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A Study of Isotopic Exchange Between Potassium Iodide and Benzyl Iodide. Solvent Effects

Joseph A. Leary

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A STUDY OF ISOTOPIC EXCHANGE BETWEEN
POTASSIUM IODIDE AND BENZYL IODIDES.
SOLVENT EFFECTS

By
Joseph A. Leary

A Thesis
In partial fulfillment of the
Requirements for the Degree of
Doctor of Philosophy in Chemistry

The University of New Mexico

1956



This dissertation, 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

DOCTOR OF PHILOSOPHY

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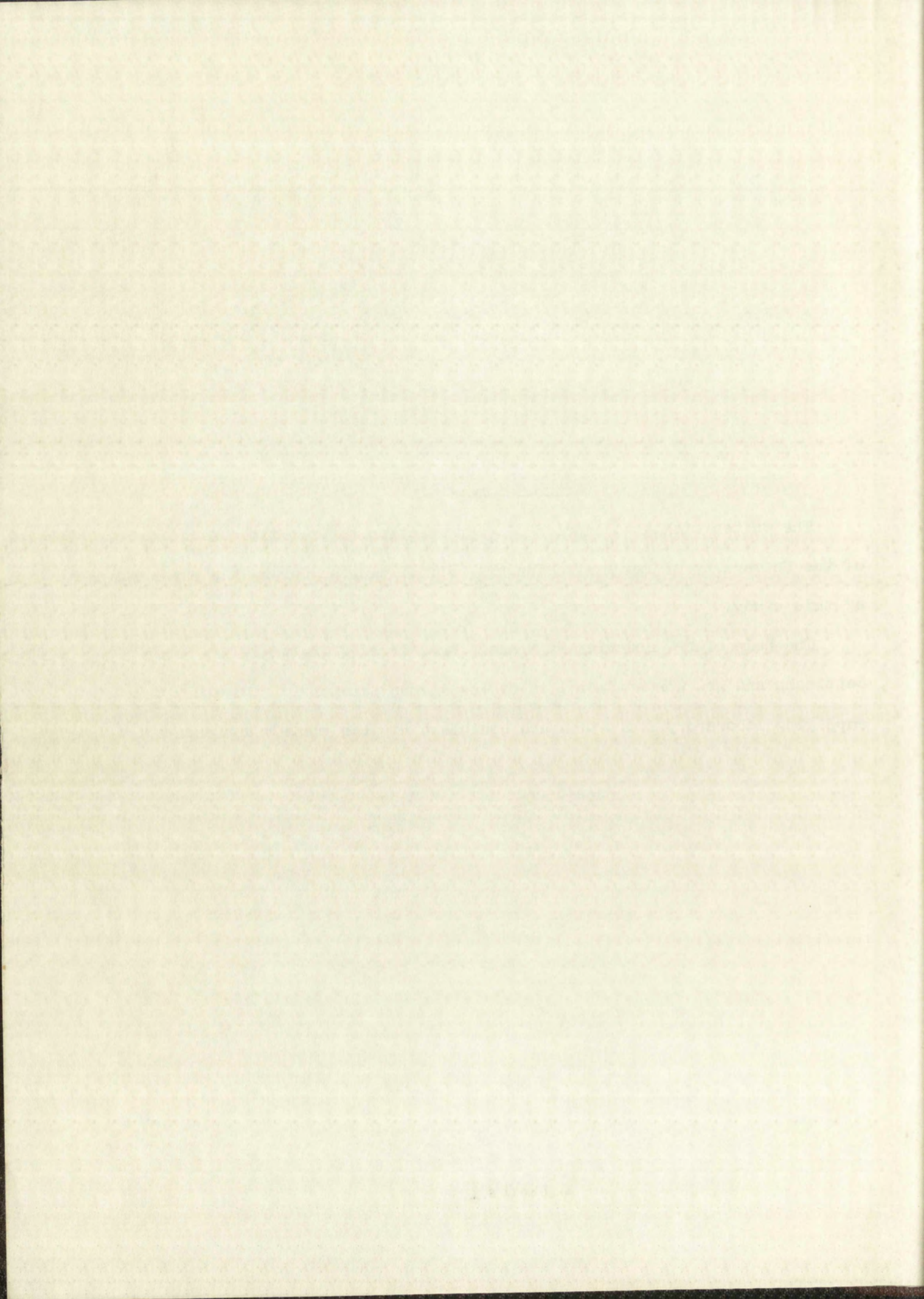


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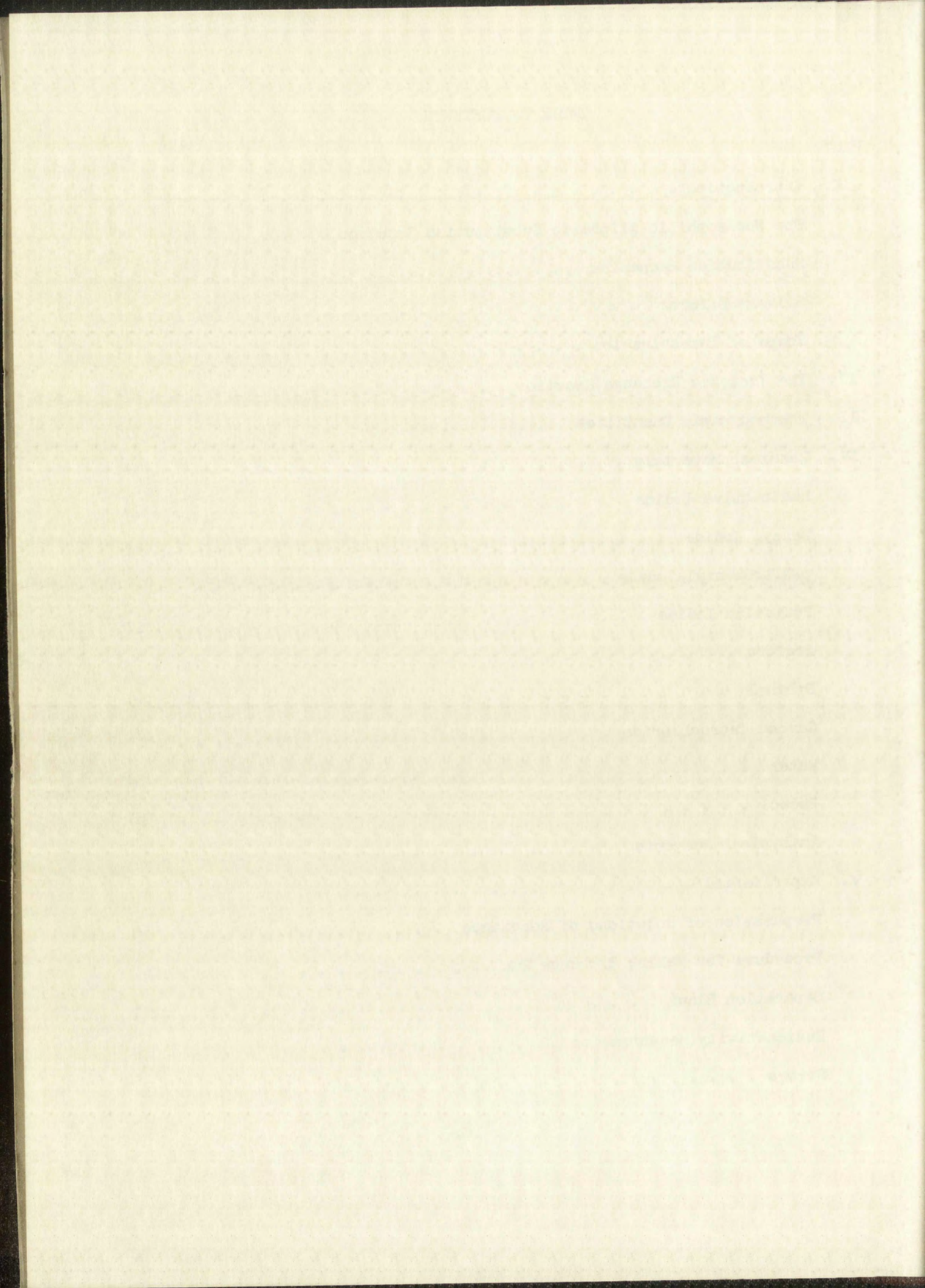
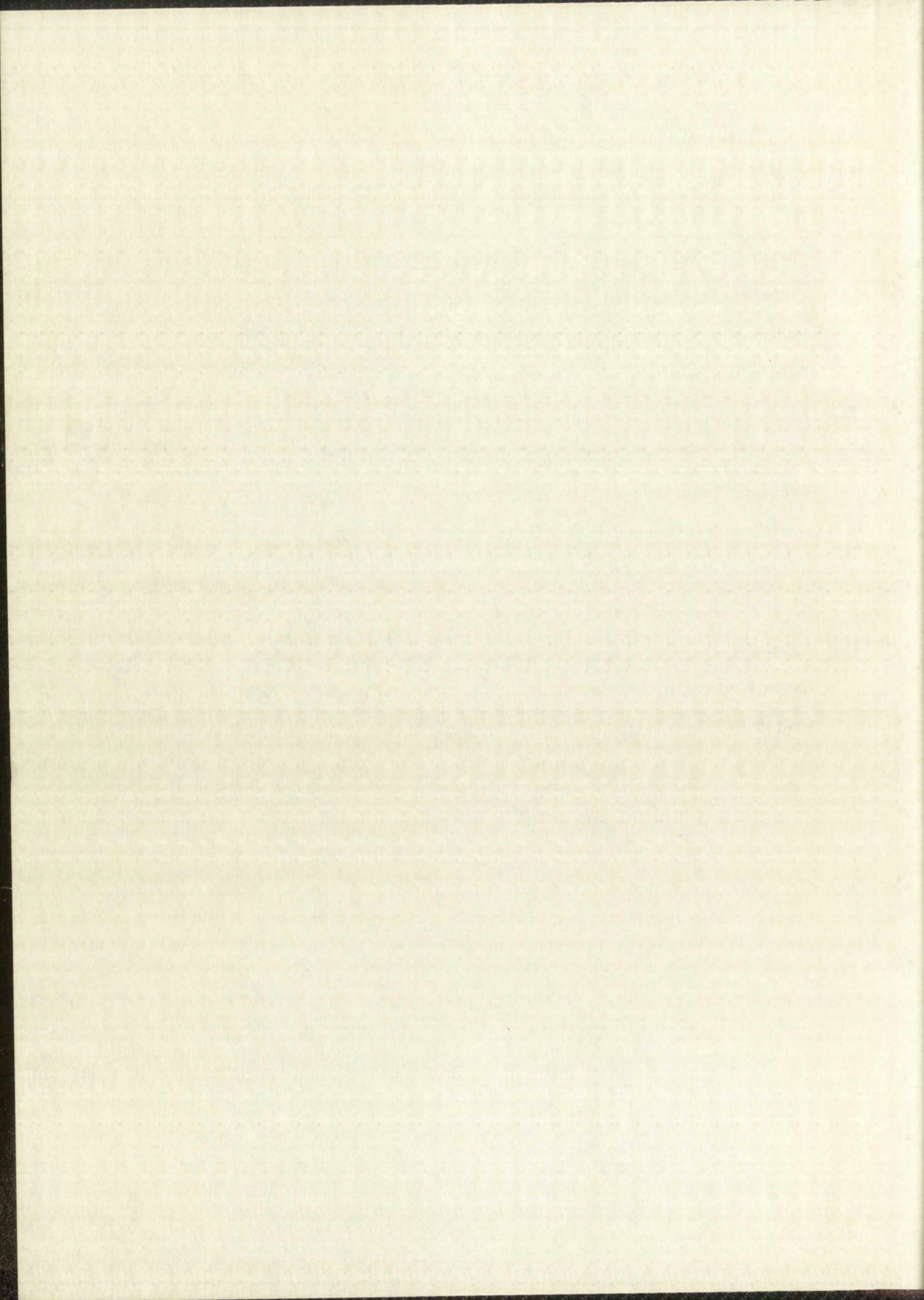


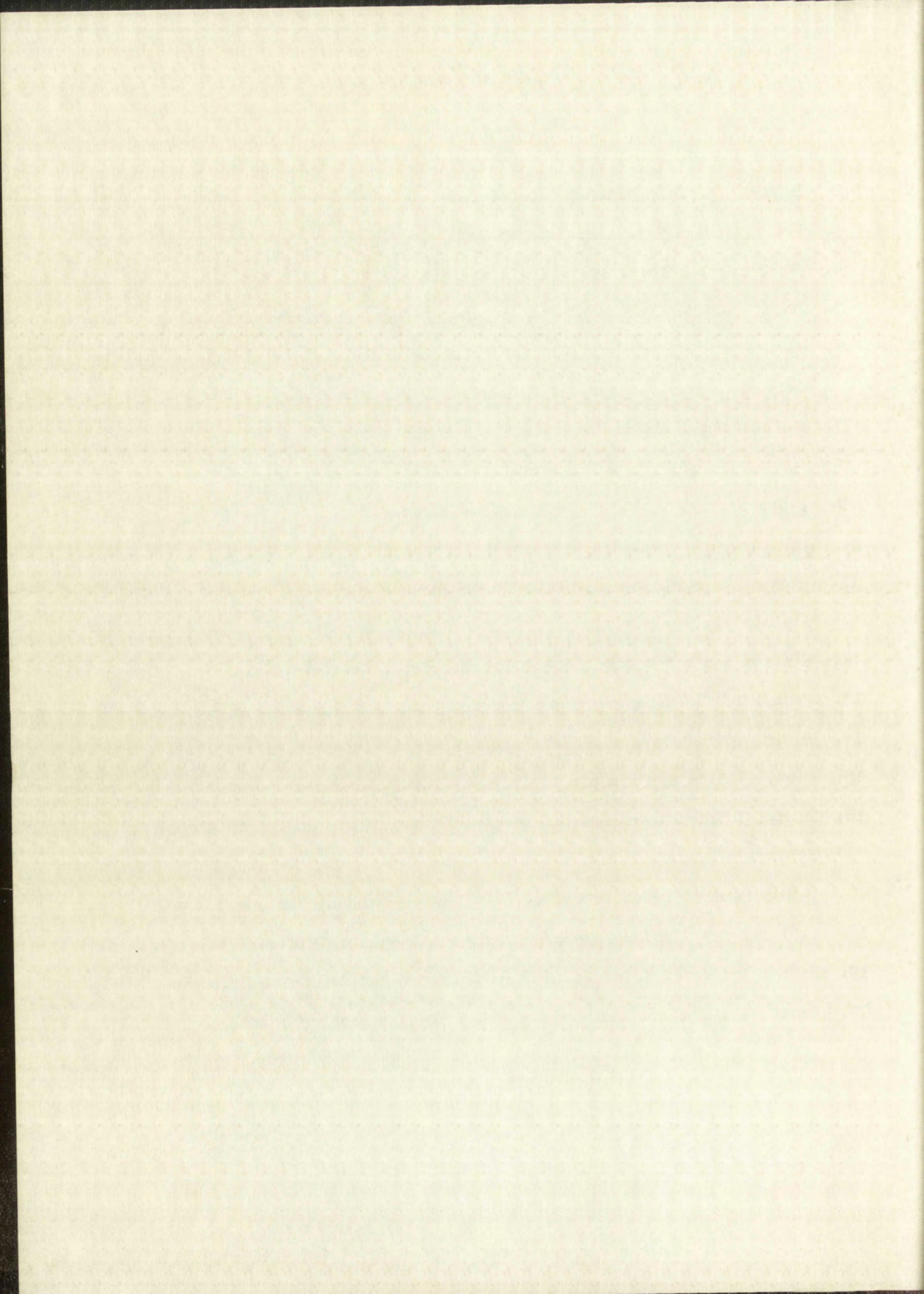
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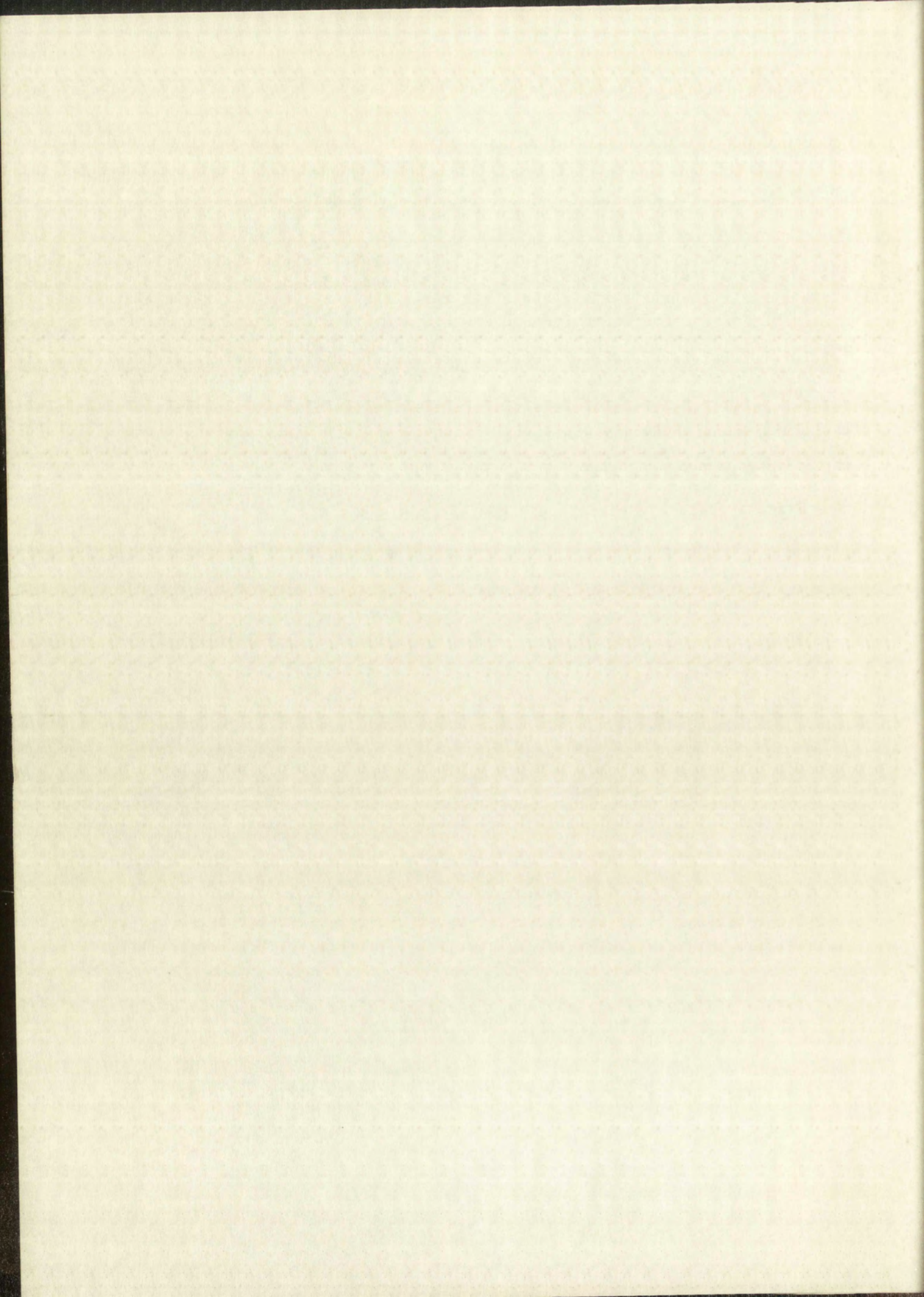
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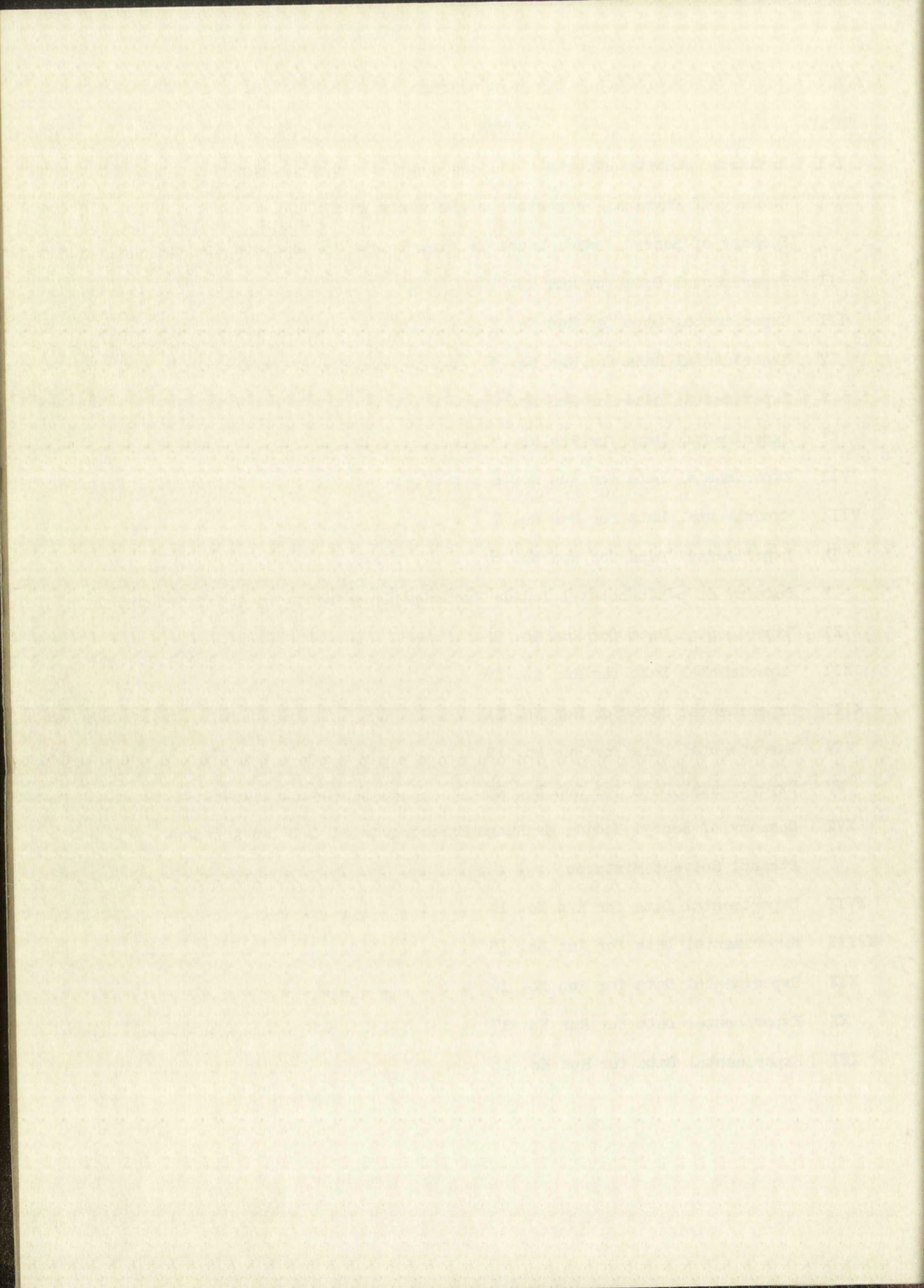
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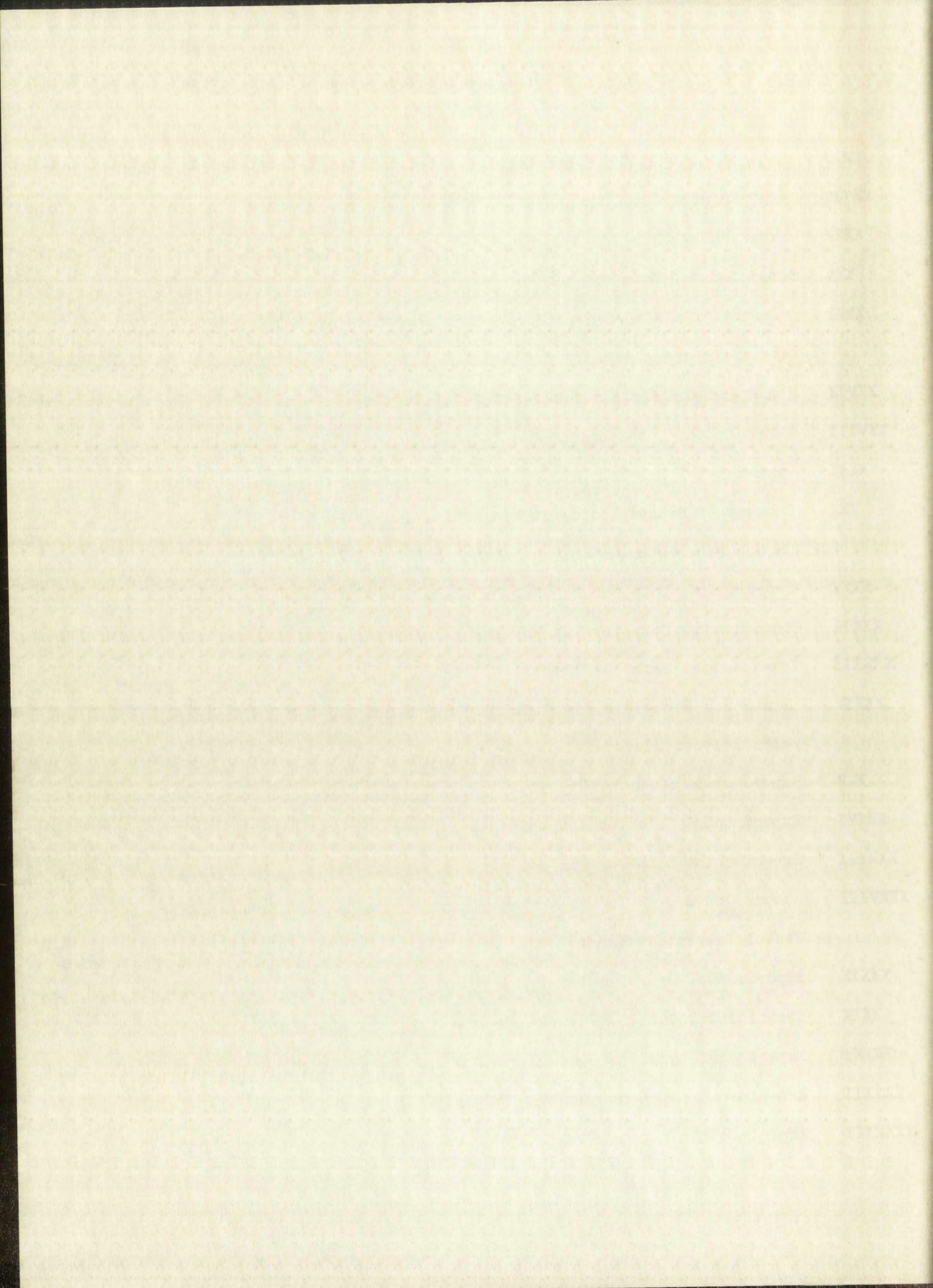
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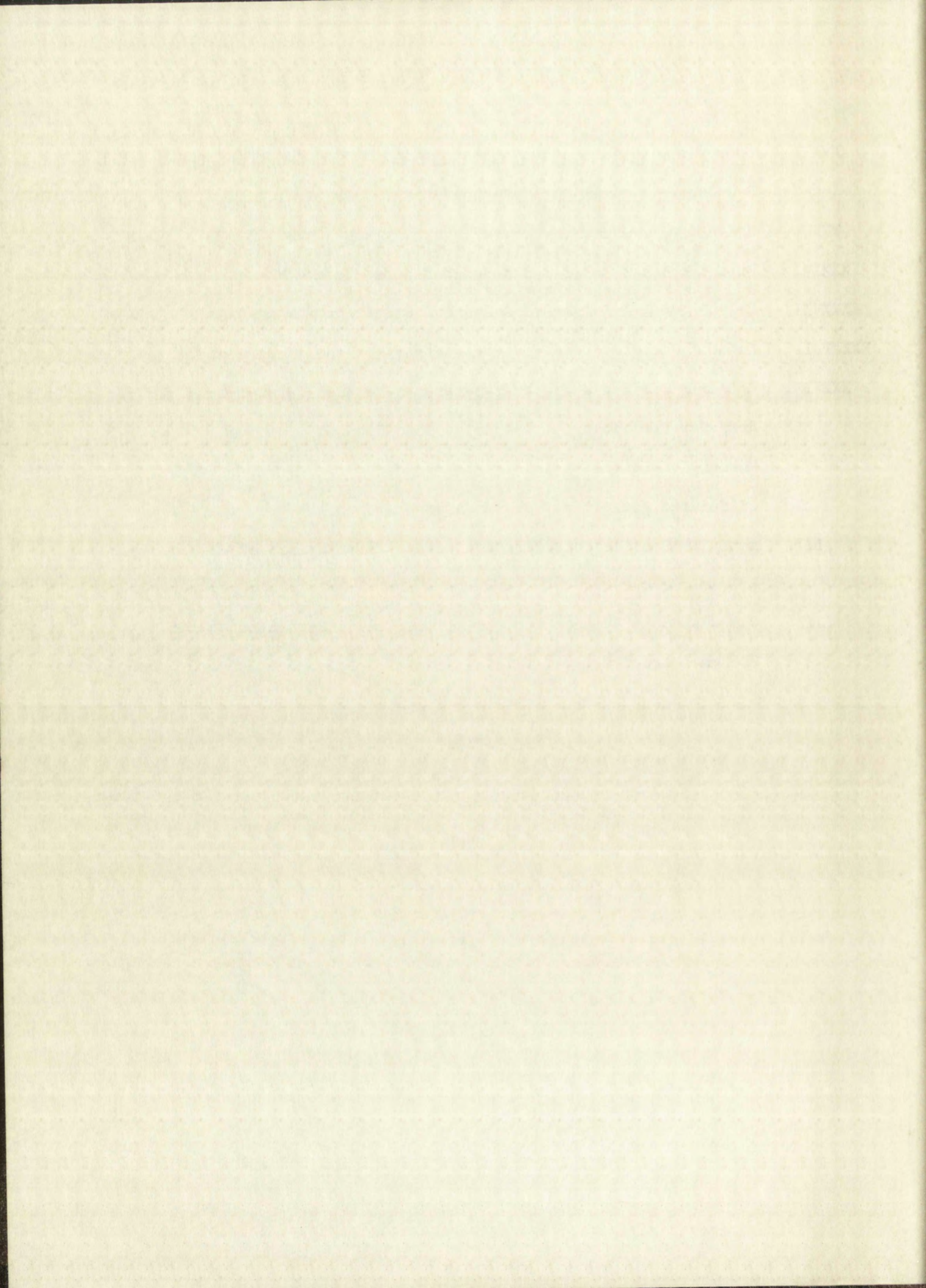
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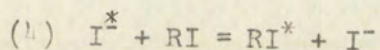
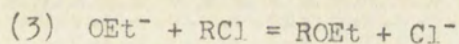
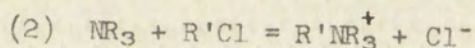
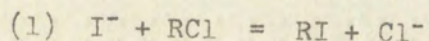
Part I

Introduction

The nucleophilic aliphatic substitution reaction. -

The kinetics of nucleophilic aliphatic substitution reactions has been studied by numerous investigators during the past fifteen years. Included in this type of reaction are well-known general reactions such as (1) the Finkelstein reaction, (2) the Menschutkin reaction, (3) the alcoholysis of alkyl halides, and (4) various isotopic exchange reactions.

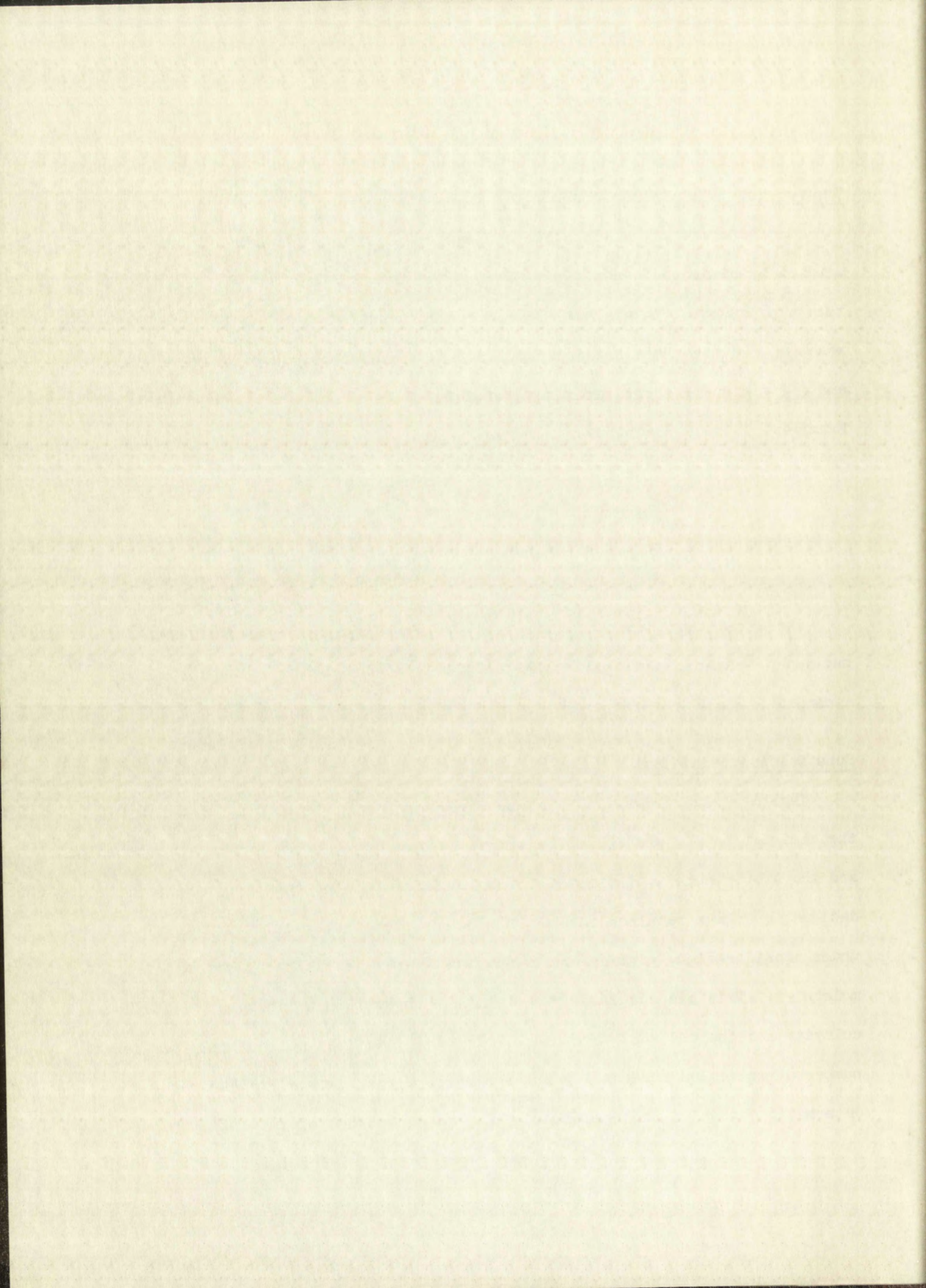
Examples of these reactions are respectively:



These reactions are all characterized by an electron transfer from a nucleophilic agent (such as I^- , NR_3 and OEt^-) to the center of substitution, accompanied by a transfer from this center to the expelled group.

Substitution mechanism. -

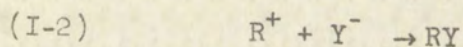
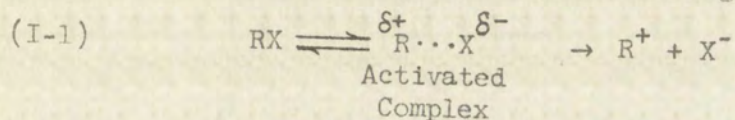
Ingold⁽¹⁾ has classified nucleophilic substitution reactions by means of the designation $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$. The symbol S_{N} stands for substitution, nucleophilic, and the Arabic numeral indicates the molecularity of the reaction. These designations have resulted in some confusion about the exact nature of the reactions under consideration, particularly in regard to participation by the solvent molecules. This has resulted from a failure to distinguish between the molecularity and the order of a reaction. Ingold⁽²⁾ defines molecularity as "the number of molecules necessarily undergoing covalency change" in the rate-determining stage of the reaction. Thus the solvating molecules that participate



by means of electrostatic interactions with reactants are not included in the rate expression.

While it is true that all reactions in polar solvents are indeed poly-molecular, the S_N1 and S_N2 designations permit classification of analogous reactions into similar mechanistic categories.

The S_N1 mechanism is considered to be a two-step process in which the rate-determining ionization step is followed by a rapid combination of the resulting carbonium ion with the substituting agent:



The rate equation that is consistent with the S_N1 mechanism is

$$(I-3) \quad R = k_1 (RX)$$

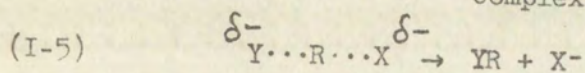
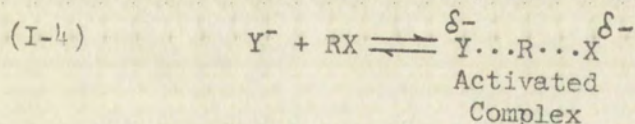
where

R = the reaction rate

k_1 = first-order rate constant

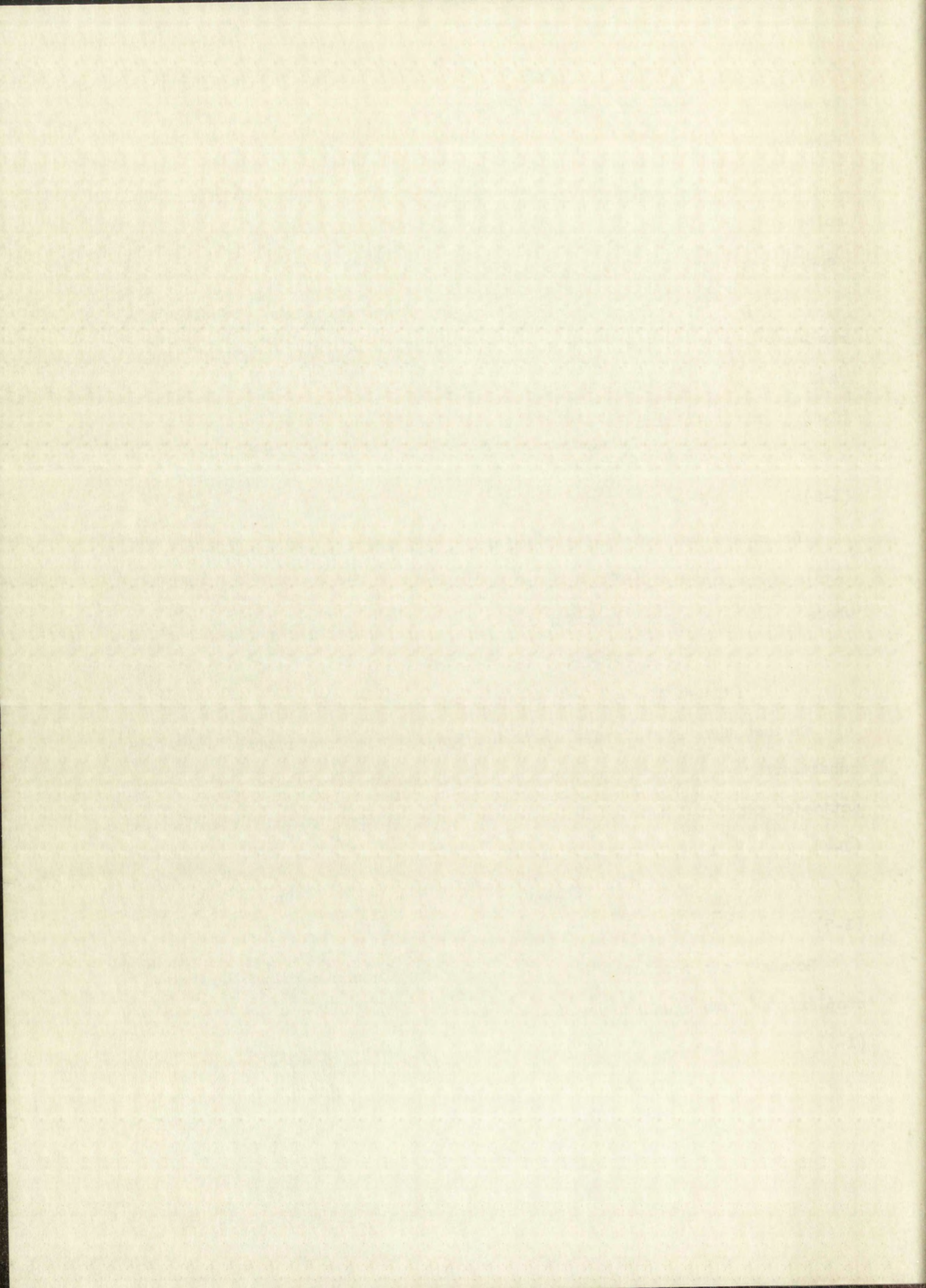
(RX) = the concentration of reactant RX

On the other hand the S_N2 mechanism is a synchronous process wherein the substituting agent combines with the compound being substituted to form an activated complex, followed by the elimination of the displaced group or ion:



Because both reactants are involved in the formation of the activated complex, the rate equation is bimolecular and

$$(I-6) \quad R = k_2 (RX) (Y^-)$$



where k_2 = second order rate constant

(Y^-) = the concentration of substituting agent

By showing that the rates of racemization of 2-iodooctane, ^(3a)

∞ - phenylethyl bromide, ^(3b) and ∞ -bromopropionic acid ^(3c) were

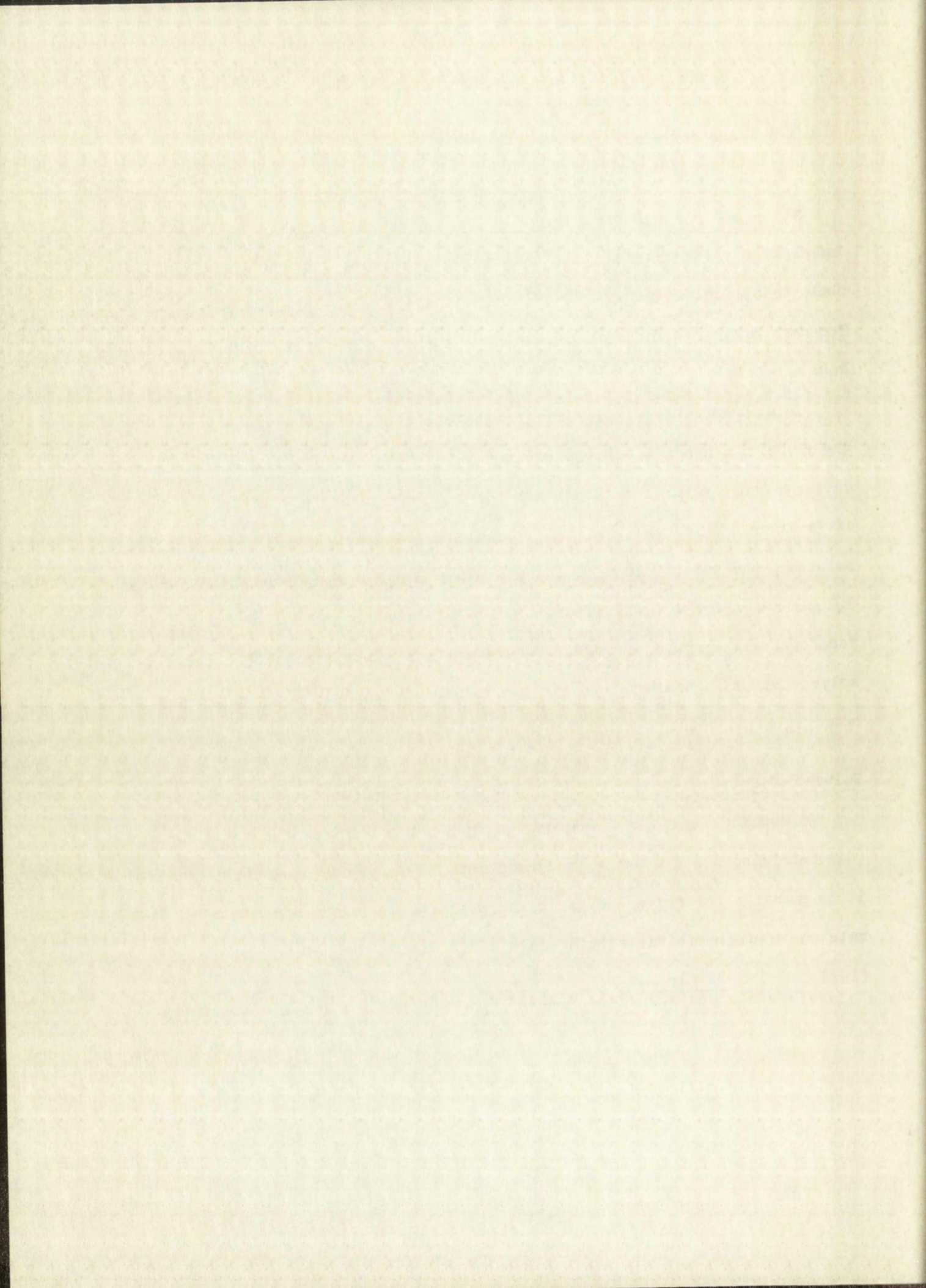
identical with the rates of halide isotopic exchange, it has been demonstrated that the S_N2 mechanism is a "back-side" attack on the tetrahedral carbon atom. The most favorable angle of approach is 180° from the existing carbon-to-halide bond direction.

In a given solvent the inductive effect on electron release will control the reaction mechanism in most instances. ^(4a) Because the S_N1 mechanism depends on the release of an electron by the seat of substitution to the expelled group, it is favored in cases involving a more polar reactant. In aqueous ethanol solution, the substitution of alkyl bromides has been observed to follow the S_N2 mechanism for methyl and ethyl, with a change to the S_N1 mechanism when isopropyl and tertiary butyl bromides were being substituted. By altering the solvent medium, isopropyl bromide can be made to follow either mechanism, or a combination of both. ⁽⁵⁾

Solvent effects. -

By considering the differences in free energy between reactants in a vacuum (dielectric constant = unity) and reactants in solution (dielectric constant = D), it is possible to derive the following expression for the dependence of the specific rate constant on the dielectric constant of the medium for an ion-molecule reaction: ^(6a)

$$(I-7) \quad \frac{d}{d\left(\frac{1}{D}\right)} (\ln k) = \frac{\epsilon^2 z_A^2}{2kT} \left(\frac{1}{r_A} - \frac{1}{r_{\ddagger}} \right)$$



where ϵ = unit charge
 Z_A = charge on the ion A
 \bar{k} = the Boltzman constant
 T = the absolute temperature
 r_A = radius of the ion A
 r_+ = radius of the activated complex

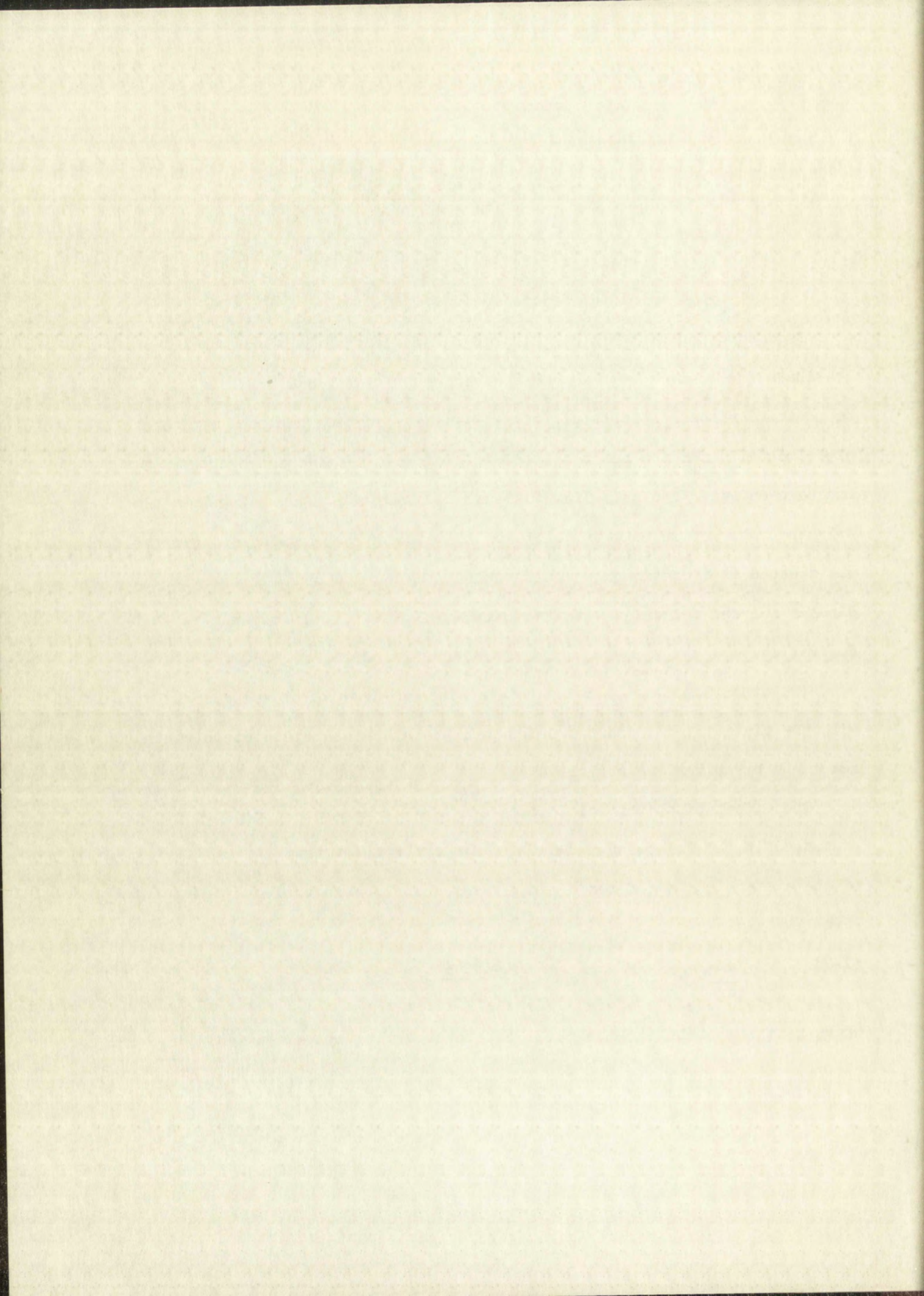
From equation (I-7) it can be seen that a plot of $\ln k$ against $1/D$ should be linear for a given reaction at a given temperature, and that the slope should be positive since r_+ is larger than r_A . This equation has been verified experimentally for the reaction between isopropyl bromide and hydroxyl ions⁽⁷⁾, and between water and sulfonium cations⁽⁸⁾. However, in deriving equation (I-7) only the interaction between reactants in solution was considered. The solvent was treated as a continuum of uniform dielectric constant. Interaction of dipolar solvent molecules with the reactants has not been included in the derivation.

Two other important effects on the rate constant which are closely associated with the dielectric constant are ion-pair formation and specific solvation of the reactants by solvent molecules.

The effect of solvent dielectric constant on ion-pair formation can be evaluated in the following manner.⁽⁹⁾ It can be shown that the radial distribution of the average number of ions, dn_2 , which are close to an ion of charge $Z_1\epsilon$ is given by

$$(I-8) \quad \frac{dn_2}{dr} = 4\pi n_2 r^2 e^{-\frac{Z_1 Z_2 \epsilon^2}{DrkT}}$$

where r is the radial distance. If Z_1 and Z_2 are of opposite sign, $\frac{dn_2}{dr}$ has a



minimum value at

$$(I-9) \quad r_{\min.} = \frac{Z_1 Z_2 e^2}{2 D k T}$$

This minimum value is referred to as the Bjerrum distance, and it is arbitrarily assumed that ions inside of a sphere of radius $r_{\min.}$ are associated, while those ions that are outside are free.

