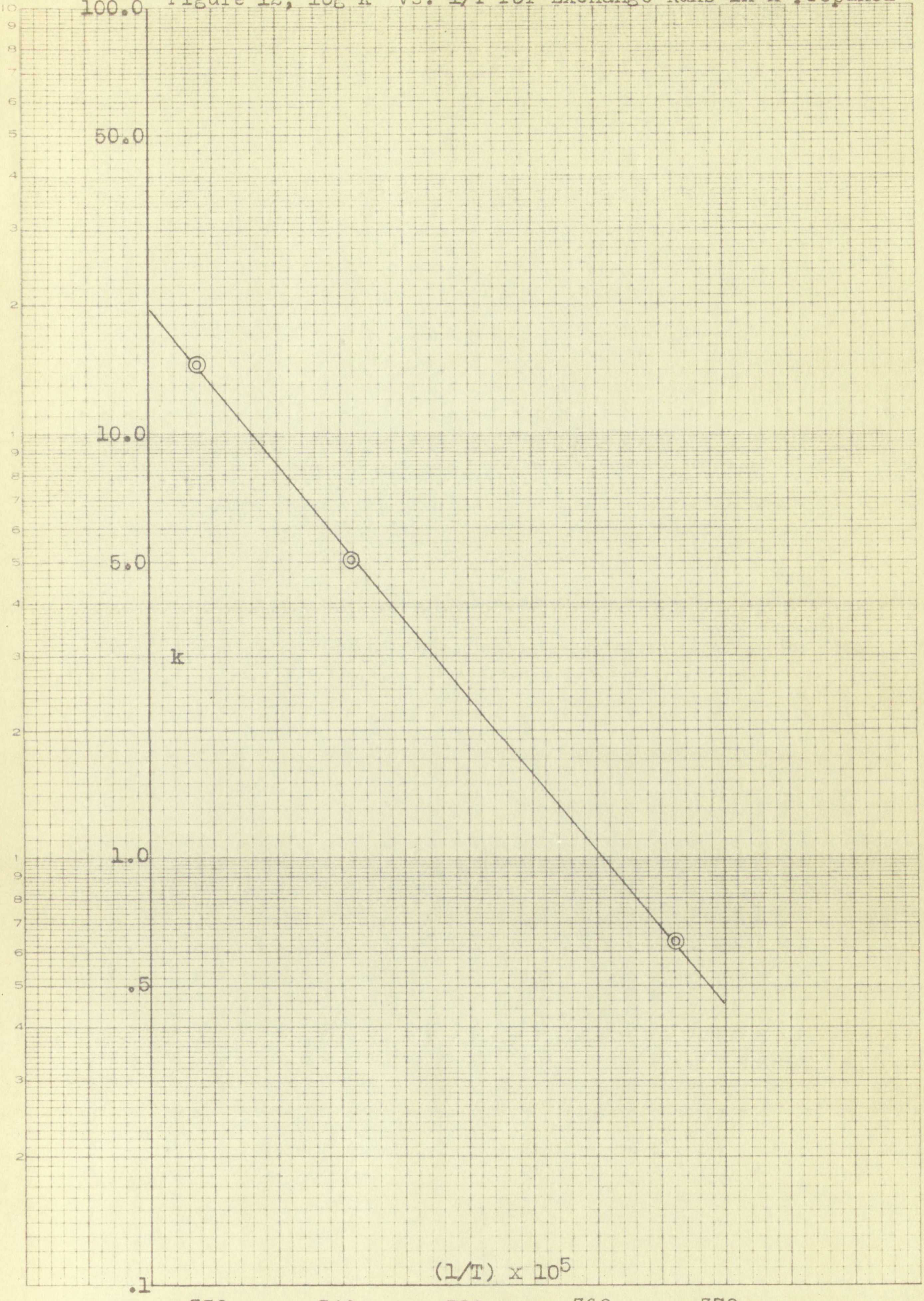