It can be seen from equation (I-9) that at a given temperature the formation of ion-pairs is increased by increasing the magnitudes of Z_1 or Z_2 , or by decreasing the dielectric constant. If the dielectric constant is sufficiently large, $r_{\min.}$ becomes smaller than the distance of closest approach and there and there is no available volume within which ion-pairs can form.

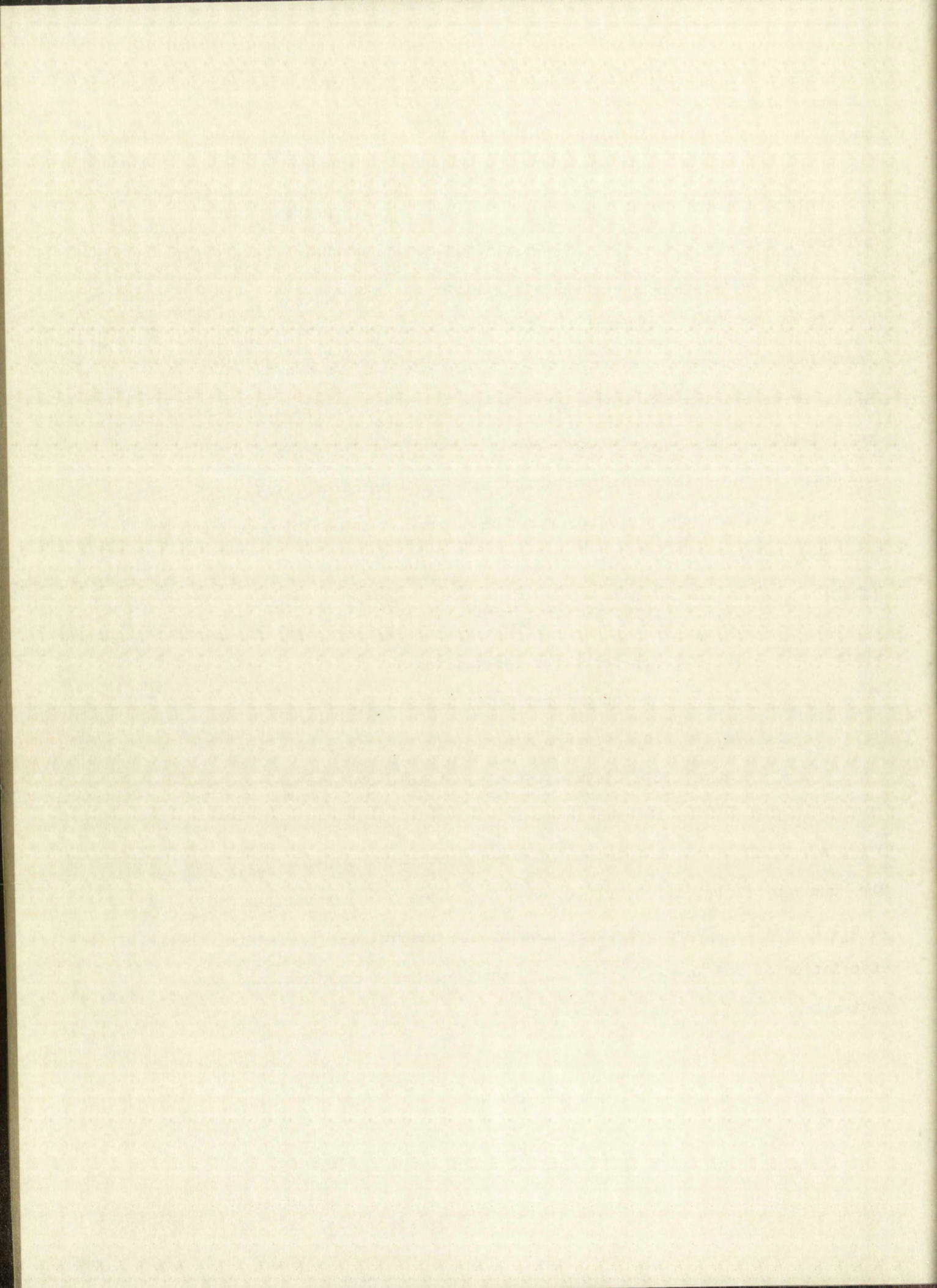
For a uni-univalent electrolyte, the degree of association of ions is also proportional to the concentration:

$$(I-10) \quad \alpha = \frac{4 \pi C A}{1000} \left(\frac{e}{D k T} \right)^3 \bar{\Phi}(r, a_i, D, T)$$

Where α = the degree of association
 C = the concentration of electrolyte
 A = the Avogadro number
 a_i = the distance of closest approach of the two oppositely-charged ions

$\bar{\Phi}(r, a_i, D, T)$ = a function of the indicated variables.

The function $\bar{\Phi}(r, a_i, D, T)$ has been evaluated ⁽¹⁰⁾ for various values of r , a_i , D , and T . Therefore it is possible to compute the theoretical degree of association if one knows the ion size, the dielectric constant, and the concentration.



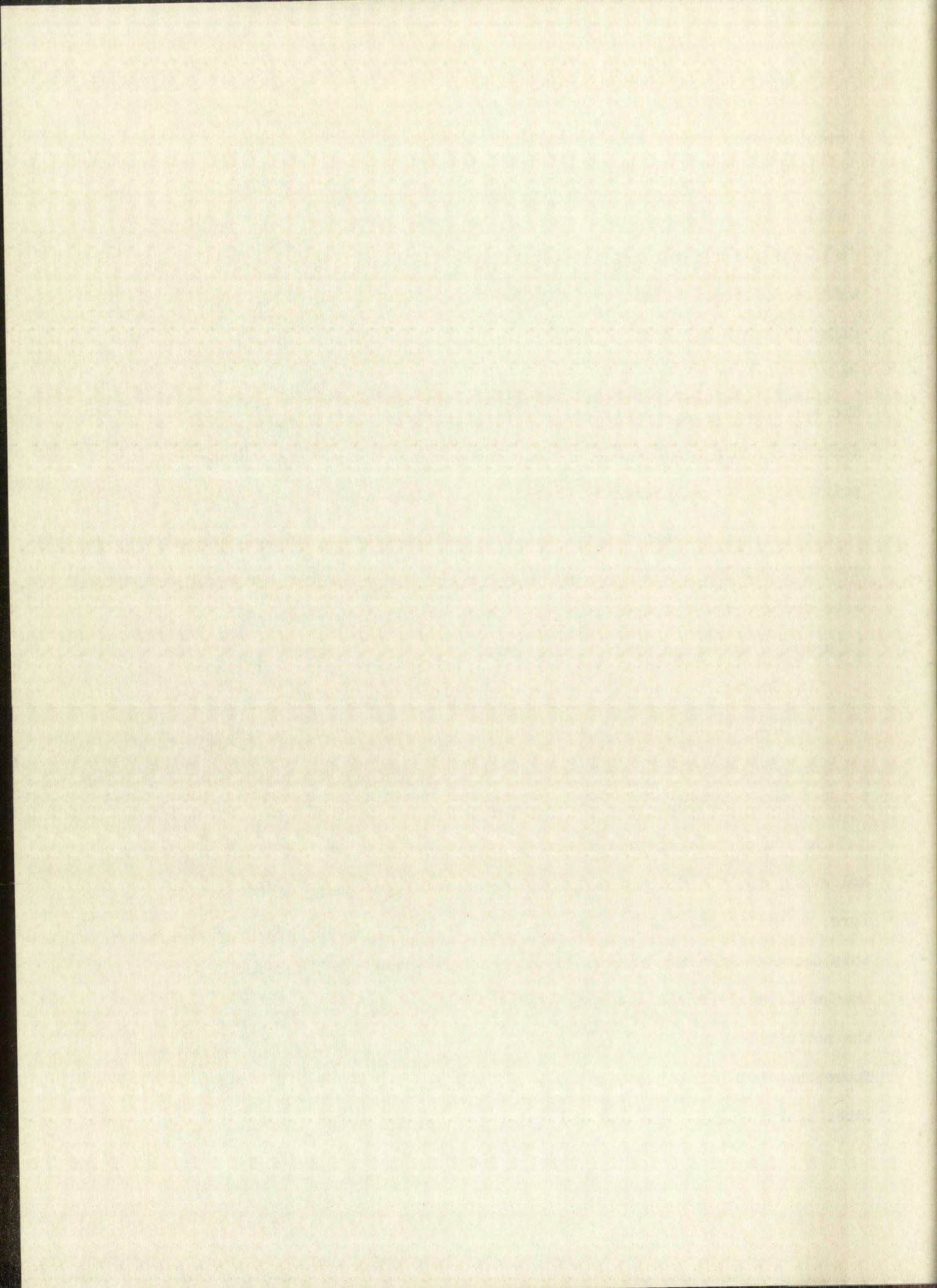
Experimentally this effect has been observed in the measurement of the conductance of tetraisoamylammonium nitrate in dioxane-water mixtures.⁽¹¹⁾

In the S_N2 isotopic exchange reaction between alkali halides and organic halides, it has been demonstrated⁽¹²⁾ that the iodide ion from the inorganic salt is the nucleophilic agent, rather than the ion pair. Thus ion-pair formation will decrease the second-order specific rate constant by decreasing the effective substituent concentration. This effect has been observed⁽¹³⁾ in the exchange reaction between p-nitrobenzyl bromide and chloride ion in dioxane-water mixtures. The specific rate constant for this reaction at first increases with $1/D$ in accordance with equation (I-7), then decreases as D is further reduced to the point where ion-pair formation becomes significant.

The effect of specific solvation on the rate constant can be predicted qualitatively by considering the degree of solvation of the reactants as compared with that of the activated complex. Three reasonable assumptions are necessary in order to make such predictions:

1. Solvation increases with the magnitude of the charge of the species.
2. Solvation decreases with increasing dispersal of a given charge.
3. The decrease of solvation due to the dispersal of a charge will be less than that due to charge destruction.

An ion or polar molecule in a polar solvent orients and attracts solvent molecules, thereby doing work at the expense of the energy of the system. Therefore, solvation results in a decrease in the energy of a reacting species, and this decrease directly affects the activation energy of the reaction. If the charge on the activated complex is more dispersed than the charge on the reactants, the activated complex will be solvated to a lesser extent in a polar solvent. Therefore, increasing solvent polarity will decrease the reaction rate. On the other hand if a polar activated complex is formed from less polar reactants,



increasing solvent polarity greatly increases the reaction rate. The nucleophilic substitution reactions can be classified according to charge-type, and the expected solvent effects shown in Table (I-1) have been predicted. ^(4b)

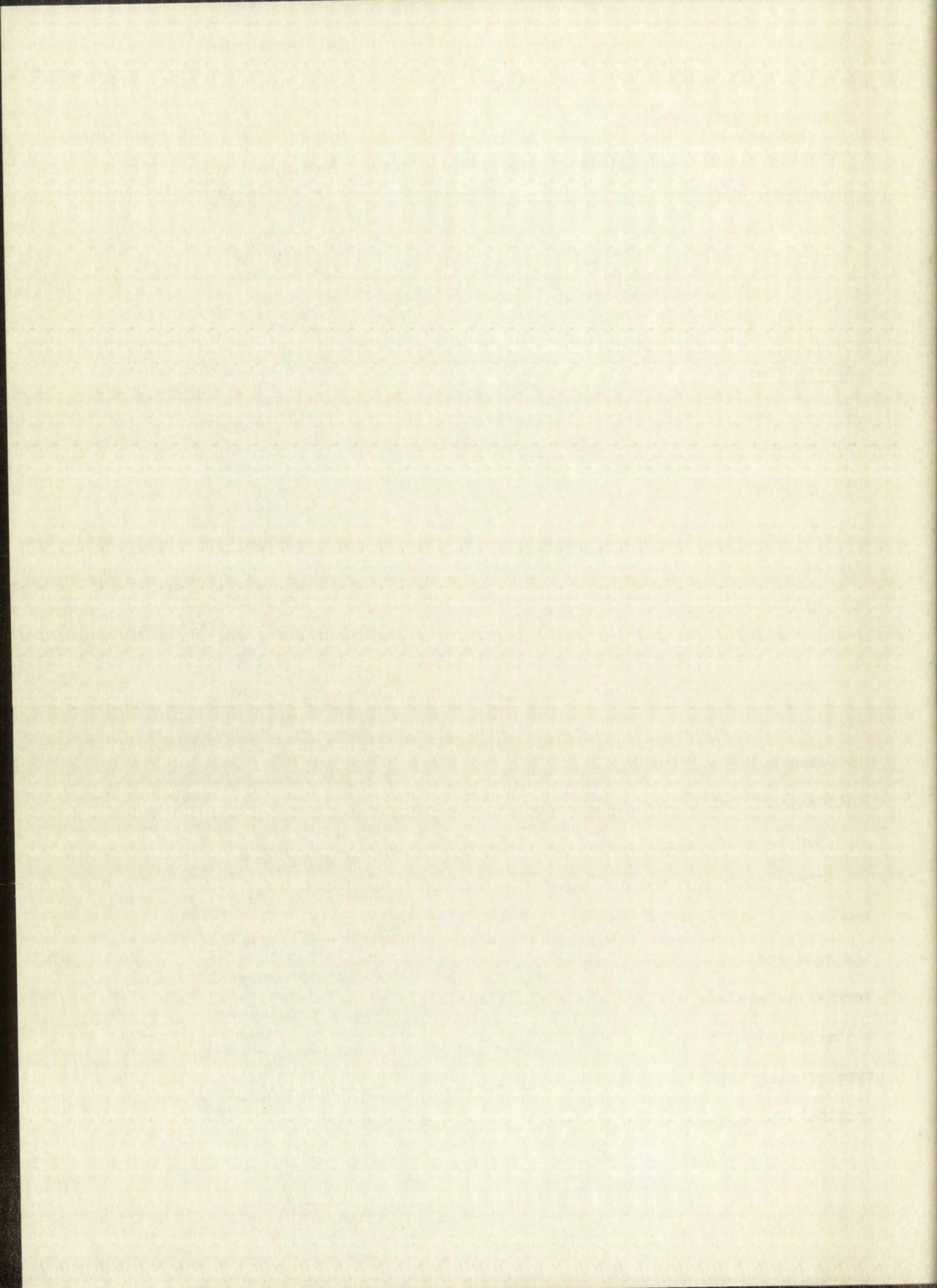
TABLE (I-1)
Predicted Solvent Effects

Reactant Charge type	Transition state charge disposition	Effect of increased polarity on rate
1) $Y^- + RX$	$\delta^-_{Y \cdots R \cdots X} \delta^-$	small decrease
2) $Y + RX$	$\delta^+_{Y \cdots R \cdots X} \delta^-$	large increase
3) $Y^- + RX^+$	$\delta^-_{Y \cdots R \cdots X} \delta^+$	large decrease
4) $Y + RX^+$	$\delta^+_{Y \cdots R \cdots X} \delta^+$	small decrease
5) RX	$\delta^+_{R \cdots X} \delta^-$	large increase
6) RX^+	$\delta^+_{R \cdots X} \delta^+$	small decrease

According to Ingold, solvent polarity will increase with increasing dipole moment of the solvent molecules, and will decrease with increased shielding of the dipole charges. For increasing the rate of the Menschutkin reaction, the following solvent order has been found experimentally:

Methanol > Ethanol > Acetone > Benzene > Cyclohexane

The relative values of "small" or "large" effects predicted in Table (I-1) are not clearly defined. For example, in the hydrolysis of isopropyl bromide the rate constant is decreased 50 per cent by increasing the water in ethanol from zero to 40 per cent by volume. This is truly a small effect, as predicted for a charge type (1) reaction in Table (I-1). On the other hand, for this same type of reaction (the isotopic exchange reaction between bromide ion and n-butyl bromide), LeRoux and Sugden found that increasing the water in acetone from zero



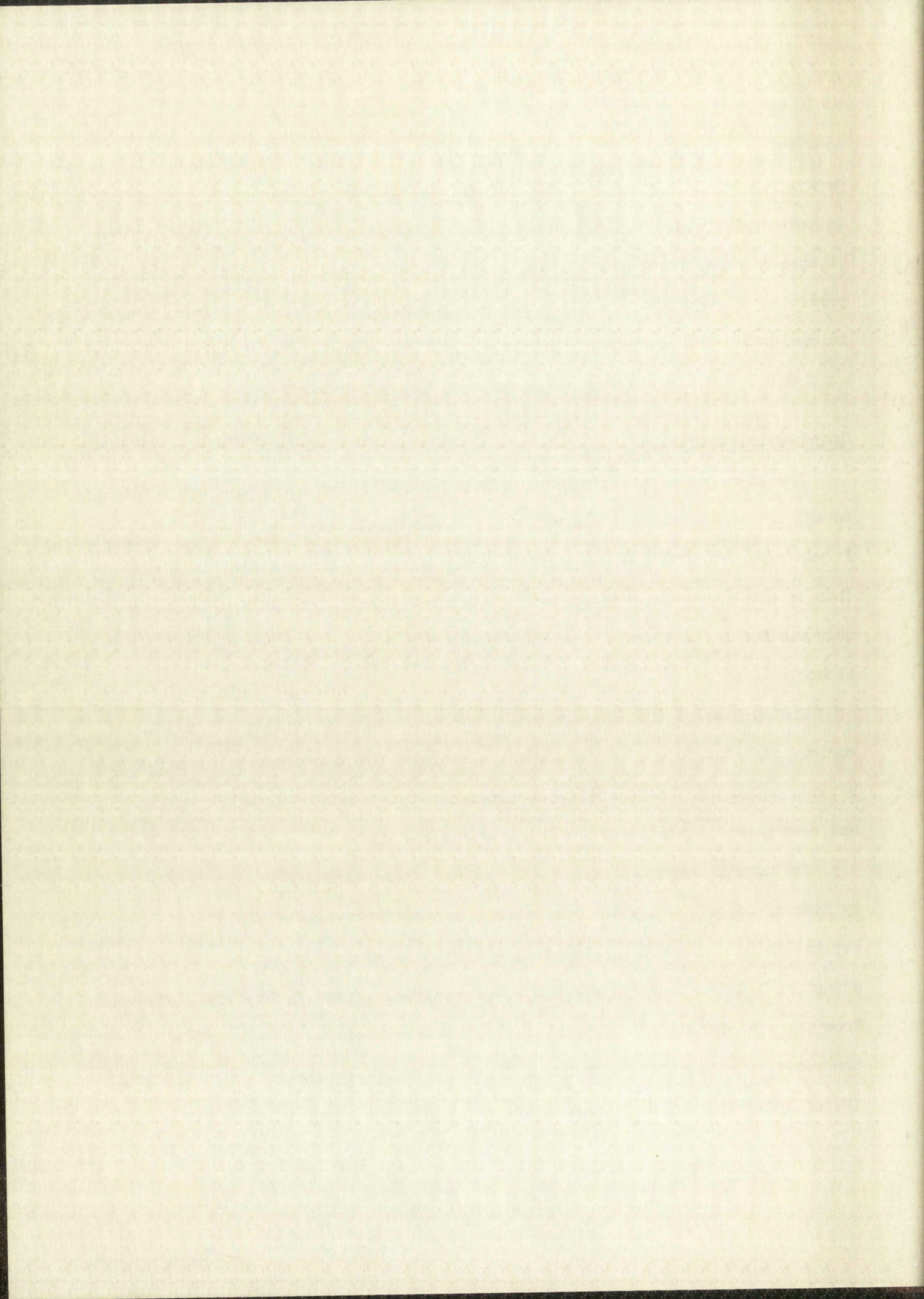
to 10 per cent by volume resulted in a twenty-fold decrease in the rate constant.⁽¹⁴⁾ In the S_N2 isotopic exchange reaction between iodide ion and benzyl iodide, Stillson⁽¹⁵⁾ has reported that changing from the solvent ethanol to acetone increased the rate constant by a factor of approximately 700. Thus it appears that the theory of Hughes and Ingold is valuable primarily for predicting the direction of the change in reaction rate with polarity, rather than in predicting the degree of the change. At the present time there is no theory available for predicting the magnitudes of these changes.

Scope of investigation. -

The kinetics of the isotopic exchange reaction between potassium iodide and benzyl iodide in alcoholic solution has been studied thoroughly by Stillson.⁽¹⁵⁾ It was reported that the reaction was much faster in ethanol-acetone mixtures than in absolute ethanol. However, it was not possible to determine whether this was due to acceleration of the reaction by acetone, or to inhibition by ethanol.

The purpose of this investigation was to elucidate further the effect of various solvents on the same exchange reaction. The isotopic exchange reaction between potassium iodide and p-nitrobenzyl iodide was also studied, because it had been investigated in alcoholic solution by Purlee.⁽¹⁶⁾

The results reported here indicate that these exchange reactions are inhibited by hydroxylic solvents which are capable of forming hydrogen bonds. An equilibrium expression for solvation of the iodide ion has been derived by considering the effect of hydrogen bonding between iodide ion and a hydroxylic solvent molecule. From the equilibrium constant, evaluated experimentally, it is possible to predict the reaction rate within experimental error in dilute solutions (up to approximately 1M) of hydroxylic solvent in acetone.

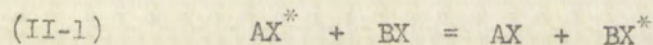


Part II

The Isotopic Exchange Reaction

The isotopic exchange reaction is characterized by the interchange of one isotope of an element between at least two species of the element. For analytical convenience, a radioactive isotope is usually chosen as the indicator of this exchange. Although the difference in mass between two isotopes of a light element is sufficient to cause a difference in chemical behavior, (the "isotope effect") this effect is relatively small for heavy elements. Urey⁽¹⁷⁾ has calculated that the isotope effect between I^{127} and I^{129} is about 0.5 per cent. In most isotopic exchange studies the specific rate constants are accurate to only about 3 per cent. Thus the isotope effect in an iodine exchange will not affect the specific rate constant significantly.

A simple isotopic exchange reaction involving a radioactive species X^* may be written



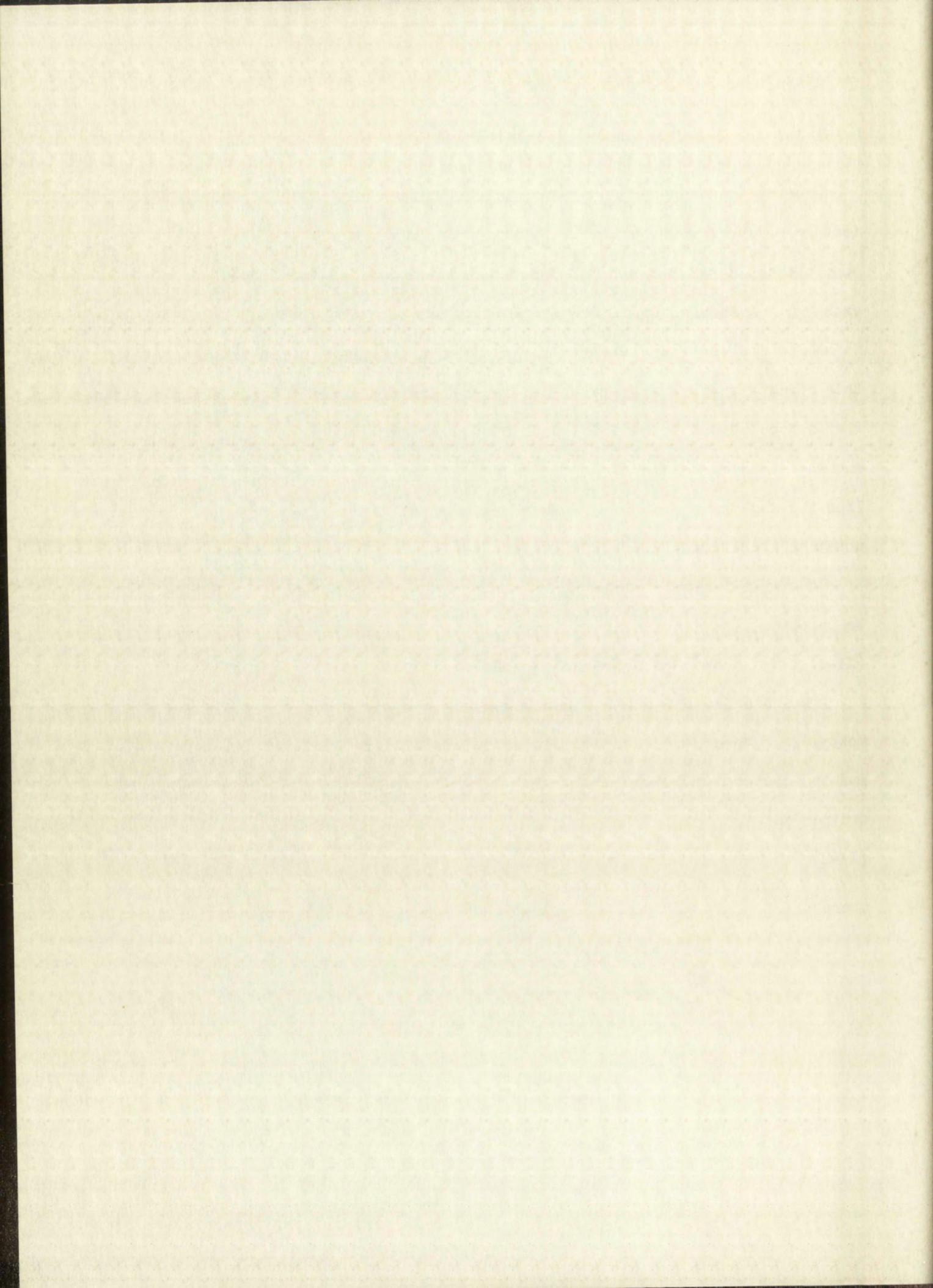
The rate law governing a simple exchange reaction was first derived by McKay.⁽¹⁸⁾ More recent derivations have been made by Duffield and Calvin,⁽¹⁹⁾ and by Prestwood and Meyers.⁽²⁰⁾ The logarithmic form of the exchange law may be written as

$$(II-2) \quad -\ln(1-F) = \frac{a+b}{ab} Rt$$

where

a = total concentration of species AX in gram atoms of X per liter (this includes AX^*)

b = total concentration of species BX in gram atoms of X per liter (this includes BX^*)



R = the constant rate of exchange of X atoms between AX and BX,
in gram-atoms per liter per unit time.

t = time of exchange

F = the fraction exchanged

$(1-F)$ = the fraction not exchanged

The fraction exchanged may be defined in terms of specific activities, i.e.,
the radioactivity per unit mass

$$(II-3) \quad F = \frac{(S_{BX})_t - (S_{BX})_0}{(S_{BX})_{\infty} - (S_{BX})_0}$$

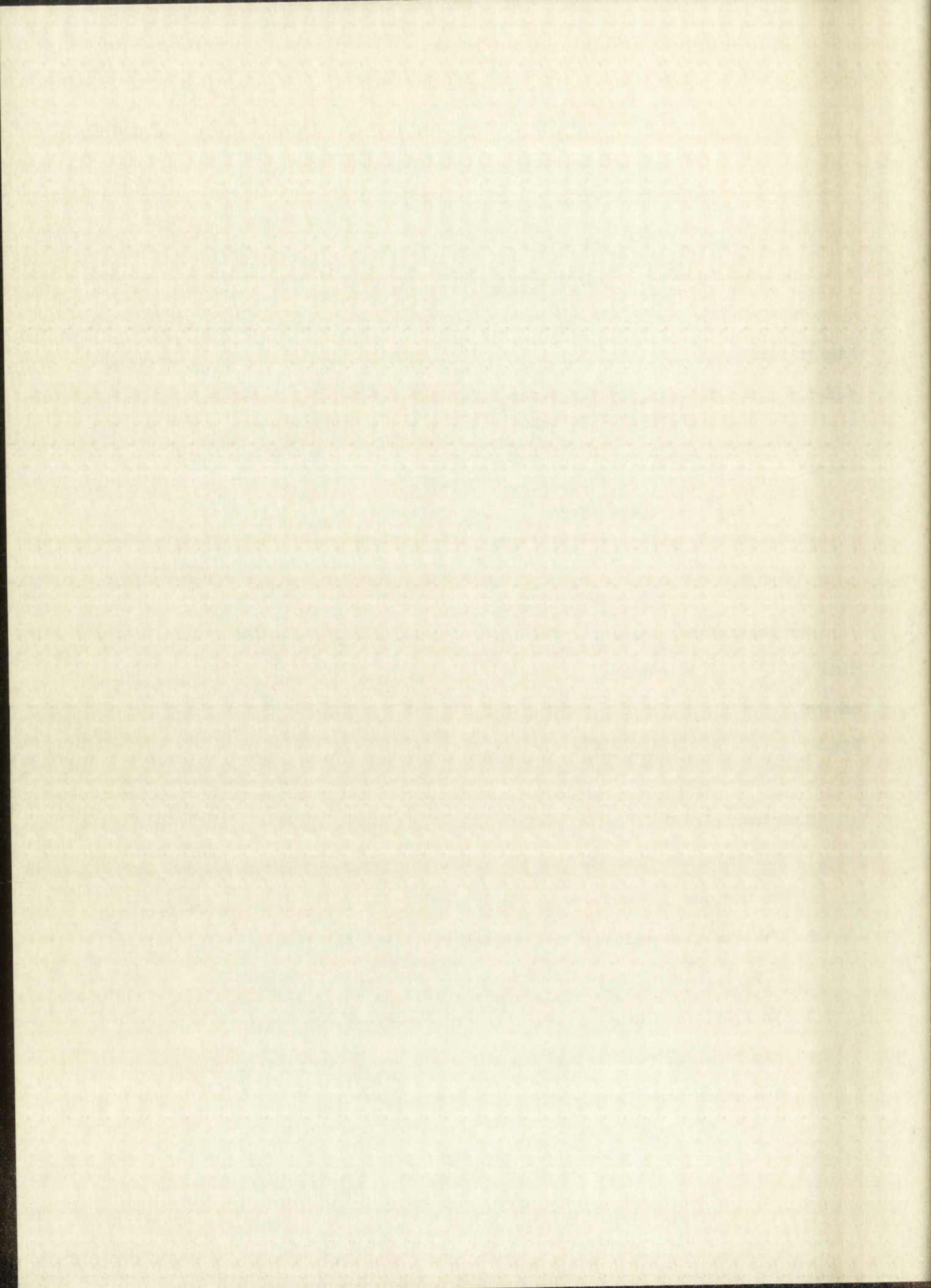
where $(S_{BX})_t$ = the specific activity of BX at time t
 $(S_{BX})_0$ = the specific activity of BX at time $t = 0$
 $(S_{BX})_{\infty}$ = the specific activity of BX when the exchange has gone
to completion.

For convenience the rate of exchange can be expressed in terms of the "half-time", $t_{1/2}$ for the reaction, which is the time when the fraction exchange equals one-half.

$$(II-4) \quad R = \frac{0.693 \text{ ab}}{(a + b)t_{1/2}}$$

Experimentally R is determined in the following manner:

1. Aliquots are removed from the reaction mixture of known composition at various time intervals and AX and BX are chemically separated.
2. The fraction exchange is computed for each time interval from equation (II-3), by counting the radioactivity in each reactant.
3. $\ln(1-F)$ is plotted against t , a straight line is drawn through the experimental points, and the value of $t_{1/2}$ is determined graphically.
4. The value of R is computed from equation (II-4).



The value of the rate of exchange is not directly useful as a criterion of specific reaction rate because it depends on reactant concentrations which vary from experiment to experiment. The rate constant, defined as the rate of exchange when the reactants are at unit activity, is a better criterion for comparison of reaction rates in different media.

In order to determine the rate constant it is necessary to consider the reaction mechanisms discussed in Part I. If the reaction is of the S_N1 type,

$$(II-5) \quad R = k_1(a)$$

where k_1 is the unimolecular specific rate constant.

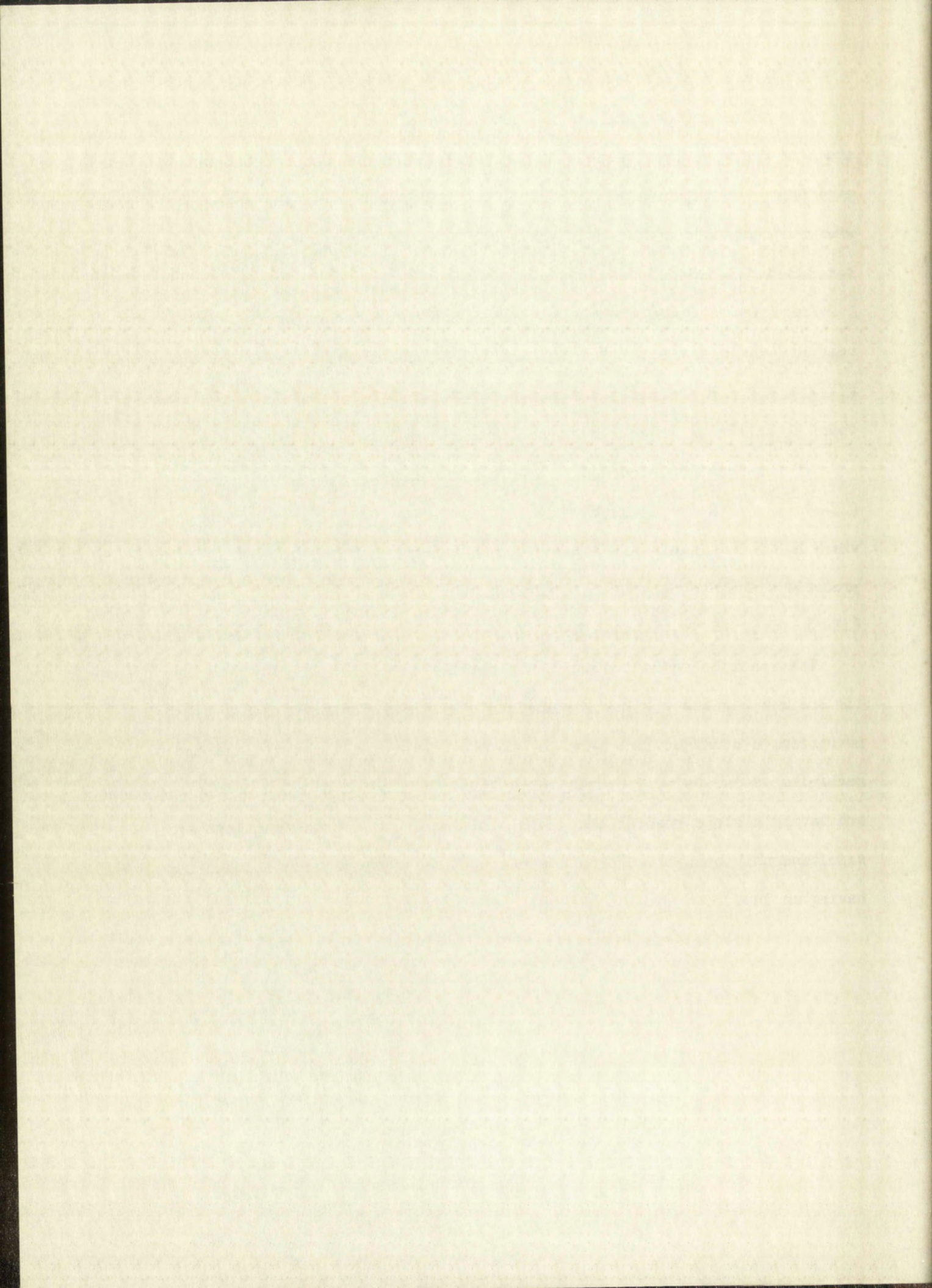
If the reaction proceeds by the S_N2 mechanism

$$(II-6) \quad R = k_2(a)(b)$$

where k_2 is the bimolecular specific rate constant. In the case where the reaction proceeds simultaneously by both mechanisms

$$(II-7) \quad R = k_1(a) + k_2(a)(b)$$

The reaction mechanism can be determined experimentally by plotting $R/(a)$ as the ordinate against (b) as the abscissa. If the reaction proceeds by the S_N1 mechanism, a straight line parallel to the abscissa will result. If the S_N2 mechanism is exclusively operative, a straight line passing through the origin and having a slope greater than zero will result. If both reactions are simultaneously operative, then a straight line of slope greater than zero having an intercept equal to k_2 will be obtained.



Part III

Thermodynamic Quantities

According to transition state theory, in an ideal solution of reactants and activated complex the specific rate constant can be expressed as

$$(III-1) \quad k = e \frac{\bar{k}T}{h} e^{\Delta S^*/R} e^{-E_a/RT}$$

\bar{k} = the Boltzman constant

T = the absolute temperature

h = Planck's constant

ΔS^* = standard entropy of activation

E_a = experimental activation energy

R = universal gas constant

The above equation, derived from the statistical treatment of reaction rates, is comparable to the empirical Arrhenius equation

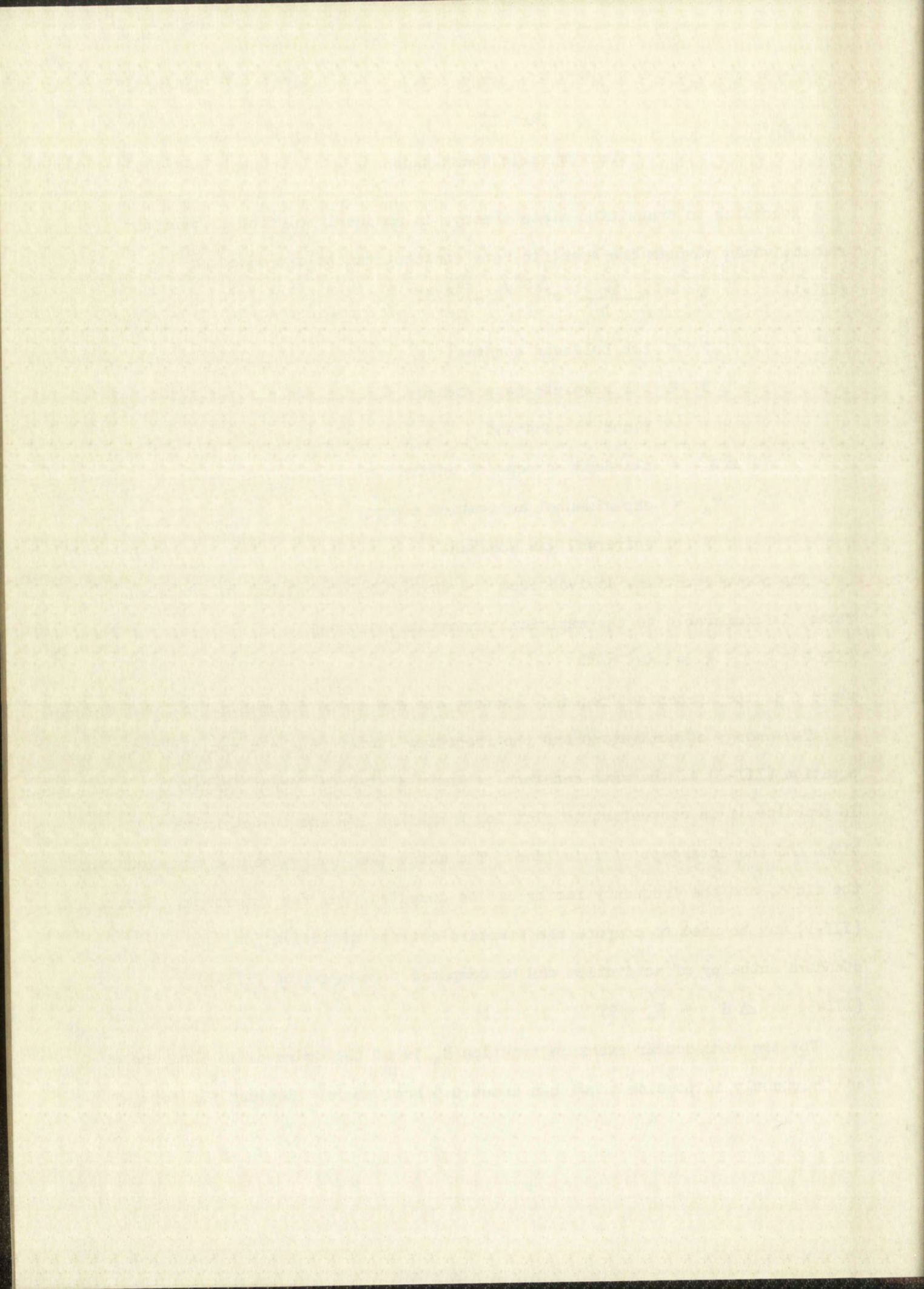
$$(III-2) \quad k = Ae^{-E_a/RT}$$

where A is the Arrhenius frequency factor, assumed to be independent of temperature.

The energy of activation and the frequency factor can be computed from equation (III-2) if the rate constant is known at two different temperatures. In practise it is convenient to plot $\log k$ against $1/T$ and to determine the slope and the intercept of this line. The activation energy can be computed from the slope, and the frequency factor can be computed from the intercept. Equation (III-1) may be used to compute the standard entropy of activation, and the standard enthalpy of activation can be computed from equation (III-3) ⁽²¹⁾

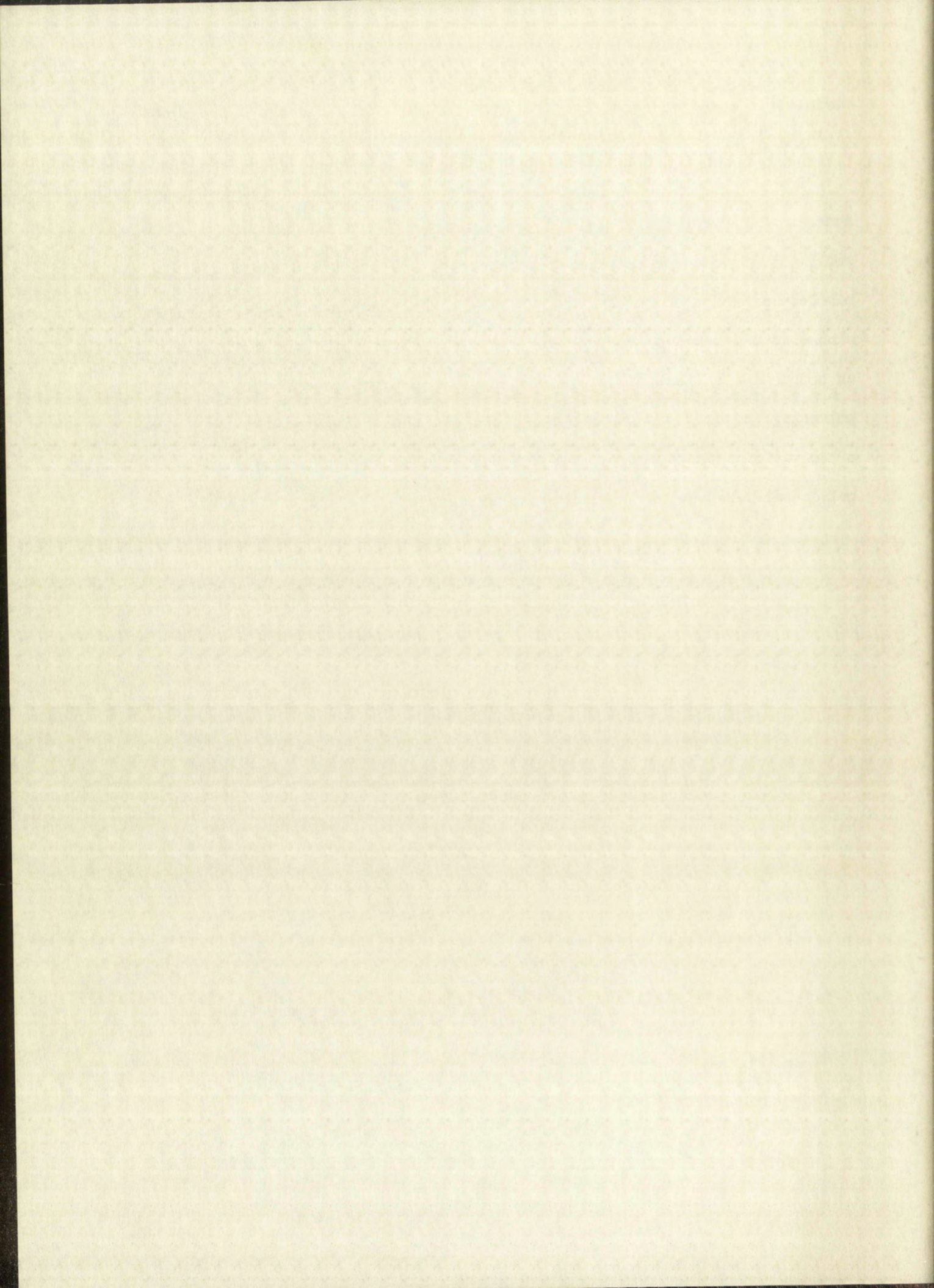
$$(III-3) \quad \Delta H^* = E_a - RT$$

For the bimolecular exchange reaction E_a is of the order of 17 Kcal./mole, and frequently is precise to within about 0.5 Kcal./mole. Because the term RT



normally is equal to about 0.6 Kcal., the usual approximation is to equate ΔH^* and E_a .

Both the standard entropy of activation and the activation energy are of interest in interpreting reaction mechanism in solution. Because relatively small entropy changes occur in the reactants and activated complex in the bimolecular reaction mechanism involving large organic molecules, the entropy change is a measure of changes in degree of solvation of the activated complex as compared with that of the reactants. For a given reaction in different solvents, the differences in entropy reflect the differences in the degree of solvation. On the other hand the differences in activation energies reflect differences in the energy of solvation.



Part IV

Chemical Materials

Radioactive iodine. -

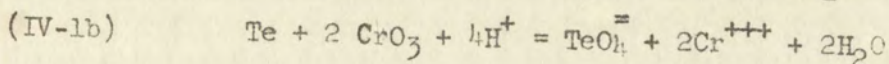
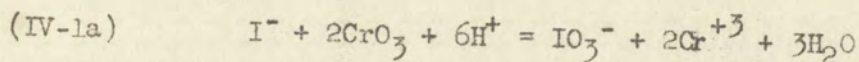
The radioactive tracer used throughout this investigation was eight-day iodine-131, formed by the n, γ reaction of tellurium-130 and subsequent decay of tellurium-131. Iodine-127 and iodine-129 are also formed from tellurium-126 and tellurium-128 by this reaction; iodine-127 is stable and iodine-129 is a long-lived beta emitter. Therefore, practically all of the radioactivity is due to the isotope iodine-131.

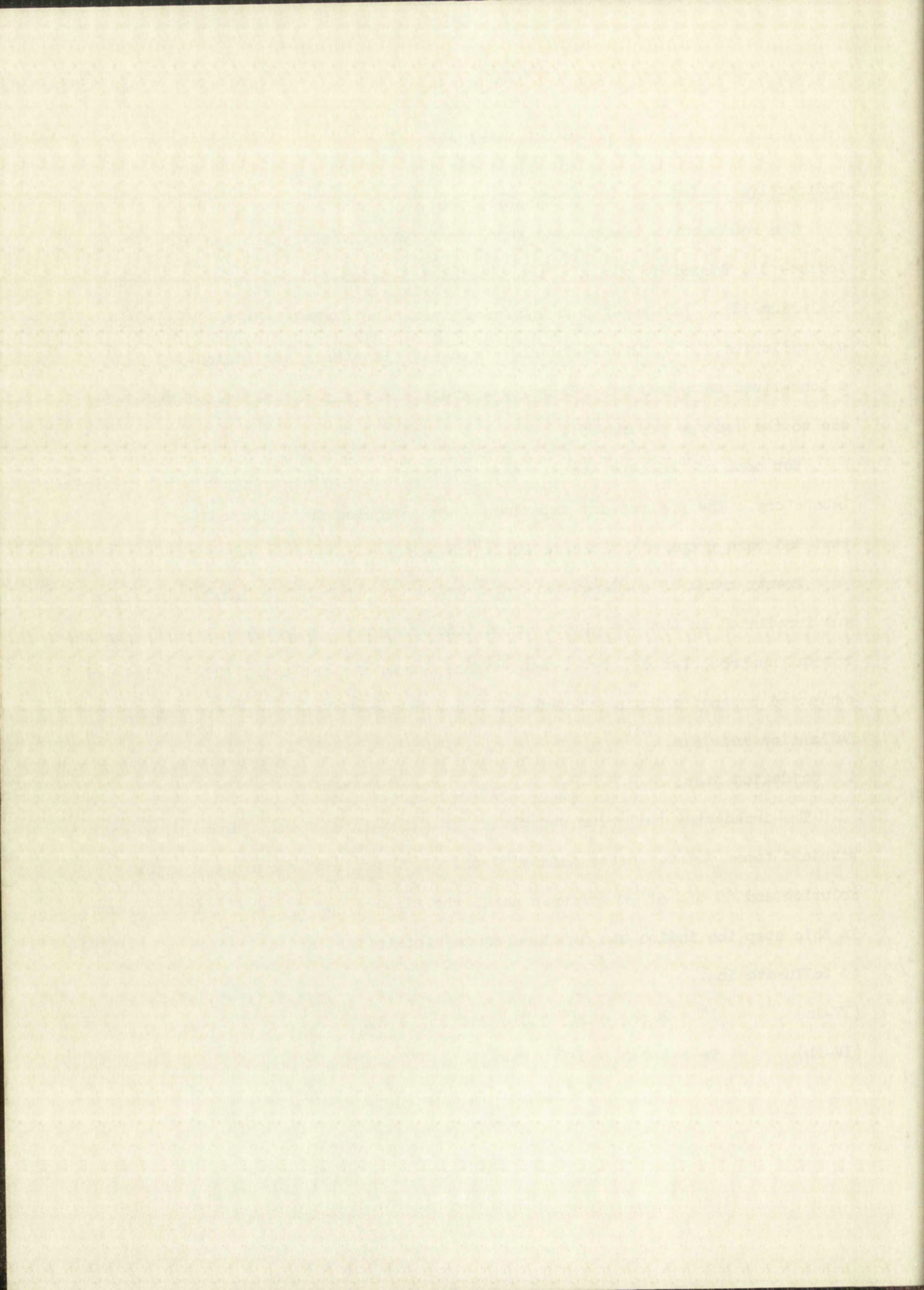
For most of the experiments radiiodine was obtained from Oak Ridge National Laboratory. The preliminary experiments were carried out with iodine tracer that had been prepared by the following method.

Twenty grams of powdered tellurium metal was sealed in a Lucite container and irradiated in the Los Alamos Scientific Laboratory homogeneous reactor in a thermal neutron flux of 10^{11} neutrons/cm²/sec. for ten days. The iodine was extracted by the following procedure, which is a modification of the method of Ballantine and Cohn.⁽²²⁾

1. Oxidation step:

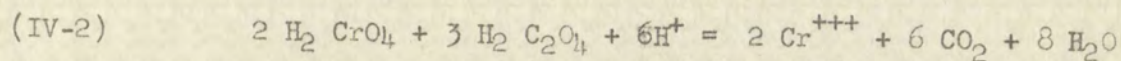
The irradiated tellurium was placed in a two-liter Pyrex flask fitted with a standard taper joint. After adding 52 ml. of 50 per cent chromium trioxide solution and 60 ml. of 9M sulfuric acid, the mixture was refluxed for two hours. In this step the iodine was oxidized to the iodate ion, and tellurium was oxidized to tellurate ion.



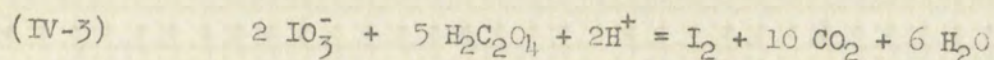


2. Reduction step:

After cooling the acid-dichromate solution, 20 grams of solid oxalic acid dihydrate and 40 ml. of 9M sulfuric acid were added in small portions through the reflux condenser. This addition was followed by a change of color from brown to green as the dichromate ion was reduced to chromic ion, and carbon dioxide was evolved as shown in equation (IV-2).



Iodate ion was reduced as shown in equation (IV-3).



The solution was refluxed for two hours to assure complete reduction of the iodate. Tellurate ion was not reduced in this step.

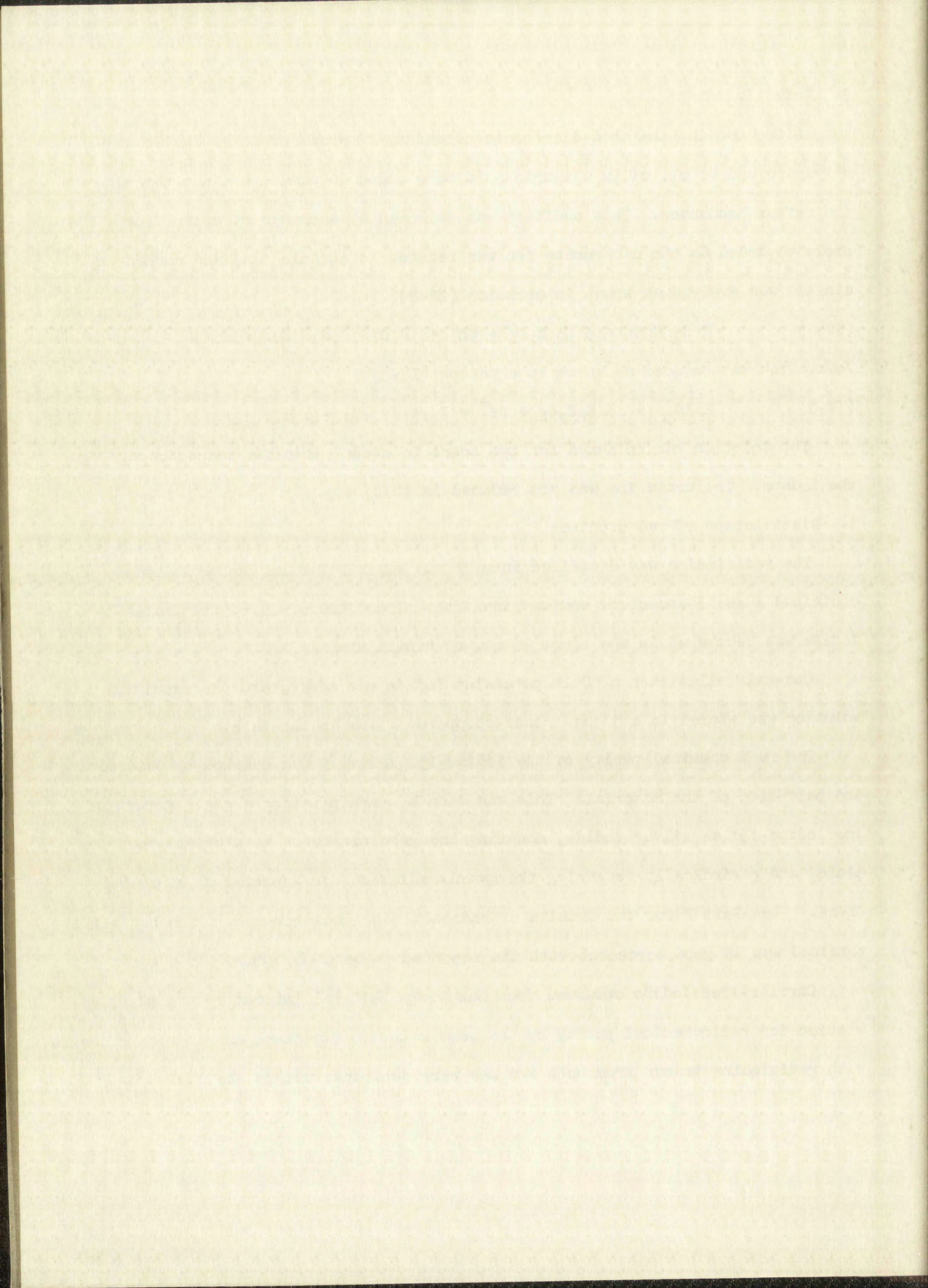
3. Distillation of radioiodine:

The radioiodine was distilled into 10 ml. of 0.1M sodium carbonate which contained a small amount of sodium bisulfite. Practically all of the radioiodine was recovered in the first 25 ml. of distillate.

One-half milliliter of 0.1M potassium iodide was added, and the resulting solution was stored in a 50 ml. glass-stoppered flask in the dark.

The radiochemical purity of the iodine-131 activity was checked by determining the half-life of the material. This was done by precipitating a small amount of the iodine-131 as silver iodide, mounting the precipitate on an aluminum counting plate, and periodically measuring the gamma-radiation for a period of eight half-lives. (See Part V) for the details of radioactivity measurements.) The half-life obtained was in good agreement with the reported value of 8.0 days.⁽²³⁾

Carrier-free iodine obtained from Oak Ridge National Laboratory was also checked for radiochemical purity by the same method. Duplicate exchange experiments with radioiodine tracer from both sources were identical within the limits of



experimental error. No carrier iodine was added to the iodine-131 tracer solutions obtained from Oak Ridge National Laboratory.

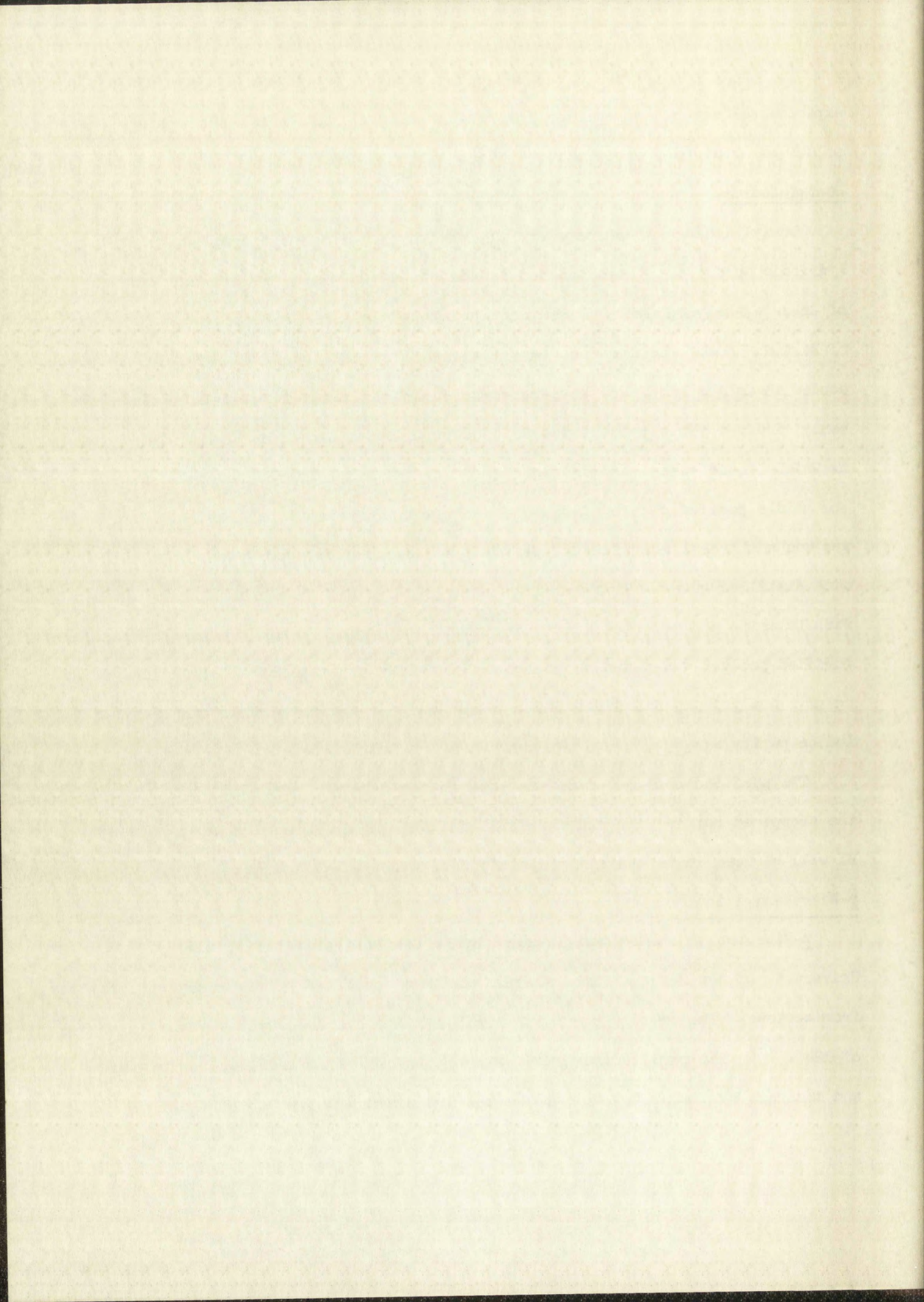
Benzyl iodide. -

Benzyl iodide was prepared by allowing benzyl alcohol to react with hydriodic acid.⁽²⁴⁾ Three hundred and twenty seven grams (20 per cent excess) of Baker's Analyzed C.P. 47 per cent hydriodic acid was refluxed with 108 grams of Eastman Kodak chlorine-free benzyl alcohol for one hour. The mixture was then cooled in an ice bath and the aqueous supernatant liquid decanted from the crude benzyl iodide. This product was dried over Drierite for three days. The crude brownish liquid benzyl iodide was then distilled twice at reduced pressure. Only the middle portion of the distillate was saved from each distillation. The product was washed three times with a 2 per cent sodium bisulfite solution, then twice with distilled water. This purified benzyl iodide was then dried for three days with Drierite and decanted into a dry glass stoppered 100 ml. flask. The final purified product was composed of long needle-like crystals of a very faint yellow color. Analysis by a modified Volhard method^(25a) indicated that the benzyl iodide purity was 99.8 ± 0.3 per cent based on iodide content.

The purified benzyl iodide was kept in the dark in the solid state by covering the stoppered bottle with aluminum foil and storing in a refrigerator. The symbol BI will be used in tables and graphs to designate benzyl iodide.

p-Nitrobenzyl iodide. -

p-Nitrobenzyl iodide was prepared by E. Lee Purlee of the Chemistry Department, University of New Mexico. The material had been purified by ~~six~~ recrystallizations from acetone. The melting point was 126.5-127.0°, compared with a reported value of 124°. ⁽²⁶⁾ The purified material was composed of white needle-like crystals and analysis by a modified Volhard method indicated 100.3 ± 0.3 per cent



p-nitrobenzyl iodide. This material was stored in the same manner as the benzyl iodide, i.e., in a dark container in the refrigerator. The symbol PNBI will be used in tables and graphs to designate p-nitrobenzyl iodide.

Potassium iodide. -

J. T. Baker Chemical Company Analytical Grade potassium iodide was dried for twenty-four hours at 110°C , and stored in a vacuum desiccator without further purification.

Acetone. -

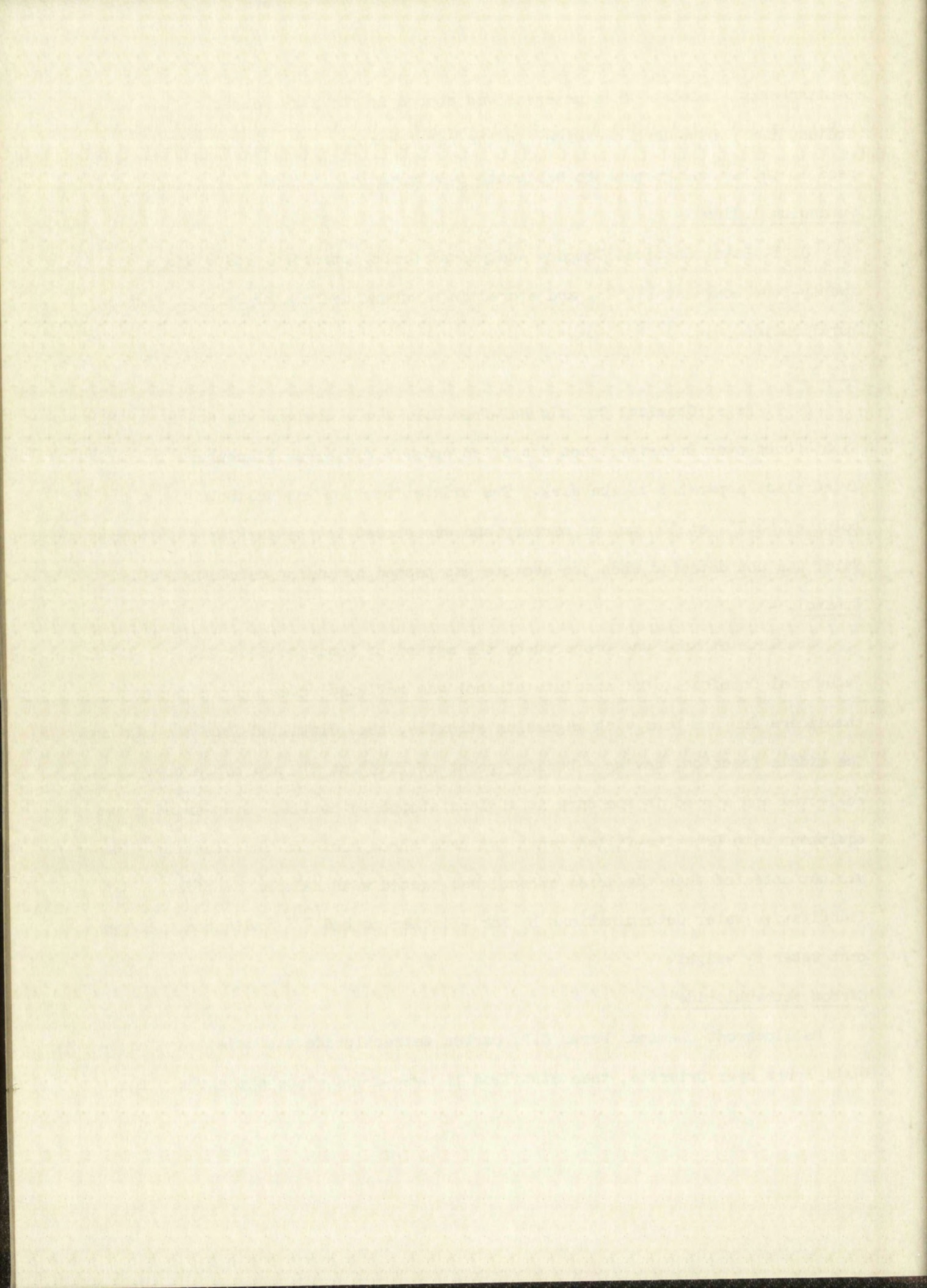
J. T. Baker Chemical Co. alcohol-free C.P. grade acetone was dried for forty-eight hours over Drierite, then distilled under a dry argon atmosphere in oven-dried glass apparatus in the dark. The middle fraction was collected at a boiling point of 48.7° at 580 mm. of mercury and was stored in the dark at room temperature. Water was not detected when the acetone was tested by adding calcium carbide.

Ethanol. -

Absolute ethanol was prepared by the method of Lund and Bjerrum. ⁽²⁷⁾ U. S. Industrial Chemicals, Co. absolute ethanol was refluxed under a dried argon atmosphere for one hour with magnesium ethoxide, then distilled from the mixture. The middle fraction, having a boiling point of 72.3° at 570 mm. of mercury was collected and stored in the dark in a glass stoppered bottle. Oven-dried glass equipment with Drierite-filled vents was used throughout the purification. Water was not detected when the dried ethanol was tested with calcium carbide. Quantitative water determinations by Karl-Fischer method ⁽²⁸⁾ indicated 0.10 per cent water by weight.

Carbon tetrachloride. -

Mallinckrodt Chemical Works C.P. carbon tetrachloride was dried for forty-eight hours over Drierite, then distilled in oven-dried glass apparatus. The



middle fraction was collected at a boiling point of 68.0° at 580 mm. of mercury, and was stored in the dark at room temperature.

Water. -

Ordinary tap water was distilled from alkaline potassium permanganate solution and then passed through a resin column. This product was redistilled from alkaline potassium permanganate, and the middle portion having a conductivity of 0.08×10^{-6} mho was stored in a glass-stoppered bottle at room temperature.

Phenol. -

Eastman Kodak phenol was fractionally distilled through a six-bulb Snyder column. The middle fraction was collected at a boiling point of 172.0 to 172.2° at 590 mm. of mercury. This material was stored at 10° in the dark.

All solvents were flushed for four hours with argon that had been passed through a chromous chloride solution to remove oxygen, followed by concentrated sulfuric acid, and a Drierite column to remove water.

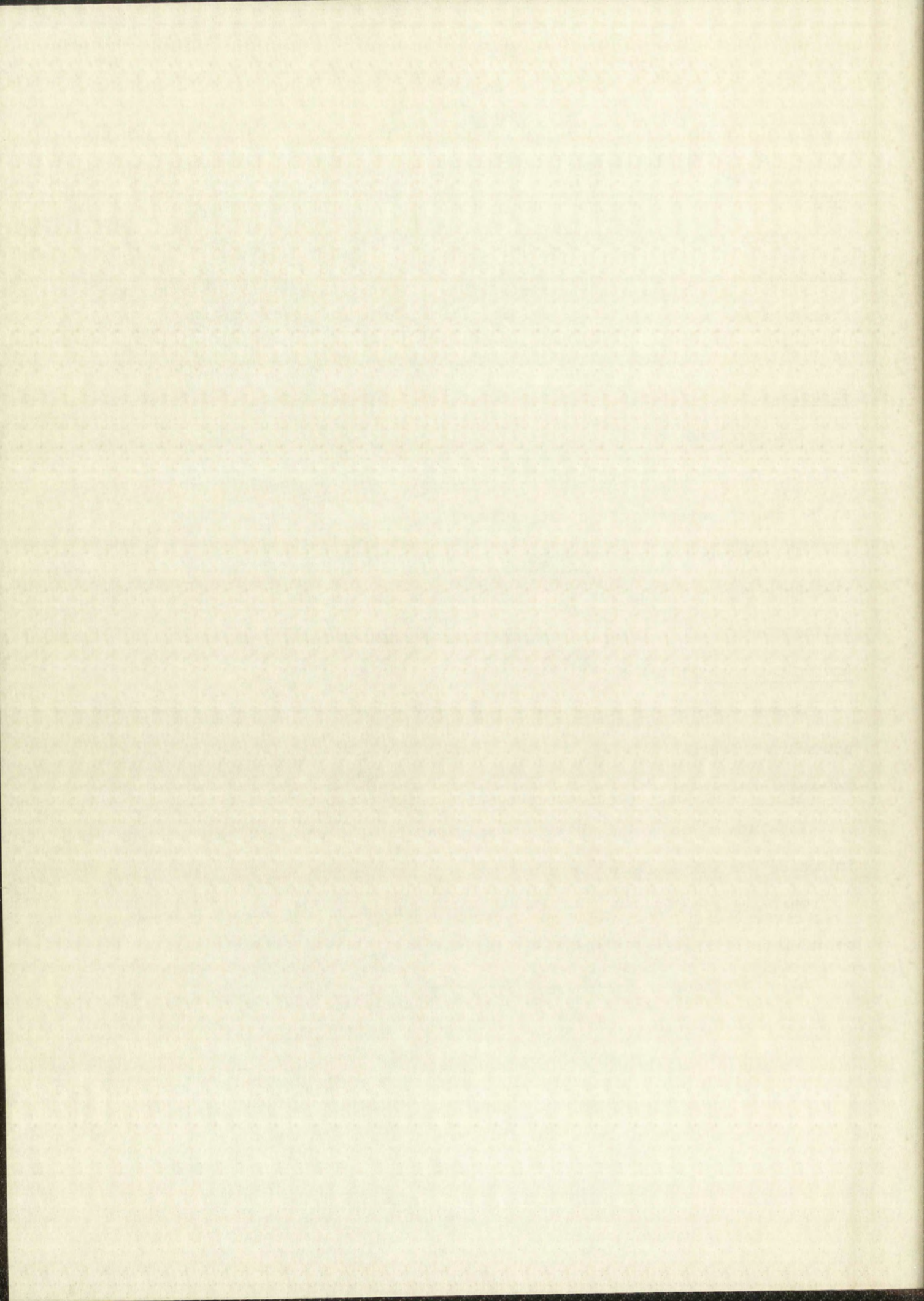
Analytical reagents. -

Standard solutions of silver nitrate (Mallinckrodt Chemical Works) and potassium thiocyanate (Merck Analytical Reagent) were prepared by the methods of Kolthoff and Sandell. (25b)

A saturated solution of ferric ammonium alum (40 per cent) was used as the indicator for iodide determination by the Volhard method.

The potassium thiocyanate was standardized against the silver nitrate solution using the ferric ammonium alum indicator.

All analytical solutions were stored in the dark in glass-stoppered bottles.



Part V

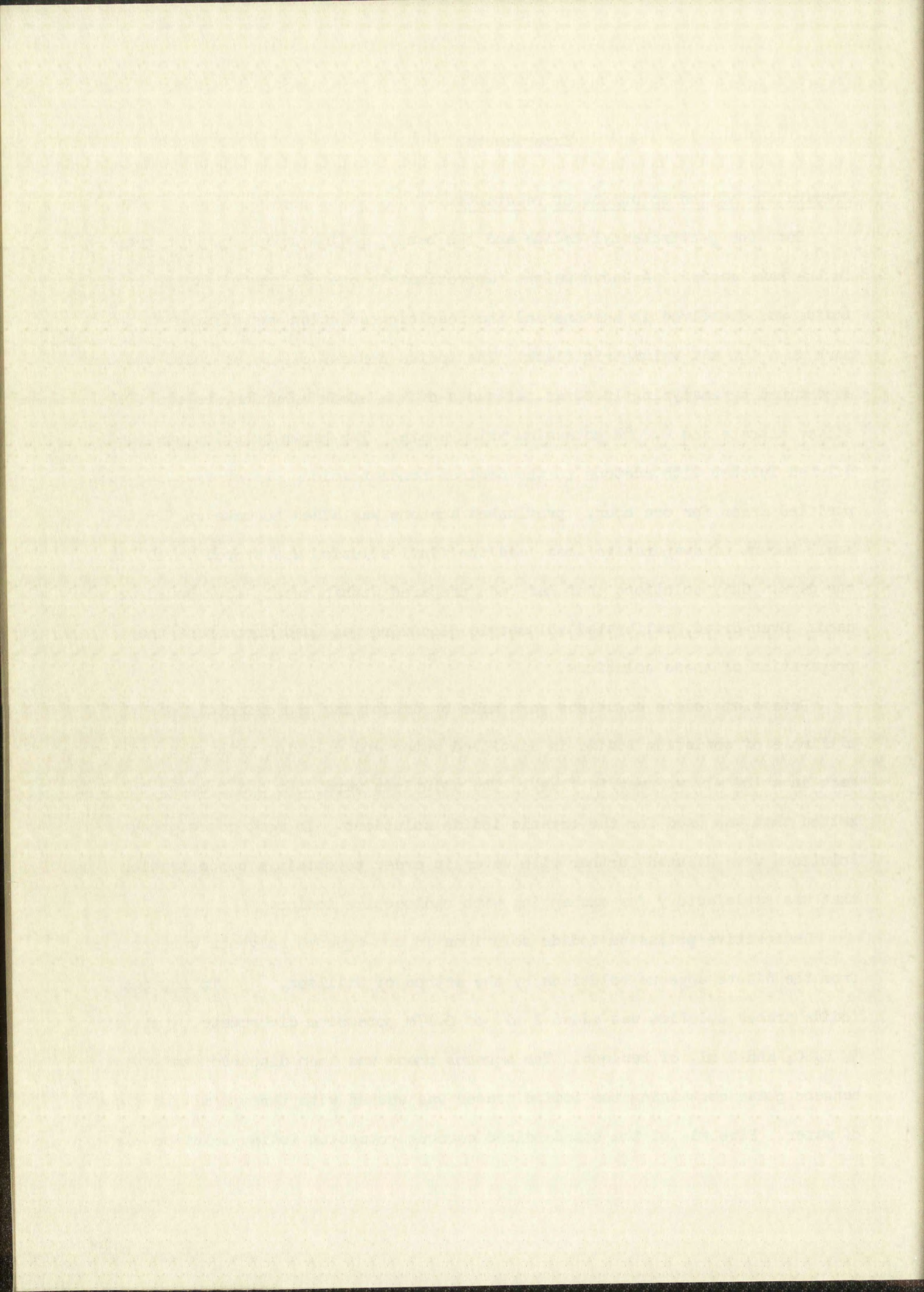
Experimental

Preparation of the solutions of reactants. -

Both the p-nitrobenzyl iodide and the benzyl iodide solutions were prepared in the same manner. A known weight (approximately one millimole) of the organic iodide was dissolved in acetone and the resulting solution was diluted to the mark in a 100 ml. volumetric flask. The iodide content of the solution was then determined by analyzing 10.00 ml. aliquots of the stock solution, using 0.01N silver nitrate and 0.005N potassium thiocyanate. The known solution was then diluted further with acetone to the desired concentration. After flushing with purified argon for one hour, preflushed acetone was added to make up for the small amount of evaporative loss, and the final solution was stored at 10° in the dark. Only solutions that had been prepared within twenty-four hours were used. Oven-dried, calibrated volumetric glassware was used throughout the preparation of these solutions.

Potassium iodide solutions were made by dissolving approximately one millimole of potassium iodide in distilled water and diluting with water to the mark in a 100 ml. volumetric flask. The solutions were then analyzed by the same method that was used for the organic iodide solutions. In most cases, these solutions were diluted further with water in order to obtain a concentration that was satisfactory for exchanging with radioactive iodine.

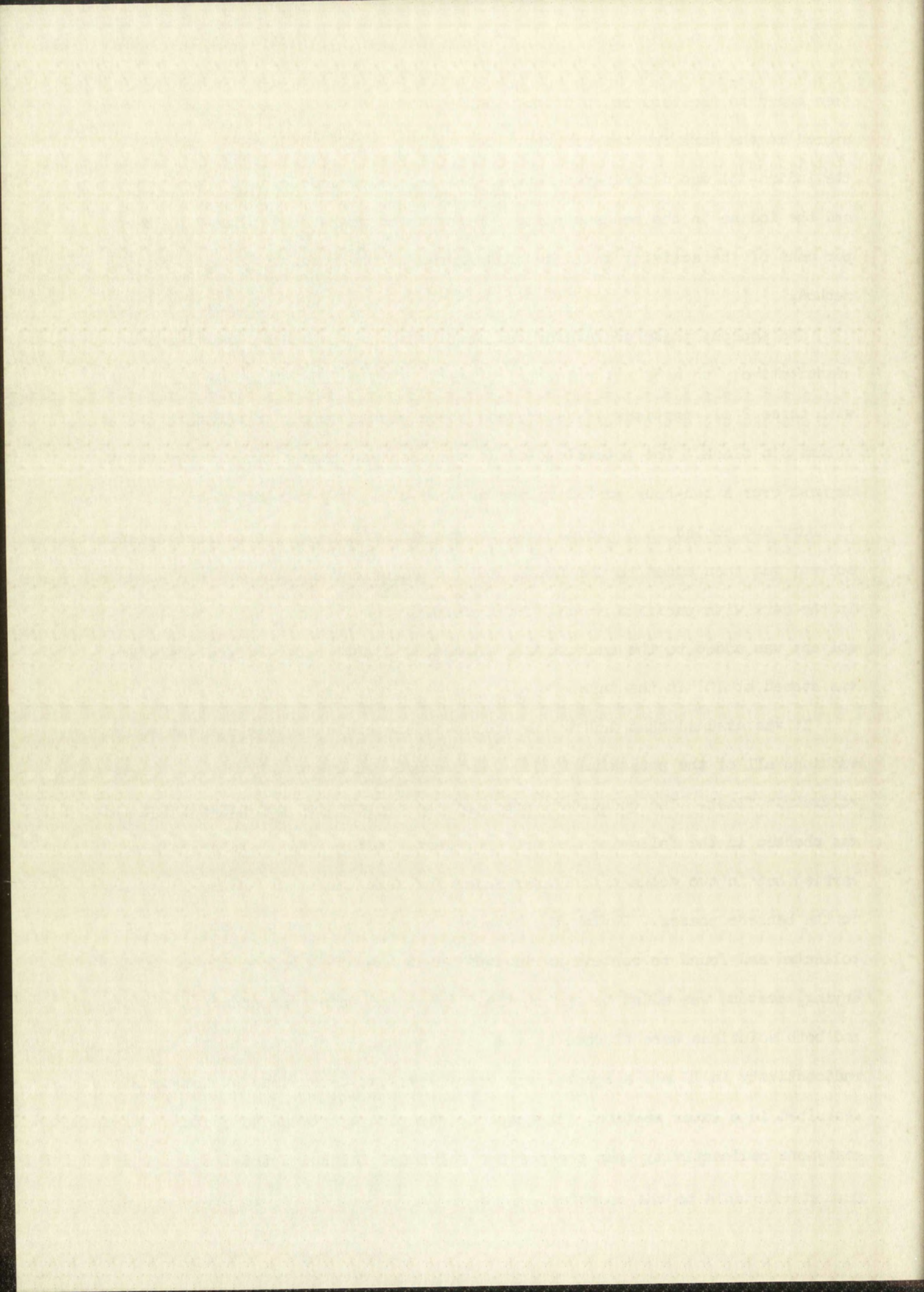
Radioactive potassium iodide solutions in non-aqueous solvents were prepared from the dilute aqueous solutions by the method of Stillson.⁽¹⁵⁾ To aqueous iodide tracer solution was added 2 ml. of 0.17M potassium dichromate, 4 ml. of 3M H₂SO₄ and 2 ml. of benzene. The aqueous phase was then discarded and the benzene phase containing the iodine tracer was washed with three 2 ml. portions of water. Five ml. of the standardized aqueous potassium iodide solution was



then added to the benzene solution, and the mixture was shaken periodically and stored in the dark for ten minutes. Due to the rapid iodide-iodine exchange,⁽²⁹⁾ the iodine-131 was distributed between the potassium iodide in the aqueous phase and the iodine in the benzene phase. By using carrier-free iodine-131, over 90 per cent of the activity could be transferred to the potassium iodide by this method.

The aqueous phase containing radioactive potassium iodide was then transferred quantitatively to a 50 ml. volumetric flask. The benzene phase was again washed with three 2 ml. portions of water, and these washes were also added to the same volumetric flask. The potassium iodide solution was then slowly evaporated to dryness over a ten-hour period in the absence of light, then dried at 110° for 16 hours and cooled in a vacuum desiccator over Drierite. The desired organic solvent was then added to the flask, and the solution was flushed for two hours in the dark with purified argon. At the end of the flushing operation, preflushed solvent was added to the mark in the volumetric flask, and the final solution was stored at 10° in the dark.

It was assumed that during the iodide-iodine exchange step and subsequent washings all of the potassium iodide was transferred quantitatively to the final volumetric flask. The quantitateness of the evaporation and dissolution step was checked in the following manner. Duplicate iodide-iodine exchanges were carried out in two volumetric flasks using the same amount of iodine-131 tracer in the benzene phases. During the evaporation step, the evaporated water was collected and found to contain an insignificant amount of radioiodine. After drying, acetone was added to one of the flasks, and water was added to the other and both solutions were flushed in the usual manner. After dissolution, the radioactivity in 10 ml. aliquots from each flask was determined by the methods described in a later section. The aqueous solution was found to contain 0.5 per cent more radioactivity than the acetone solution. Although this was greater than that attributable to the counting errors (± 0.2 per cent), it is not a serious



source of error.

All of the stock solutions of exchange reactants were corrected for temperature variations. The following equations ⁽³⁰⁾ were used to calculate the molar volumes given in Table (V-1).

$$\text{Ethanol: } d_t = 0.78506 - 0.0038591 (t-25) - 0.0656 (t-25)^2 - 0.085 (t-25)^3$$

Carbon Tetrachloride:

$$d_t = 1.63255 - 0.0019110 t - 0.06690 t^2$$

$$\text{Acetone: } d_t = 0.81248 + 0.0011142 t - 0.06315 t^2$$

Where

d_t = density, g./ml./ at temperature t

t = temperature, °C

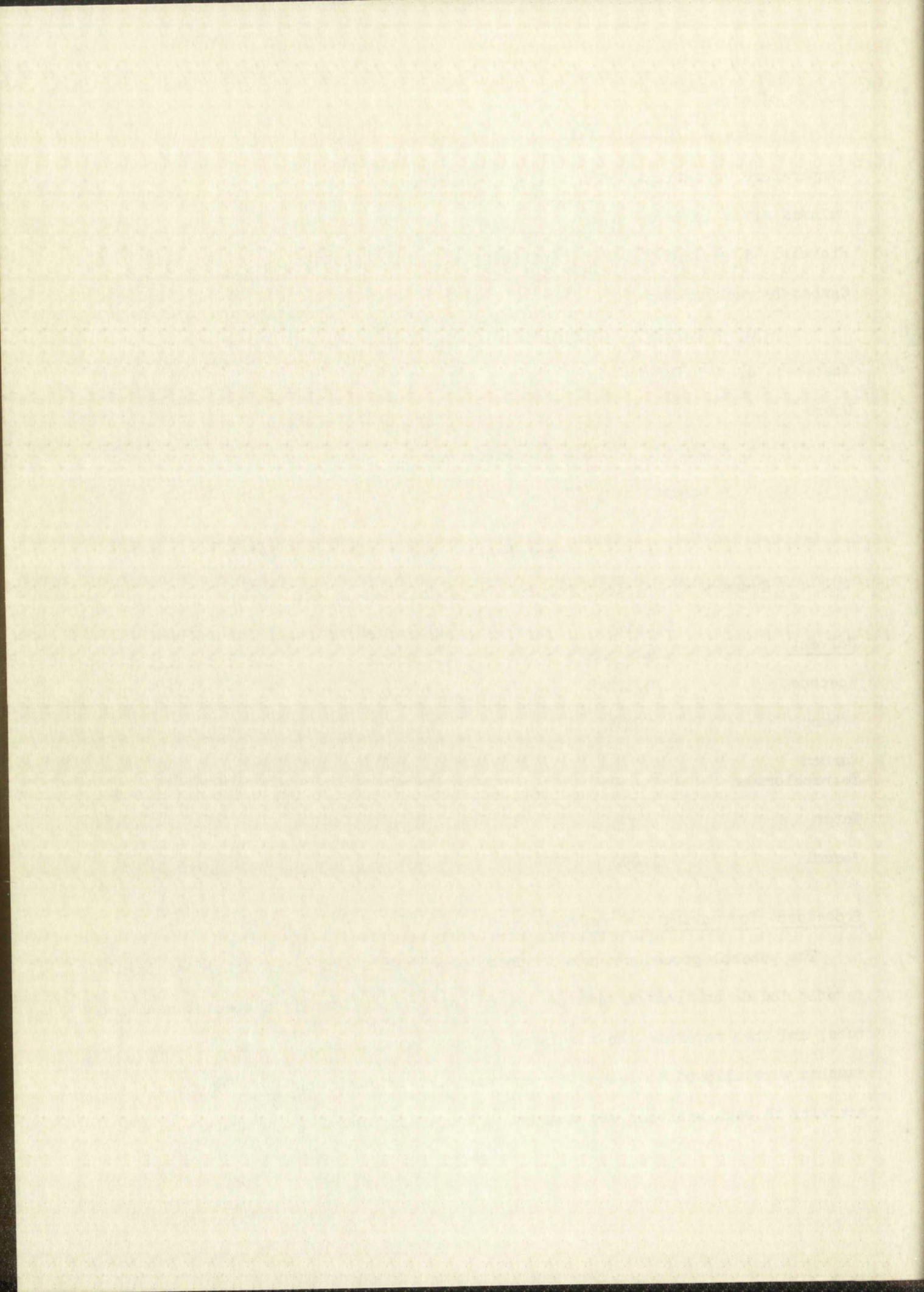
Table(V-1)

Summary of Physical Properties of Solvents at 0°C

<u>Solvent</u>	<u>Density,</u> <u>g/ml.</u>	<u>Molecular</u> <u>Weight</u>	<u>Molar Volume,</u> <u>ml.</u>
Acetone	0.81248	58.08	71.48
Ethanol	0.8061	46.07	57.15
Carbon Tetrachloride	1.6326	143.84	88.10
Water	0.99988	18.02	18.02
Phenol	1.092	94.12	86.19

Procedure: for making the exchange run. -

The general procedure used in these experiments was to mix thermostatted organic iodide and radioactive potassium iodide solutions in a special reaction tube, and then separate the reactants after a known reaction time. Several samples were allowed to react for various times in each run, and the radioactivity in each reactant was measured after separation. As discussed in a

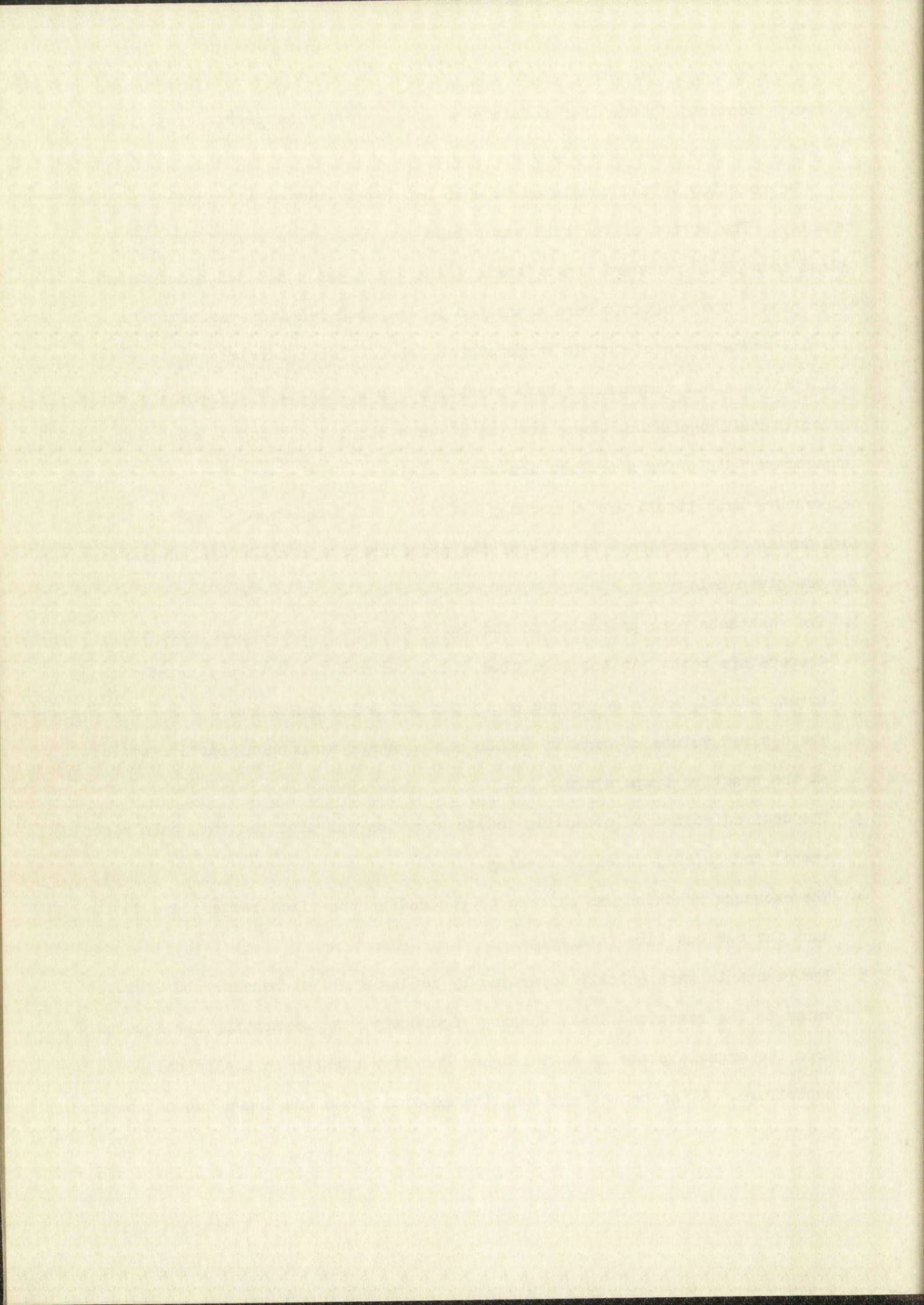


Following section, it was then possible to compute the experimental rate constant for the given reaction conditions.

The reaction vessel consisted of a 16 mm. Pyrex tube of approximately 25 ml. capacity. The bottom of the tube was sealed and drawn to a point; the top was joined to a 12/18 standard taper female joint which was sealed with a standard taper plug. The reactants were separated in the same reaction vessel.

All exchange reactions at temperatures above 0° were carried out in an insulated constant temperature bath maintained to within 0.05° by means of an Aminco thermal regulator. Reactions at 0° were carried out in the same constant temperature bath using a crushed ice-water mixture. During all runs the constant temperature bath liquid was vigorously stirred. All samples were kept in the dark during the reaction. Details of the procedure for carrying out an exchange run are given below:

1. The reactants were precooled to the desired temperature in the constant temperature bath. At the same time, the reaction flasks were flushed with argon, sealed, and also precooled to the desired temperature.
2. The desired volume of organic iodide was pipetted into each reaction vessel at the reaction temperature.
3. The desired volume of potassium iodide solution was pipetted into each reaction vessel and quickly mixed by shaking.
4. The exchange reaction was allowed to proceed at the fixed temperature in the dark for various time intervals.
5. The reactants were quickly separated by adding 2 ml. of benzene and 2 ml. of water to the reaction flask, shaking vigorously, and separating the aqueous from the organic phase by centrifuging for five minutes in a clinical centrifuge. After centrifugation, the aqueous phase was drawn out of the



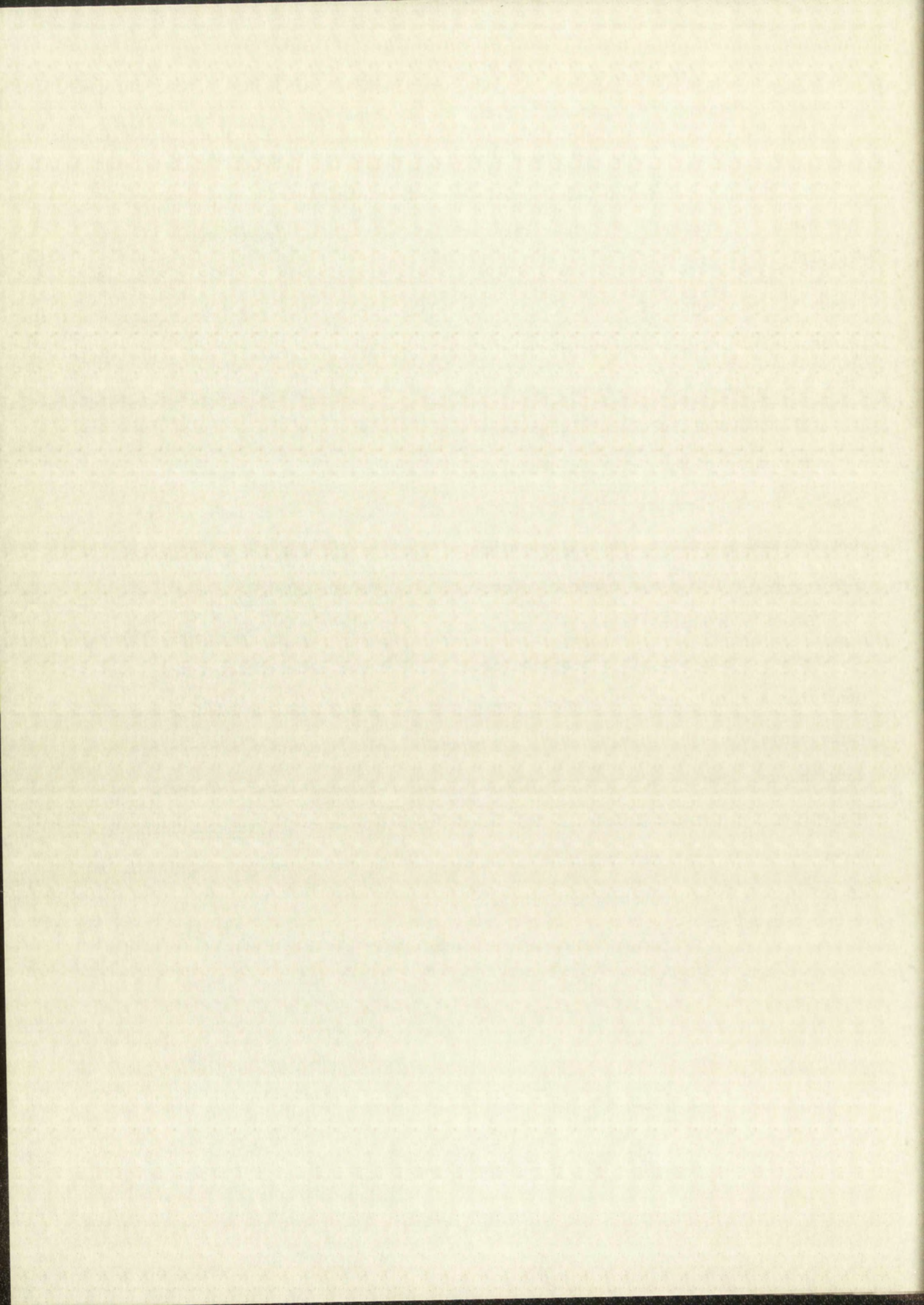
bottom of the flask by means of a capillary pipette, and added to a calibrated counting tube. The organic phase was washed three times with water and separated in the same manner. These washes were also added to the counting tube for the aqueous phase. The washed organic phase containing the organic iodide was then transferred by means of a new capillary pipette to a second counting tube. The reaction vessel was rinsed twice with benzene and the rinse solutions were added to the second counting tube. Each of the counting tubes was diluted to the calibration mark, using water for the potassium iodide solution and benzene for the organic iodide solution. Both solutions were then mixed thoroughly.

6. The amount of iodine-131 radioactivity in each sample was determined and the fraction exchange was computed by means of equation (II-3).
7. By separating different samples after different reaction times, it was possible to obtain the fraction exchanged, F , as a function of exchange time, t .

Separation blank. -

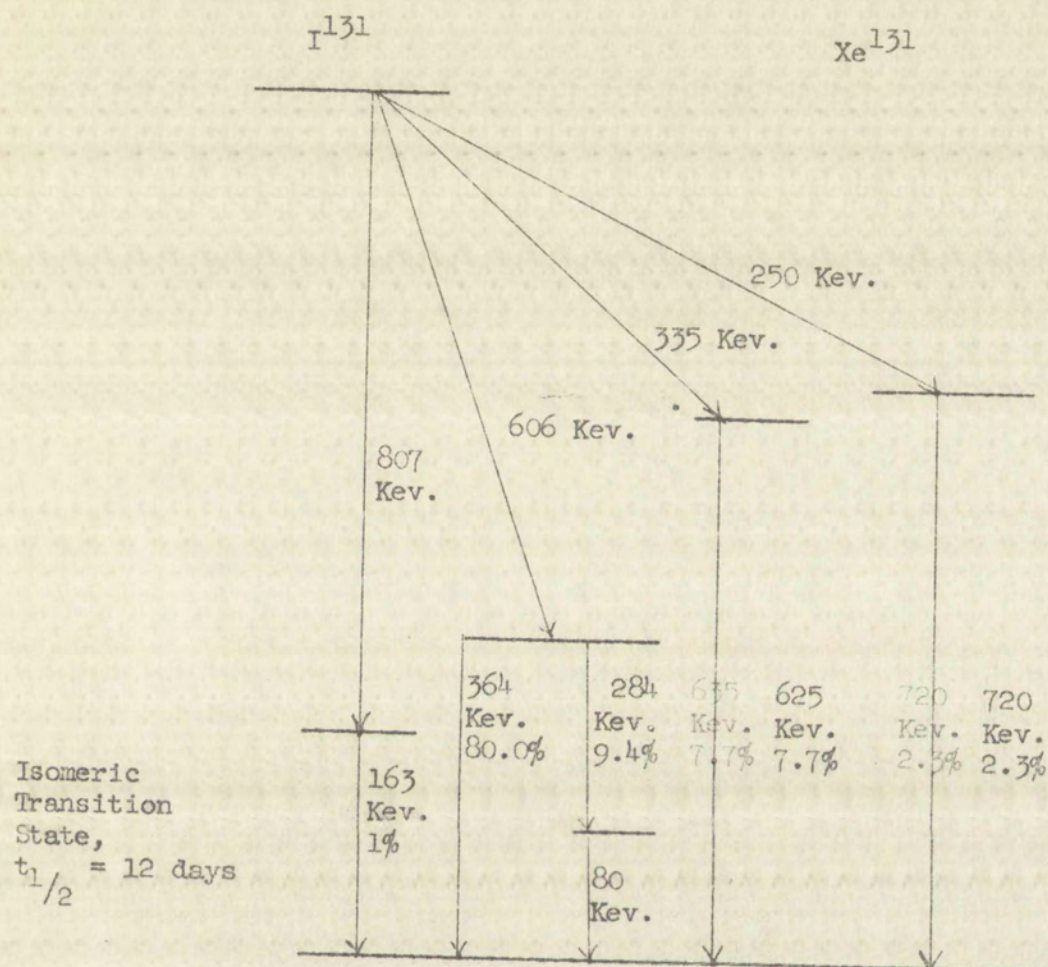
In each experiment at least one blank sample was run with purified acetone in place of the acetone solution of organic iodide. The same amount of potassium iodide solution was added that was used in the reaction samples. After the run was completed, this "blank" solution was separated and counted in the same manner as the reaction samples.

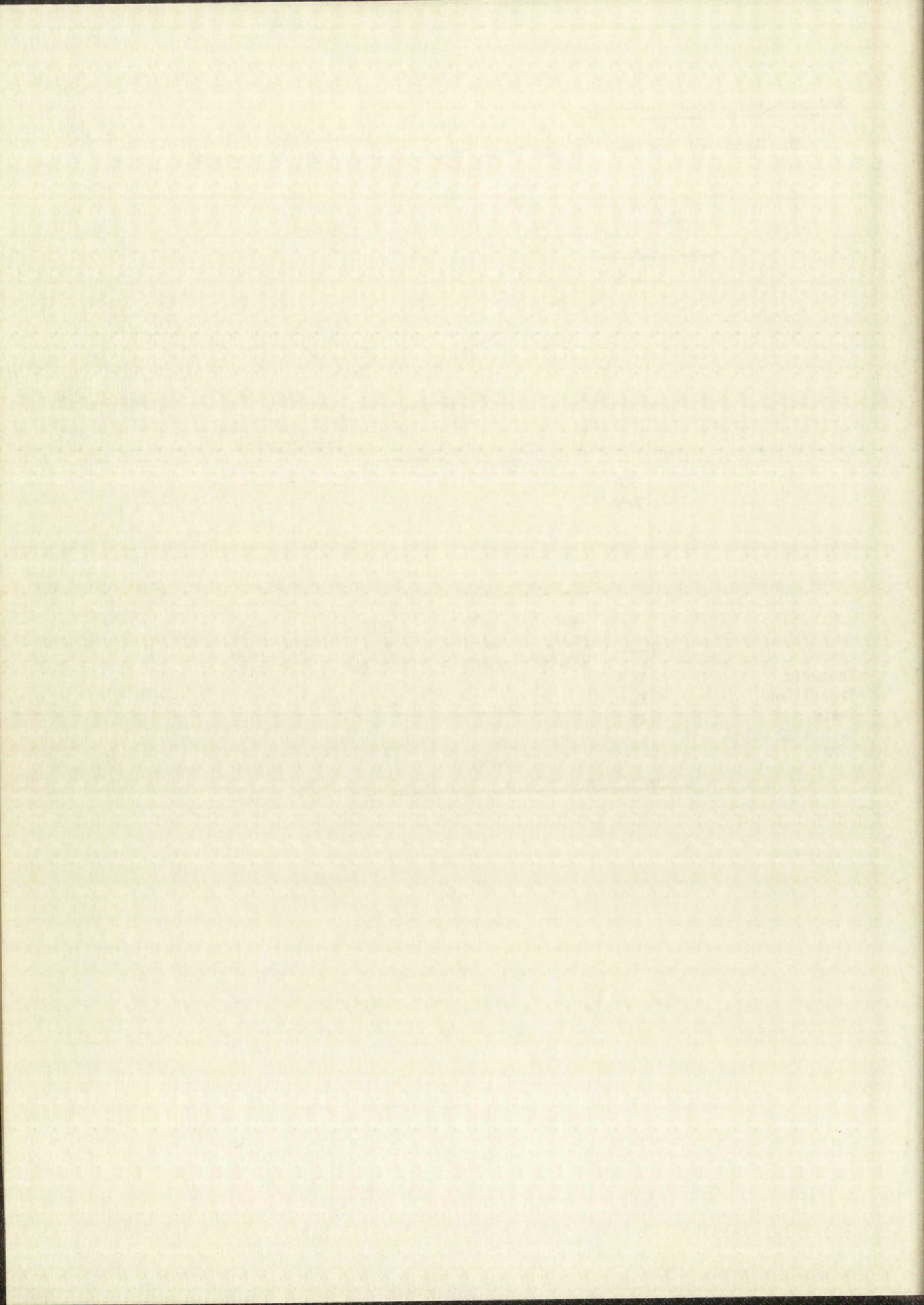
The amount of iodine activity extracted into the benzene phase from the blank was dependent on the acetone used in the experiments, but it was independent of the potassium iodide concentration. Blanks as high as 12 per cent of the potassium iodide were obtained with acetone that had not been stored in the dark.