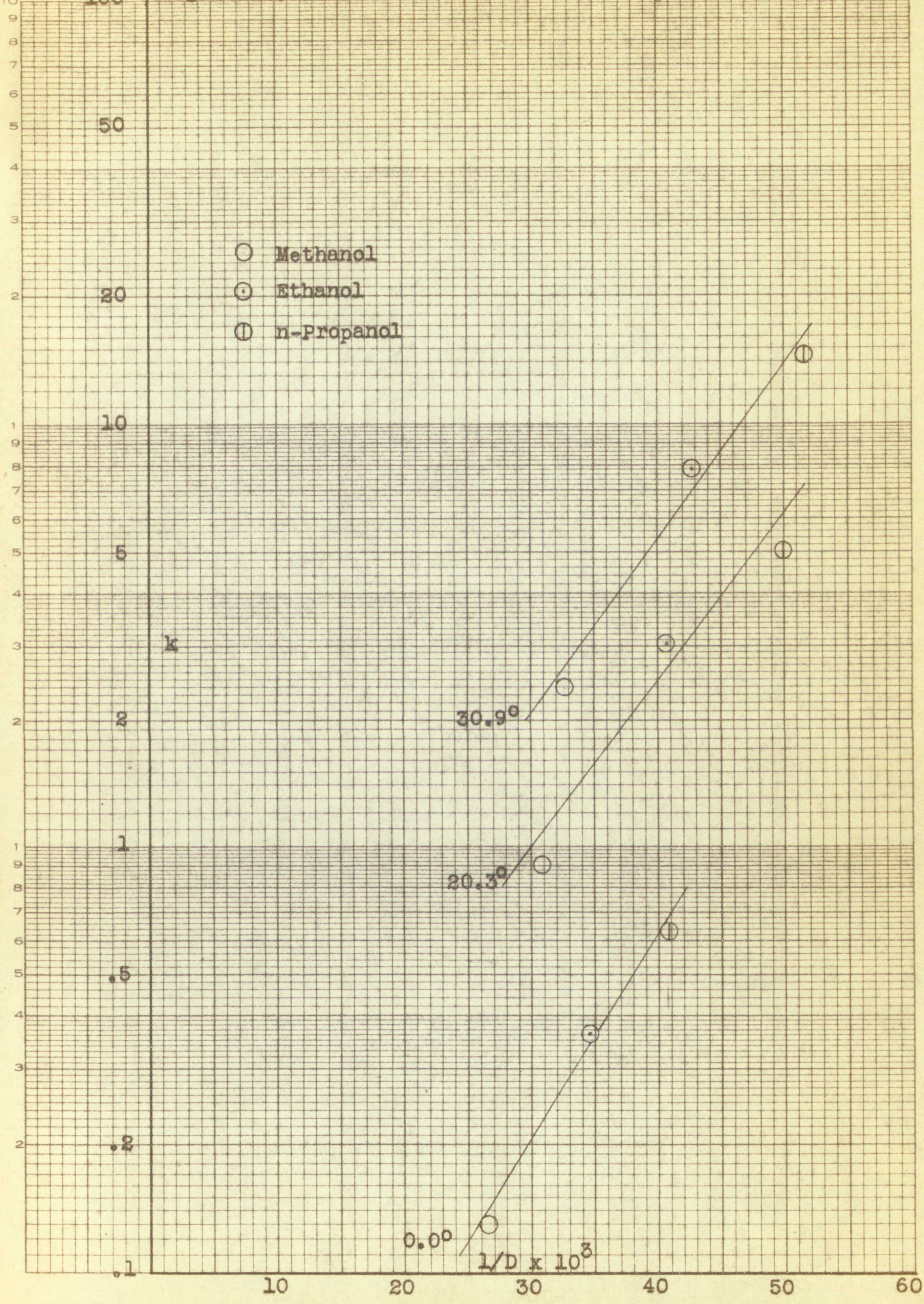


Figure 13, Dielectric constant Effect upon Exchange Rates



Discussion

Energies of Activation and Entropies of Activation for the p-Nitrobenzyl Iodide - Iodide Ion Exchange

The experimental energies of activation, found in table XXXII, increase slightly in passing through the solvent series methanol, ethanol, n-propanol. This increase results in a slight decreasing effect upon the rates of exchange. The entropies of activation, found in table XXXIII, increase in passing through the solvent series methanol, ethanol, n-propanol. These increases result in corresponding increases upon the rates of exchange.

A more explicit comparison of the relative magnitudes of the effects of entropy of activation and energy of activation is obtained by comparing the entropy factors and activation energy factors of table XXXIV. The large relative increases in the entropy factors in passing through the solvent series methanol, ethanol, n-propanol at a given temperature exceed the relative decreases in the activation energy factors for the corresponding solvent series at the same temperature. Thus the observed increases in the rates of exchange for the solvent series methanol, ethanol, n-propanol may be attributed to the dominating influence of

the increases in the entropies of activation.

Expression of the Specific Rate Constants in the Arrhenius Form

The specific rate constants for the p-nitrobenzyl iodide - iodide ion exchange in the various solvents may be expressed in the Arrhenius form as follows:

$$k = 5.362 \times 10^{11}\, e^{-15,759/RT} \qquad \text{(methanol)} \tag{V-14}$$

$$k = 8.134 \times 10^{12}\, e^{-16,688/RT} \qquad \text{(ethanol)} \tag{V-15}$$

$$k = 2.041 \times 10^{13}\, e^{-16,888/RT} \qquad \text{(n-propanol)} \tag{V-16}$$

the increase in the [illegible]

Expression of the [illegible]

in the [illegible]

The specific rate constants for [illegible] iodide - iodine [illegible] be expressed in the [illegible]

(V-14) k = [illegible]

(V-15) k = [illegible]

(V-16) k = [illegible]

Table XXXII

Energies of Activation for the p-Nitrobenzyl Iodide - iodide ion Exchange

Solvent	Energy of Activation, ΔE_X
Methanol	15,759 cal.
Ethanol	16,688 cal.
n-Propanol	16,888 cal.

Table XXXIII

Entropies of Activation for the p-Nitrobenzyl Iodide - iodide ion Exchange

Temperature----	0.0°C.	20.3°C.	30.9°C.
Solvent			
Methanol	-6.68 e.u.	-6.82 e.u.	-6.90 e.u.
Ethanol	-1.28 "	-1.42 "	-1.49 "
n-Propanol	0.551 "	0.408 "	0.334 "

Table XXXIV

Entropy Factors and Activation Energy Factors for the p-Nitrobenzyl Iodide - Iodide Ion Exchange

Solvent	Temperature °C.	Entropy Factor $e^{\Delta S^*/R} \times 10^2$	Activation Energy Factor $e^{-\Delta E_X/RT} \times 10^{13}$
Methanol	0.0	3.465	2.425
"	20.3	3.225	16.89
"	30.9	3.107	44.76
Ethanol	0.0	52.57	0.4477
"	20.3	48.93	3.757
"	30.9	47.14	9.617
n-Propanol	0.0	131.9	0.3121
"	20.3	122.8	2.477
"	30.9	118.3	7.126

Comparison of the p-Nitrobenzyl Iodide - Iodide Ion Exchange with that of Benzyl Iodide - Iodide Ion*

In every instance the rates of exchange for the p-nitrobenzyl iodide - iodide ion exchange were found to be greater than those for the benzyl iodide - iodide ion exchange. A comparison of the specific rate constants for the two exchanges is found in table XXXV.

The energies of activation for the two exchange reactions, tabulated in table XXXVI, are virtually the same. The maximum error in the experimental energies of activation is thought to be not greater than $\pm 1\%$.

Since the energies of activation exhibit little or no change, the increases in rates of exchange result from increases in the Arrhenius frequency factors, see table XXXVII, or more explicitly from increases in entropy of activation.

---

*In the tables accompanying the discussion, the data concerning the benzyl iodide exchange in methanol and ethanol was taken directly from the results of Stillson, ref.1, or calculated from his results. The data concerning the benzyl iodide exchange in n-propanol was obtained from Stillson by private communication. It should be pointed out that the results of Stillson have not been corrected for the thermal expansion and contraction of the solvents. These applied thermal corrections would result in changes in the specific rate constants to the extent of one to three per cent.

Comparison of the p-Nitrobenzyl Iodide - Iodide Ion Exchange with that of Benzyl Iodide - Iodide Ion*

In every instance the rates of exchange for the p-nitrobenzyl iodide - iodide ion exchange were found to be greater than those for the benzyl iodide - iodide ion exchange. A comparison of the specific rate constants for the two exchanges is found in table XXXV.

The energies of activation for the two exchange reactions, tabulated in table XXXVI, are virtually the same. The maximum error in the experimental energies of activation is thought to be not greater than [illegible].

Since the energies of activation undergo little or no change, the increases in rates of exchange result from increases in the Arrhenius frequency factors, see table XXXVII, or more explicitly from increases in entropy of activation.

---

*In the tables accompanying the discussion, the data concerning the benzyl iodide exchange in methanol and ethanol was taken directly from the results of Stillson, ref. 1, or calculated from his results. The data concerning the benzyl iodide exchange in n-propanol was obtained from Stillson by private communication. It should be pointed out that the results of Stillson have not been corrected for the thermal expansion and contraction of the solvents. These applied thermal corrections would result in changes in the specific rate constants to the extent of one to three per cent.