Radioactivity measurements. -

The decay of iodine-131 has been reported to follow the scheme (31)





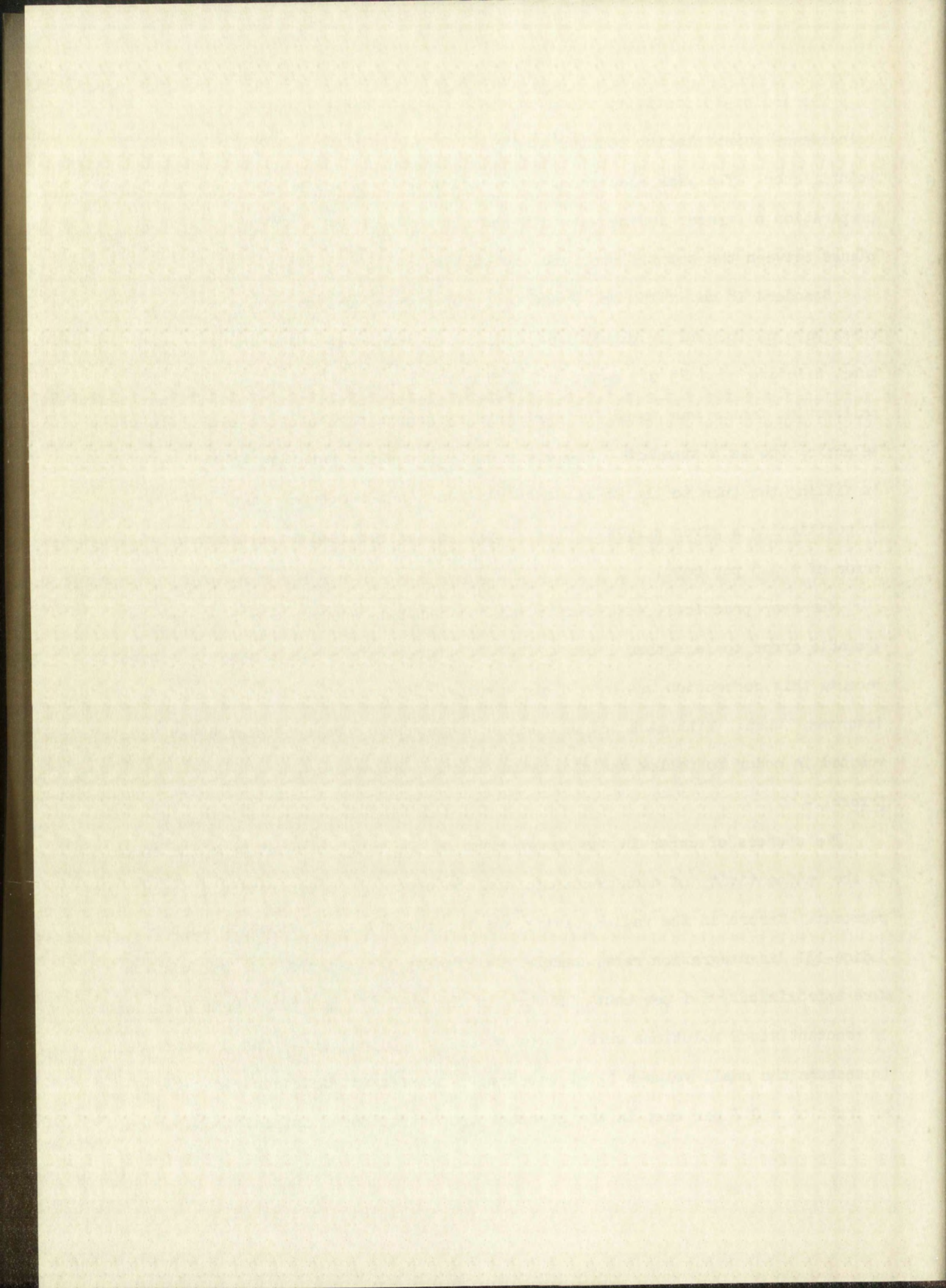
The iodine-131 activity was detected by a standard type of anti-coincidence scintillation counter employing a thallium-activated sodium iodide scintillator. The weak electromagnetic radiation from iodine-129 formed in the preparation of tracer iodine was filtered out by means of a 50 mil lead sheet placed between the scintillator and the sample.

Standard 18 mm. x 150 mm. Pyrex test tubes were used as sample holders. The tubes were calibrated by pipetting 10.00 ml. of iodine-131 solution into each tube, diluting to a 25 ml. mark, and mixing the resulting solution with air. A calibration factor was found for each tube by accurately counting each tube and selecting one as a standard. The error in the counting rate due to the error in filling the tube to the 25 ml. mark was less than ± 0.3 per cent. Variation in positioning a given sample in the sample holder resulted in an average error of ± 0.5 per cent.

Whenever practical, each sample was counted long enough to reduce the probable error to less than 1 per cent. Coincidence corrections were unnecessary, because this correction was only 1 per cent at 100,000 c/m. for the counting instrument used. With each set of samples a standard cobalt-60 source was also counted in order to follow variations in counter performance.

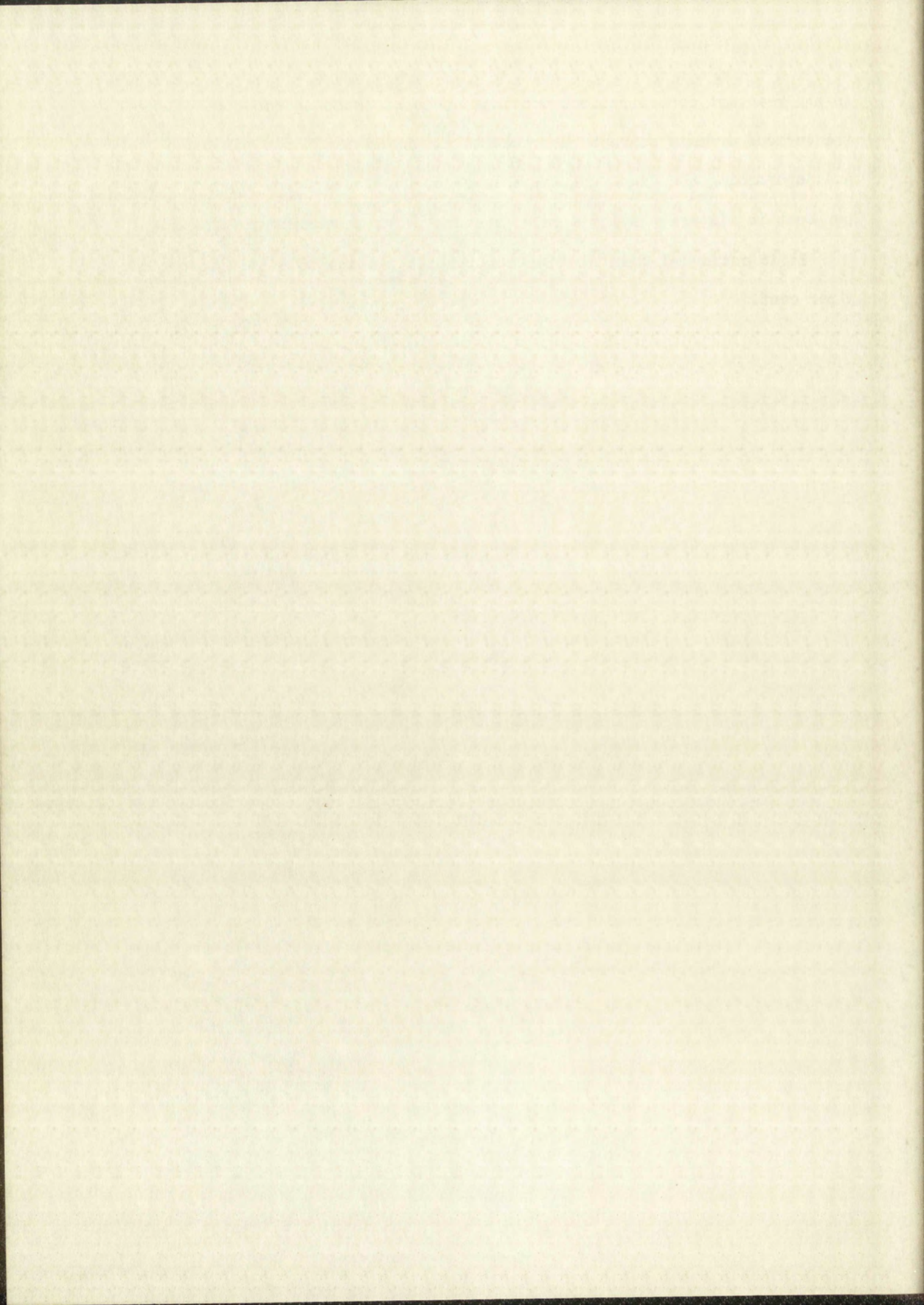
Errors. -

The sources of error in the measurement of the rate constant were the error in the radioactivity of each reactant, and the error in concentration of each reactant. Errors in the radioactivity due to statistical fluctuation in the iodine-131 disintegration rate, sample positioning, and sample tube calibration were approximately ± 1 per cent. Errors in the analysis and subsequent dilution of reactant stock solutions were approximately ± 0.5 per cent. The pipettes used to measure the small volumes (1 ml. to 5 ml.) of reactant solutions contributed an error of ± 0.7 per cent in the reactant concentrations. An additional error



in the reactant concentrations was introduced by assuming that the volumes of the various organic solvents were additive. By mixing known volumes of solvents and determining the final volume, this error was found to be approximately 1 per cent in mixtures having a mole fraction of acetone greater than 0.85.

It is estimated that the rate constant is precise to within approximately 5 per cent.



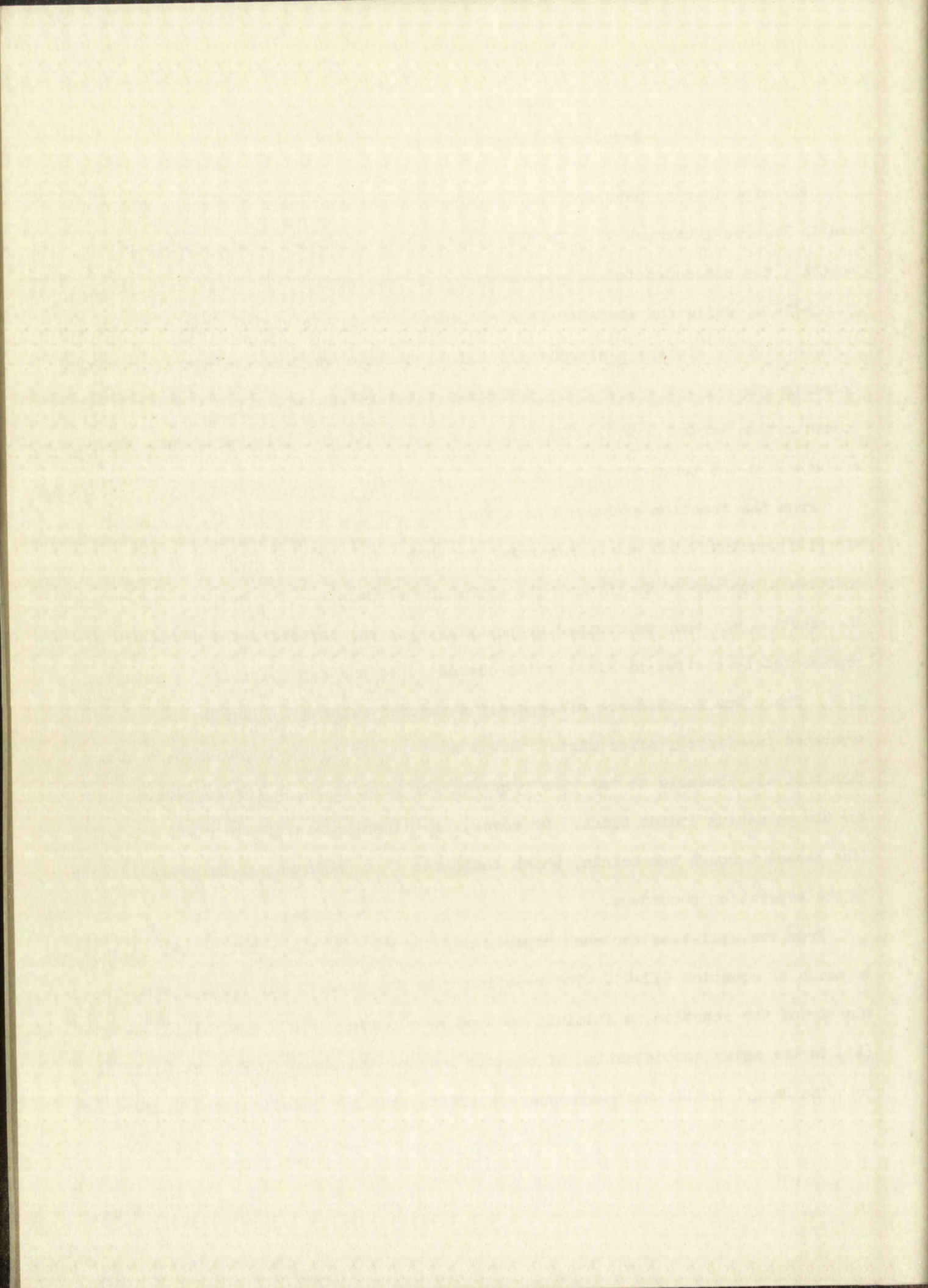
Part VI

Results and Calculations

The experimental data and results are recorded in tables I through XXXXIII and in Figures 1 through 24. In the benzyl iodide exchange studies in absolute acetone, the concentration of potassium iodide was varied from 0.00001491 to 0.0004724 M, while the concentration of benzyl iodide was varied from 0.00002912 M to 0.0001452 M. In the p-nitrobenzyl iodide exchange studies the potassium iodide concentration ranged from 0.000003454 M to 0.00003125 M, while p-nitrobenzyl iodide concentration varied from 0.000002621 M to 0.00003440 M. All experiments were conducted in the temperature range from 0° to 34.2°.

From the fraction exchanged as a function of time (see Part V), a plot of $-\ln(1-F)$ against time was constructed for each run, and a straight line of positive slope was drawn through the experimental points. The half-time for the reaction was then determined graphically. In all instances the data were well represented by a straight line, which demonstrated the applicability of equation II-2. There was no evidence of separation-induced exchange. Samples that were separated immediately after mixing showed no activity in the organic phase other than that attributable to the time required for separation, after correction for the potassium iodide blank. Moreover, the linear plots of $-\ln(1-F)$ against time passed through the origin, which indicates that there was no exchange induced by the separation procedure.

From the half-time for each experiment, the rate of the reaction was calculated by means of equation (II-4). The reaction rate was used to determine the molecularity of the reaction in absolute acetone by plotting $R/(RI)$ against (KI) where (RI) is the molar concentration of organic iodide. As shown in Figures 6 and 11 both the benzyl iodide and p-nitrobenzyl iodide exchange reactions are bimolecular,



i.e., they are both first order with respect to iodide ion and first order with respect to organic iodide.

Knowing that the reaction was bimolecular the second-order specific rate constant, k_2 , was calculated for each experiment by means of equation II-6.

Exchange experiments in absolute acetone. -

The exchange experiments in absolute acetone were carried out at different temperatures in order to determine the energy of activation and the frequency factor.

Equation III-2 can be converted to the logarithmic form

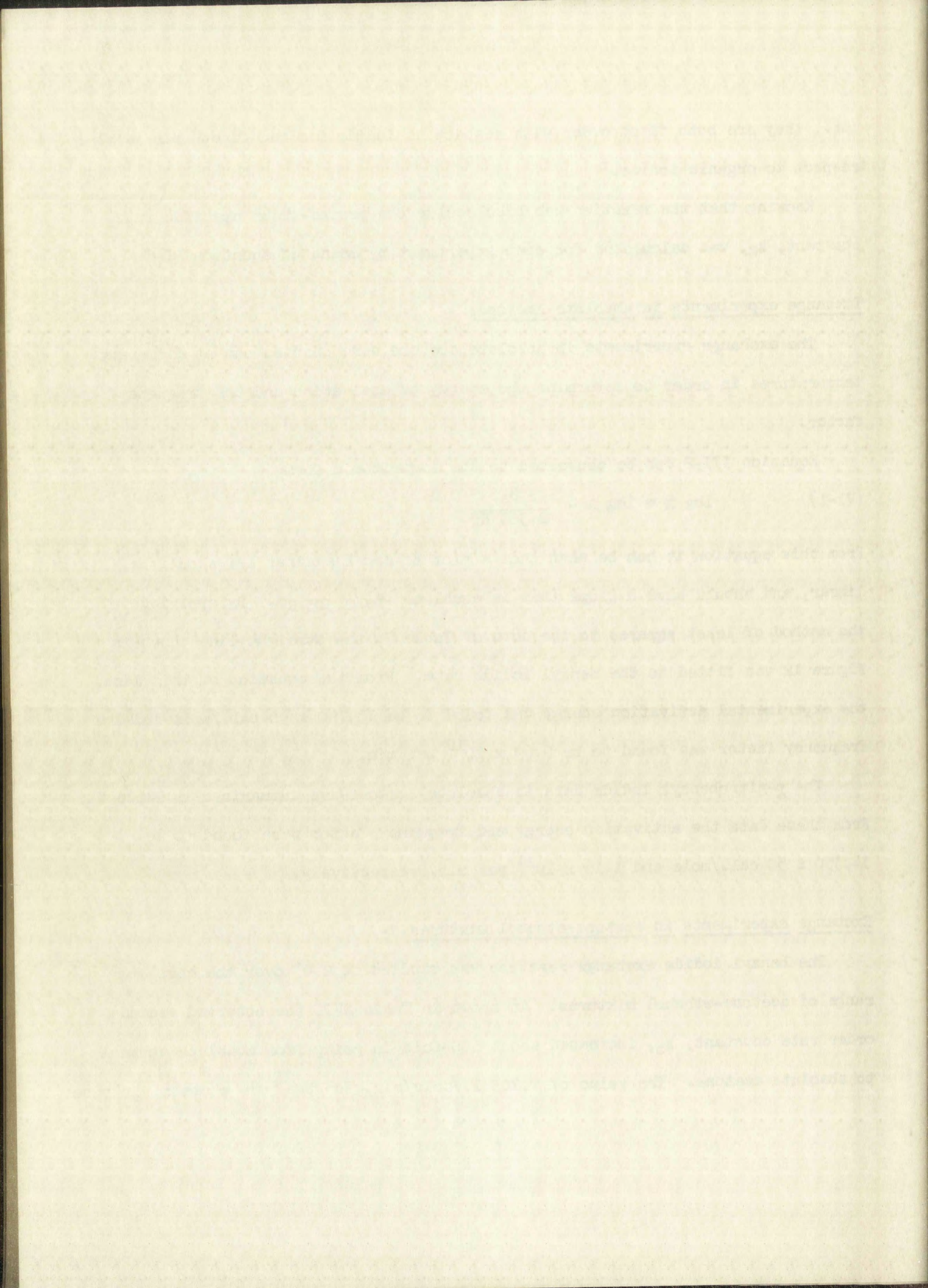
$$(VI-1) \quad \log k = \log A - \frac{E_a}{2.303 RT}$$

From this equation it can be seen that a plot of $\log k$ against $1/T$ should be linear, and should have a slope that is equal to $-E_a/2.303 RT$. By applying the method of least squares to the data of Table I, the straight line shown in Figure 12 was fitted to the benzyl iodide data. From the equation of this line, the experimental activation energy was found to be $13,720 \pm 90$ cal./mole and the frequency factor was found to be 5.69×10^{12} per min.

The *p*-nitrobenzyl iodide data in absolute acetone are summarized in Table X. From these data the activation energy and frequency factor were found to be $14,350 \pm 50$ cal./mole and 1.16×10^{14} per min. respectively.

Exchange experiments in acetone-ethanol mixtures. -

The benzyl iodide exchange reaction was studied at 0.0° over the complete range of acetone-ethanol mixtures. As shown in Table XVI, the observed second order rate constant, k_o , increased about 600-fold in going from absolute ethanol to absolute acetone. The value of 0.103 l./mole/min. for the rate constant in pure



ethanol is in agreement with the value of 0.101 ± 0.003 l./mole/min. obtained by Stillson.⁽¹⁵⁾ Because this exchange is second order in acetone, in ethanol, and in mixtures of the two,⁽¹⁵⁾ the large change in rate constant must be due to solvent effects.

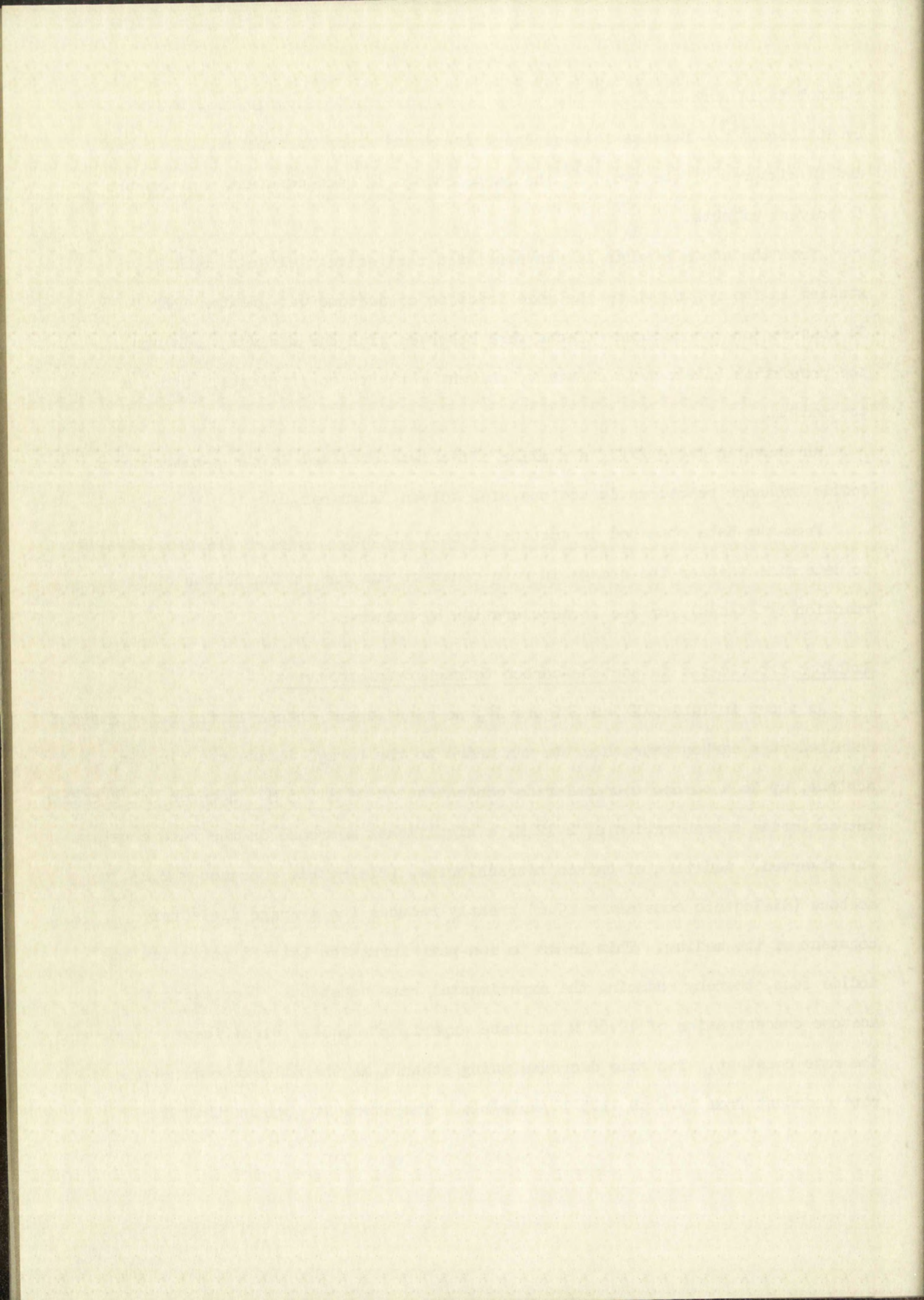
From the above results it was concluded that solvent effects could best be studied in the region where the mole fraction of acetone was greater than 0.85. In this region the maximum effects were observed with the minimum variation in the properties (dielectric constant, solvent activity coefficients, etc.) of the medium.

As shown in Table XXVI, a similar effect was obtained in the p-nitrobenzyl iodide exchange reactions in acetone-rich solvent mixtures.

From the data obtained in acetone-ethanol mixtures alone it was not possible to determine whether the change in rate constant was due to inhibition of the reaction by ethanol, or due to acceleration by acetone.

Exchange experiments in acetone-carbon tetrachloride mixtures. -

As shown in Table XXX and Figure 24, no significant change in the rate constant resulted when carbon tetrachloride was added to the benzyl iodide reaction in acetone, up to a carbon tetrachloride concentration of 1.063 M. However, at a carbon tetrachloride concentration of 2.12 M, a significant decrease in the rate constant was observed. Addition of carbon tetrachloride, (dielectric constant = 2.23) to acetone (dielectric constant = 19.6) greatly reduces the average dielectric constant of the medium. This leads to ion-pair formation between potassium and iodide ions, thereby reducing the experimental rate constant. Decreasing the acetone concentration of 12.60 M in these experiments had no significant effect on the rate constant. The same decrease using ethanol as the diluent reduced the rate constant from 59.6 to 11.5 l./mole/min. Therefore it appears that the



reaction is inhibited by ethanol, and that only relatively minor effects are caused by changes in the concentration of acetone.

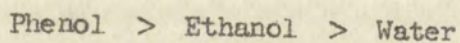
Exchange experiments in acetone-water mixtures. -

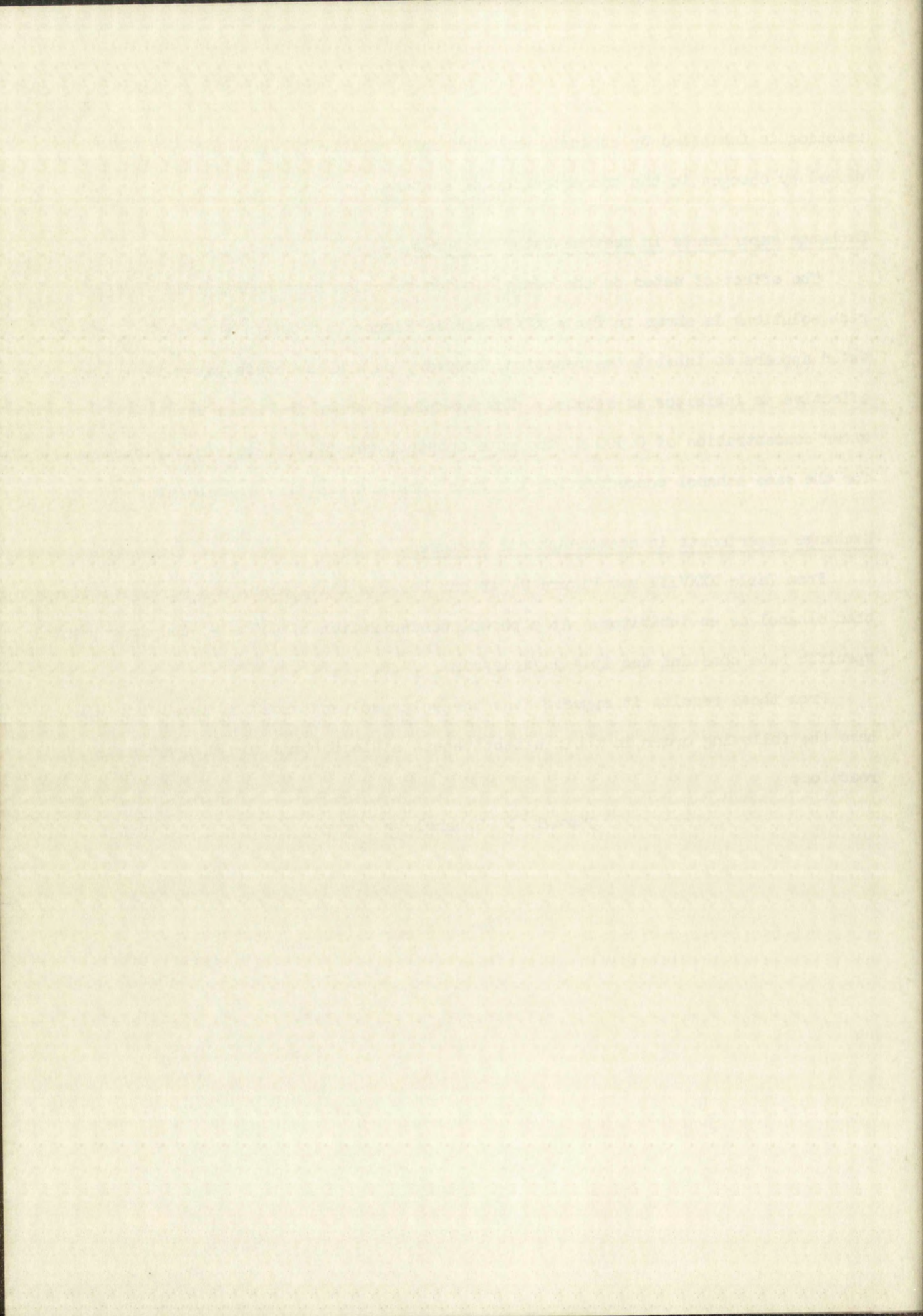
The effect of water on the benzyl iodide reaction rate constant in acetone-rich solutions is shown in Table XXXIV and in Figure 24. As in the case of ethanol, water appears to inhibit the reaction; however, on a molar basis water is not as effective an inhibitor as ethanol. For example as shown in Figure 24, at a water concentration of 0.500 M, the rate constant was 37.8 l./mole/min., whereas for the same ethanol concentration the rate constant was 31.9 l./mole/min.

Exchange experiments in acetone-phenol mixtures. -

From Table XXXVIII and Figure 24 it can be seen that phenol was more effective than ethanol as an inhibitor. At a phenol concentration of 0.500 M, the experimental specific rate constant was 15.4 l./mole/min.

From these results it appears that the polar solvents used in these experiments have the following order in their effectiveness as inhibitors for this exchange reaction:





Experimental Data for Benzyl Iodide Exchange

Experiments in Absolute Acetone

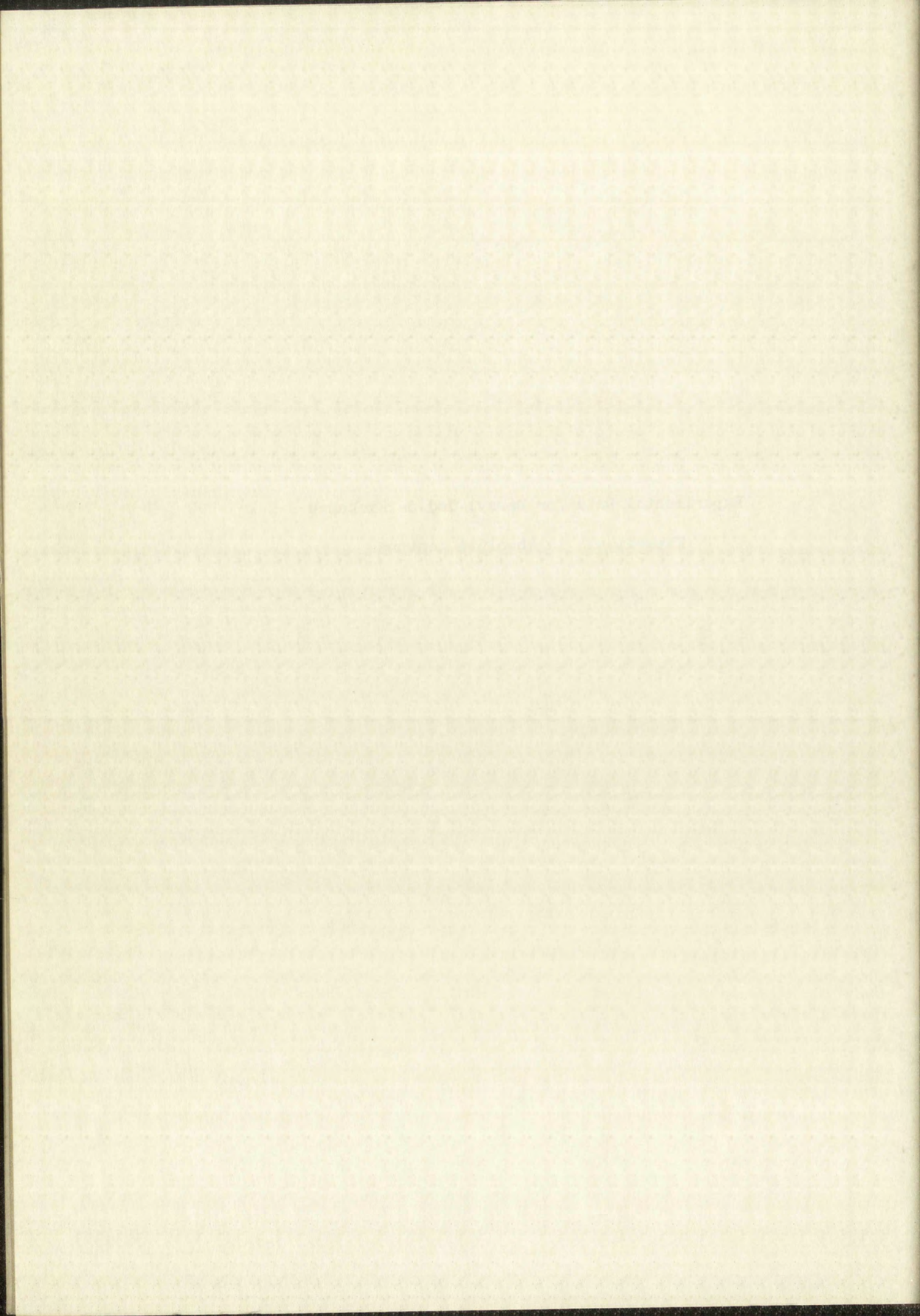


Table I

Summary of Benzyl Iodide Exchange Experiments in Absolute Acetone

Run No.	Temperature, °C	(BI), M X 10 ⁵	(KI), M x 10 ⁵	$t_{1/2}$, min.	k_2 1/mole/min.	Average k_2 , 1/mole/min.
1	0.0	4.068	2.083	196	57.5	
2	0.0	6.22	47.24	21.7	59.7	
3	0.0	9.66	12.68	52.0	59.7	
4	0.0	14.52	10.62	44.8	61.3	59.6 ± 1.0
5	17.8	2.980	6.10	28.9	264.	
6	17.8	2.980	3.052	42.7	269.	266 ± 3.
7	34.2	2.912	2.983	11.6	1016.	
8	34.2	4.370	1.491	12.1	978.	997 ± 19.

Table II
Experimental Data for Run No. 1

Temperature: 0.0°

Solvent: Absolute acetone

(BI) = 0.00004068 M

(KI) = 0.00002083 M

Aliquot	Time, (min.)	Activity in KI, (c/m)*	Activity in BI, (c/m)	Fraction Exchanged
1	32.8	5926	481	0.114
2	61.7	5592	824	0.194
3	90.0	5336	1184	0.275
4	120.0	5018	1429	0.335

$t_{1/2}$ = 196 min.

k = 57.5 l./mole/min.

Blank correction = 0.4 per cent

*c/m = counts per minute

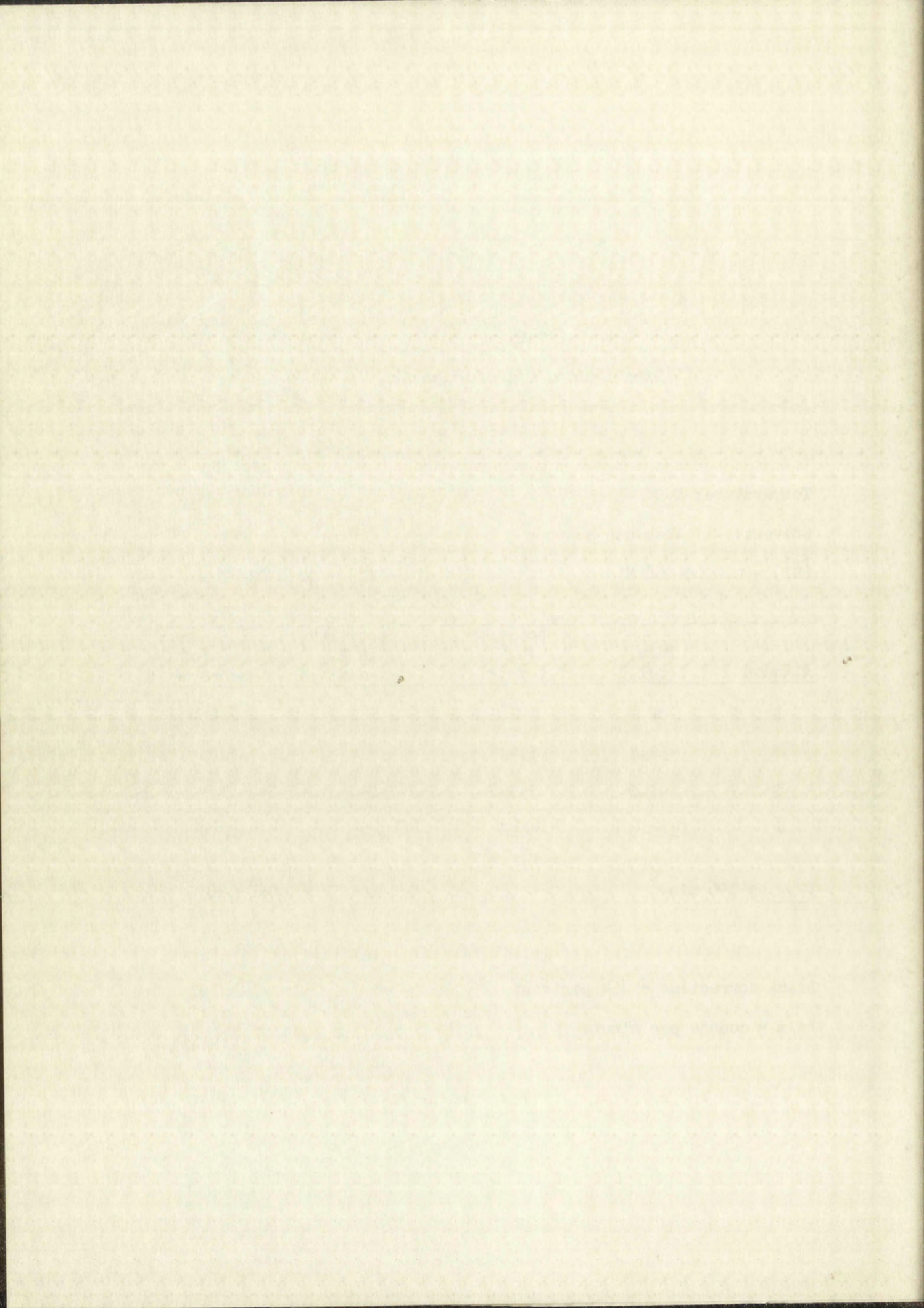


Table III
Experimental Data for Run No. 2

Temperature: 0.0°

Solvent: Absolute acetone

(BI) = 0.0000622 M

(KI) = 0.0004724 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	10.8	18,820	679	0.299
2	24.8	18,290	1254	0.551
3	38.7	18,150	1572	0.686

$t_{1/2} = 21.7$ min.

$k = 59.7$ l/mole/min.

Blank correction = 1.6 per cent

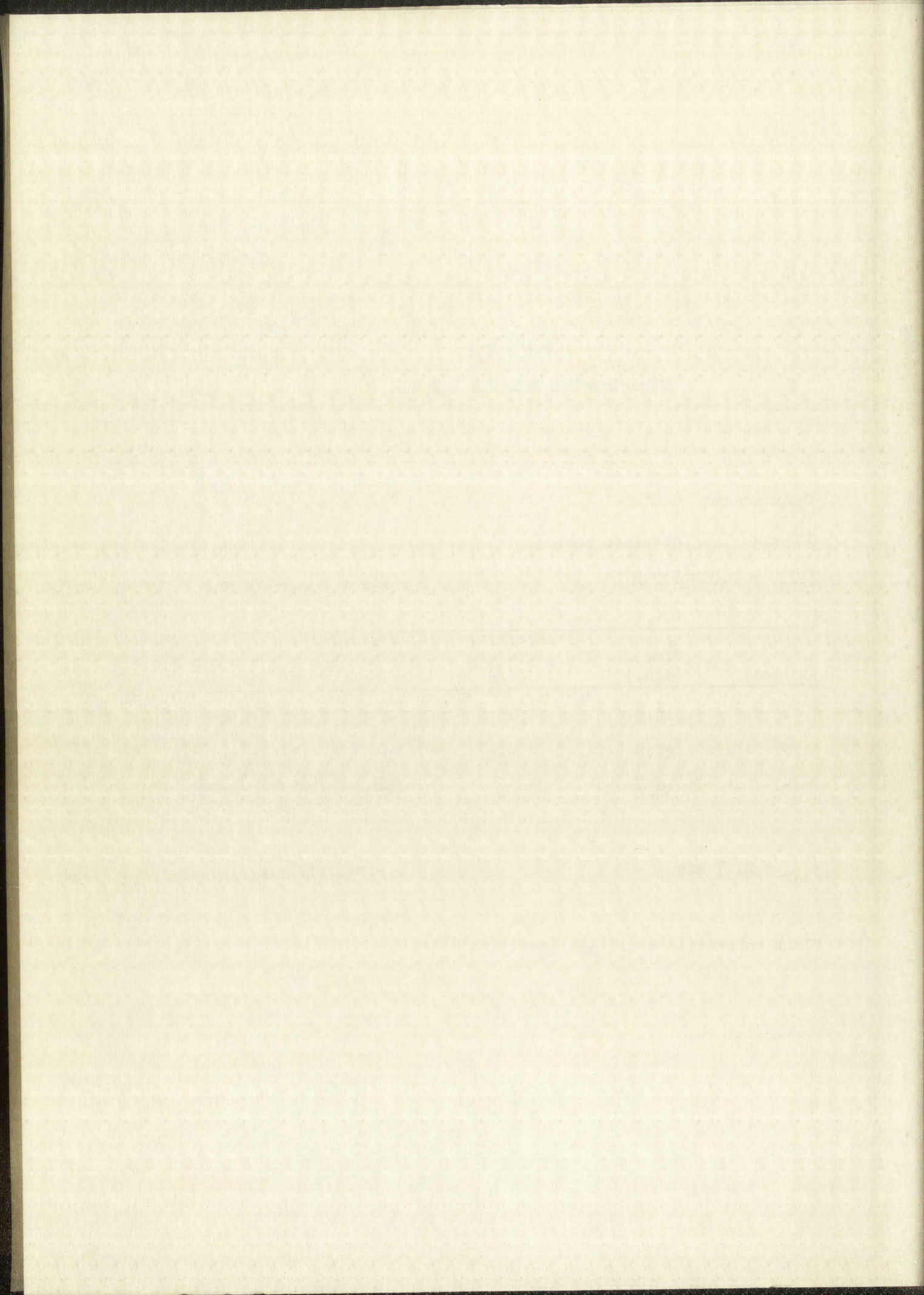


Table IV
Experimental Data for Run No. 3

Temperature: 0.0°

Solvent: Absolute acetone

(BI) = 0.0000966 M

(KI) = 0.0001268 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	24.7	1418	193	0.277
2	49.2	1266	342	0.492
3	72.0	1199	429	0.609

$t_{1/2} = 52.0$ min.

$k = 59.7$ l./mole/min.

Blank correction = 1.2 per cent

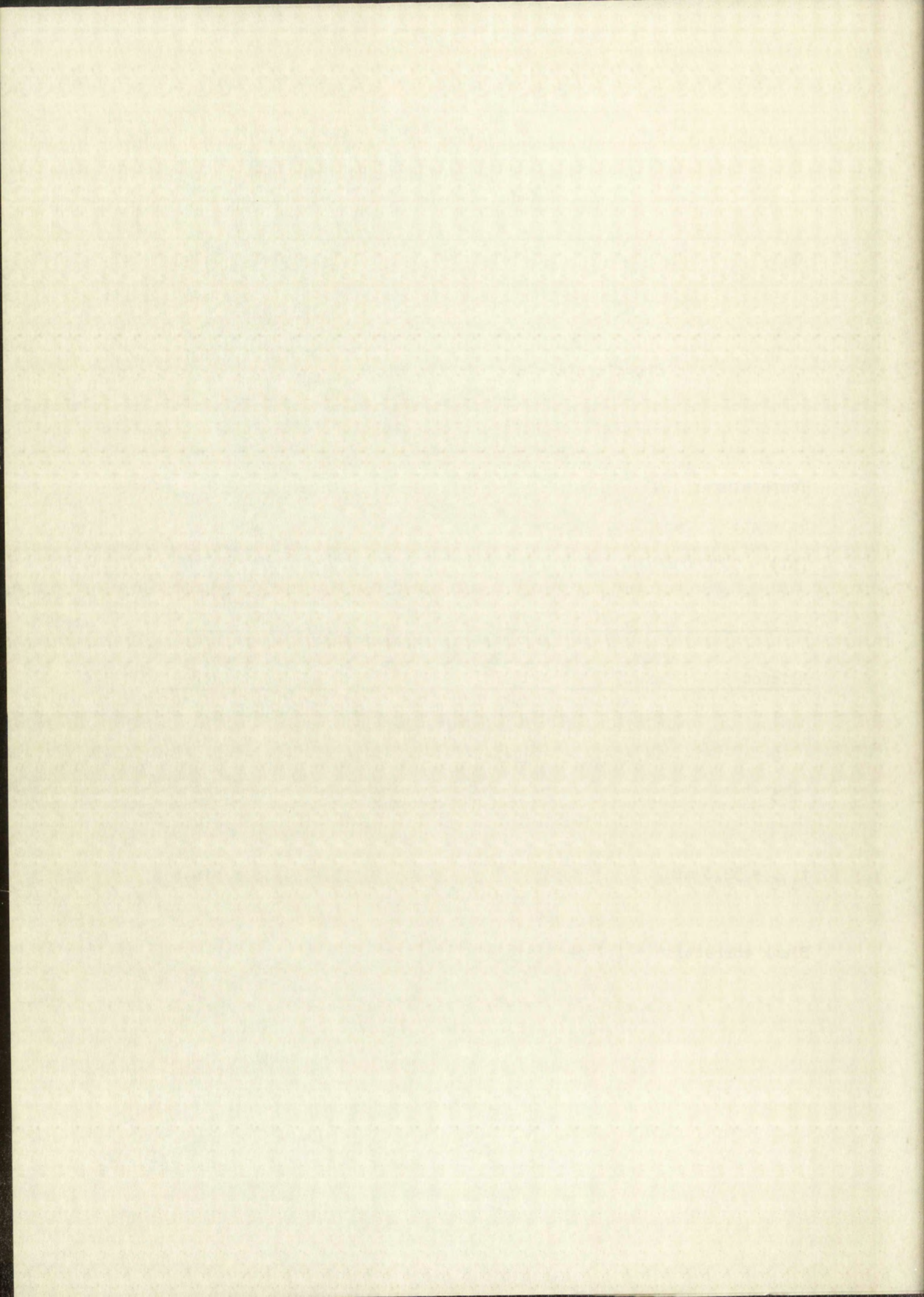


Table V
Experimental Data for Run No. 4

Temperature: 0.0°

Solvent: Absolute acetone

(BI) = 0.0001452 M

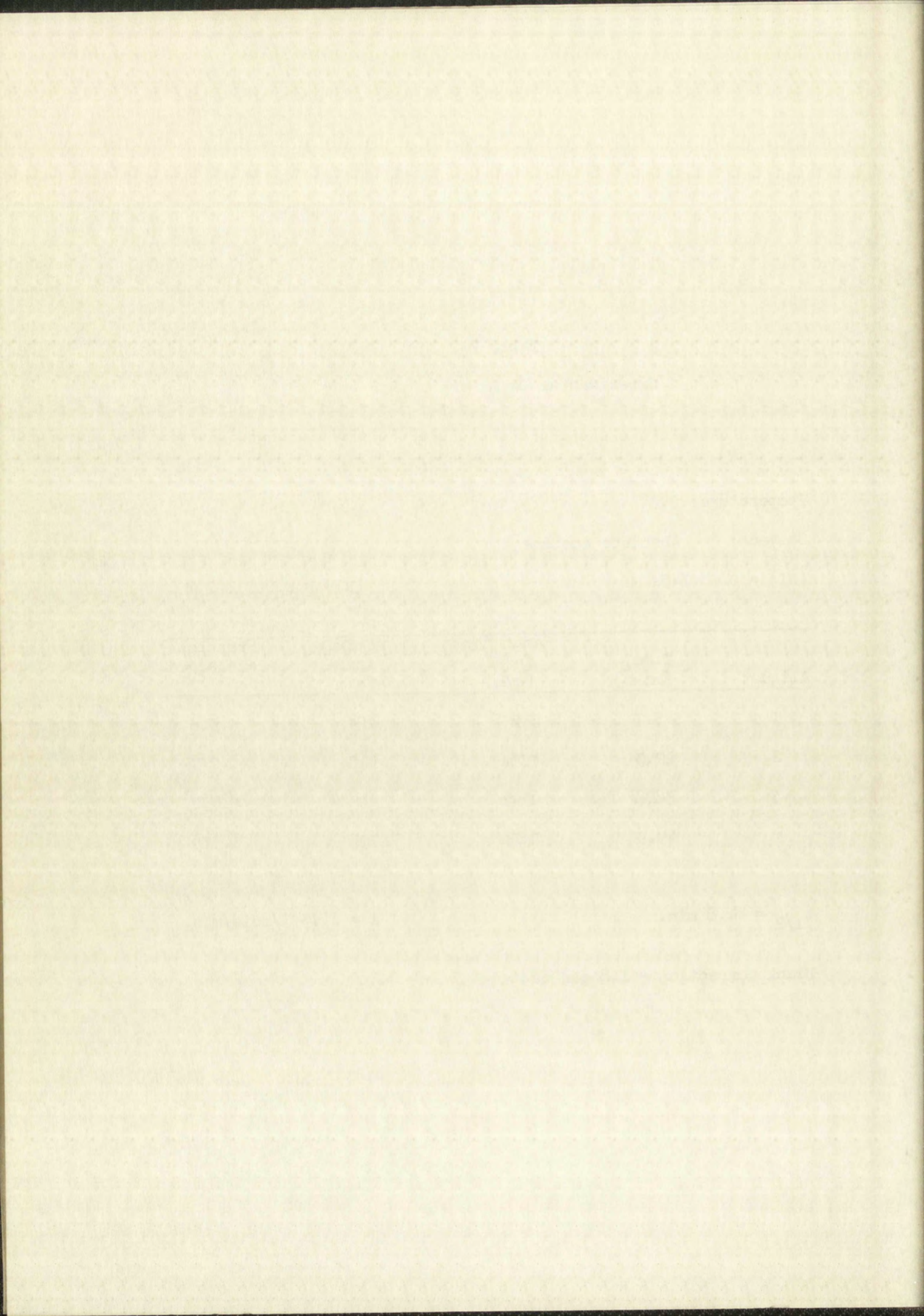
(KI) = 0.0001062 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	5.7	2367	124	0.086
2	22.3	2180	415	0.277
3	38.8	1856	655	0.452
4	49.9	1852	795	0.539

$t_{1/2} = 44.8$ min.