Table XXXV

Comparison of the Specific Reaction Rate Constants of the p-Nitrobenzyl Iodide - Iodide Ion Exchange with those of the Benzyl Iodide - Iodide Ion Exchange

Solvent	Temp.	k_a	k_b	k_b/k_a
Methanol	0.0°	.063	0.1300	2.1
Ethanol	0.0°	.101	0.3642	3.6
n-Propanol	0.0°	0.1180	0.6370	5.8
Methanol	20.3°	0.438	0.9055	2.1
Ethanol	20.3°	.834	3.056	3.7
n-Propanol	20.3°	.8733	5.057	5.8
Methanol	30.9°	1.12	2.400	2.1
Ethanol	30.9°	2.29	7.823	3.4
n-Propanol	30.9°	2.512	14.55	5.8

k_a - specific rate constant for the benzyl iodide - iodide ion exchange calculated from the data of Stillson.

k_b - specific rate constant for the p-nitrobenzyl iodide - iodide ion exchange.

Table XXXVI

Comparison of the Energies of Activation of the Benzyl Iodide - Iodide Ion Exchange with those of the p-Nitrobenzyl - Iodide - Iodide Ion Exchange

Solvent	ΔE_{x-a}	ΔE_{x-b}
Methanol	15,650 cal.	15,759 cal.
Ethanol	17,150 cal.	16,688 cal.
n-Propanol	16,837 cal.	16,888 cal.

ΔE_{x-a} experimental energy of activation for the benzyl iodide - iodide ion exchange

ΔE_{x-b} experimental energy of activation for the p-nitrobenzyl iodide - iodide ion exchange

Table XXXVII

Comparison of Frequency Factors

	A_a	A_b	A_b/A_a
Methanol	2×10^{11}	5.362×10^{11}	2.68
Ethanol	5×10^{12}	8.134×10^{12}	1.63
n-Propanol	3.5×10^{12}	2.041×10^{13}	5.8

A_a - frequency factor for benzyl iodide exchange

A_b - frequency factor for p-nitrobenzyl iodide exchange

The calculated entropies of activation for the two exchanges appear in table XXXVIII. For a given reaction, the entropies of activation are seen to vary little with temperature. In every instance the entropy of activation for the p-nitrobenzyl iodide exchange is seen to be greater than the corresponding entropy of activation for the benzyl iodide exchange.

Table XXXVIII

Comparison of the Entropies of Activation

	0.0°		20.3°		30.9°	
Solvent	ΔS_a^*	ΔS_b^*	ΔS_a^*	ΔS_b^*	ΔS_a^*	ΔS_b^*
Methanol	-8.637	-6.68	-8.780	-6.82	-8.854	-6.90
Ethanol	-2.244	-1.28	-2.386	-1.42	-2.460	-1.49
n-Propanol	-2.938	0.551	-3.080	0.408	-3.154	0.334

ΔS_a^* - entropy of activation for the benzyl iodide - iodide ion exchange

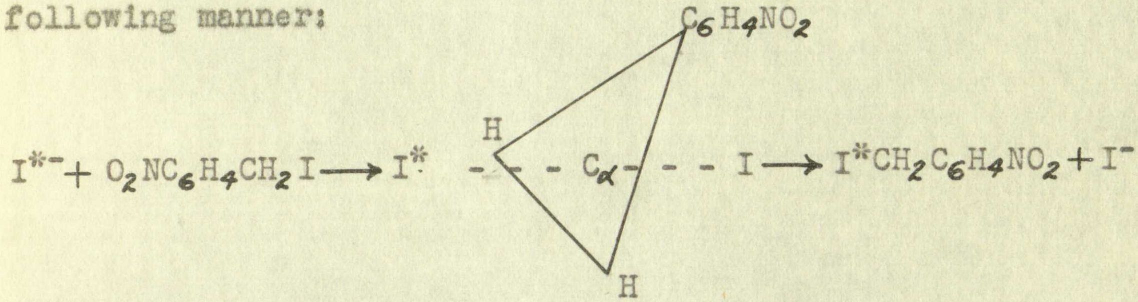
ΔS_b^* - entropy of activation for the p-nitrobenzyl iodide - iodide ion exchange

Mechanism of the Exchange Reaction

At this point it is of interest to consider the mechanism of the exchange reaction and the potential energy

changes accompanying it.[46,47]

The reaction may be visualized as occurring in the following manner:



The reaction steps are as follows:

1. I^{*-} approaches the organic molecule in such a manner that the forces of repulsion against it are minimized. It has been shown that this generally requires an approach toward the face of the tetrahedral carbon atom opposite to the carbon-halide bond and along a line extended from the tetrahedral axis of the carbon-attached halide.

2. As the attacking ion I^{*-} gets close enough to the central carbon atom, a "stretching" of the C_α-I bond results. I^{*-} finally gets sufficiently close that it competes equally with I^- for attachment to the central carbon and a "transition state" or "activated complex" is formed.

3. The activated complex decomposes, I^- is expelled and inversion of the Walden type results in the formation of ψ-I^* and I^-.

changes accompanying it.

The reaction may be visualized as occurring in the following manner:

$$I^{*-} + O_2NC_6H_4CH_2I \longrightarrow I^{*} - - \overset{C_6H_4NO_2}{\underset{H \quad H}{C}} - - I \longrightarrow I^{*}CH_2C_6H_4NO_2 + I^{-}$$

The reaction steps are as follows:

1. I^{*-} approaches the organic molecule in such a manner that the forces of repulsion [illegible] are a minimum. It has been shown that this generally involves an approach toward the face of the [illegible] carbon atom opposite to the carbon-halide bond and along a line extended from the tetrahedral axis of the carbon-attached halide.

2. As the attacking ion I^{*-} approaches close enough to the central carbon atom, a "stretching" of the C-I bond results. I^{*-} finally [illegible] sufficiently close that it competes equally with I for attachment to the central carbon and a transition state or "activated complex" is formed.

3. The activated complex decomposes, I^{-} is expelled and inversion of the molecule results in the formation of [illegible] and I^{-}.

The potential energy of the system may be discussed from the standpoint of a potential energy profile diagram[48] as shown in figure 14.

Consider an exchange reaction such as:

$$I^{*-} + \psi\text{-}I \longrightarrow I^{*}\text{-}\psi + I^{-}$$

Curve I represents the potential energy of the system in the activated state $I^{*}\text{---}\psi\text{----}I$ and is the normal attraction curve shifted upward from its normal position II. Curve II represents the potential energy of the molecule ψ-I when I^{*-} is far away, and does not interact with ψ-I. Curve III represents the normal repulsion curve when the reverse reaction is considered:

$$\psi\text{-}I^{*} + I^{-} \longrightarrow \psi\text{-}I + I^{*-}$$

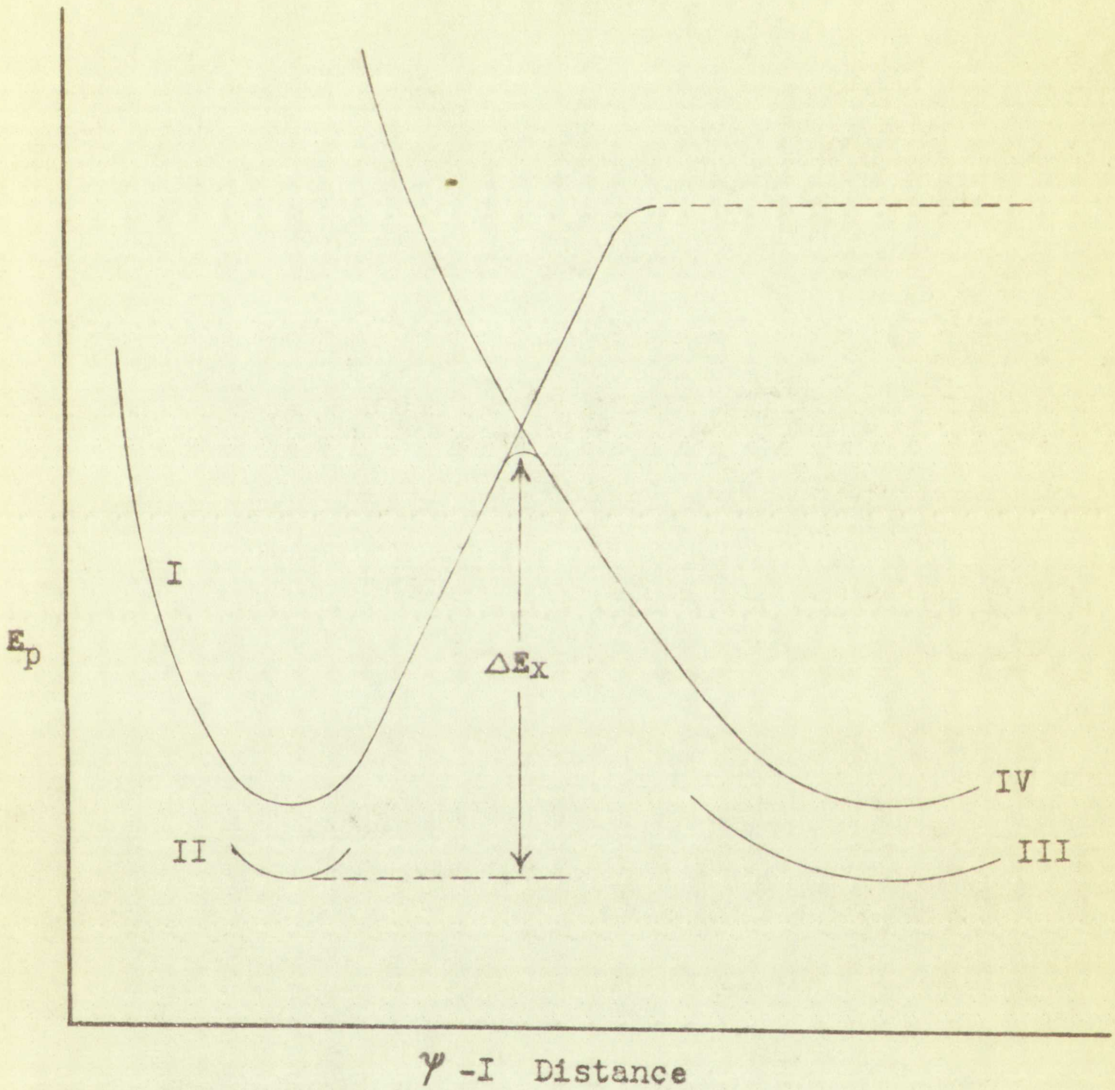
As I^{-} approaches ψ-I^{*}, the atoms of ψ-I^{*} retaining their equilibrium positions, the potential energy of the molecule increases due to the repulsion between I^{-} and ψ-I^{*}. The potential energy of the activated state is represented by curve IV.