$k = 61.3$ l./mole/min.

Blank correction = 1.8 per cent



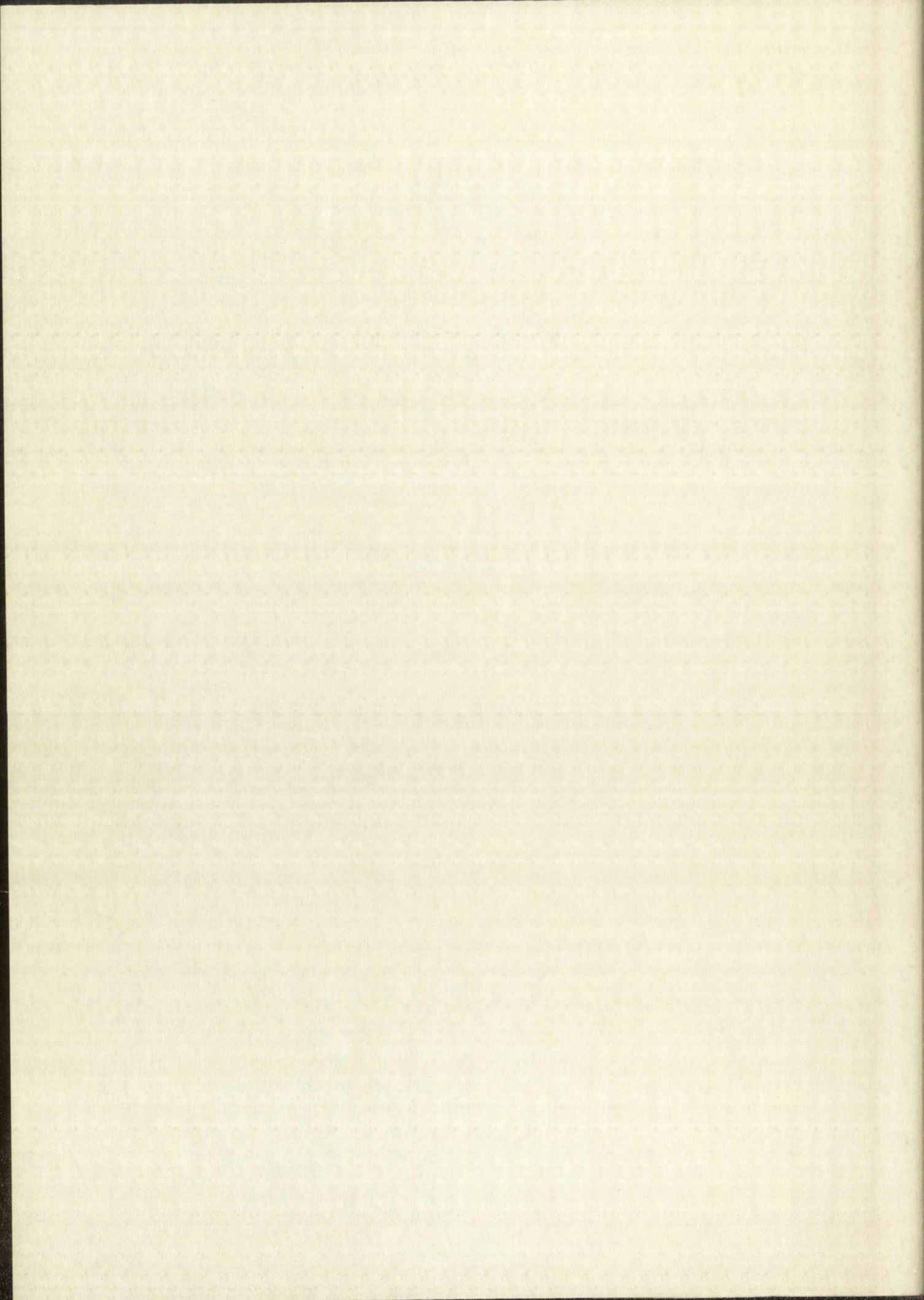
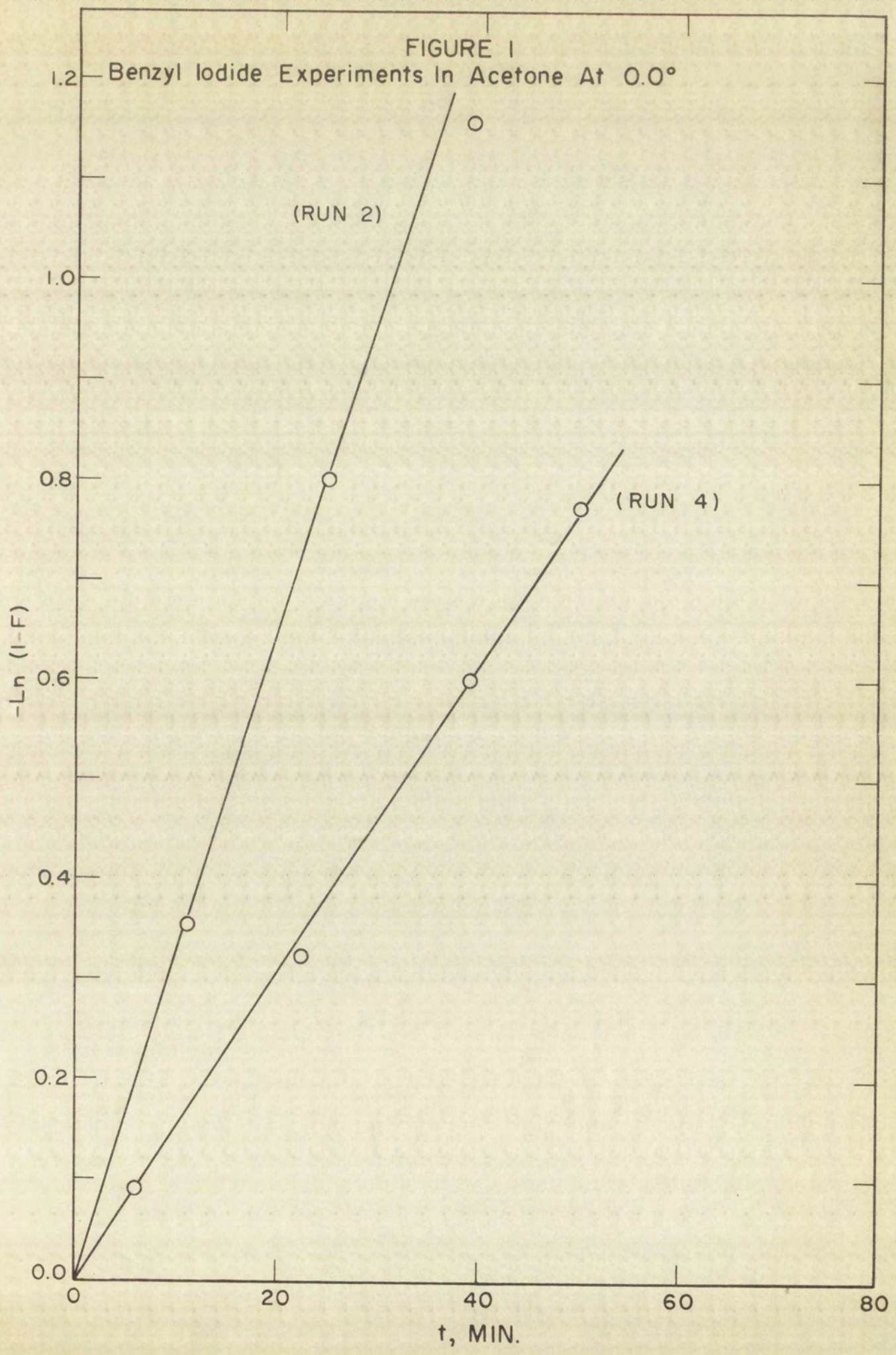
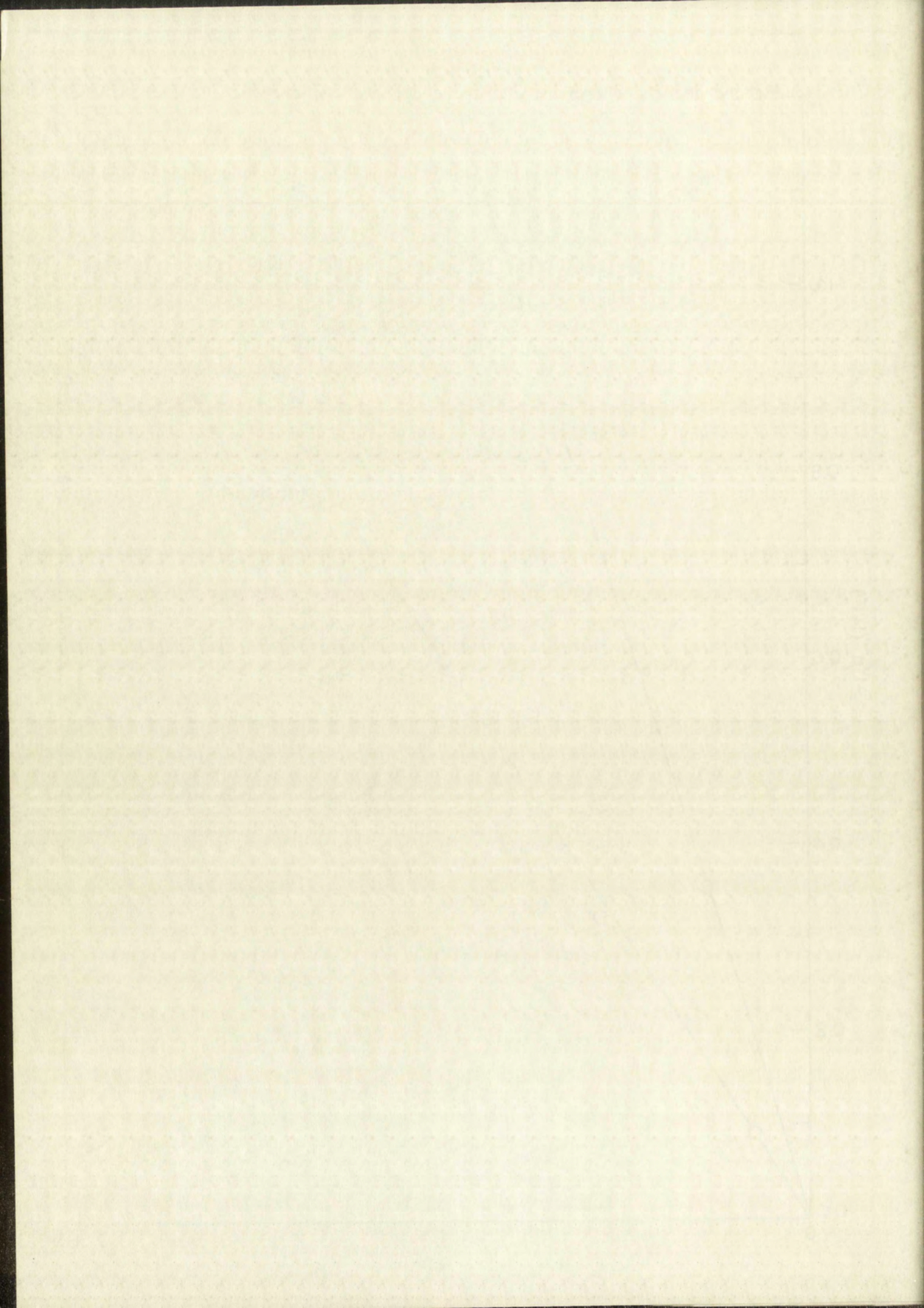


FIGURE 1

Benzyl Iodide Experiments In Acetone At 0.0°





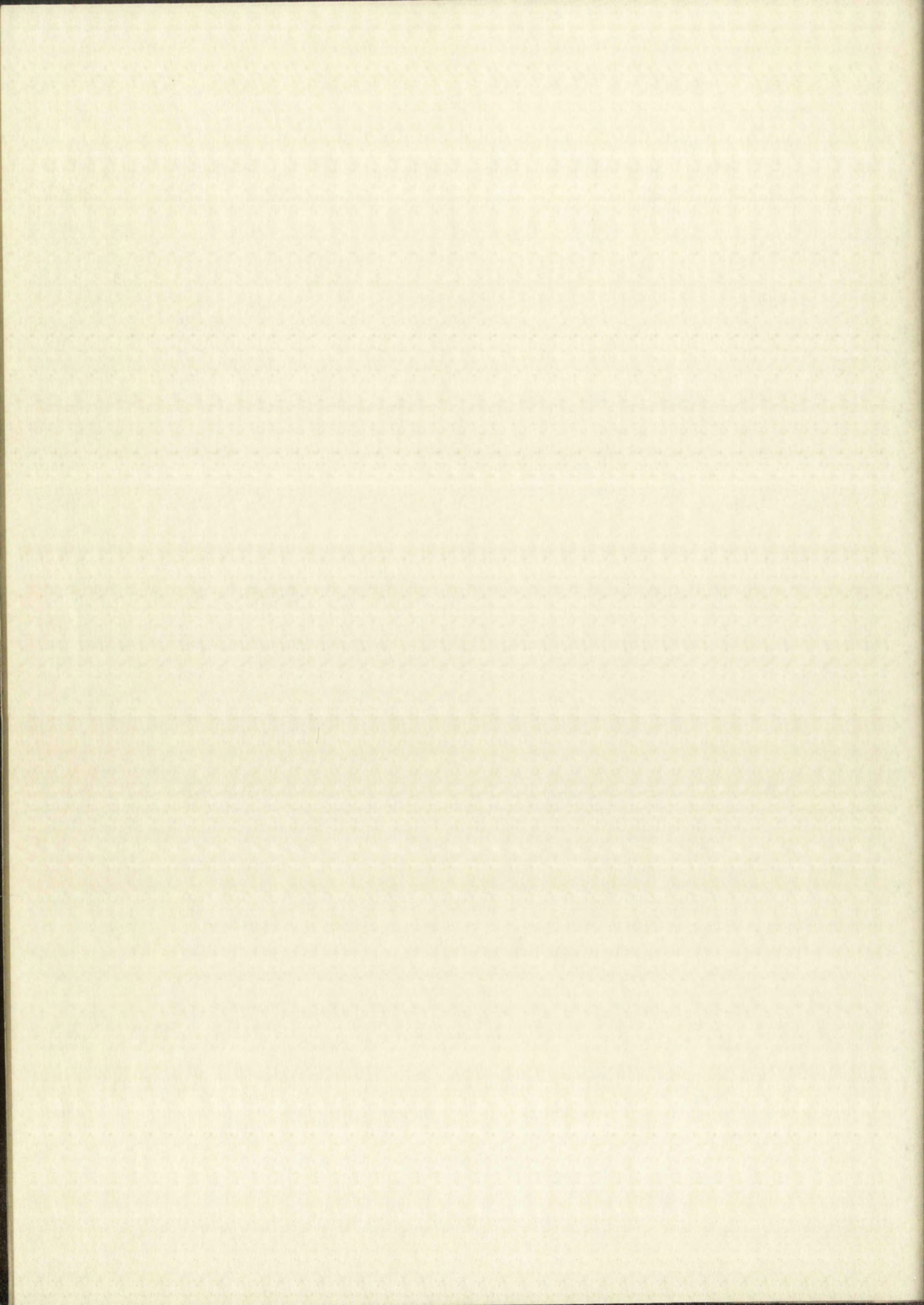
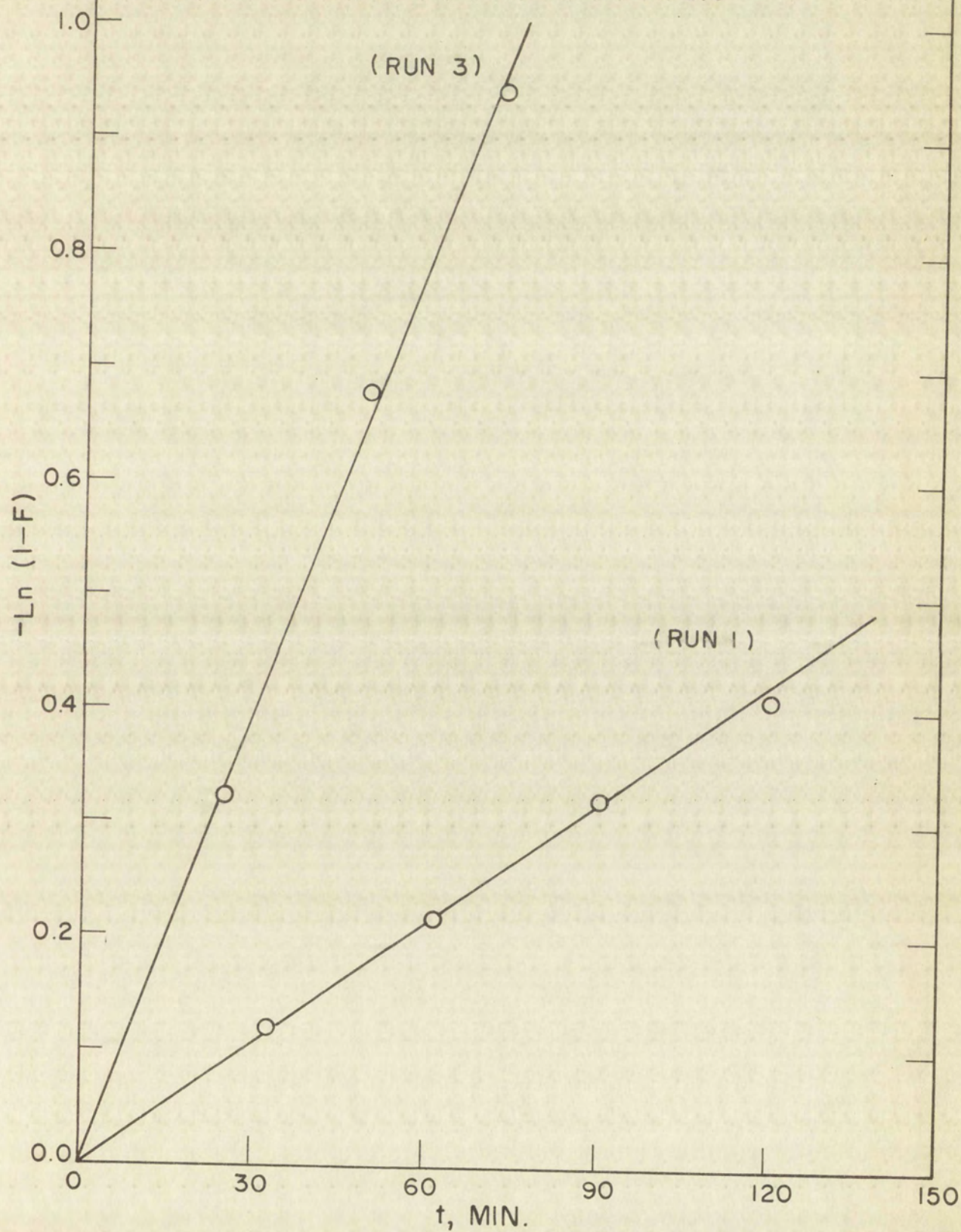


FIGURE 2
Benzyl Iodide Experiments In Acetone At 0.0°



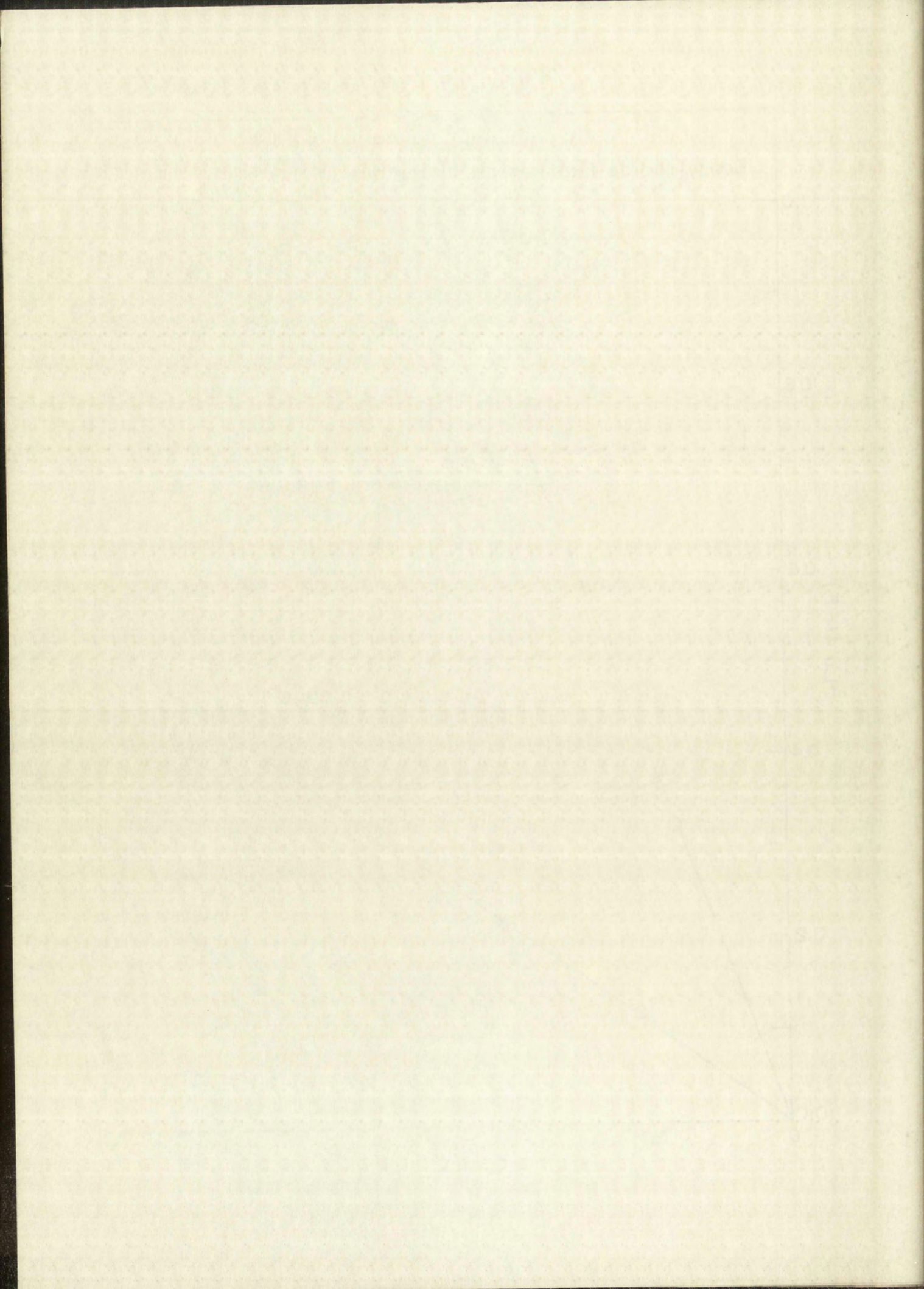


Table VI

Experimental Data for Run No. 5

Temperature: 17.8°

Solvent: Absolute acetone

(BI) = 0.00002980 M

(KI) = 0.0000610 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	7.4	38,850	2348	0.174
2	18.3	36,380	4887	0.361
3	25.5	35,700	6115	0.446

 $t_{1/2} = 28.9$ min. $k = 264$ l/mole/min.

Blank correction = 0.20 per cent

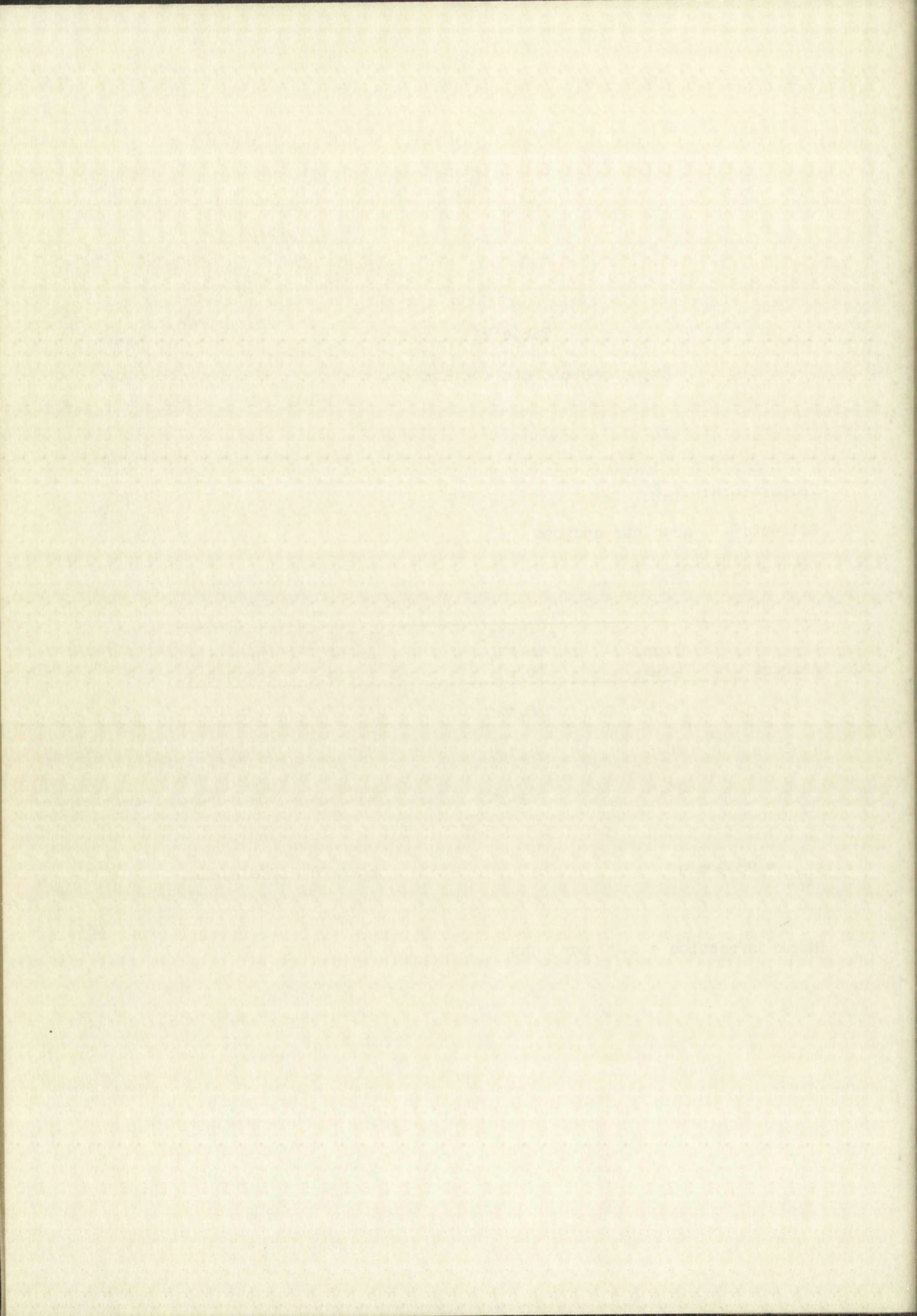


Table VII

Experimental Data for Run No. 6

Temperature: 17.8°

Solvent: Absolute acetone

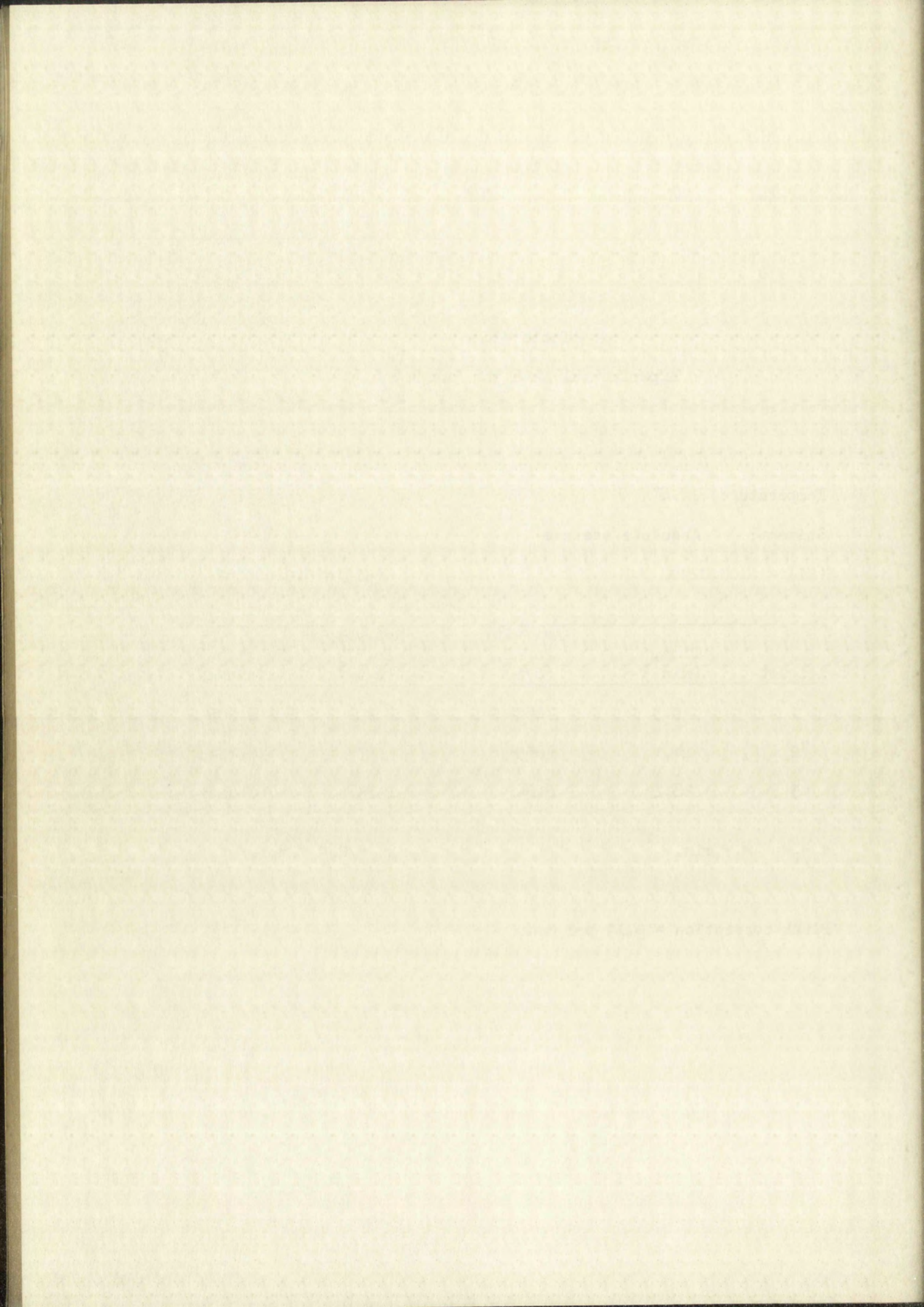
(BI) = 0.00002980 M

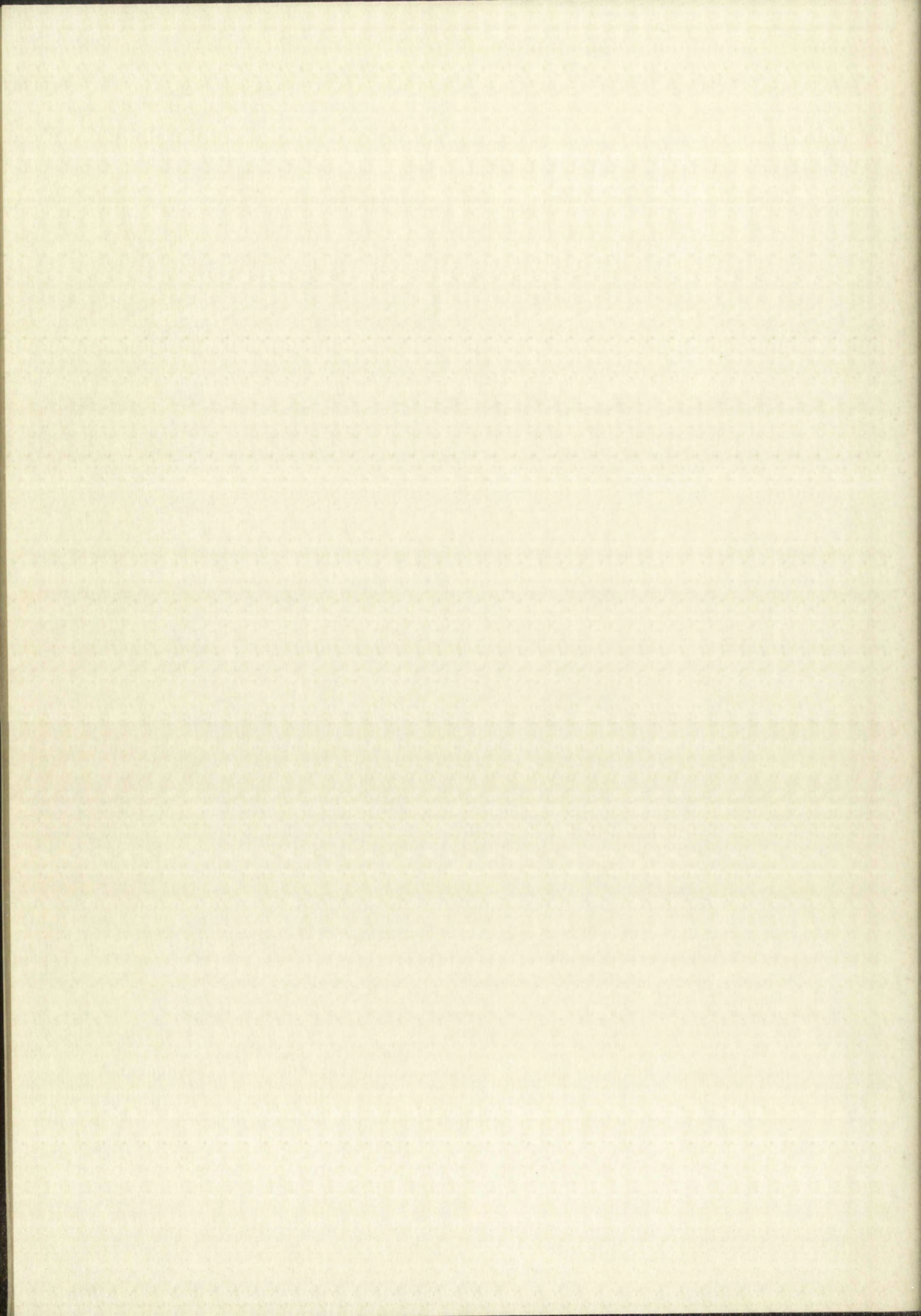
(KI) = 0.00003052 M

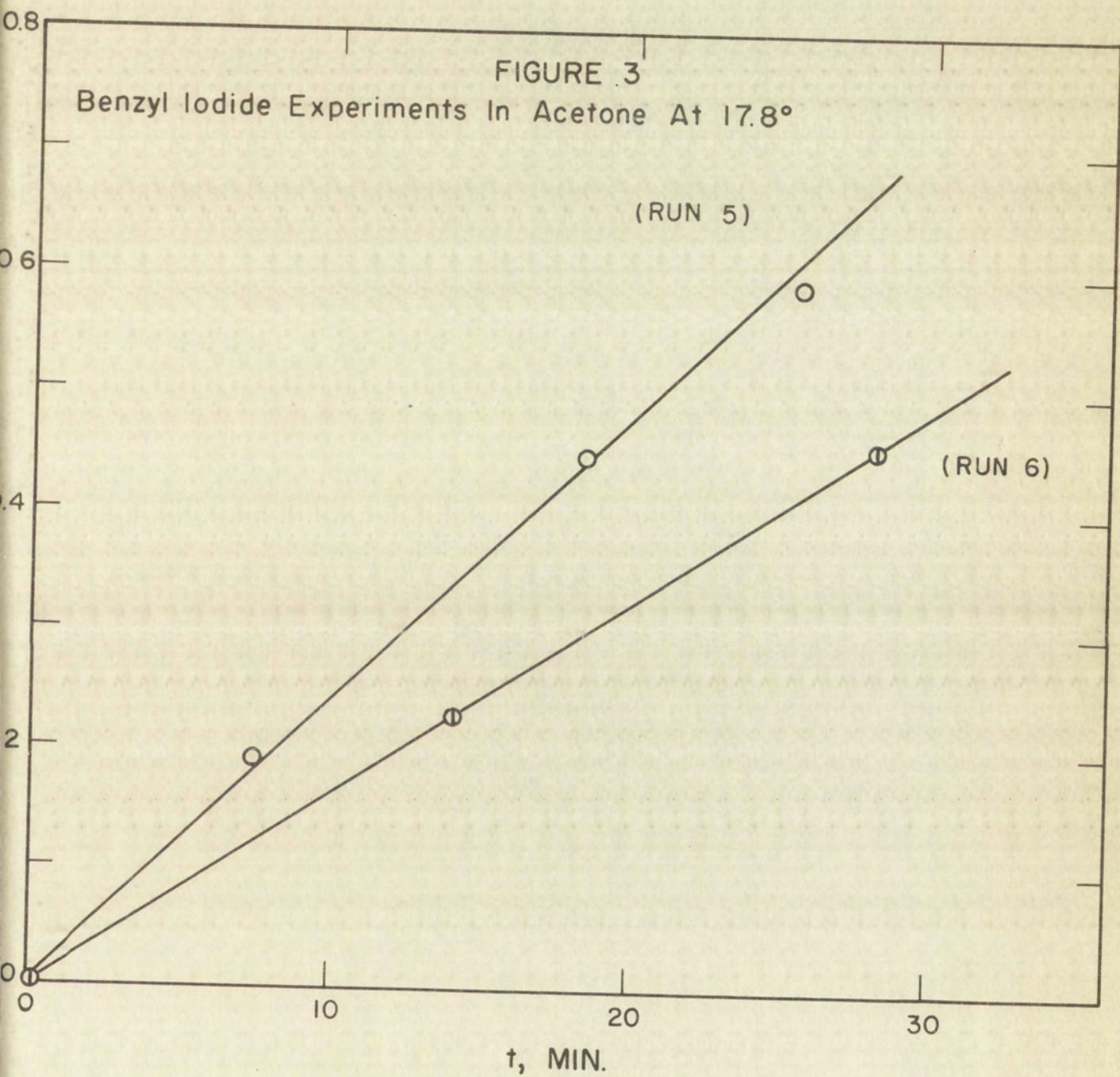
Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	0.3	7650	19	0.005
2	14.1	6855	767	0.204
3	28.1	6164	1363	0.367

 $t_{1/2} = 42.7$ min. $k = 269$ l/mole/min.

Blank correction = 0.19 per cent







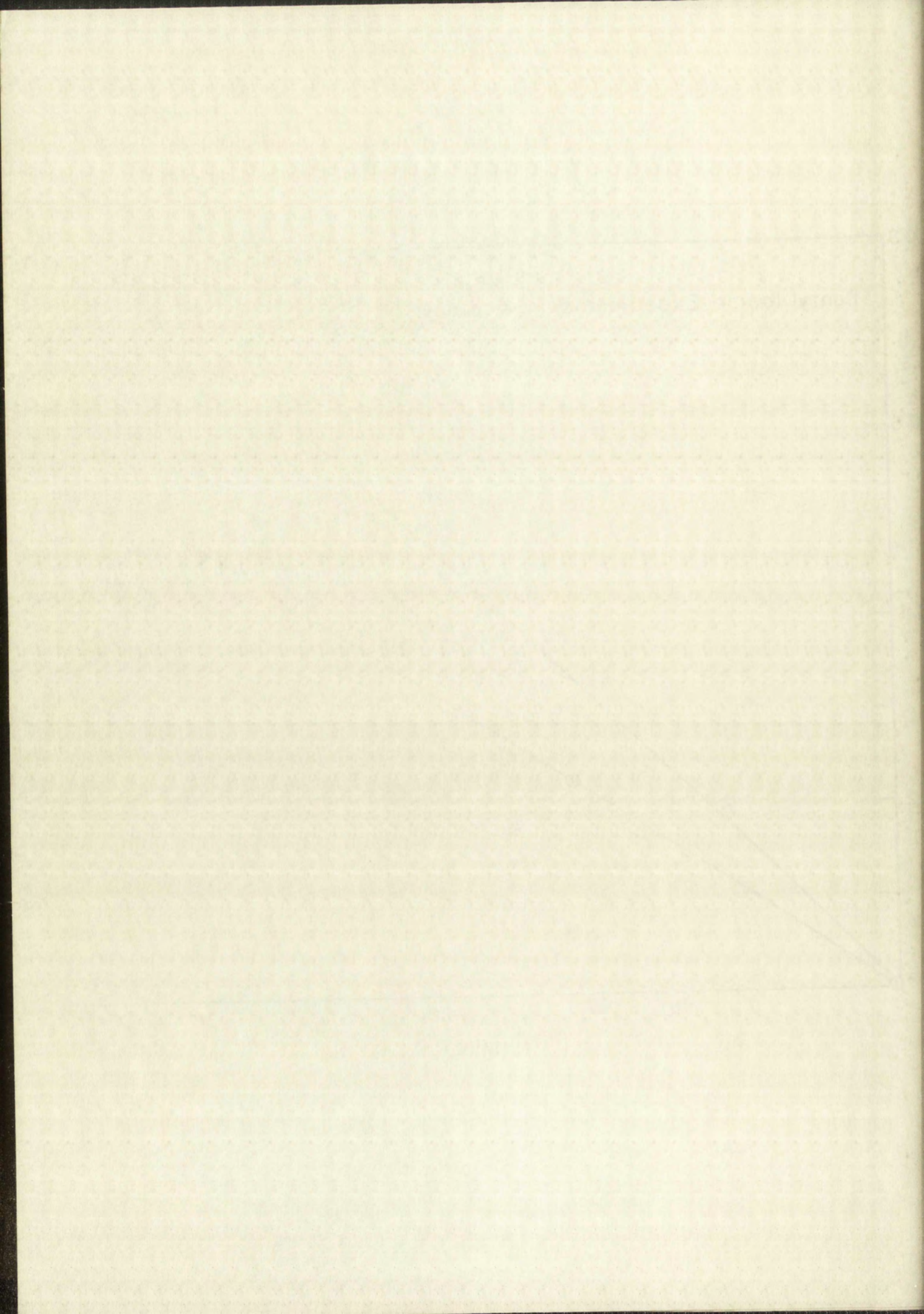


Table VIII
Experimental Data for Run No. 7

Temperature: 34.2°

Solvent: Absolute acetone

(BI) = 0.00002912 M

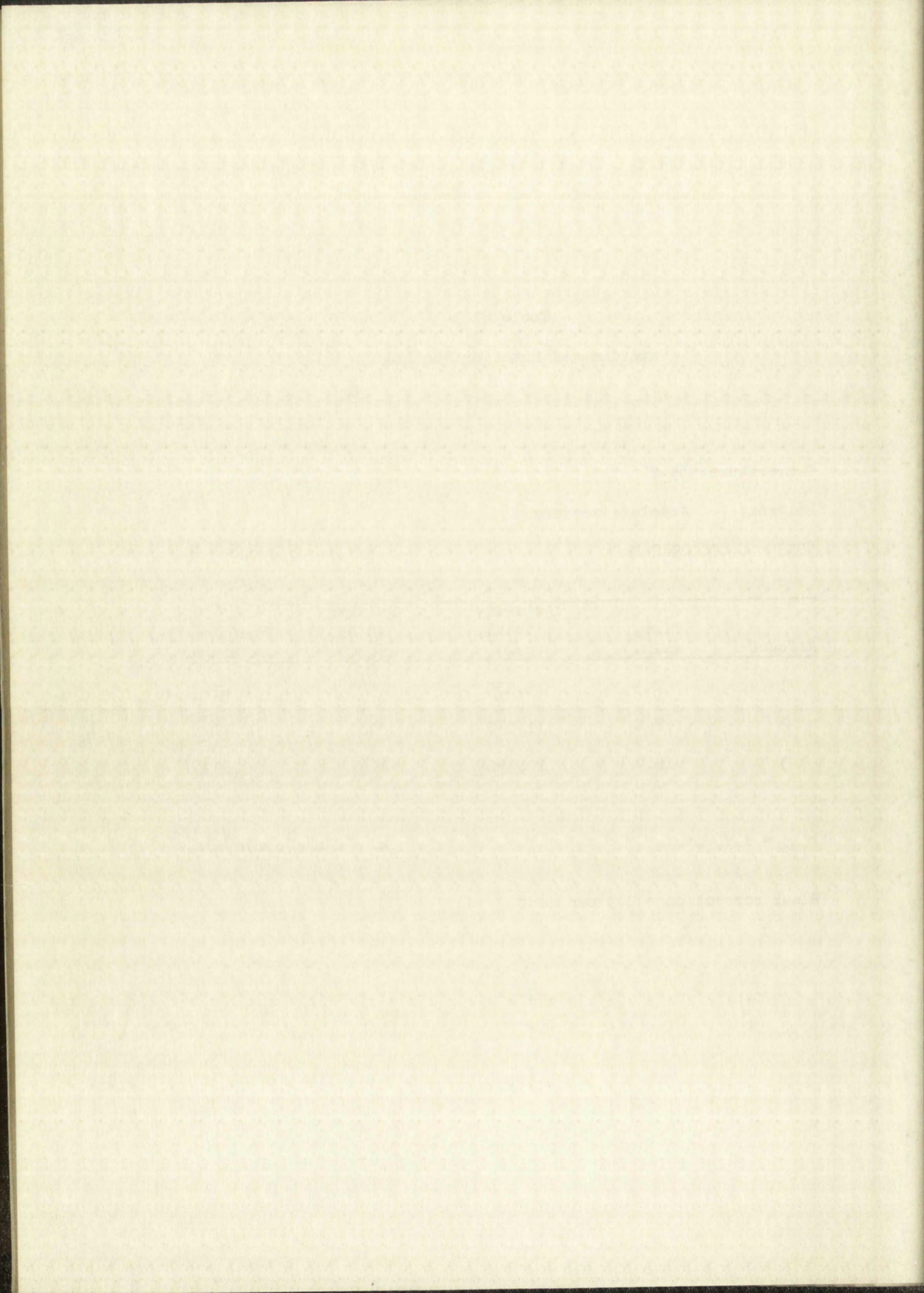
(KI) = 0.00002983 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	0.3	15,130	85	0.012
2	8.4	11,940	3035	0.410
3	16.7	10,350	4661	0.629

$t_{1/2} = 11.6$ min.

$k = 1016$ l./mole/min.