In an exchange reaction of this type the potential energy profile or the activation energy is determined by two factors:

(1) The strength of the ψ-I bond.

(2) The repulsion energy between ψ-I and I^{-}.

Figure 14, Potential Energy Profile Diagram



E_p - Potential Energy

ΔE_x - Experimental Energy of Activation

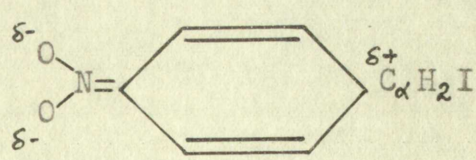
An increase in ψ-I bond strength results in a steepening of curve I, a raising of its horizontal asymptote and an increase in activation energy.

An increase in repulsion energy between ψ-I and I^- results in an upward shifting of both curves I and IV and an increase in activation energy.

An increase in ψ-I bond strength has the effect of lowering curve III. Since the difference in levels of curves III and IV is equivalent to the energy required to stretch the bond from the normal state to the activated state, curve IV is dependent upon ψ-I bond strength and will be lowered with an increase in bond strength. The result is a decrease in the energy of activation.

It is seen that an increase in ψ-I bond strength has two simultaneous and oppositely directed effects upon the energy of activation in the ion-neutral molecule exchange reaction. Should these effects be of approximately equal magnitude, changes in the energy of activation would result principally from the altering of repulsion energies.

Consider the effect of introducing a nitro group into the para position of benzyl iodide:



The introduction of the electrophilic nitro group results in a $\delta+$ charge on the tetrahedral carbon atom, C_α. This alteration of effective charge results in:

I. A strengthening of the C_α-I bond which exerts two opposing effects upon the energy of activation.

II. A decrease in the repulsion energy between the reaction center and the attacking I^{*-}. This exerts a decreasing effect upon the energy of activation.

Since the energies of activation of the two exchanges under consideration have been found to be essentially the same in corresponding reaction mediums, the resultant influences of effects (I) and (II) above apparently cancel out. The resultant effect of the p-nitro group is thus to increase the rates of exchange by increasing the entropies of activation.

Influence of the Entropy of Activation

The entropy factor, $e^{\Delta S^*/R}$, may be considered as a measure of the probability that two colliding activated-reactants result in the formation of the activated complex or transition state.[49] A negative entropy of activation implies a low probability of activated complex formation.

the introduction of [illegible] [illegible] δ+charge on the [illegible] [illegible] of effective [illegible] [illegible]

I. [illegible] [illegible] two opposing effects [illegible] [illegible]

II. a decrease [illegible] [illegible] [illegible] relative [illegible] [illegible] creasing effect upon the energy of [illegible]

Since the energies of [illegible] changes under consideration [illegible] [illegible] the same [illegible] [illegible] influence of effects (I) and (II) [illegible] [illegible] cat. The resultant effect [illegible] [illegible] increase the rates [illegible] [illegible] of activation.

Influence of the [illegible] of Activation

The entropy [illegible] measure of the probability [illegible] [illegible] reactants result in the [illegible] [illegible] or transition state. [illegible] implies a low probability [illegible] [illegible]

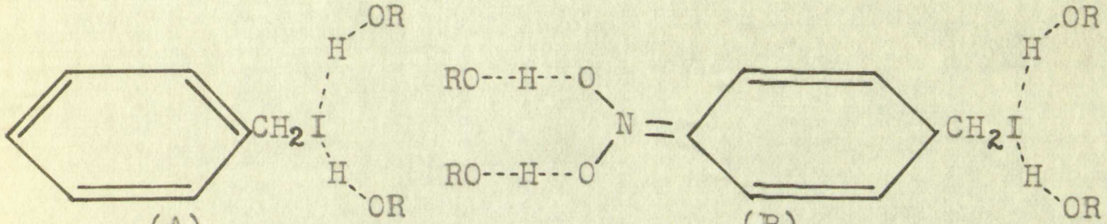
Furthermore, reactions of complex molecules are associated with decreases in entropy of activation.[50] Increases in entropy of activation imply that the reacting molecules are less complex in nature.

The increases in the entropies of activation resulting from the introduction of the p-nitro group into benzyl iodide suggest that the reacting organic molecules are less complex in nature. Also, the increases in entropy of activation for the p-nitrobenzyl iodide exchange indicate a decreasing complexity of the reactant molecules in passing through the solvent series methanol, ethanol, n-propanol.

Consider now the effects of solvation. Since varying degrees of solvent-organic molecule interaction result in varying degrees of molecular complexity, changes in entropy of activation may reflect variation in solvation. The increases in entropies of activation for the p-nitrobenzyl iodide exchange therefore suggest that solvation decreases in passing through the solvent series methanol, ethanol, n-propanol.

It is interesting to note that this decreasing effect of solvation is consistent with the hydrogen-bonding

tendencies of the solvents. The hydrogen-bonding tendencies of the solvents decrease in the order: methanol, ethanol, n-propanol. The mechanism of hydrogen-bonding is therefore suggested as a possible means of solvent-organic molecule interaction:

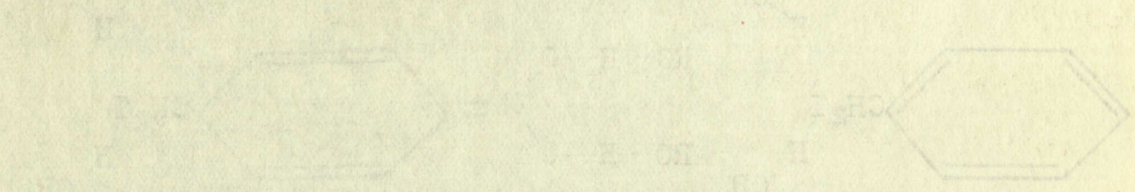


(A) (B)

Figure (A) represents hydrogen-bonding occurring with the benzyl iodide molecule. Figure (B) represents the hydrogen-bonding occurring with the p-nitrobenzyl iodide molecule. It is seen that hydrogen-bonding with the nitro group tends to stabilize the resonance structure B. Any hydrogen-bonding occurring with the oxygen atoms of the nitro group would not be expected to be involved in any entropy changes other than those arising from the stabilizing effects of hydrogen-bonding upon the resonance structure B since the nitro group is remote from the reaction center.

The increases in entropies of activation of the exchanges resulting from the introduction of the p-nitro group into benzyl iodide are consistent with the idea of hydrogen-bonding. The p-nitro group results in a decrease

tendencies of the solvents. The hydrogen-bonding tendencies of the solvents decrease in the order: methanol, ethanol, n-propanol. The mechanism of hydrogen-bonding is therefore suggested as a possible means of solvent-organic molecule interaction:



(A)

Figure (A) represents hydrogen-bonding occurring with the benzyl iodide molecule. Figure (B) represents the hydrogen-bonding occurring with the p-nitrobenzyl iodide molecule. It is seen that hydrogen-bonding with the nitro group tends to stabilize the resonance structure B. Any hydrogen-bonding occurring with the oxygen atoms of the nitro group would not be expected to be involved in any entropy changes other than those arising from the stabilizing effects of hydrogen-bonding upon the resonance structure B since the nitro group is remote from the reaction center.

The increases in entropies of activation of the exchanges resulting from the introduction of the p-nitro group into benzyl iodide are consistent with the idea of hydrogen-bonding. The p-nitro group results in a decrease

of electron density around the reaction center of the molecule and the iodide atom. This decrease in electron density tends to decrease the extent of hydrogen-bonding, thereby resulting in a less complex reactant molecule. This is in agreement with the increases in the entropies of activation observed in going from exchanges with benzyl iodide to those of p-nitro-benzyl iodide.