Blank correction = 0.3 per cent



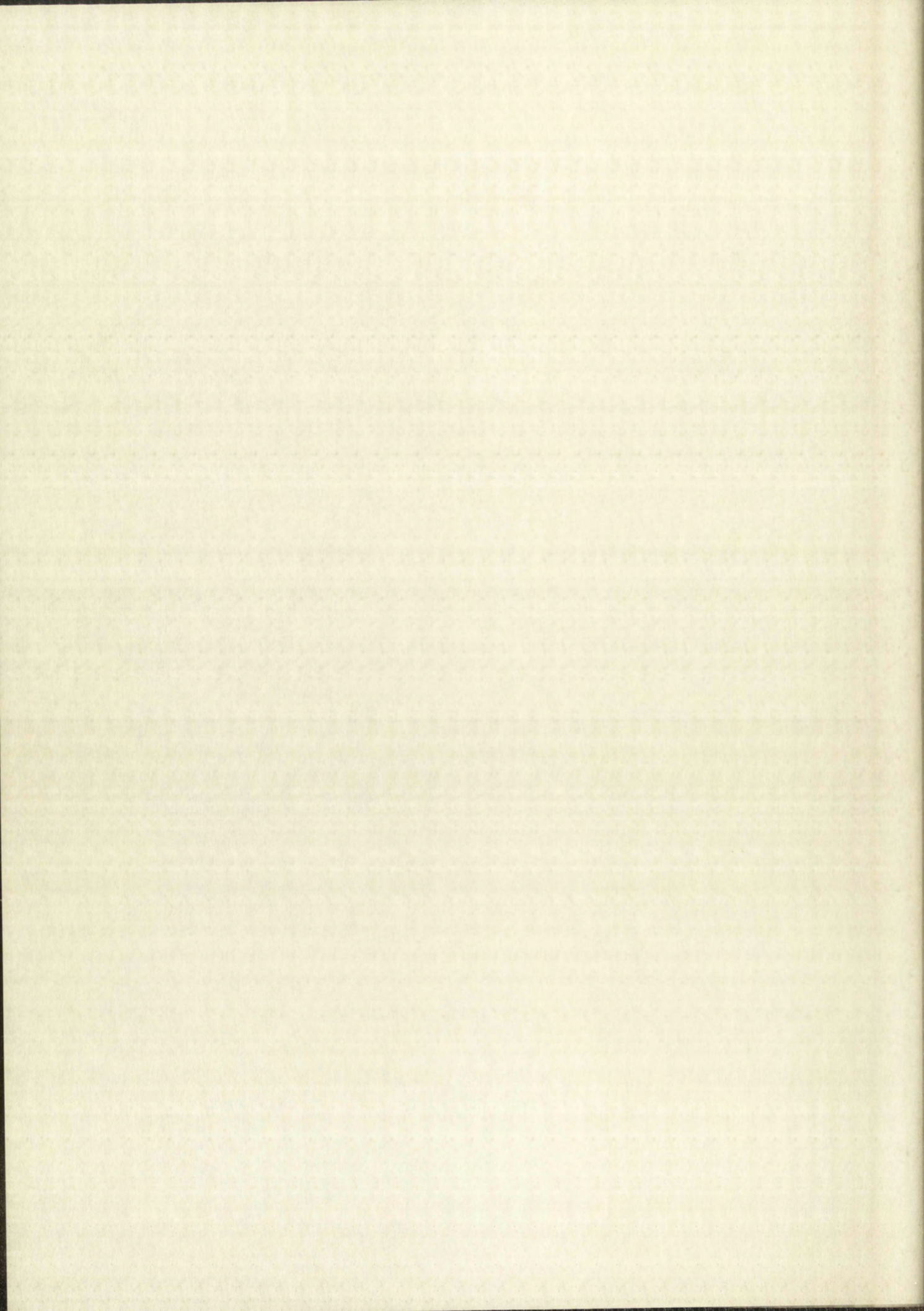
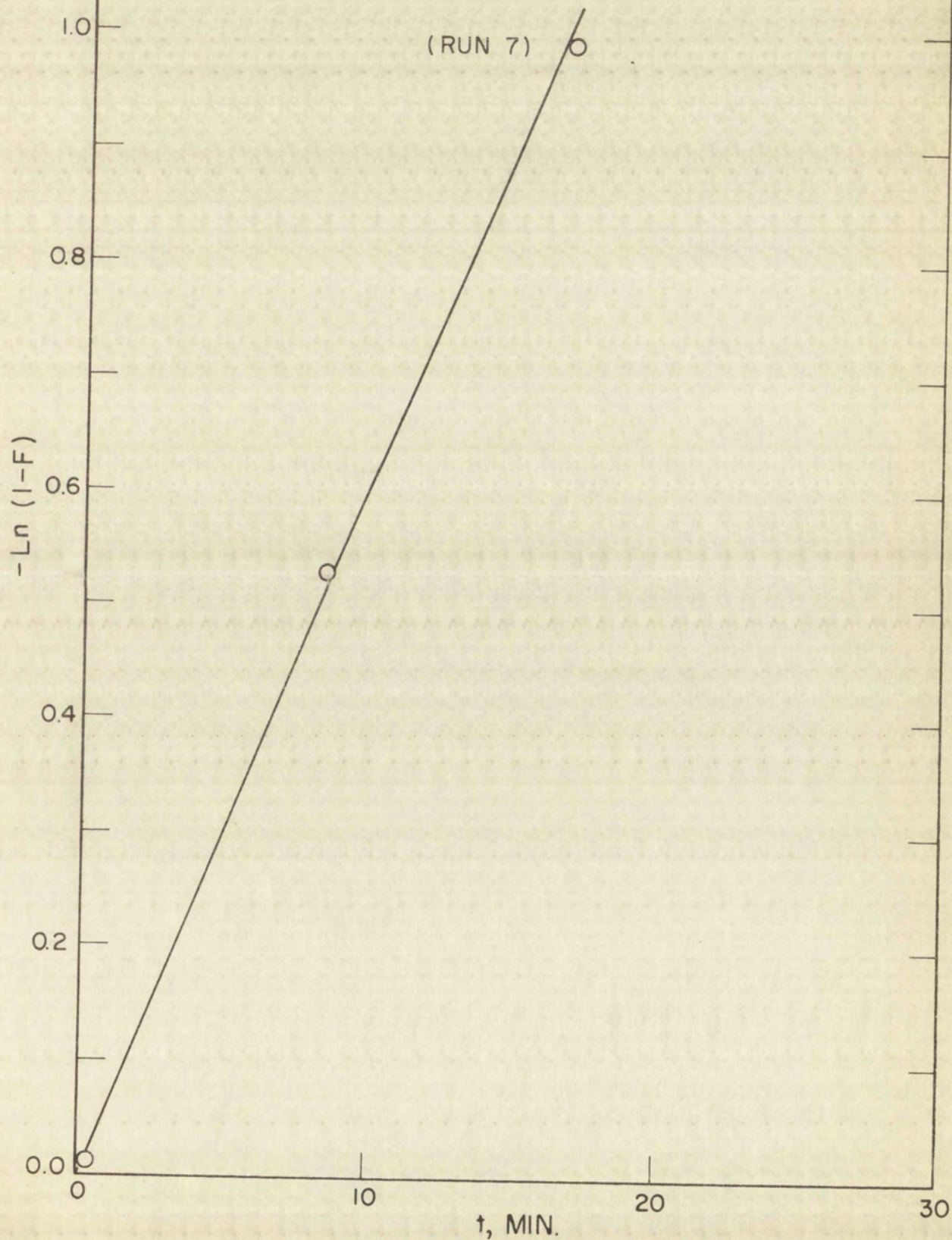


FIGURE 4

Benzyl Iodide Experiment In Acetone At 34.2°



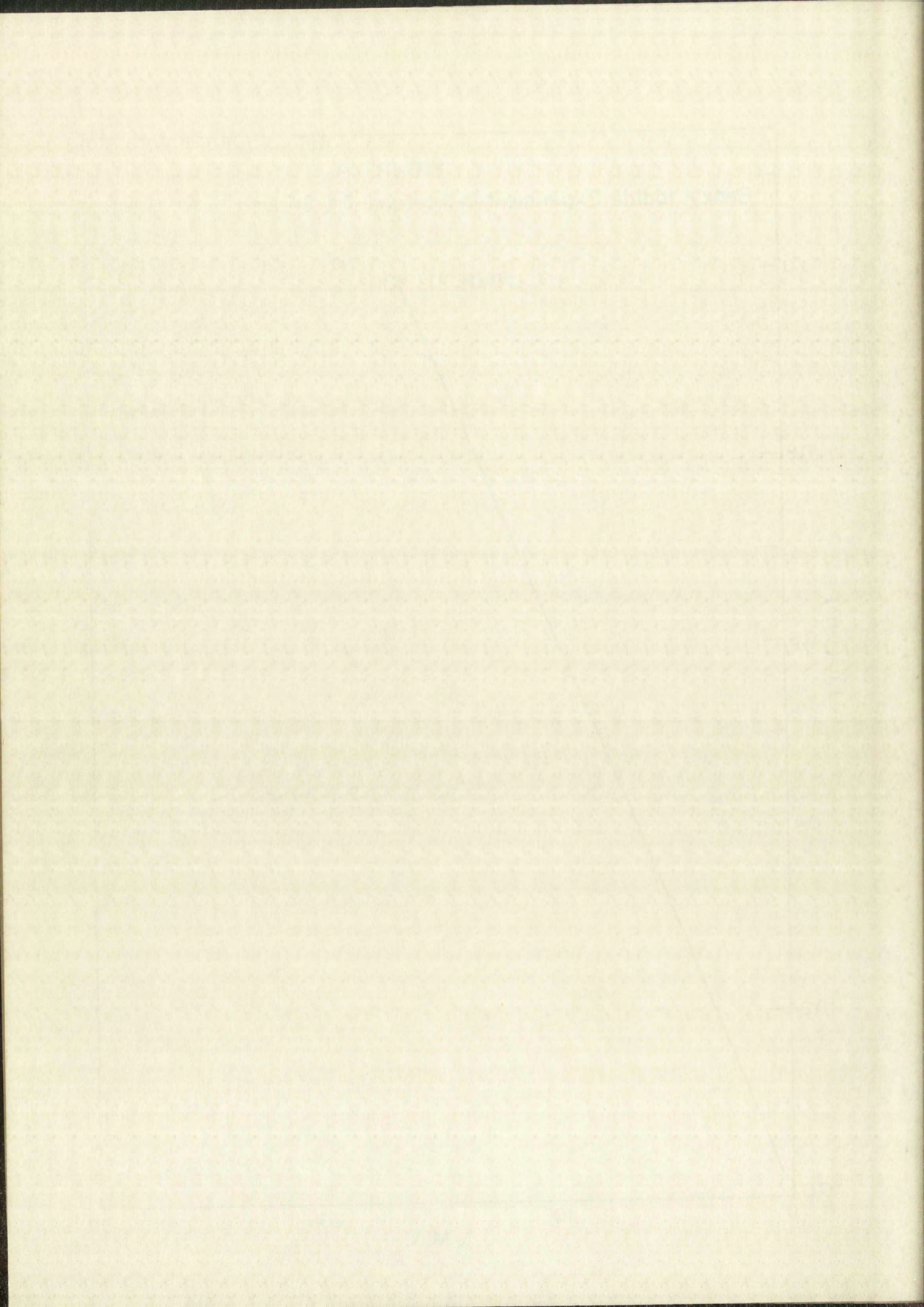


Table IX
Experimental Data for Run No. 8

Temperature: 34.2°

Solvent: Absolute acetone

(BI) = 0.00004370 M

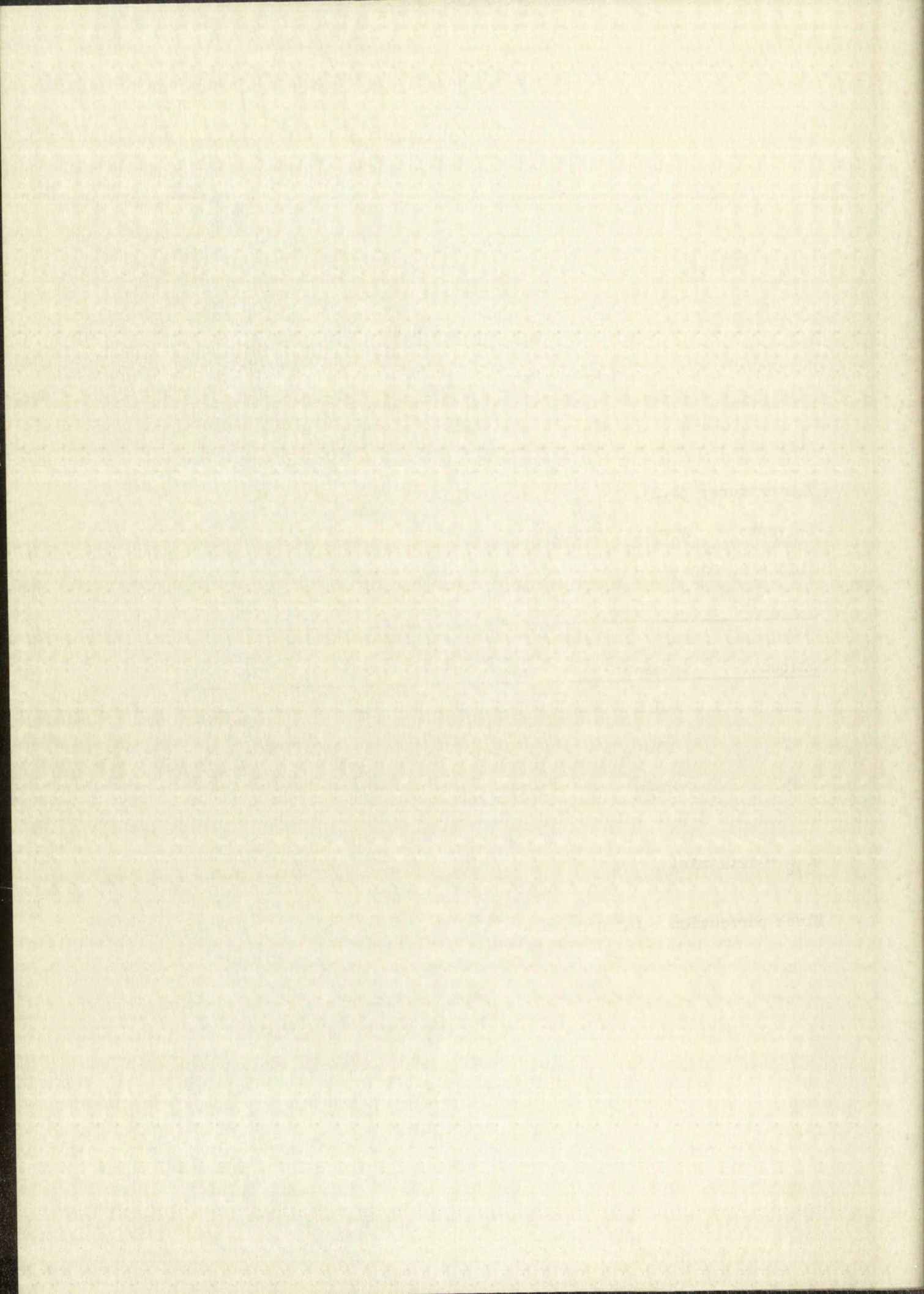
(KI) = 0.00001491 M

Aliquot	Time (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	8.8	5553	2333	0.397
2	15.4	4371	3357	0.583
3	25.1	3452	4242	0.739

$t_{1/2} = 12.1$ min.

$k = 978$ l/mole/min.

Blank correction = 0.5 per cent



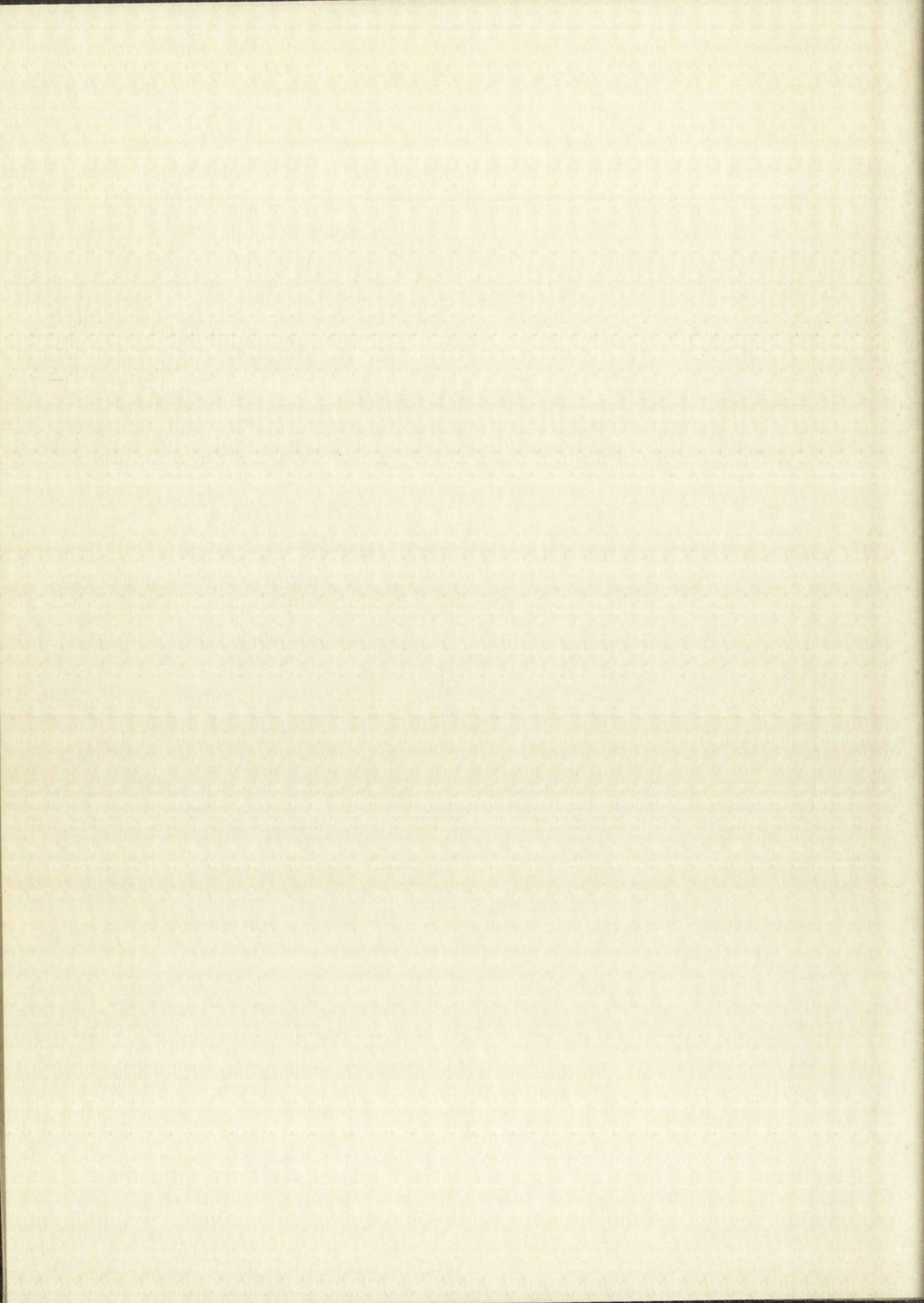
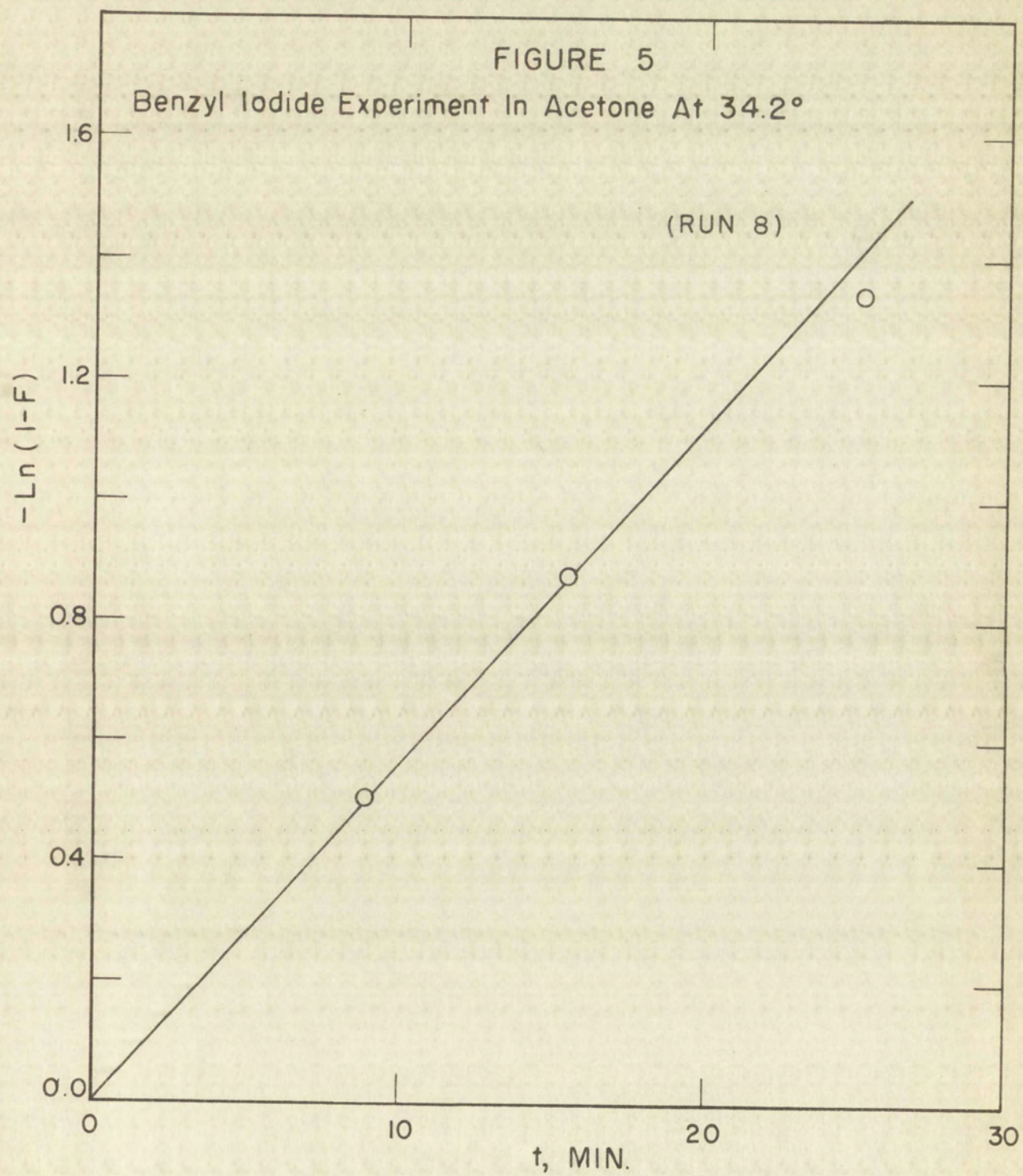
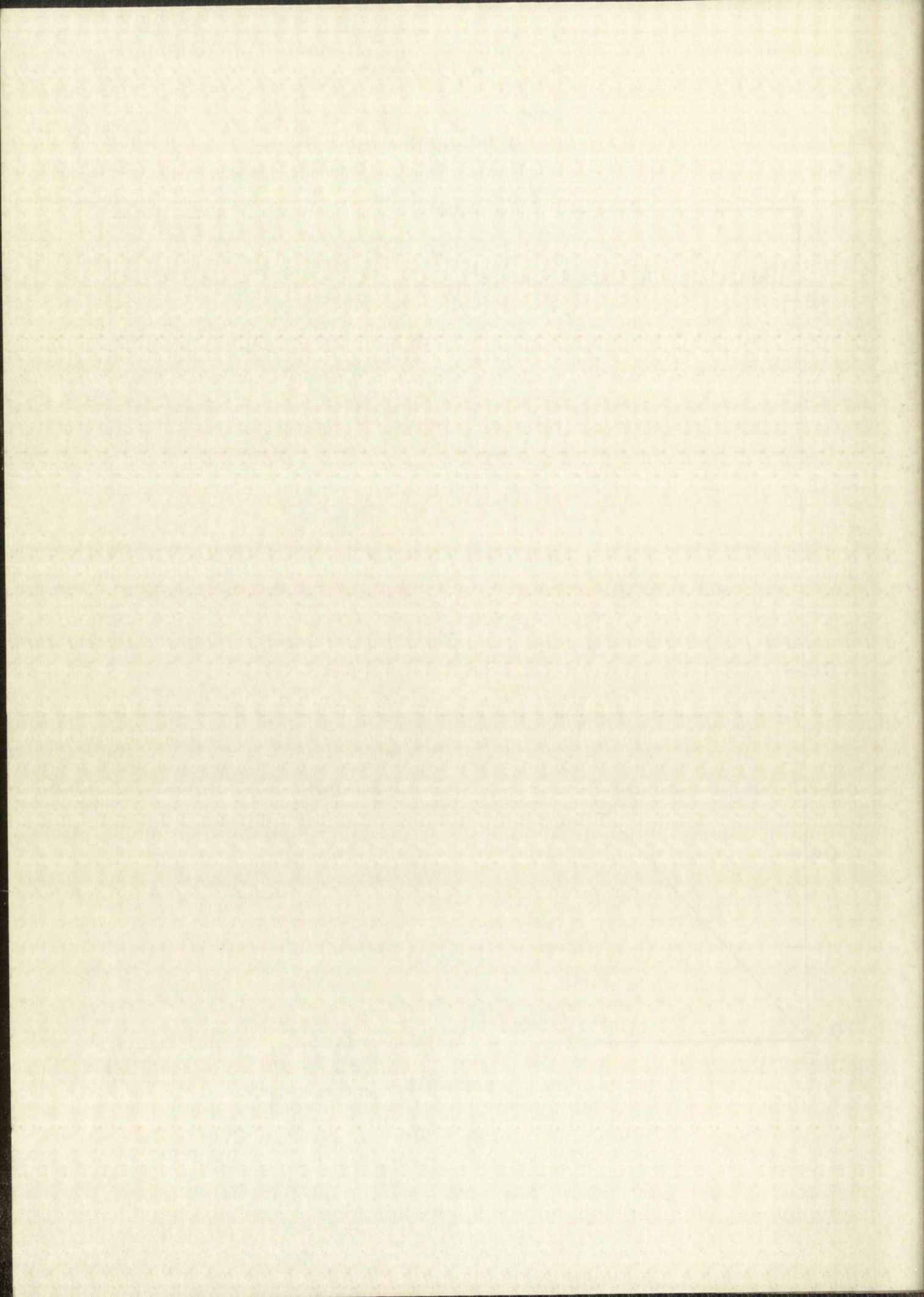


FIGURE 5

Benzyl Iodide Experiment In Acetone At 34.2°





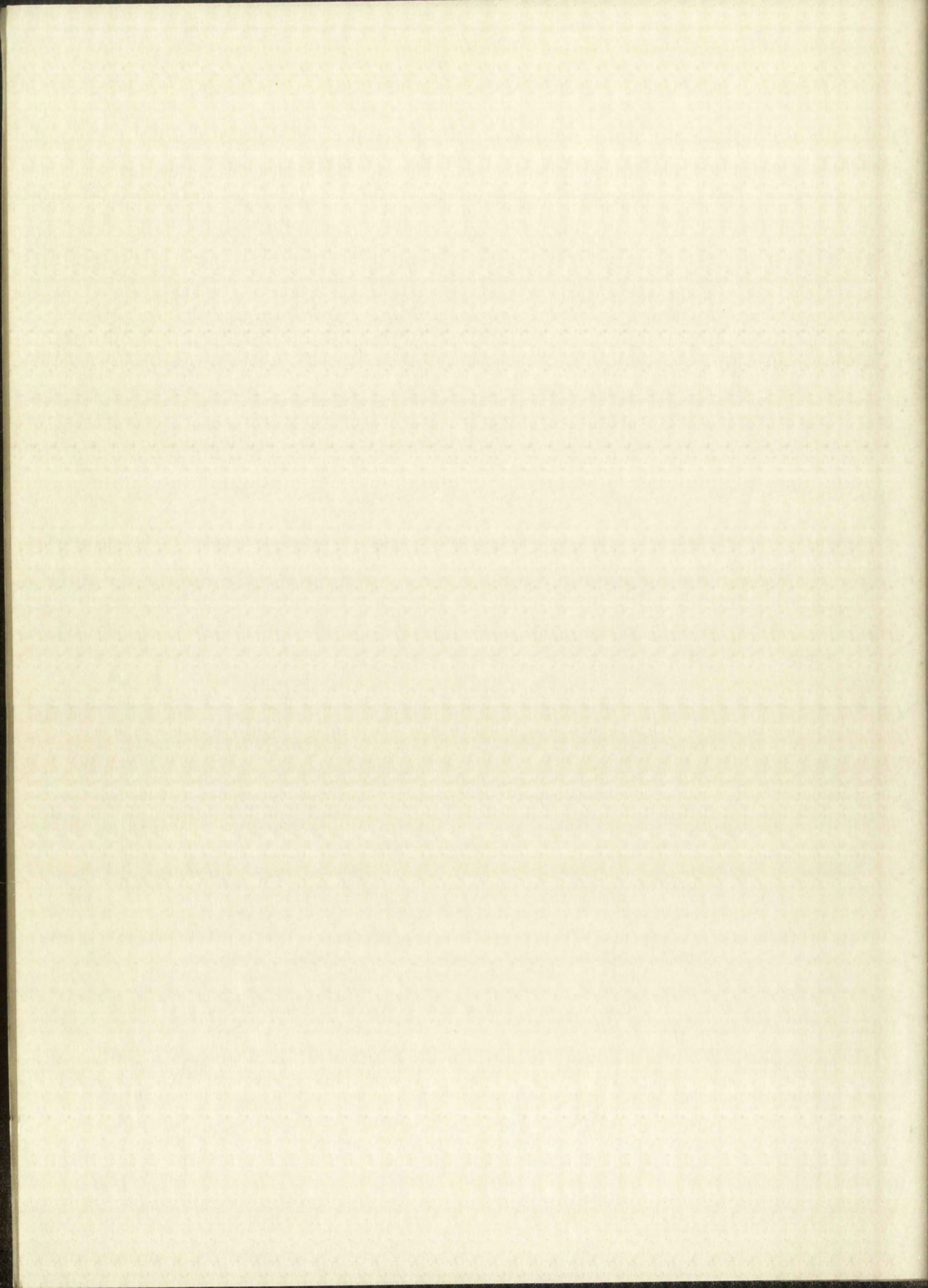
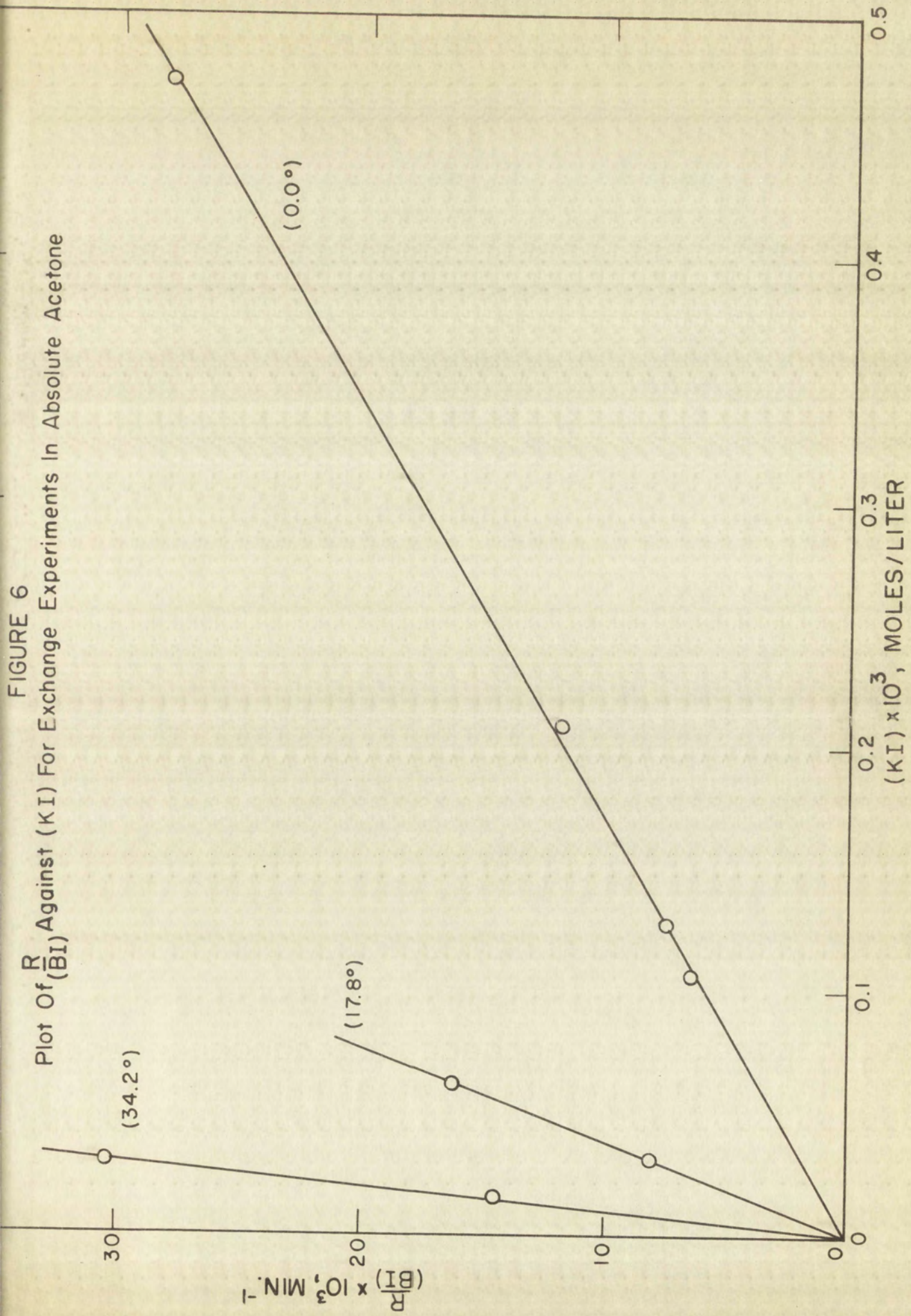
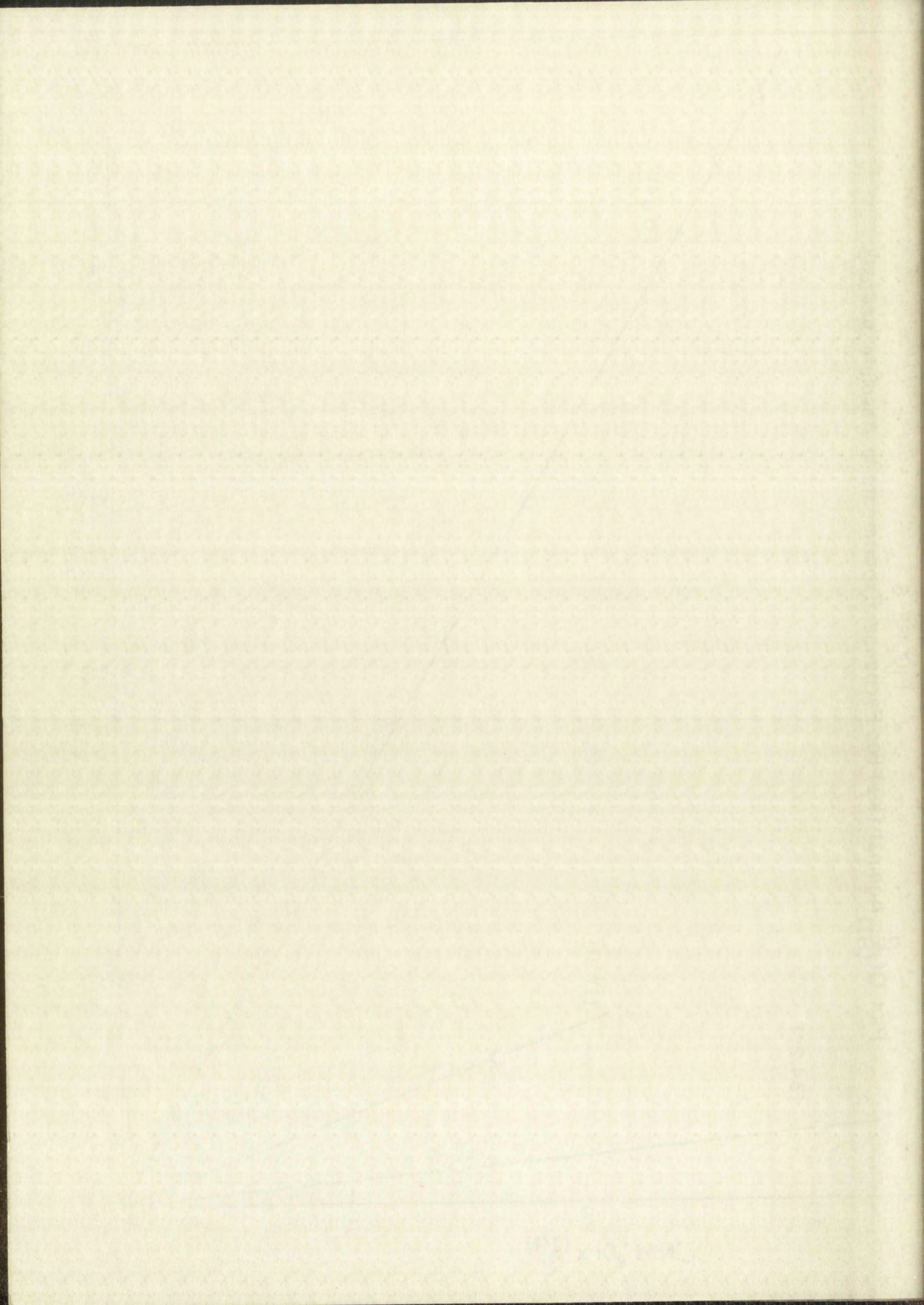


FIGURE 6
Plot Of $\frac{R}{(BI)}$ Against (KI) For Exchange Experiments In Absolute Acetone





Experimental Data for p-Nitrobenzyl Iodide

Exchange Experiments in Absolute Acetone

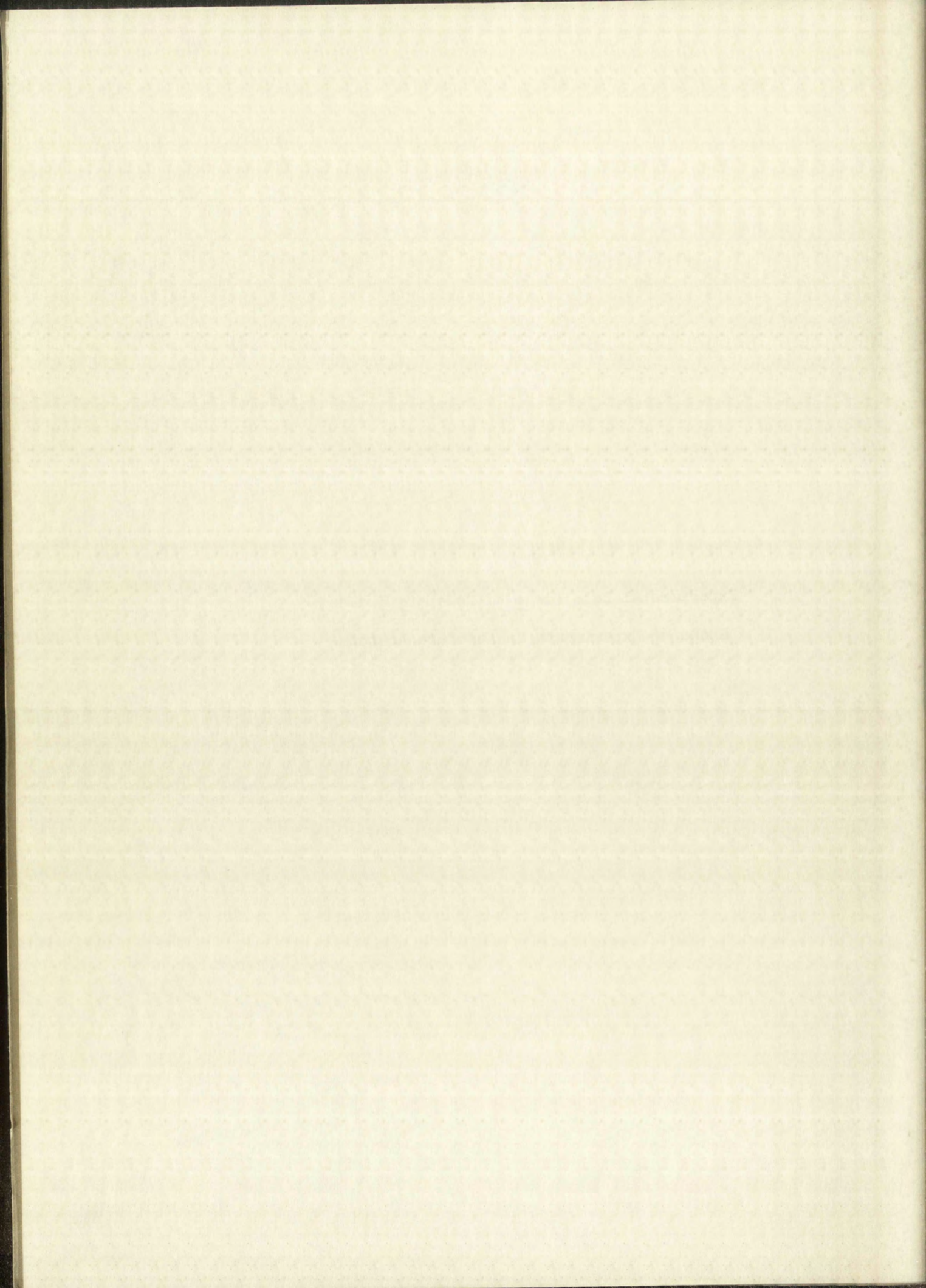


Table X

Summary of p-Nitrobenzyl Iodide Exchange Experiments in
Absolute Acetone

Run. No.	Temperature, °C	(PNBI), M x 10 ⁵	(KI), M x 10 ⁵	^t _{1/2} , min.	k ₂ , l./mole/min.	Average k, l./mole/min.
9	0.0	2.580	3.125	32.8	370	
10	0.0	3.440	2.083	33.5	375	372 ± 3
11	16.0	0.2621	0.757	42.4	1604	
12	16.0	0.524	0.505	41.4	1627	
13	16.0	0.776	0.3454	38.3	1613	1615 ± 8

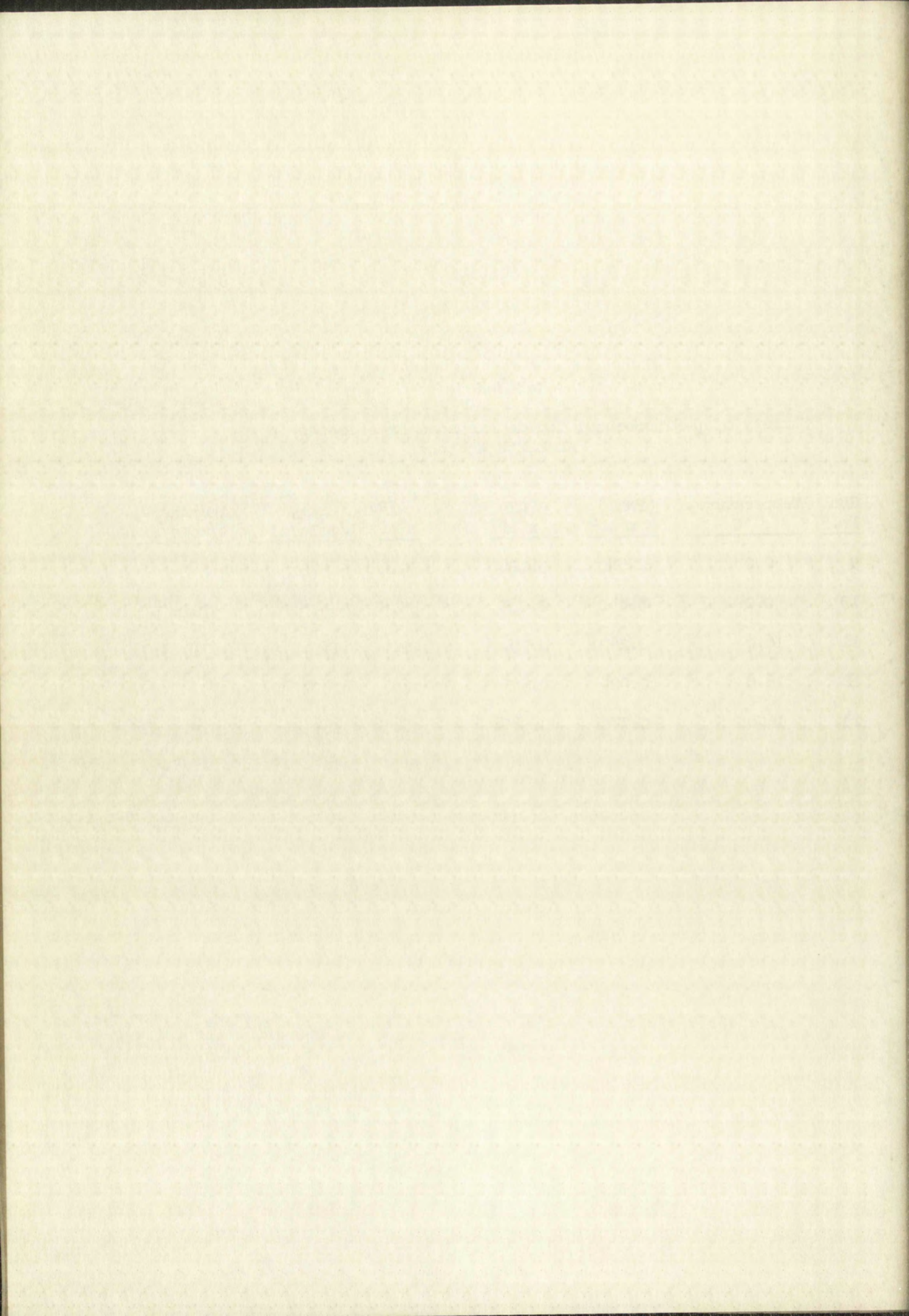


Table XI
Experimental Data for Run No. 9

Temperature: 0.0°

Solvent: Absolute acetone

(PNBI) = 0.00002580 M

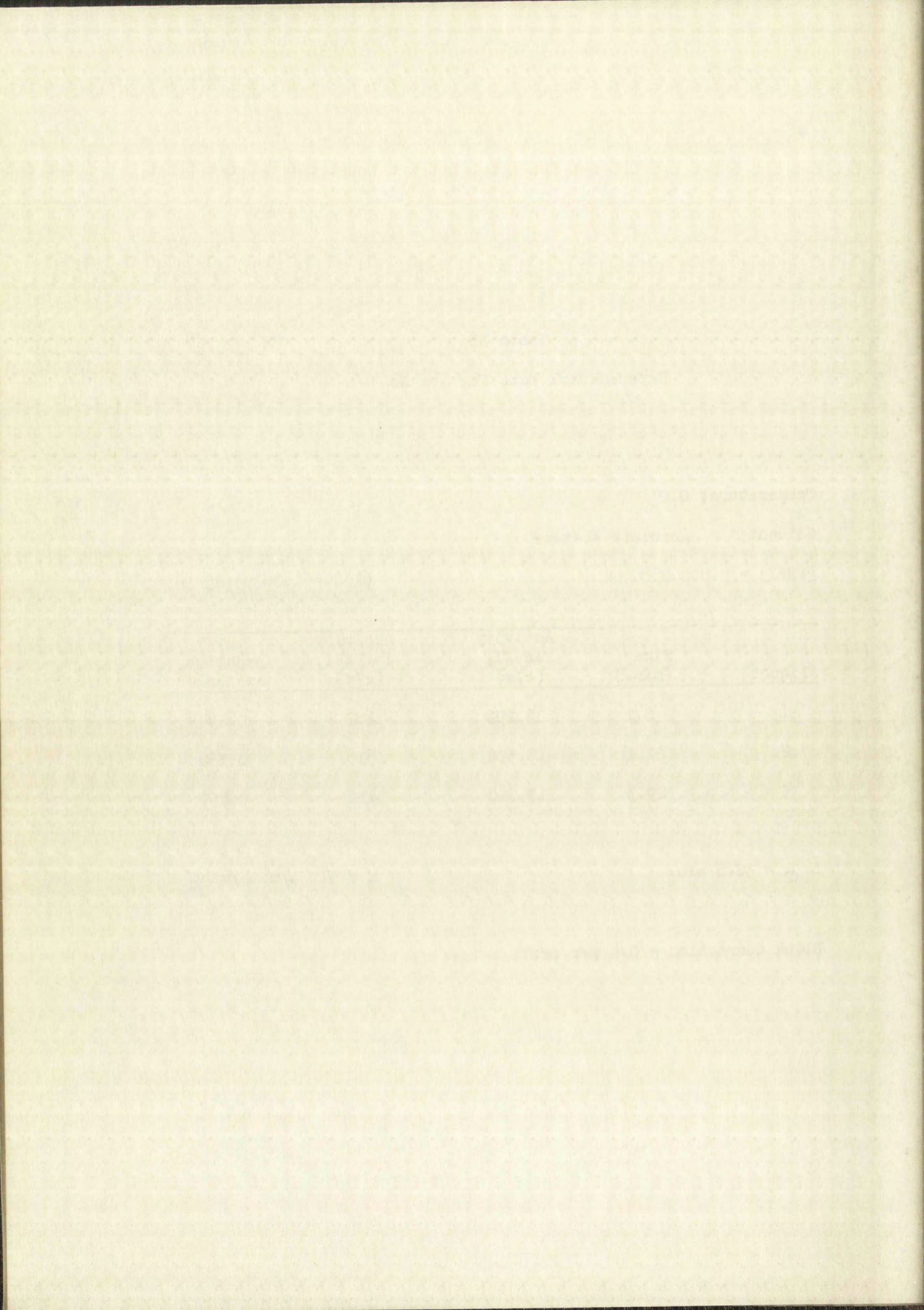
(KI) = 0.00003125 M

Aliquot	Time (min.)	Activity in KI, (c/m)	Activity in PNBI, (c/m)	Fraction exchanged
1	8.1	15,290	1187	0.154
2	21.1	13,500	2640	0.362
3	29.3	13,020	3410	0.459

$t_{1/2} = 32.8$ min.

$k = 370$ l/mole/min.