BIBLIOGRAPHY

1. P. Stillson, Ph.D. Dissertation, The University of New Mexico (1951).

2. E. D. Hughes, J. Chem. Soc., 968 (1946).

3. E. D. Hughes, Trans. Faraday Soc., 37, 603 (1941).

4. E. D. Hughes and C. K. Ingold, J. Chem. Soc., 244 (1935).

5. E. D. Hughes, C. K. Ingold and C. S. Patel, J. Chem. Soc., 526 (1933).

6. E. D. Hughes, Trans. Faraday Soc., 37, 608 (1941).

7. L. C. Bateman, K. A. Cooper, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 925 (1940).

8. E. D. Hughes and C. K. Ingold, J. Chem. Soc., 246 (1935).

9. E. D. Hughes, Trans. Faraday Soc., 37, 623 (1941).

10. I. Dostrovsky and E. D. Hughes, J. Chem. Soc., 157, 161, 169 (1946).

11. E. D. Hughes and C. K. Ingold, J. Chem. Soc., 252 (1935).

12. L. C. Bateman, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 1011, 1017 (1940).

13. K. J. Laidler, Chemical Kinetics, 1st ed., The McGraw-Hill Book Company, Inc., New York, 1950, pp. 130, 131.

14. C. C. J. Fontein, Rec. trav. chim., 47, 635 (1928).

15. C. A. Lobry de Bruyn and E. Steger, Rec. trav. chim., 18, 14, 311 (1899).

16. E. D. Hughes, C. K. Ingold and U. G. Shapiro, J. Chem. Soc., 225 (1936).

17. E. D. Hughes and C. K. Ingold, J. Chem. Soc., 1571 (1933).

18. E. Bergman, M. Polanyi and A. Szabo, A. physyk, Chem., B. 20, 161 (1933).

19. S. Glasstone, K. J. Laidler and H. Eyring, The Theory of Rate Processes, 1st ed., The McGraw-Hill Book Company, Inc., New York, 1941, pp. 415, 417.

20. S. Glasstone, K. J. Laidler and H. Eyring, op. cit., ch. Iv,VII.

21. O. E. Meyers and R. J. Prestwood, Radioactivity Applied to Chemistry, Edited by A. C. Wahl and N. A. Bonner, John Wiley and Sons, Inc., New York, 1951, ch.1.

22. J. Bigeleisen, J. Chem. Phys., 17, 675 (1949).

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

24. H. McKay, Nature, 997 (1938).

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

26. G. Friedlander and J. Kennedy, Introduction to Radiochemistry, John Wiley and Sons, Inc., New York, 1949, pp. 285-288.

27. O. E. Myers and R. J. Prestwood, loc. cit.

28. G. Friedlander and J. Kennedy, op. cit., pp. 346, 391.

29. A. W. Kenney and W. T. Sprague, J. Chem. Soc., Supplements & Index, 323-326 (1949).

30. H. Finkelstein, Ber., 43, 1531 (1910).

31. H. Finkelstein, loc. cit.

32. S. M. McElvain, Characterization of Organic Compounds, The Macmillan Co., New York, 1947, pp. 40-42.

33. I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, The Macmillan Co., New York, 1946, pp. 475, 573.

34. H. Lund and N. Bjerrum, Ber., 64, 210 (1931).

35. I. M. Kolthoff and E. B. Sandell, op. cit., pp. 568, 569.

36. P. Stillson, op. cit.

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

38. I. M. Kolthoff and E. B. Sandell, op. cit., p. 573.

39. I. M. Kolthoff and E. B. Sandell, op. cit., p. 573.

40. O. E. Myers and R. J. Prestwood, loc. cit.

41. N. A. Lanze, et. al., Handbook of Chemistry, 6th edition, Handbook Publishers Inc., Sandusky, Ohio (1946).

42. International Critical Tables, 6, 1927, table 4.

43. G. Ackerlöf, J. Am. Chem. Soc., 54, 4125 (1932).

44. K. J. Laidler, loc. cit.

45. D. V. Widder, Advanced Calculus, Prentice-Hall, Inc., New York, 1947, p. 108.

46. S. Glasstone, K. J. Laidler and H. Eyring, op. cit., pp. 85-86, 95-98.

47. C. N. Hinshelwood, K. J. Laidler, and E. W. Timm, J. Chem. Soc., 848 (1938).

48. S. Glasstone, K. J. Laidler and H. Eyring, op. cit., pp. 139-142.

49. S. Glasstone, K. J. Laidler and H. Eyring, op. cit. p. 24.

50. S. Glasstone, K. J. Laidler and H. Eyring, op. cit., pp. 22, 23.

RR