Blank correction = 0.4 per cent



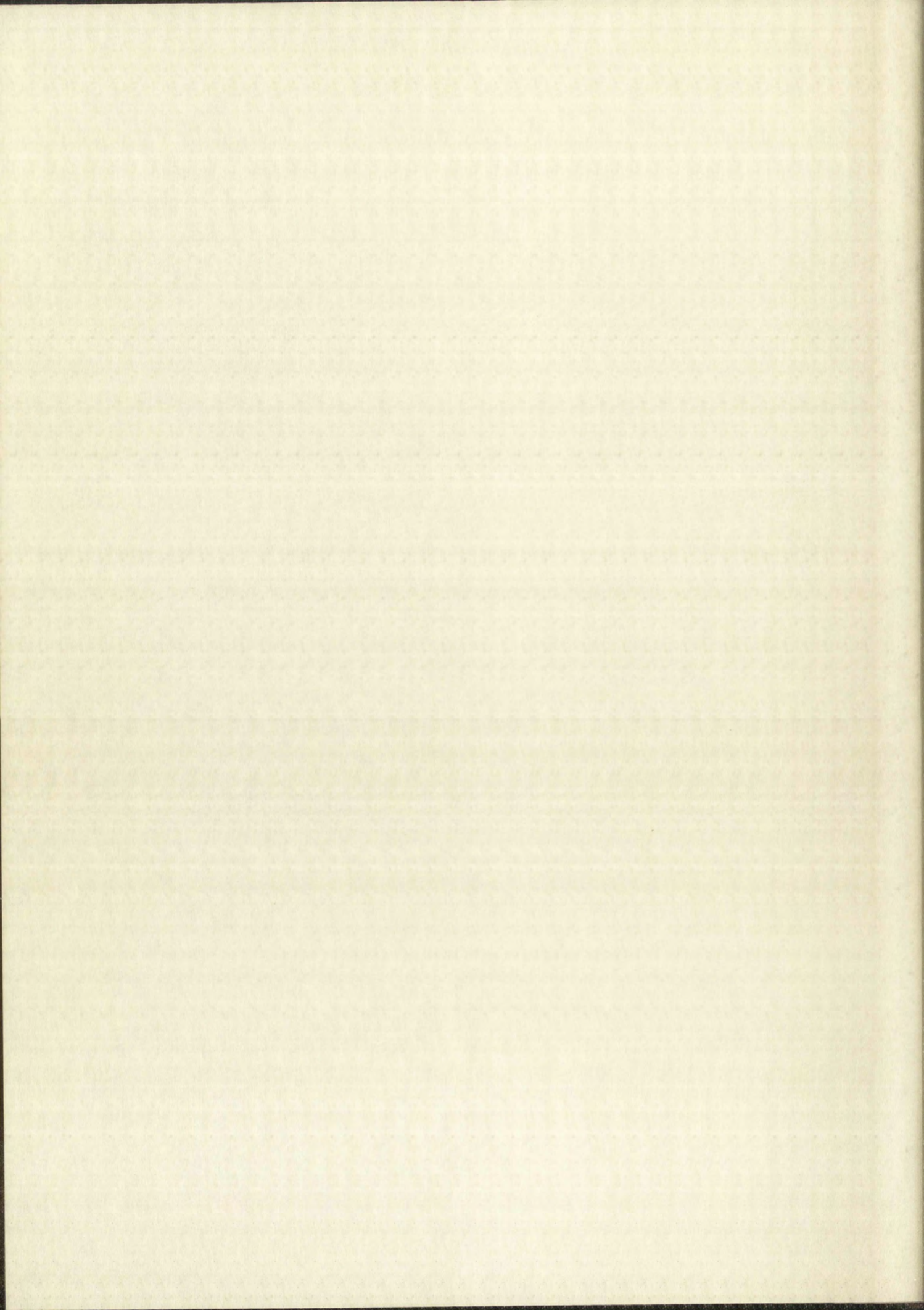
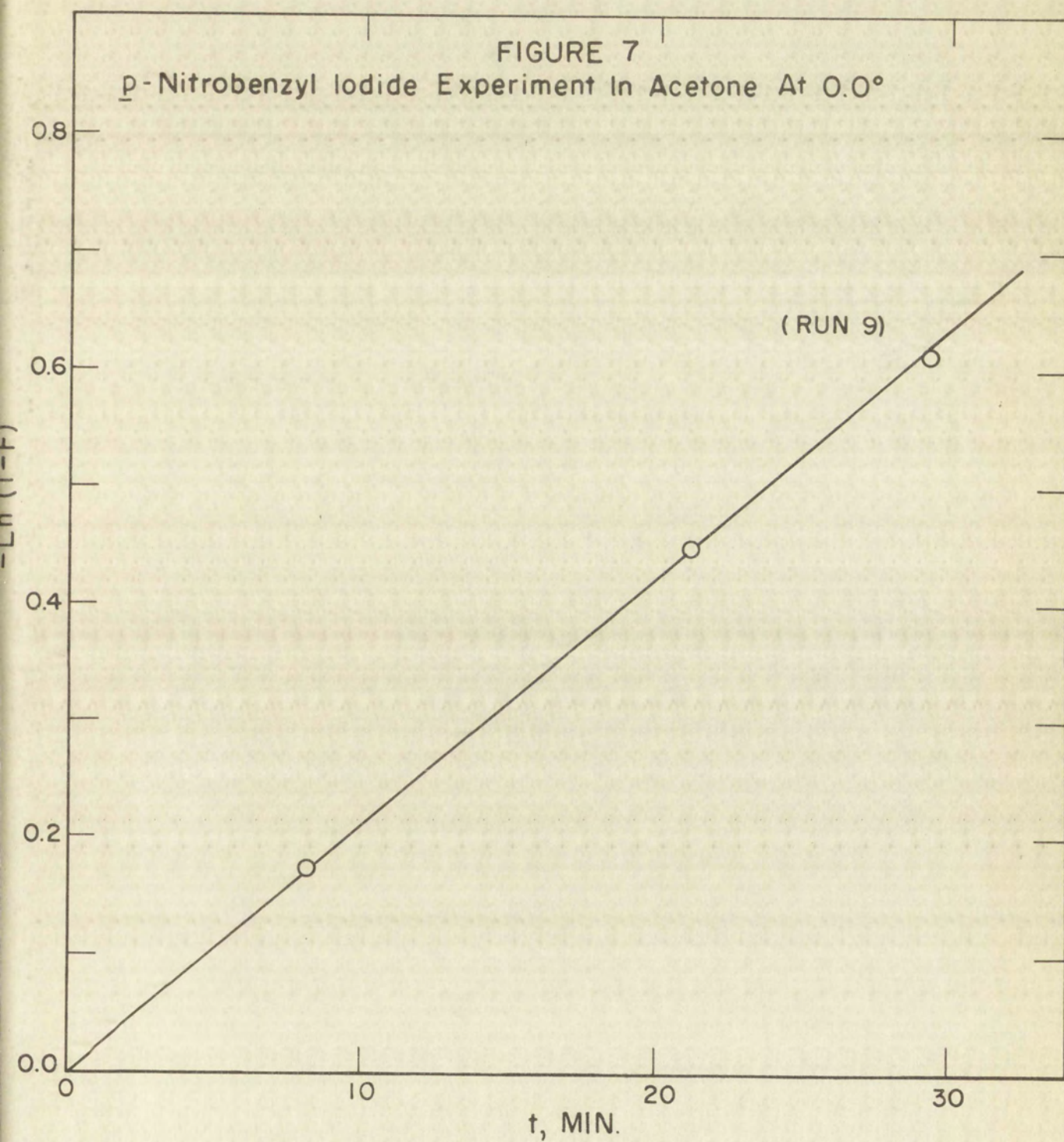


FIGURE 7

p-Nitrobenzyl Iodide Experiment In Acetone At 0.0°



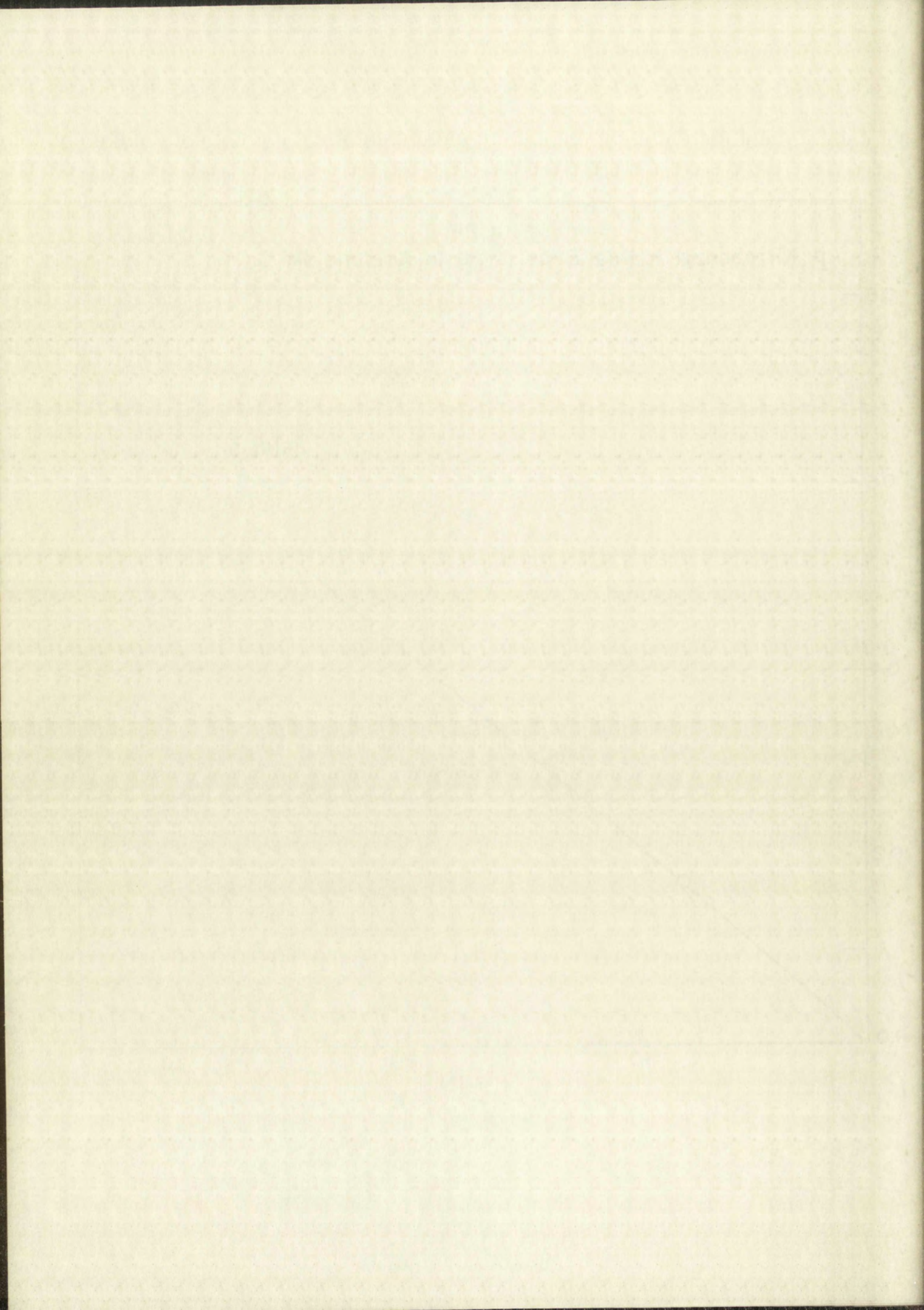


Table XII

Experimental Data for Run No. 10

Temperature: 0.0°

Solvent: Absolute acetone

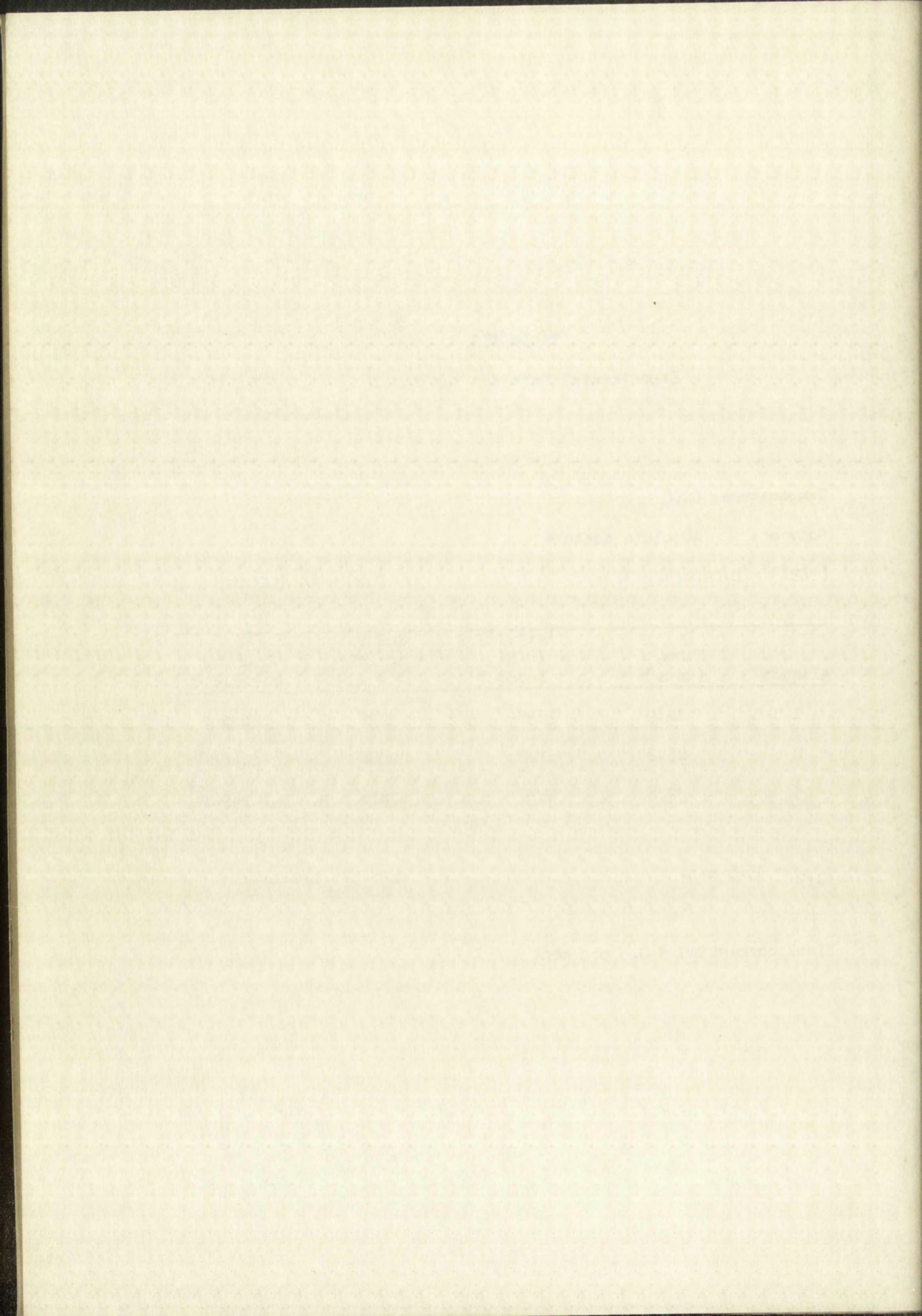
(PNBI) = 0.00003440 M

(KI) = 0.00002083 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in PNBI, (c/m)	Fraction exchanged
1	11.9	7235	1126	0.216
2	25.2	6122	2084	0.408
3	32.8	5676	2511	0.492

 $t_{1/2} = 33.5$ min. $k = 375$ l./mole/min.

Blank correction = 0.4 per cent



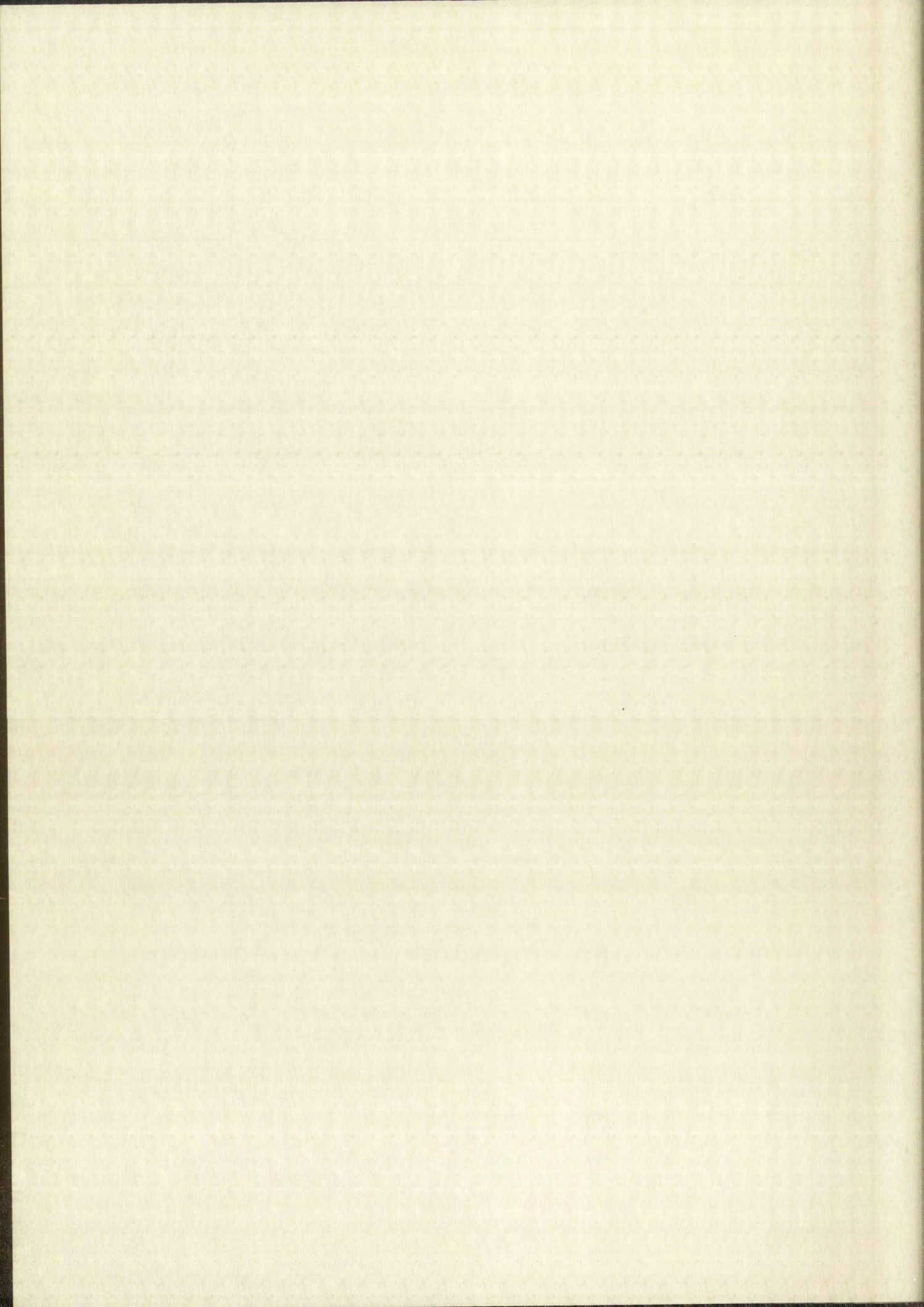
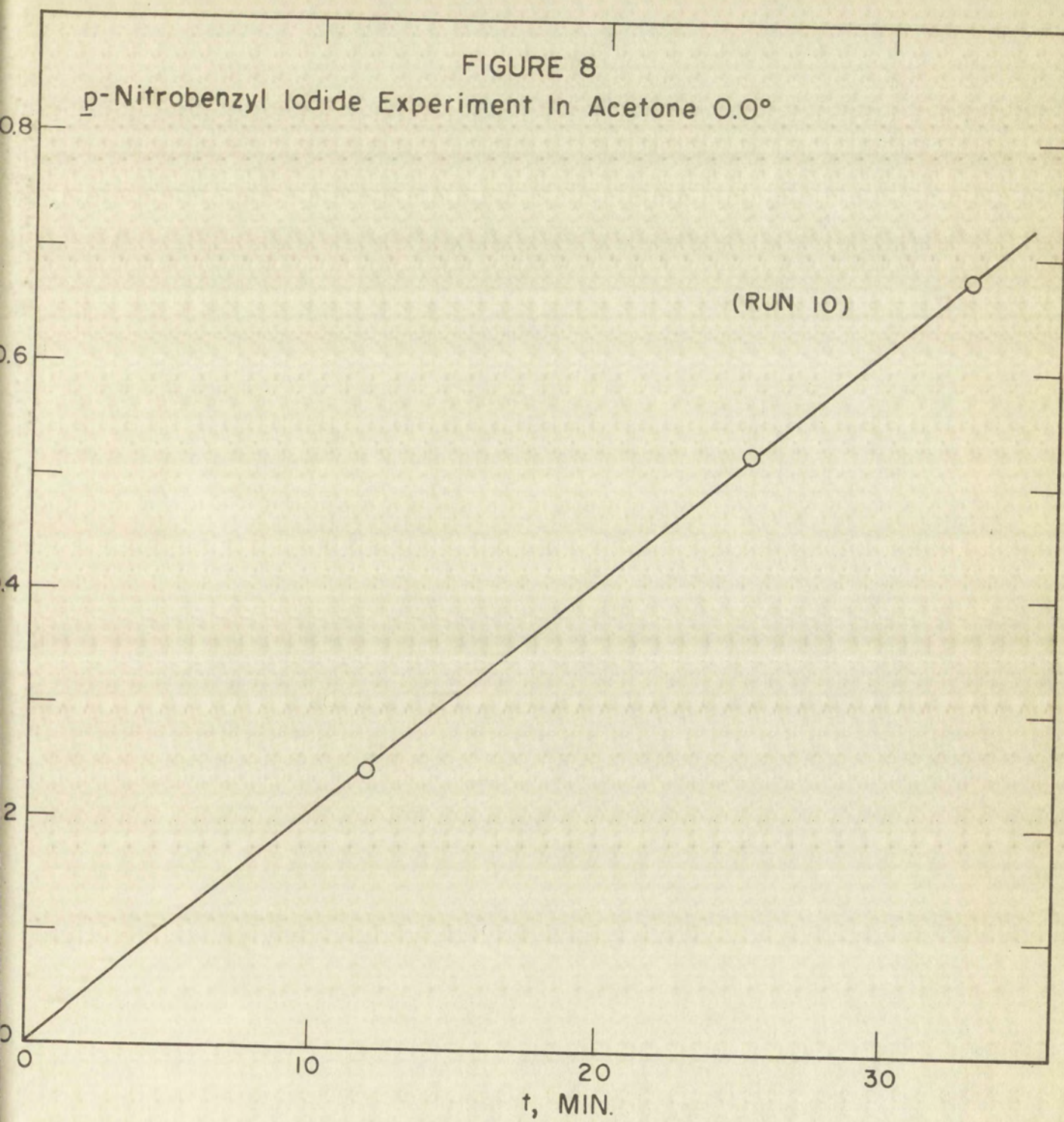


FIGURE 8

p-Nitrobenzyl Iodide Experiment In Acetone 0.0°



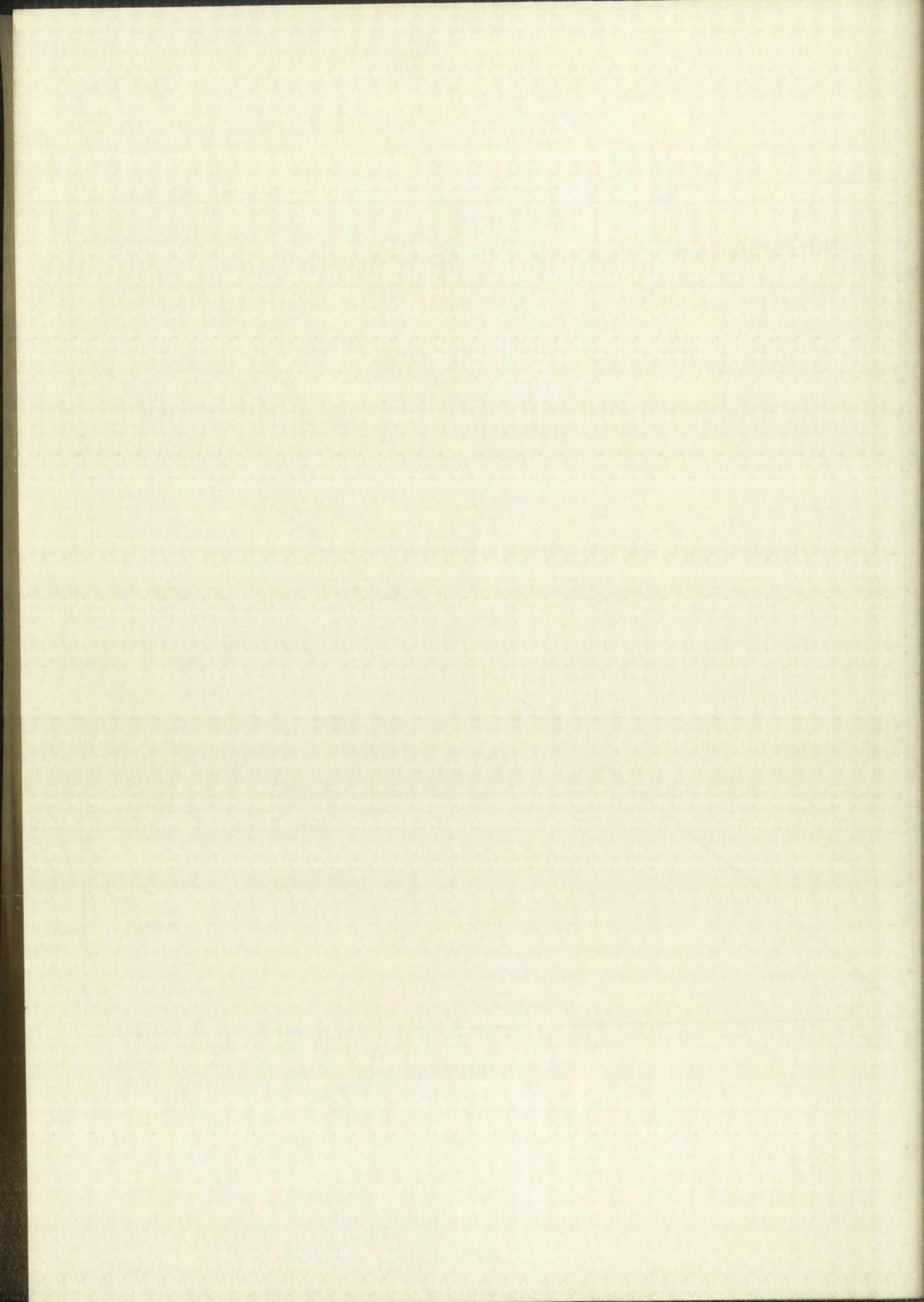


Table XIII

Experimental Data for Run No. 11

Temperature: 16.0°

Solvent: Absolute acetone

(PNBI) = 0.000002621 M

(KI) = 0.00000757 M

Aliquot	Time (min.)	Activity in KI, (c/m)	Activity in PNBI, (c/m)	Fraction exchanged
1	0.3	9541	0	0
2	18.0	8932	699	0.265
3	37.9	8745	1202	0.461
4	56.5	8551	1589	0.589

 $t_{1/2} = 42.4$ min. $k = 1604$ l./mole/min.

Blank correction = 2.2 per cent

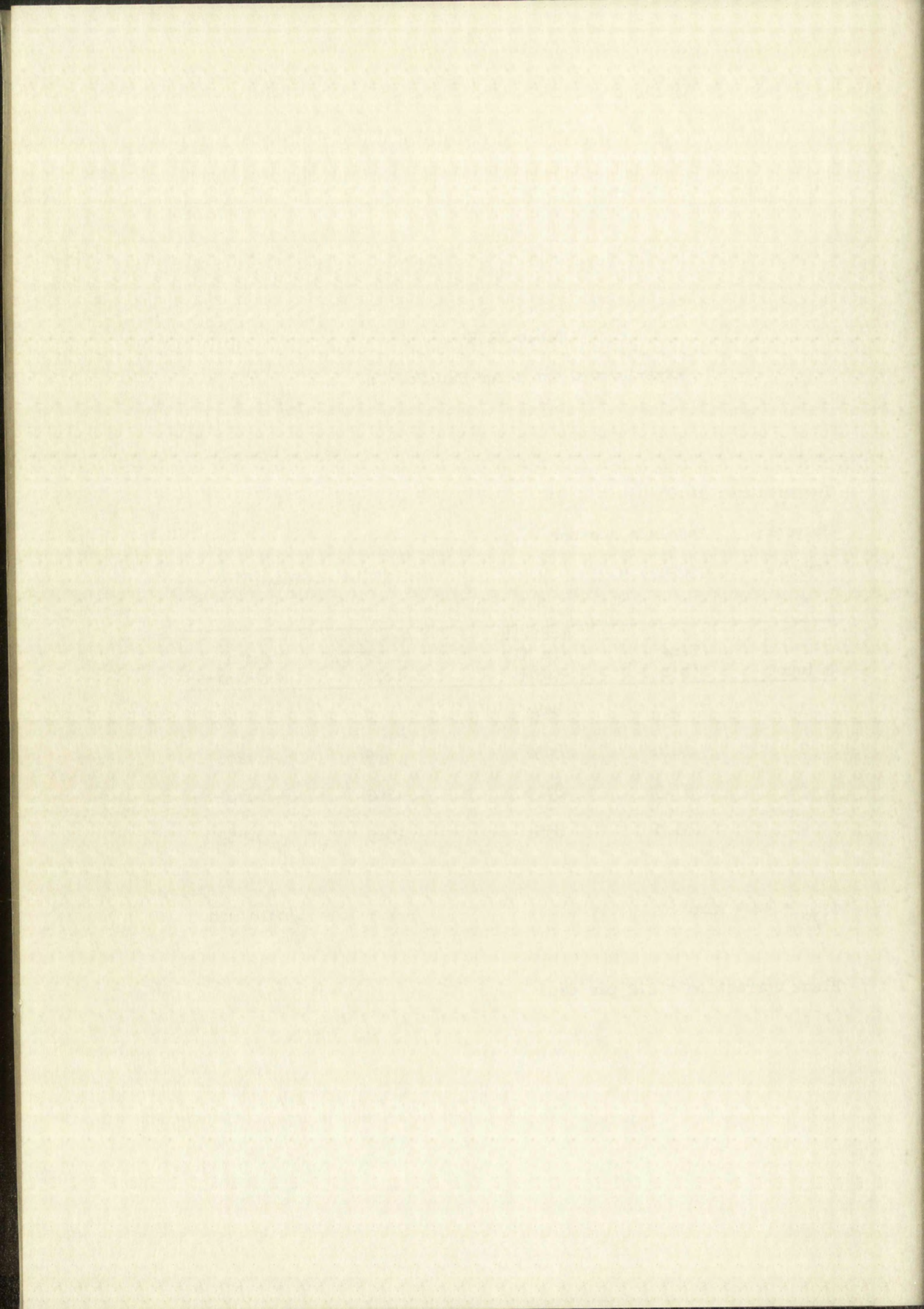


Table XIV

Experimental Data for Run No. 12

Temperature: 16.0°

Solvent: Absolute acetone

(PNBI) = 0.00000524 M

(KI) = 0.00000505 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in PNBI, (c/m)	Fraction exchanged
1	14.7	6728	942	0.241
2	31.8	5847	1540	0.410
3	48.5	5509	2129	0.547

 $t_{1/2} = 41.4$ min. $k = 1627$ l./mole/min.

Blank correction = 2.3 per cent

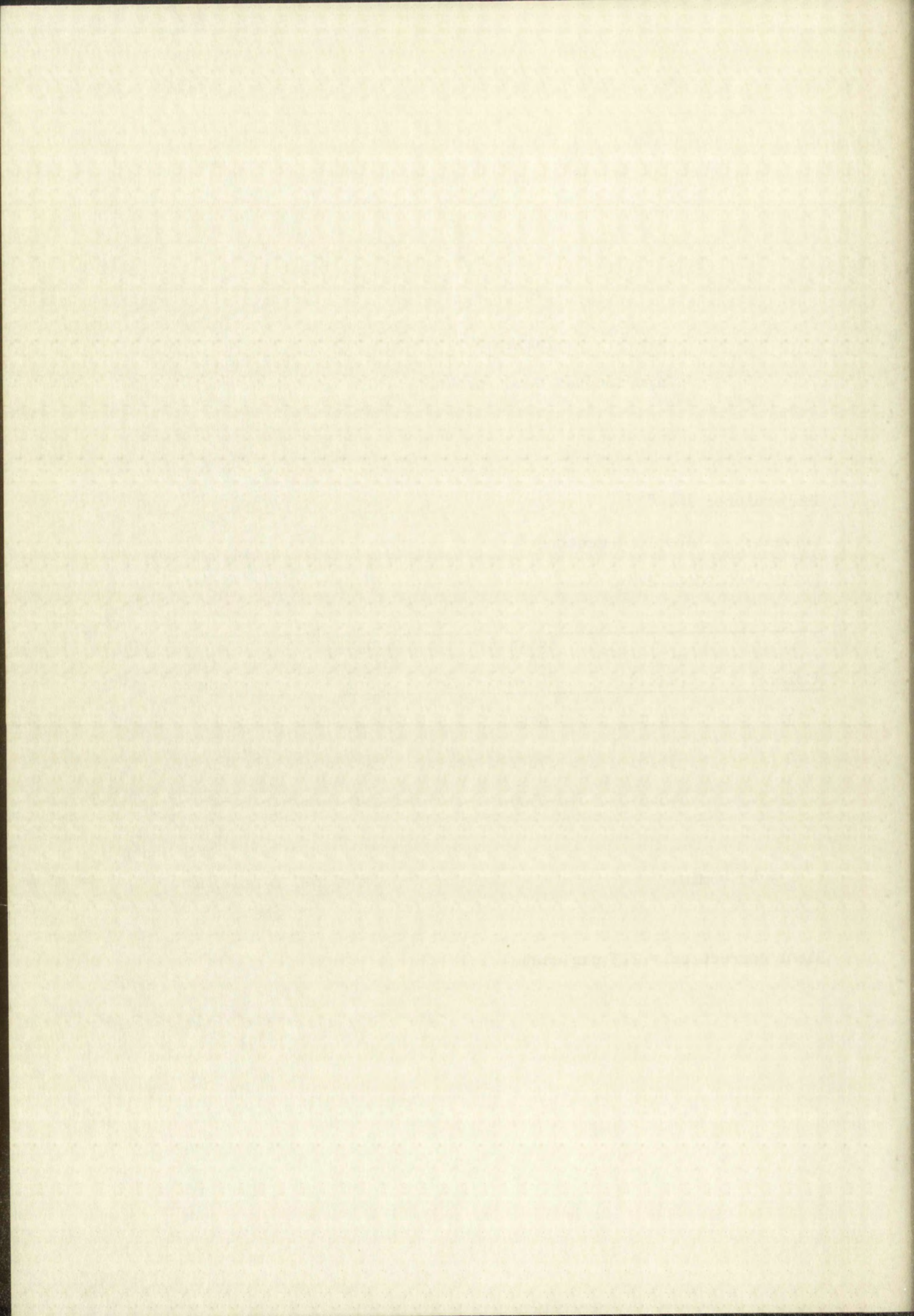


Table XV

Experimental Data for Run No. 13

Temperature: 16.0°

Solvent: Absolute acetone

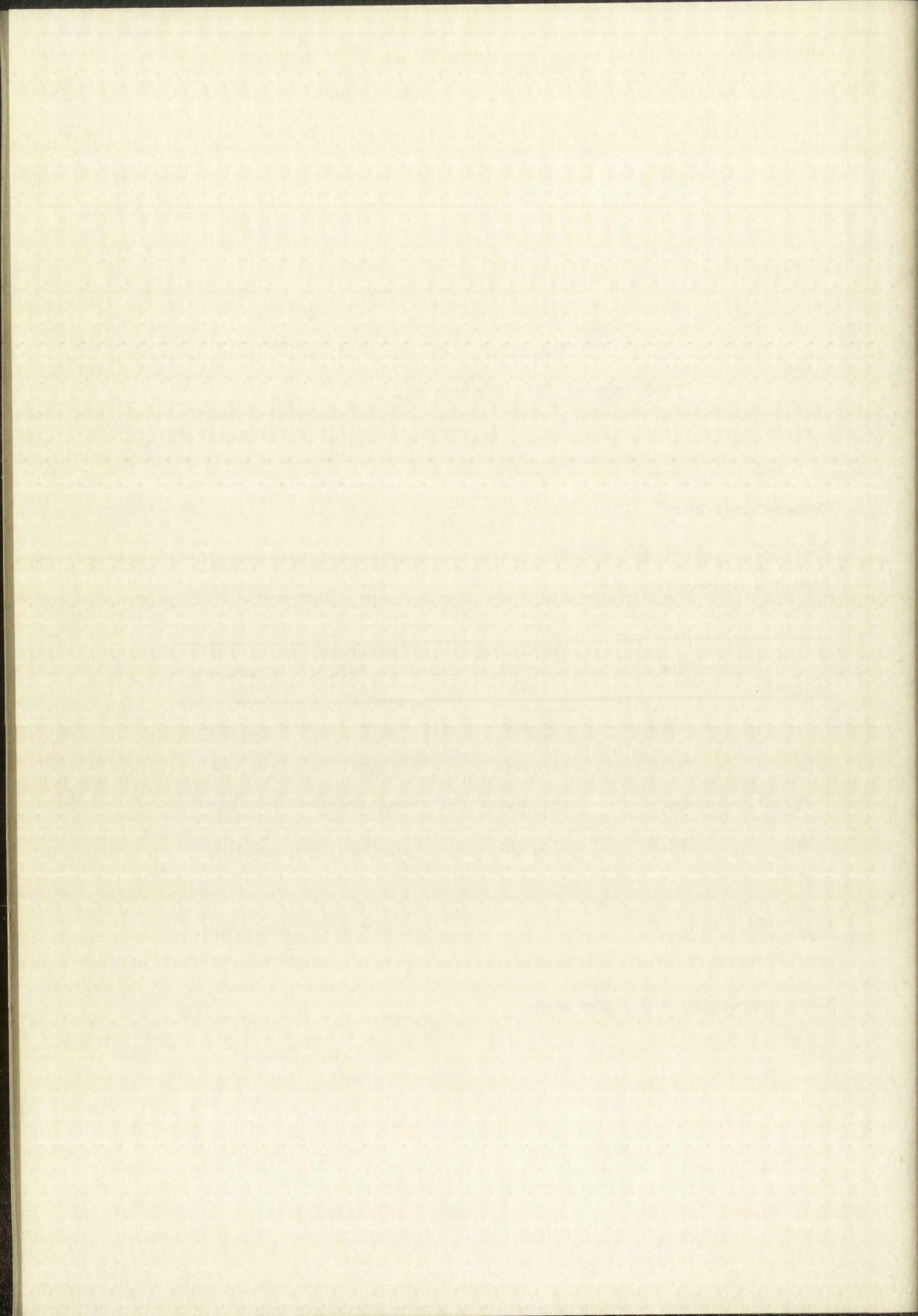
(PNBI) = 0.00000776 M

(KI) = 0.000003454 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in PNBI, (c/m)	Fraction Exchanged
1	15.2	19,490	3870	0.239
2	31.9	16,100	7393	0.455
3	46.1	14,390	9260	0.566
4	58.8	13,190	10,750	0.649

 $t_{1/2} = 38.3$ min. $k = 1613$ l/mole/min.

Blank correction = 2.7 per cent



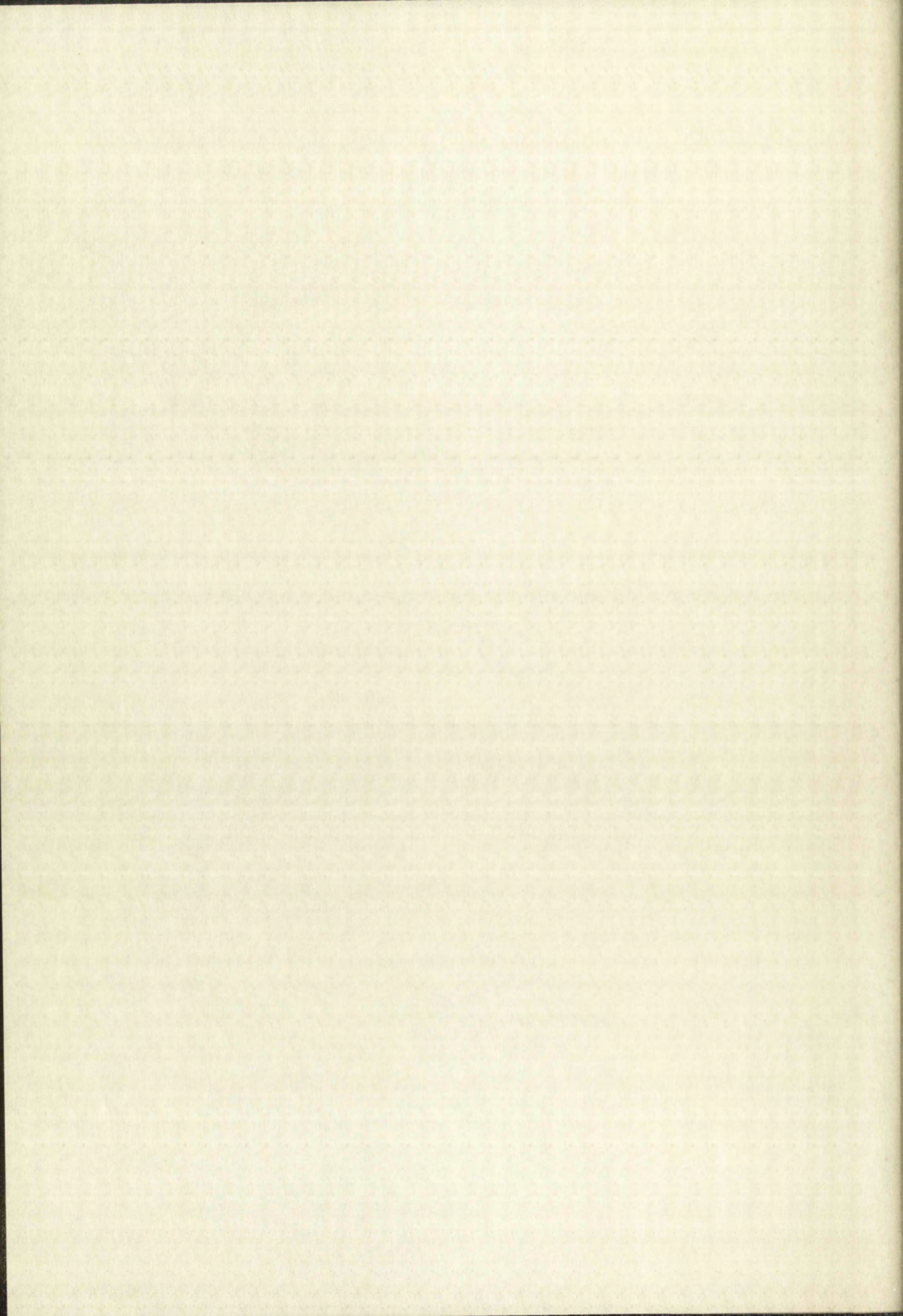
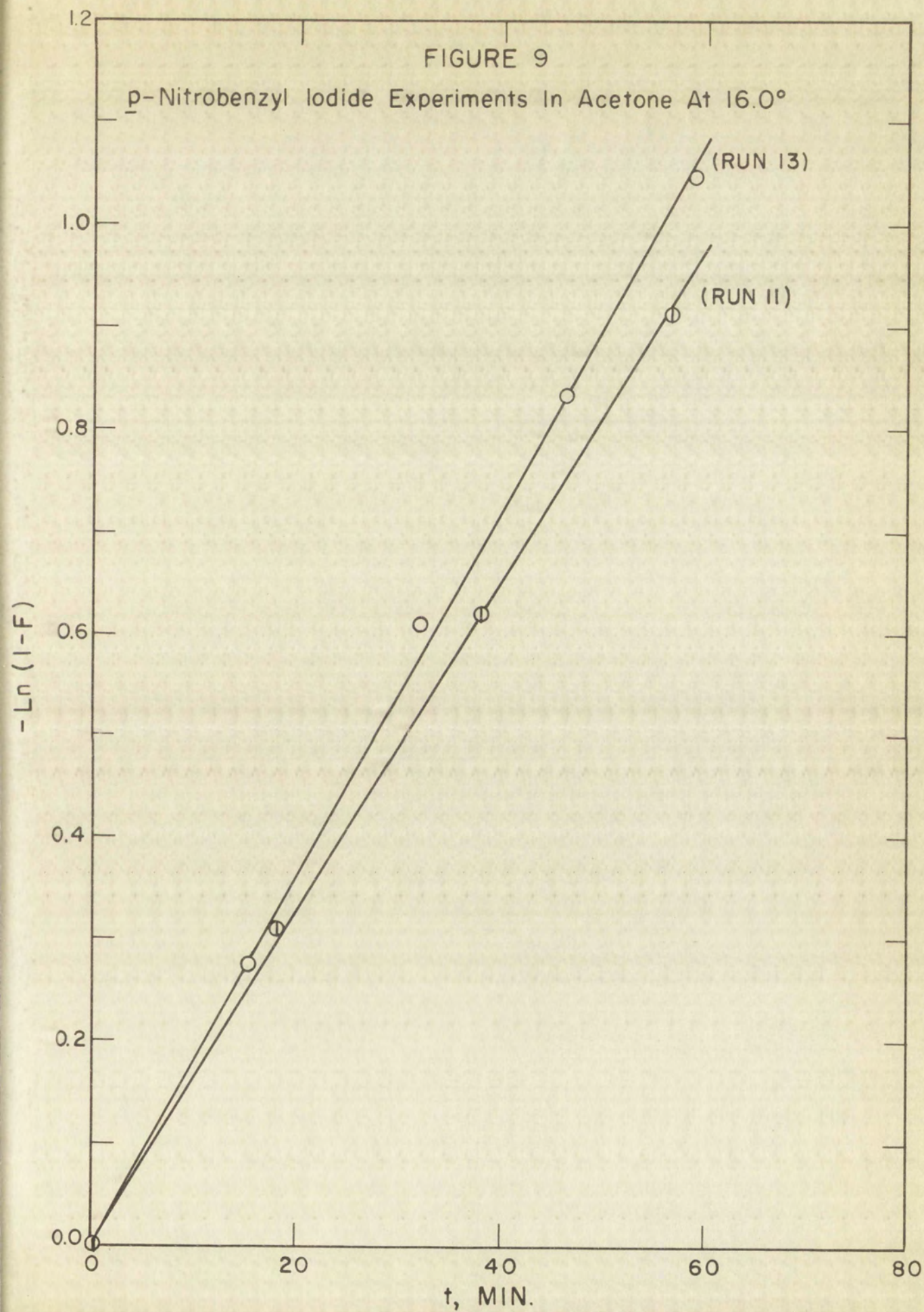
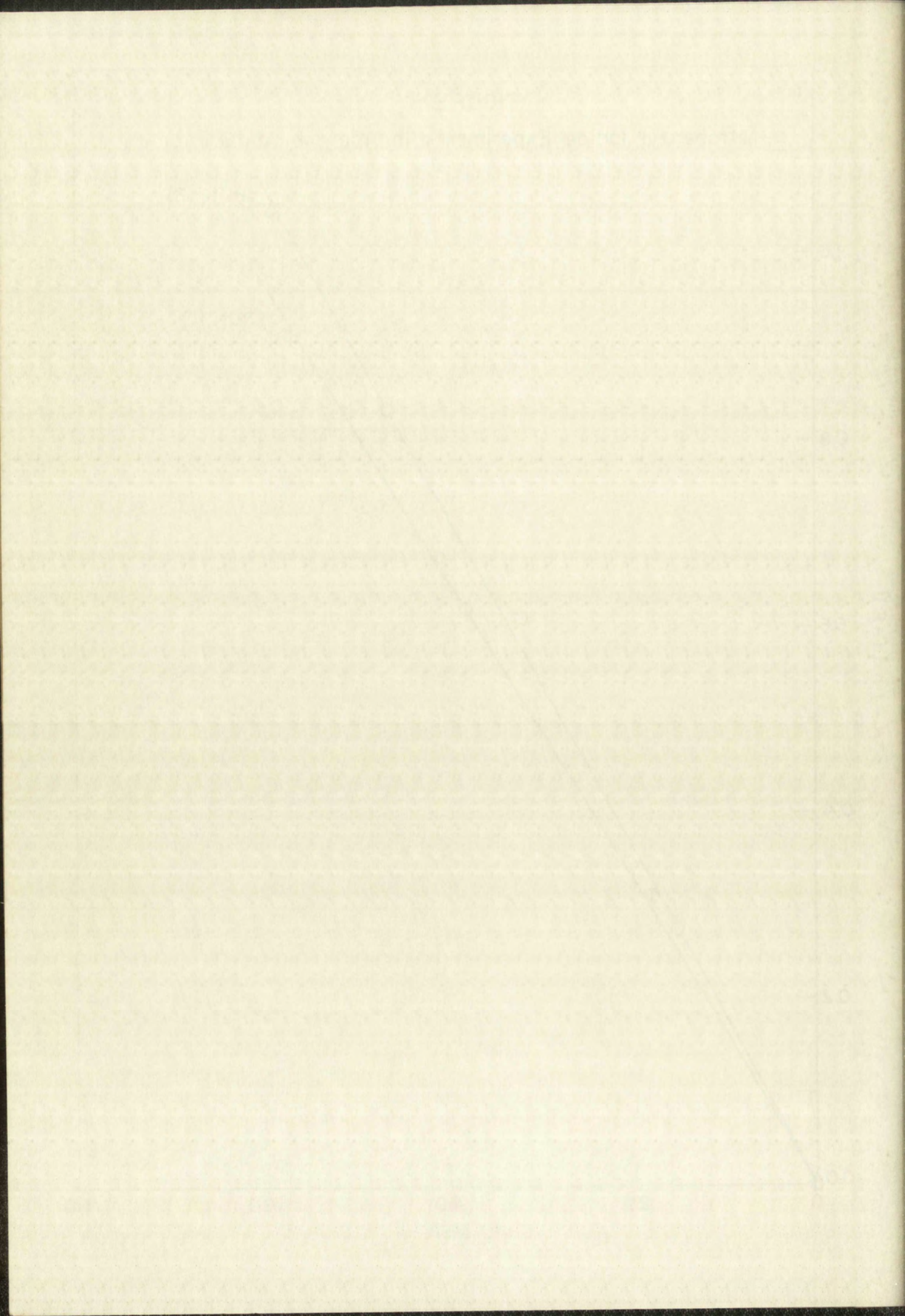
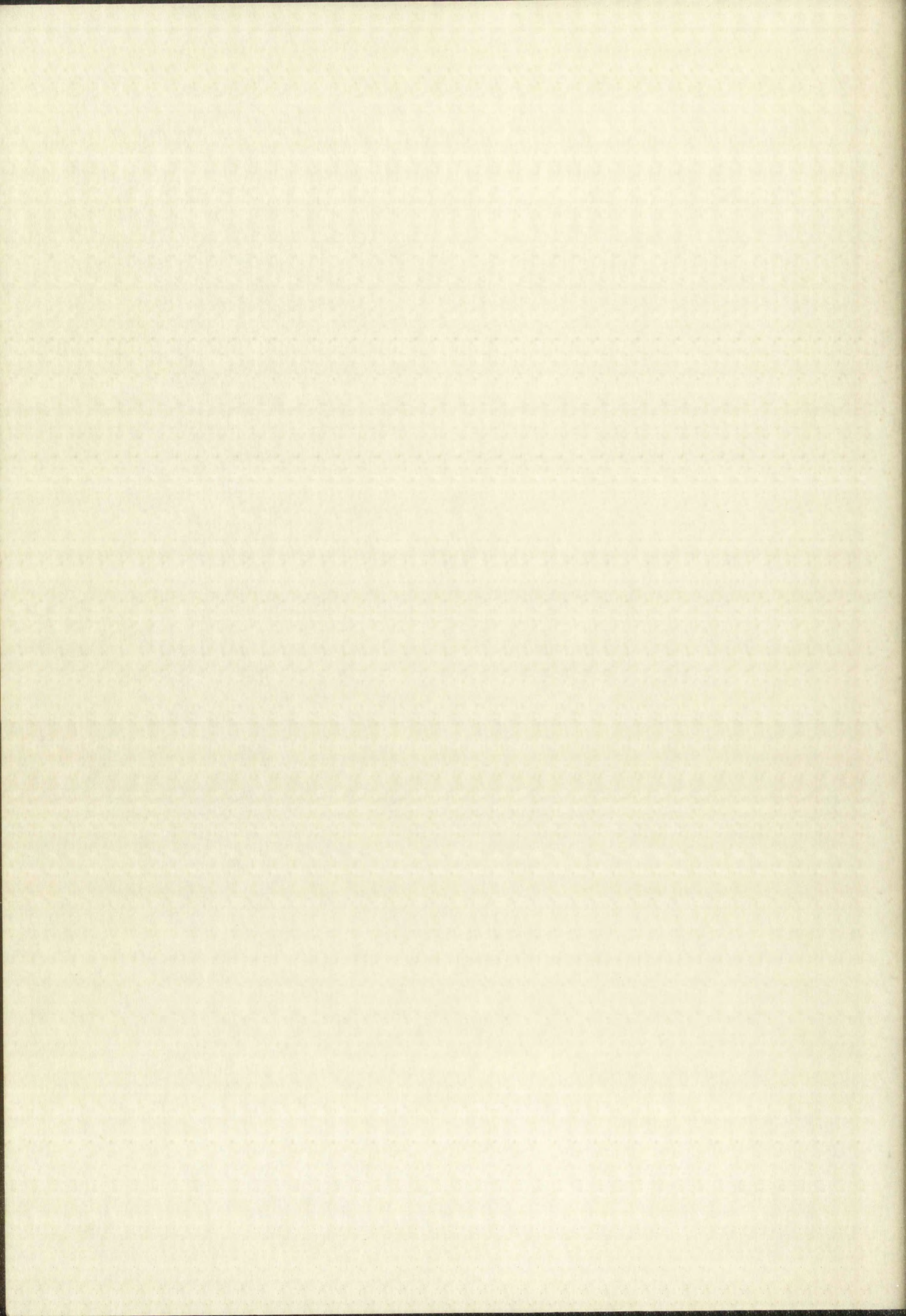


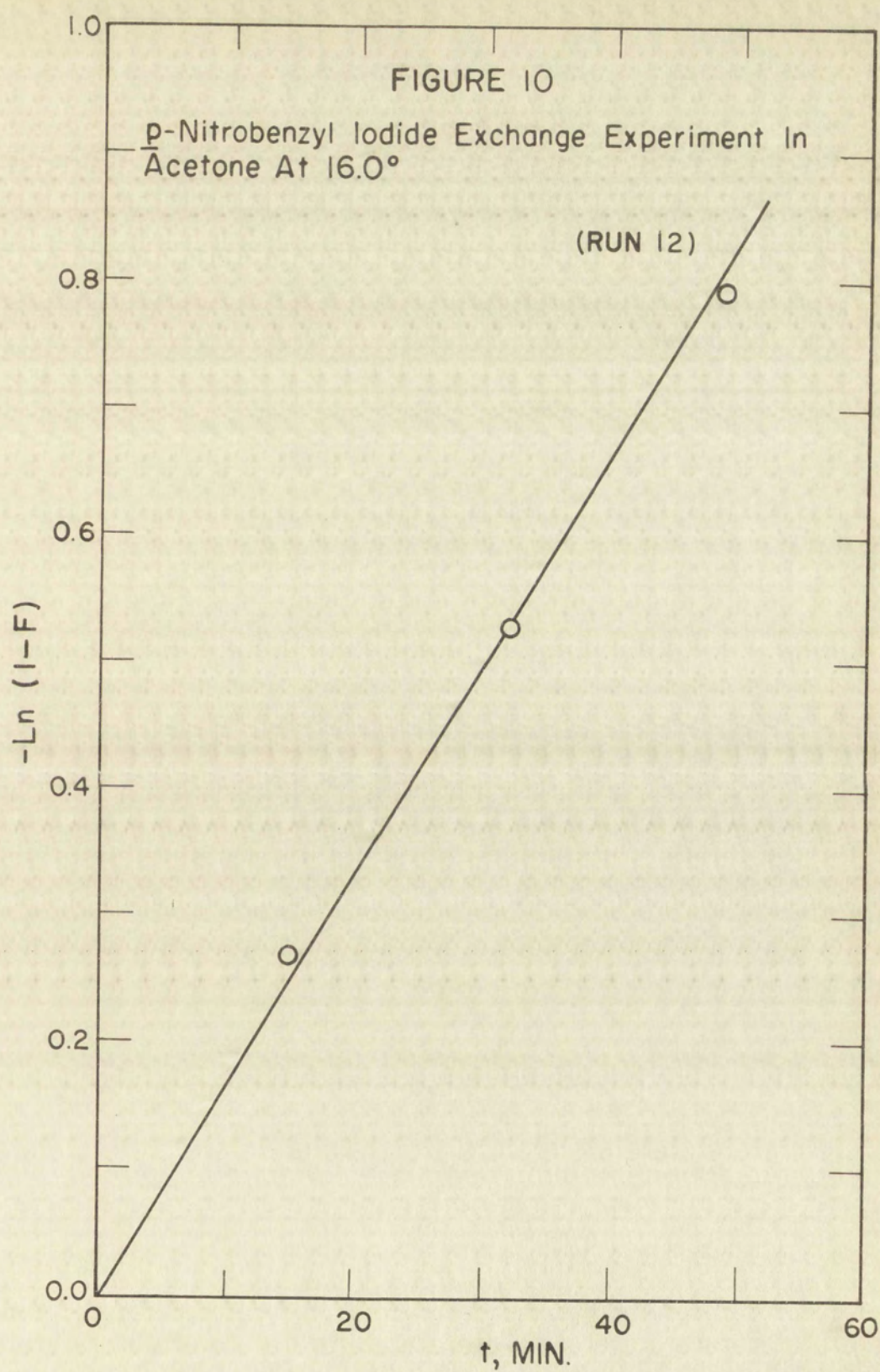
FIGURE 9

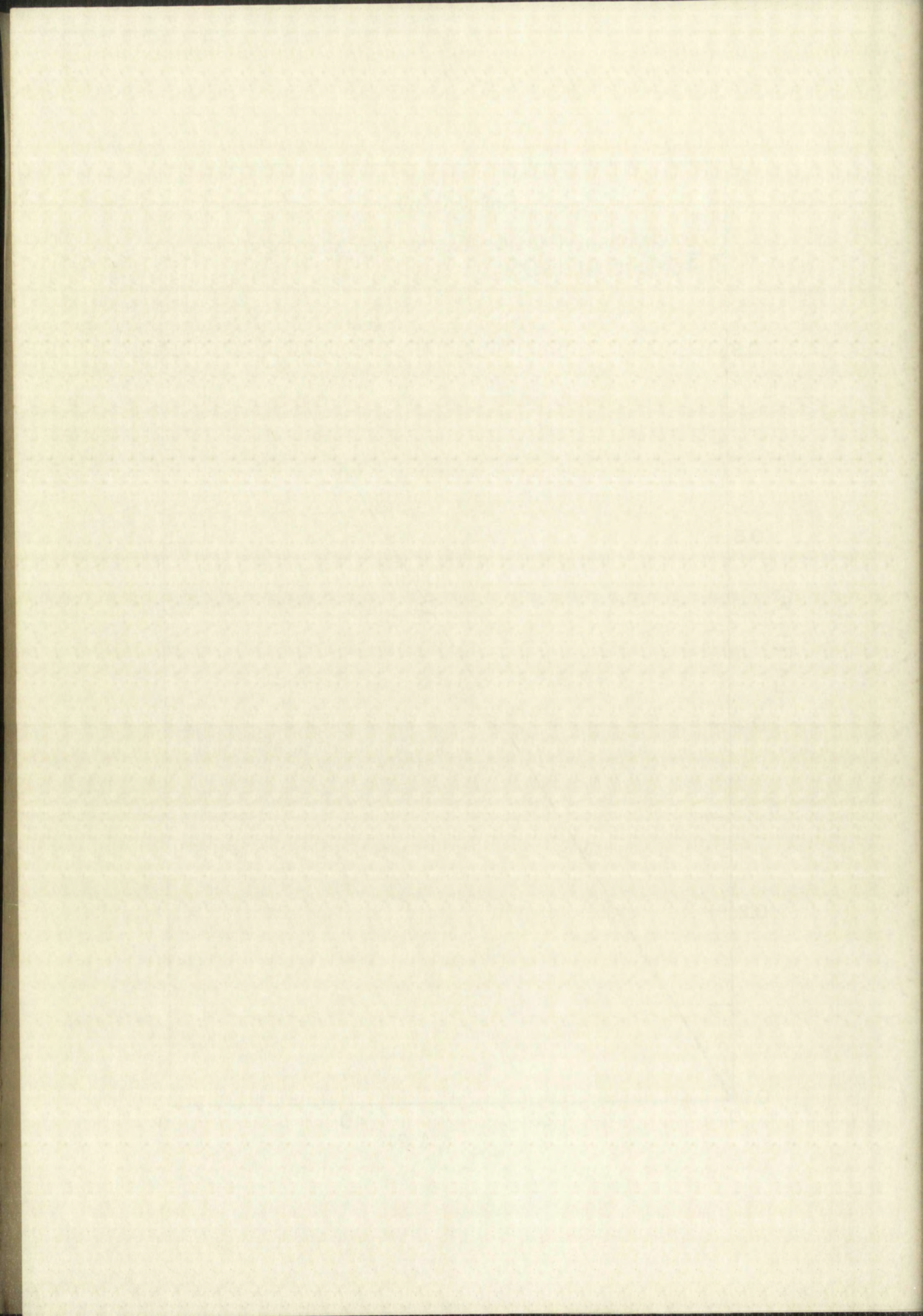
p-Nitrobenzyl Iodide Experiments In Acetone At 16.0°

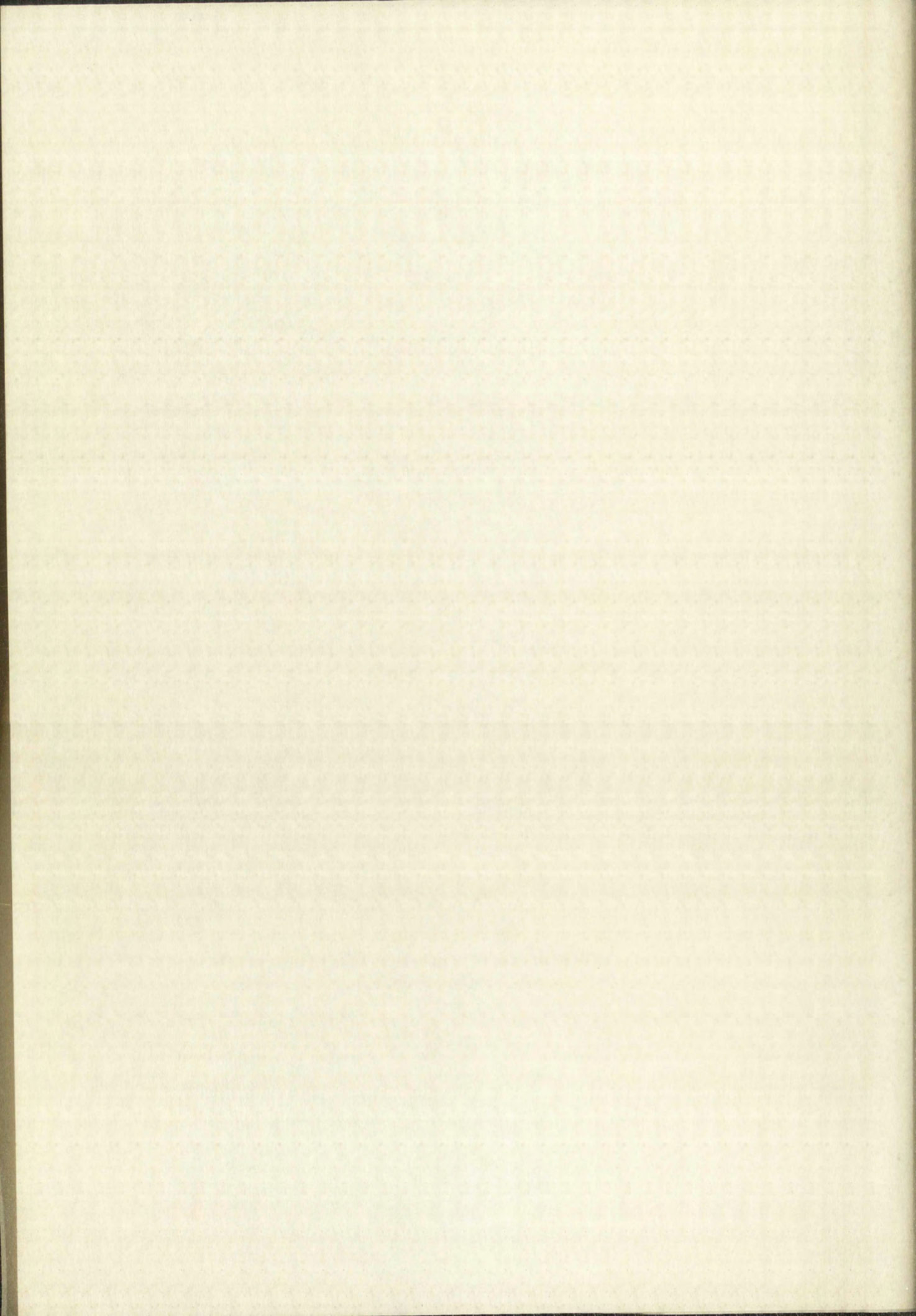


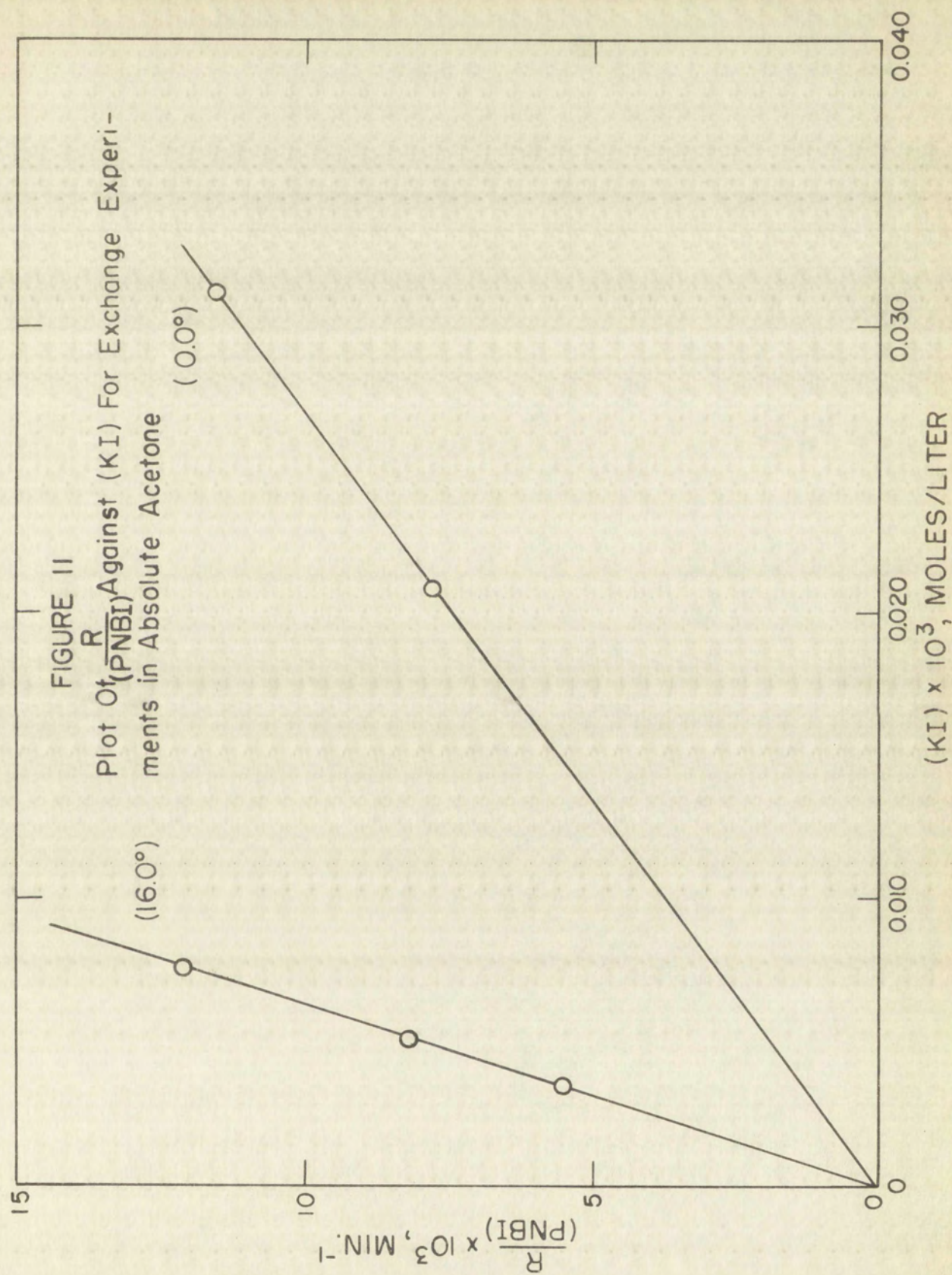












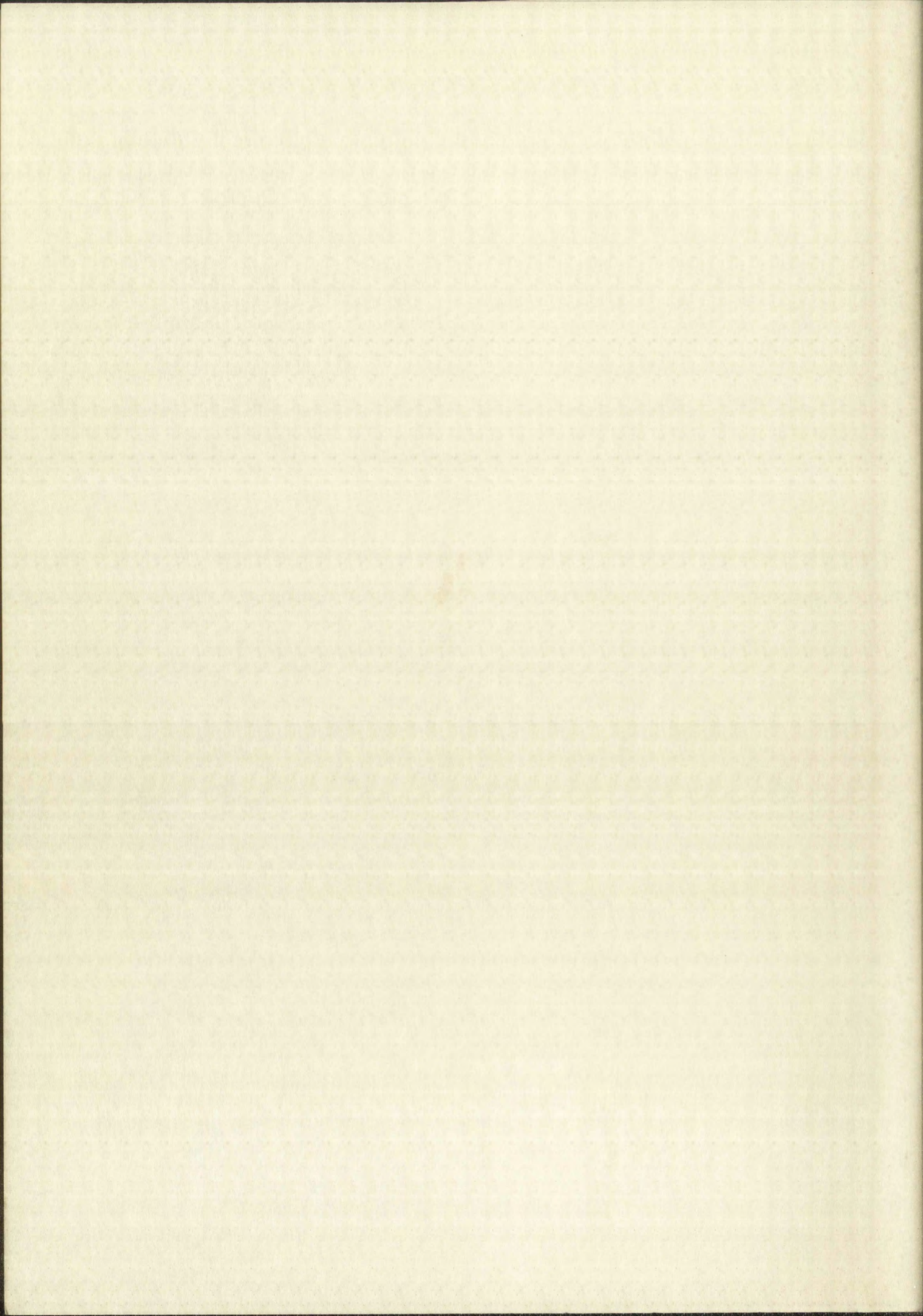
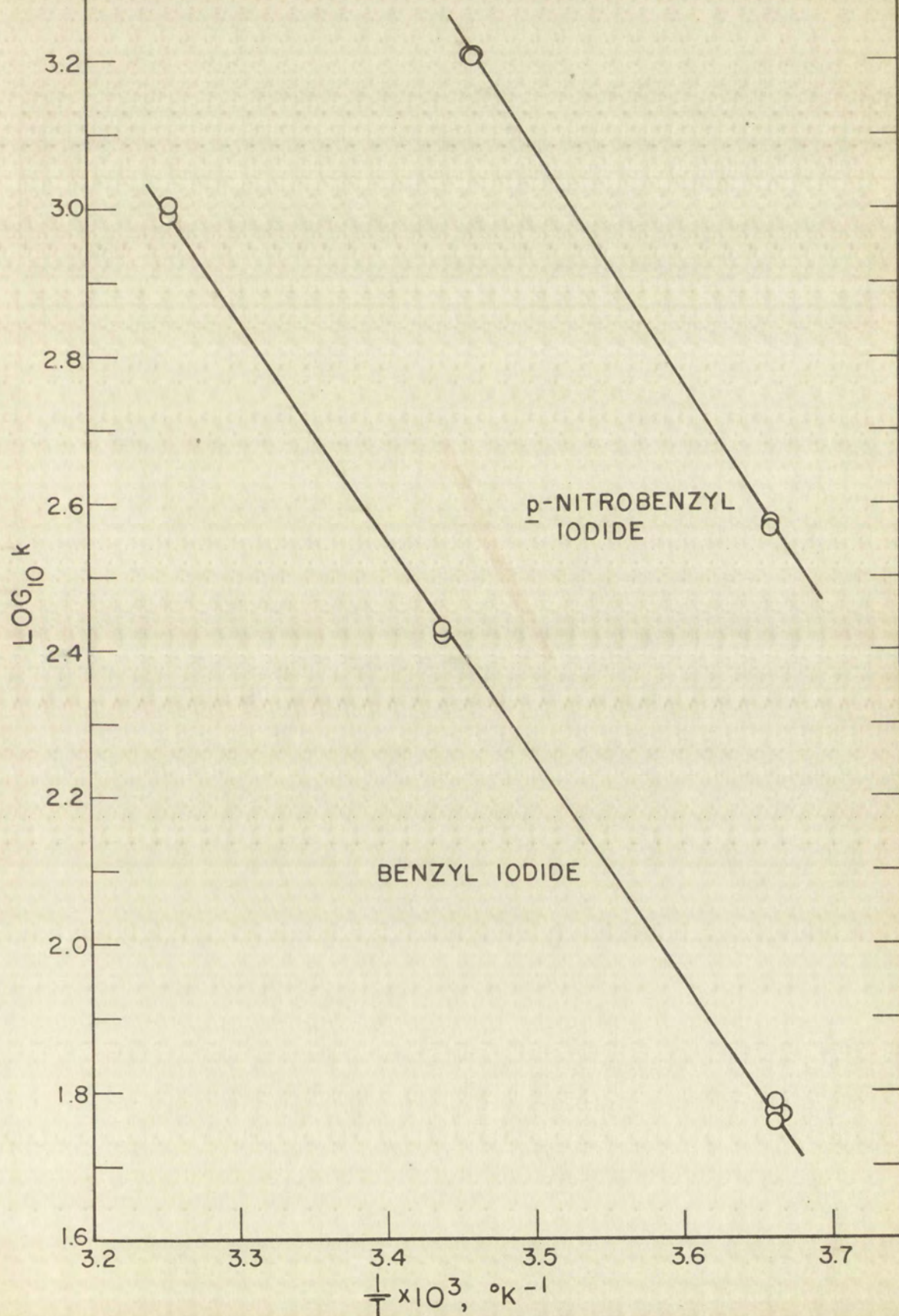
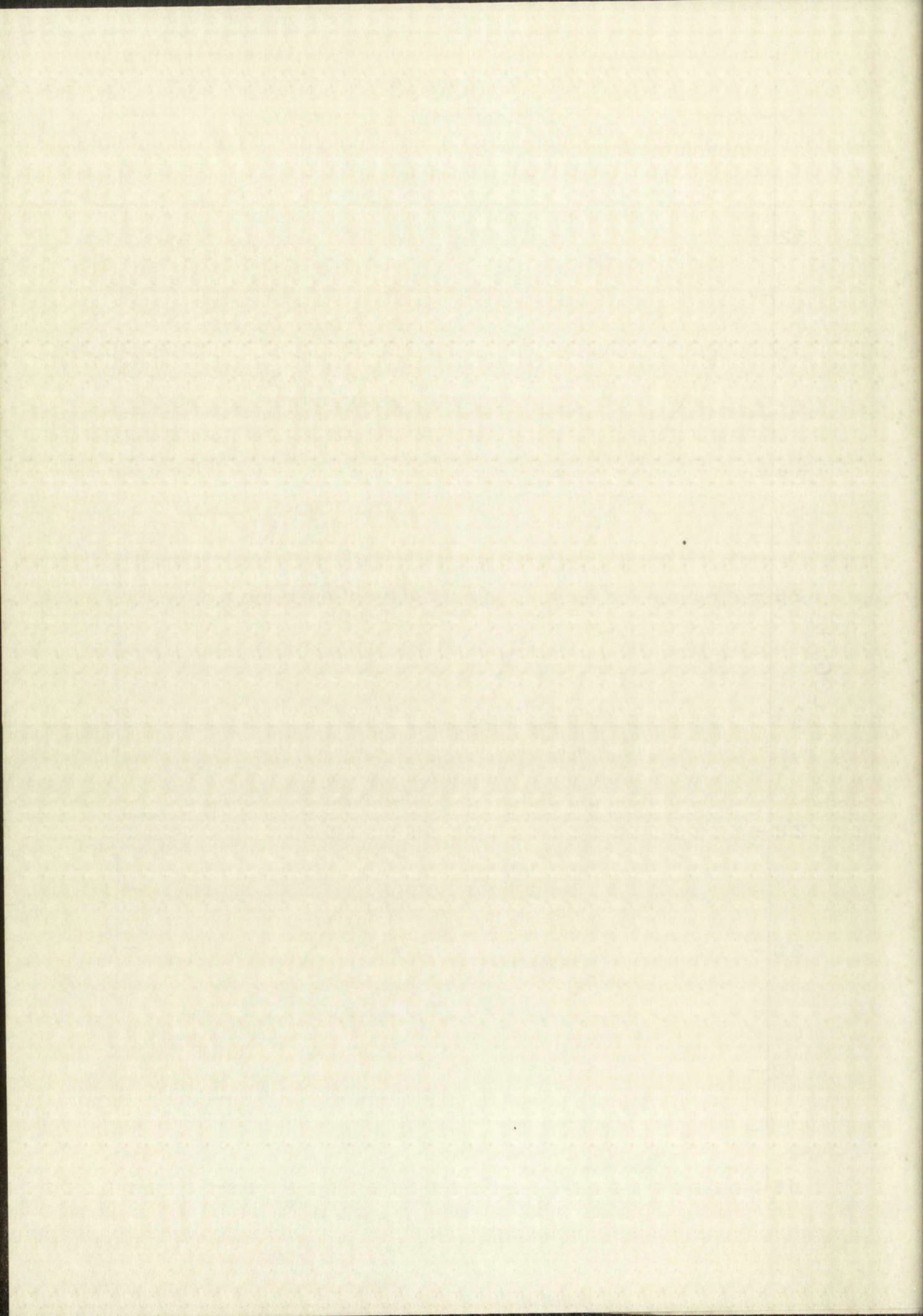


FIGURE 12

Plot Of $\log_{10} k$ Against $\frac{1}{T}$ For Experiments In Absolute Acetone





Experimental Data for Benzyl Iodide Exchange
Experiments in Acetone-Ethanol Mixtures at 0.0°

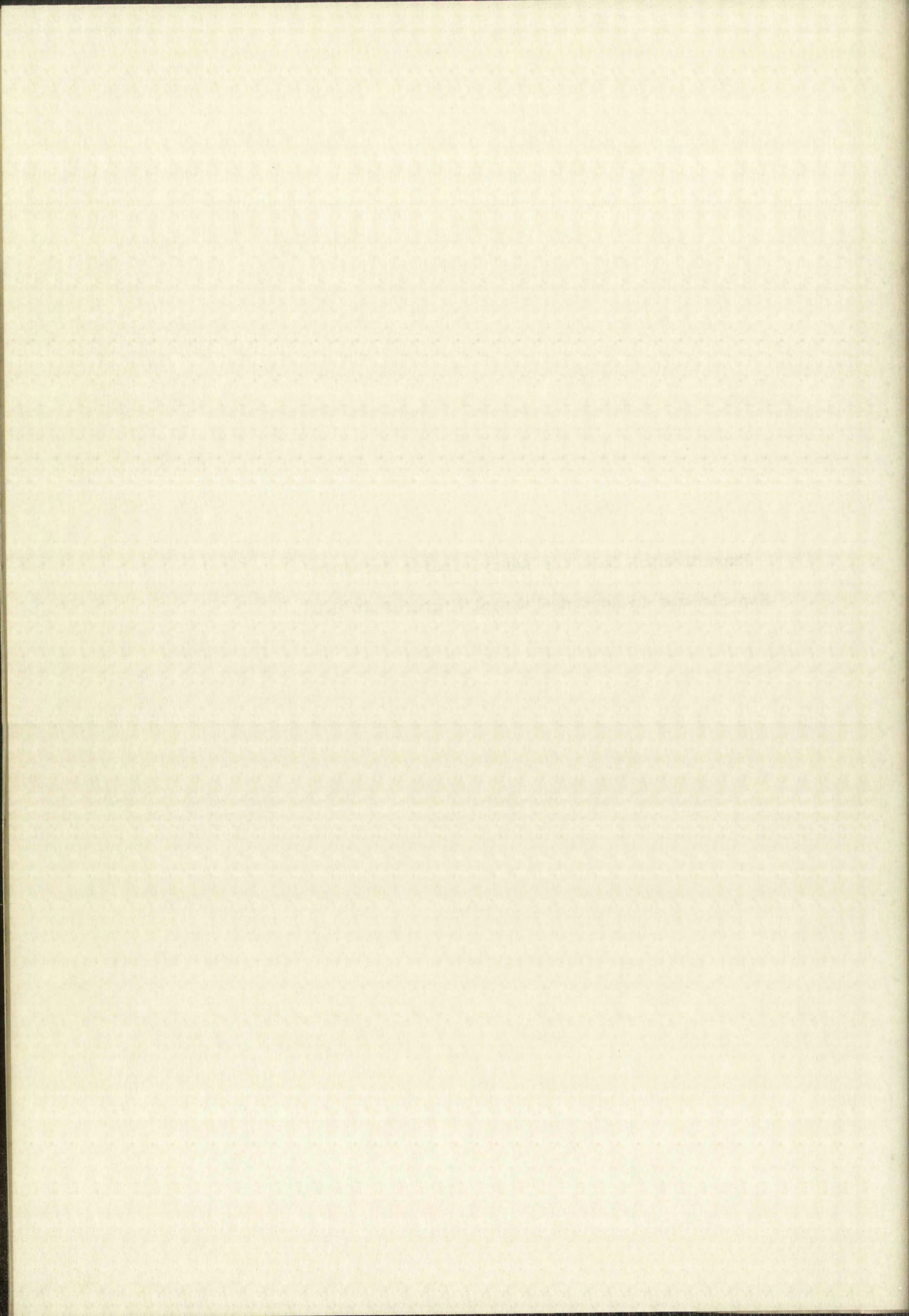


Table XVI

Summary of Benzyl Iodide Exchange Experiments at 0.0° in
Acetone-Ethanol Solvent Mixtures

Run No.	$((\text{CH}_3)_2\text{CO}),$ M	$(\text{C}_2\text{H}_5\text{OH}),$ M	$(\text{BI})_3$ $\text{M} \times 10^3$	$(\text{KI})_3$ $\text{M} \times 10^3$	$t_{1/2},$ min.	$k,$ l./mole/min.
(avg.) ¹	14.00	0.0	-	-	-	59.6
14	13.73	0.351	0.2728	0.2592	35.2	37.0
15	13.40	0.753	0.2598	0.2592	53.1	25.2
16	12.60	1.75	0.980	0.0635	57.8	11.5
17	7.01	8.75	12.27	6.43	36.1	1.03
18	7.01	8.75	12.08	6.41	35.3	1.06
19	5.60	10.50	5.61	7.72	74.0	0.702
20	4.67	11.67	8.06	8.54	78.3	0.532
21	0.0	17.53	22.45	12.86	188.	0.104
22	0.0	17.53	15.70	12.79	236.	0.103

1. From Table I.

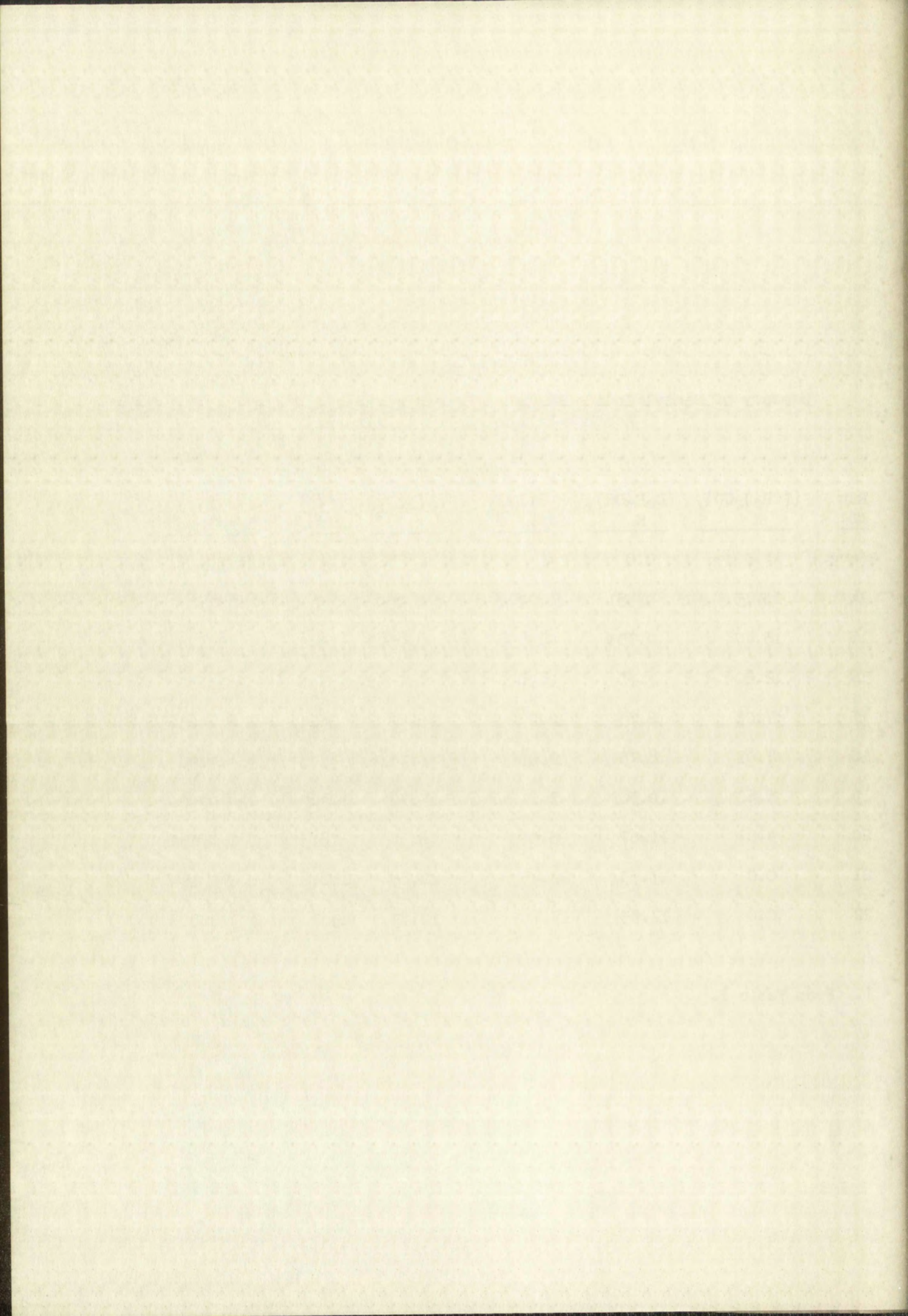


Table XVII

Experimental Data for Run No. 14

Solvent Composition: 13.73 M Acetone

0.351 M Ethanol

(BI) = 0.0002728 M

(KI) = 0.0002592 M

Aliquot	Time (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	0.3	2607	12	0.009
2	10.2	2375	249	0.185
3	22.5	2092	494	0.373
4	57.9	1776	932	0.672

 $t_{1/2} = 35.2 \text{ min.}$ $k = 37.0 \text{ l/mole/min.}$

Blank correction = 1.6 per cent

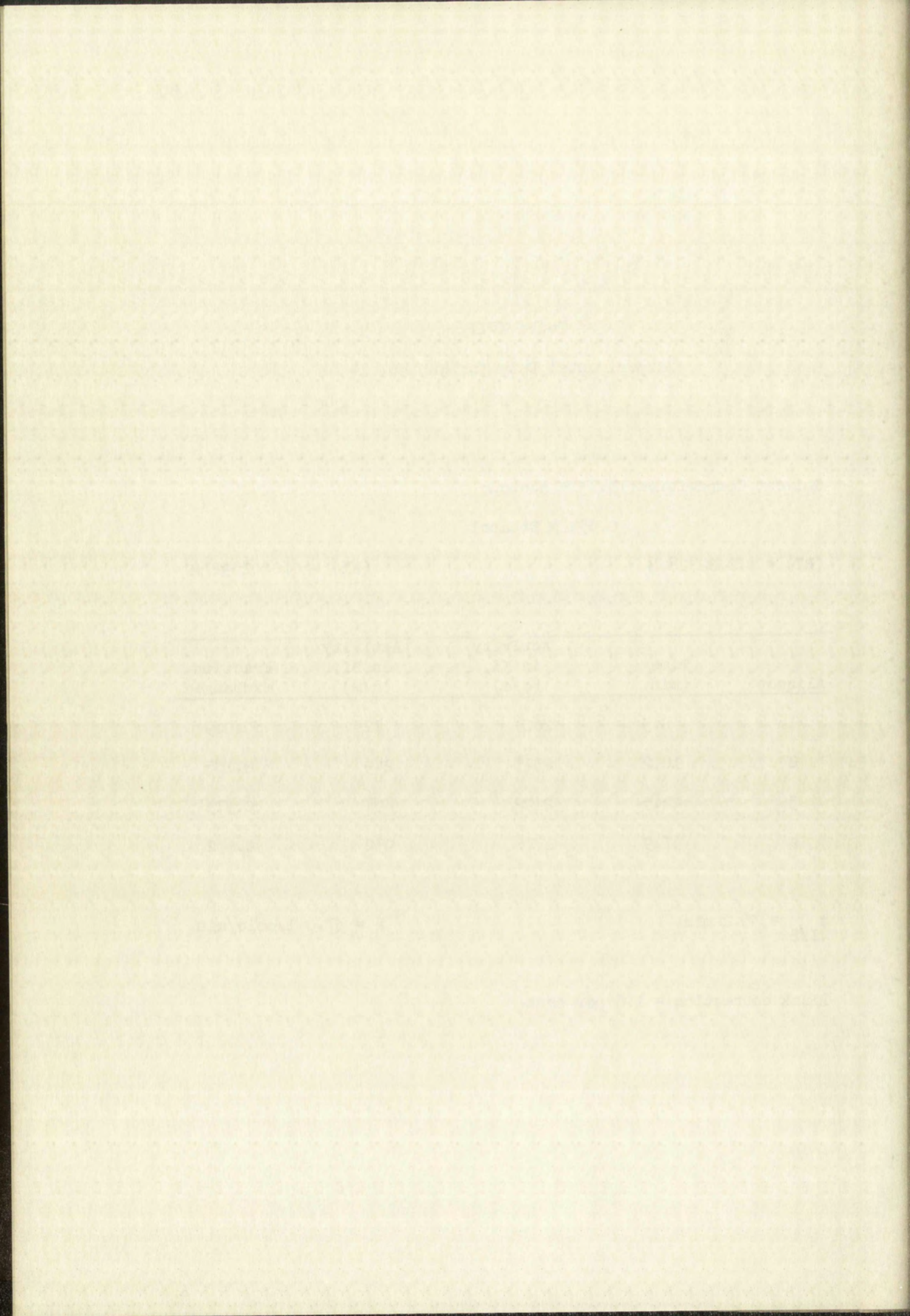


Table XVIII

Experimental Data for Run No. 15

Solvent composition: 13.40 M Acetone

0.753 M Ethanol

(BI) = 0.0002598 M

(KI) = 0.0002592 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	21.6	2317	326	0.246
2	44.5	2041	559	0.429
3	69.7	1789	781	0.607

 $t_{1/2} = 53.1 \text{ min.}$ $k = 25.2 \text{ l/mole/min.}$

Blank correction = 1.6 per cent

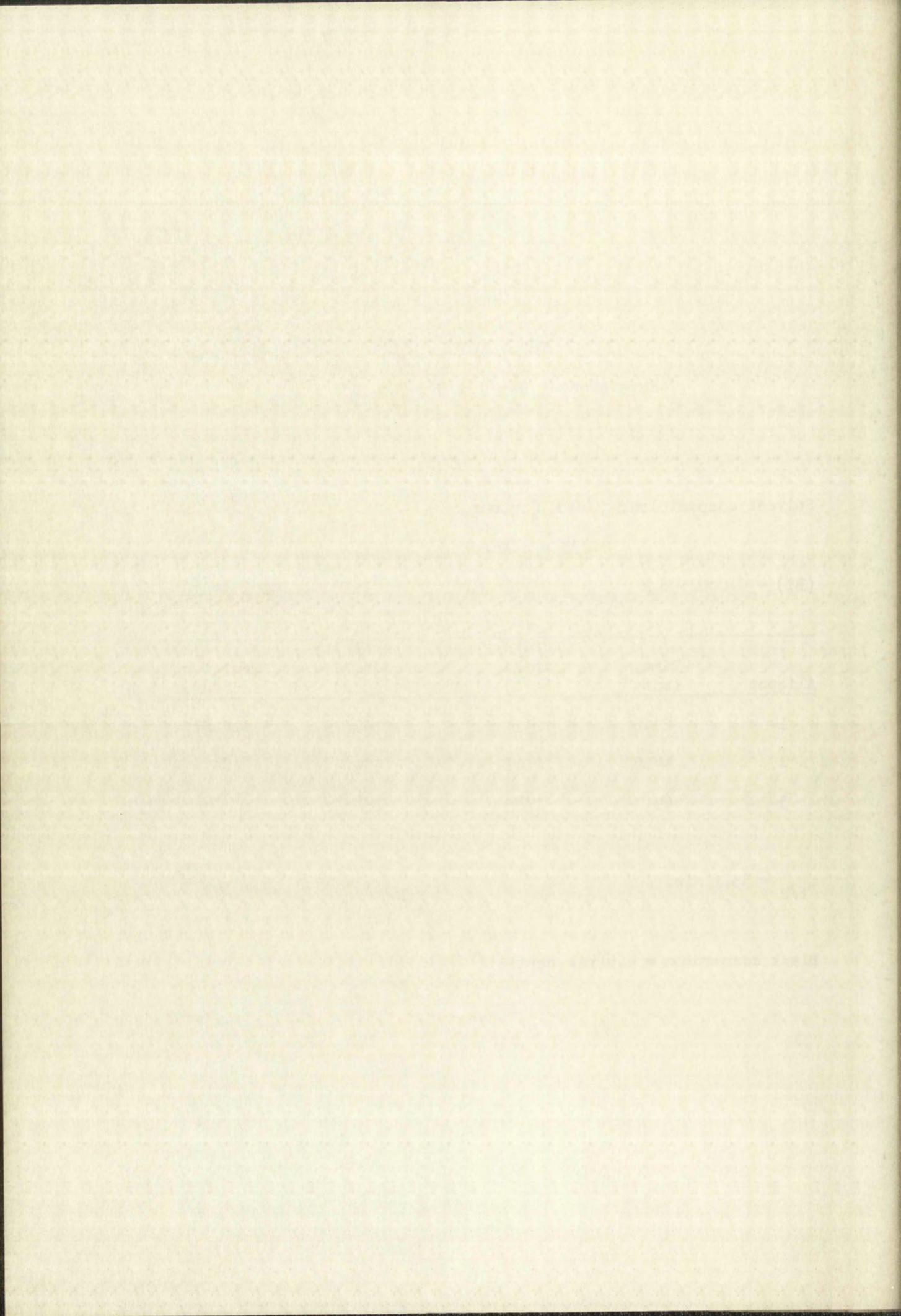


Table XIX

Experimental Data for Run No. 16

Solvent composition: 12.60 M Acetone

1.75 M Ethanol

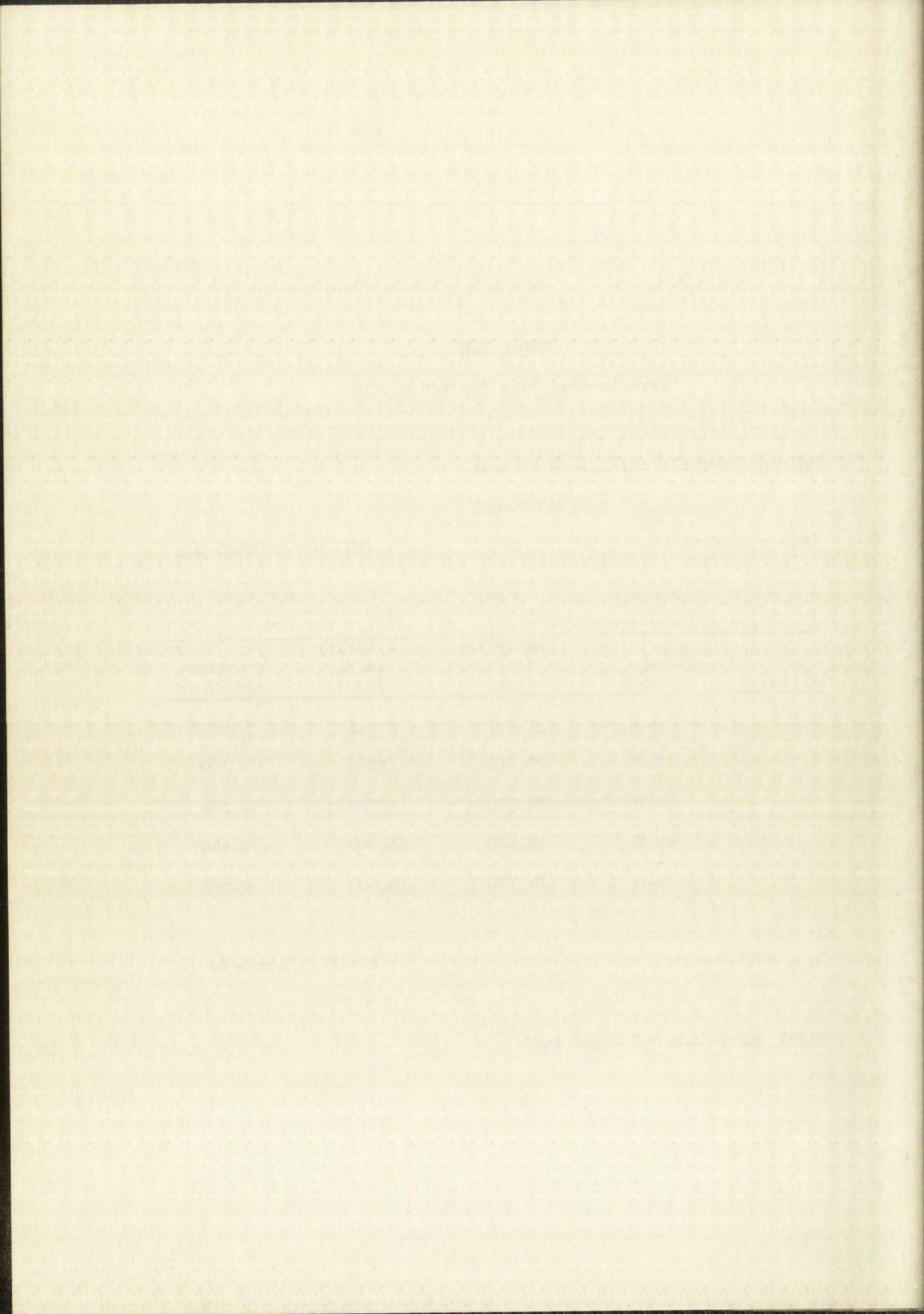
(BI) = 0.000980 M

(KI) = 0.0000635 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	0.3	30,770	11	0.0004
2	15.7	25,500	5262	0.182
3	32.8	22,240	9730	0.324
4	49.0	18,620	13,540	0.448
5	70.8	14,780	16,600	0.563

 $t_{1/2} = 57.8$ min. $k = 11.5$ l./mole/min.

Blank correction = 2.2 per cent



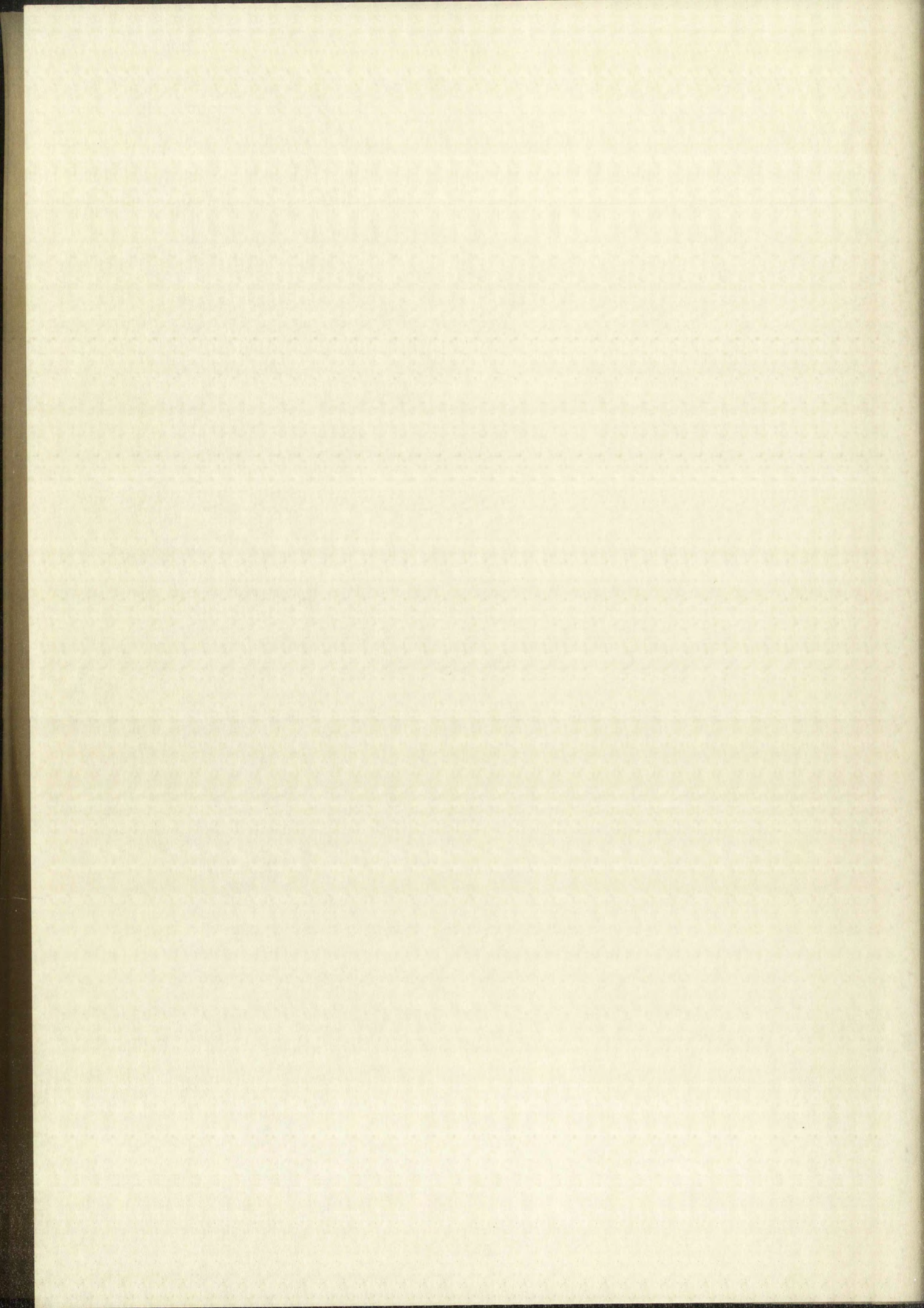
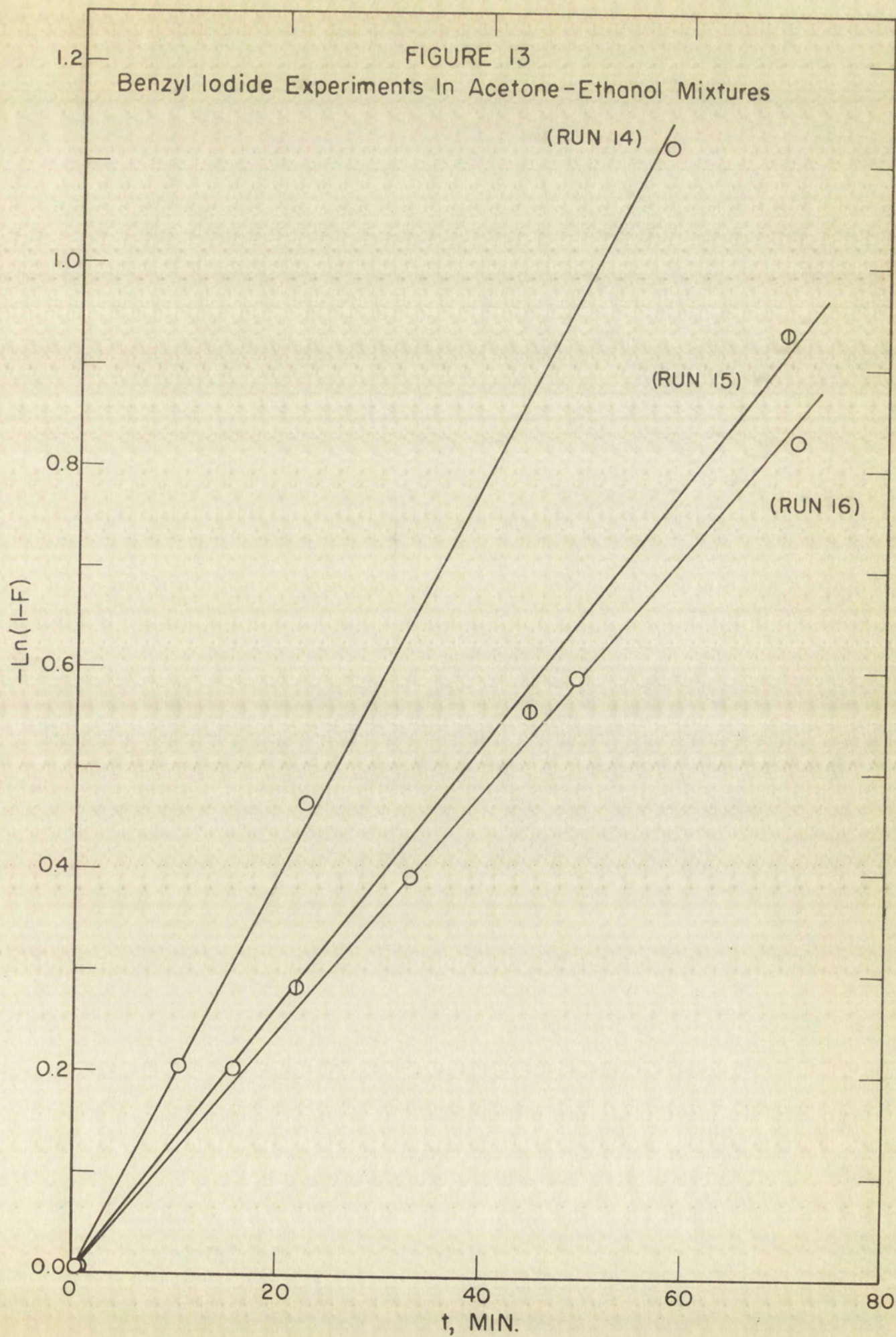


FIGURE 13
Benzyl Iodide Experiments In Acetone-Ethanol Mixtures



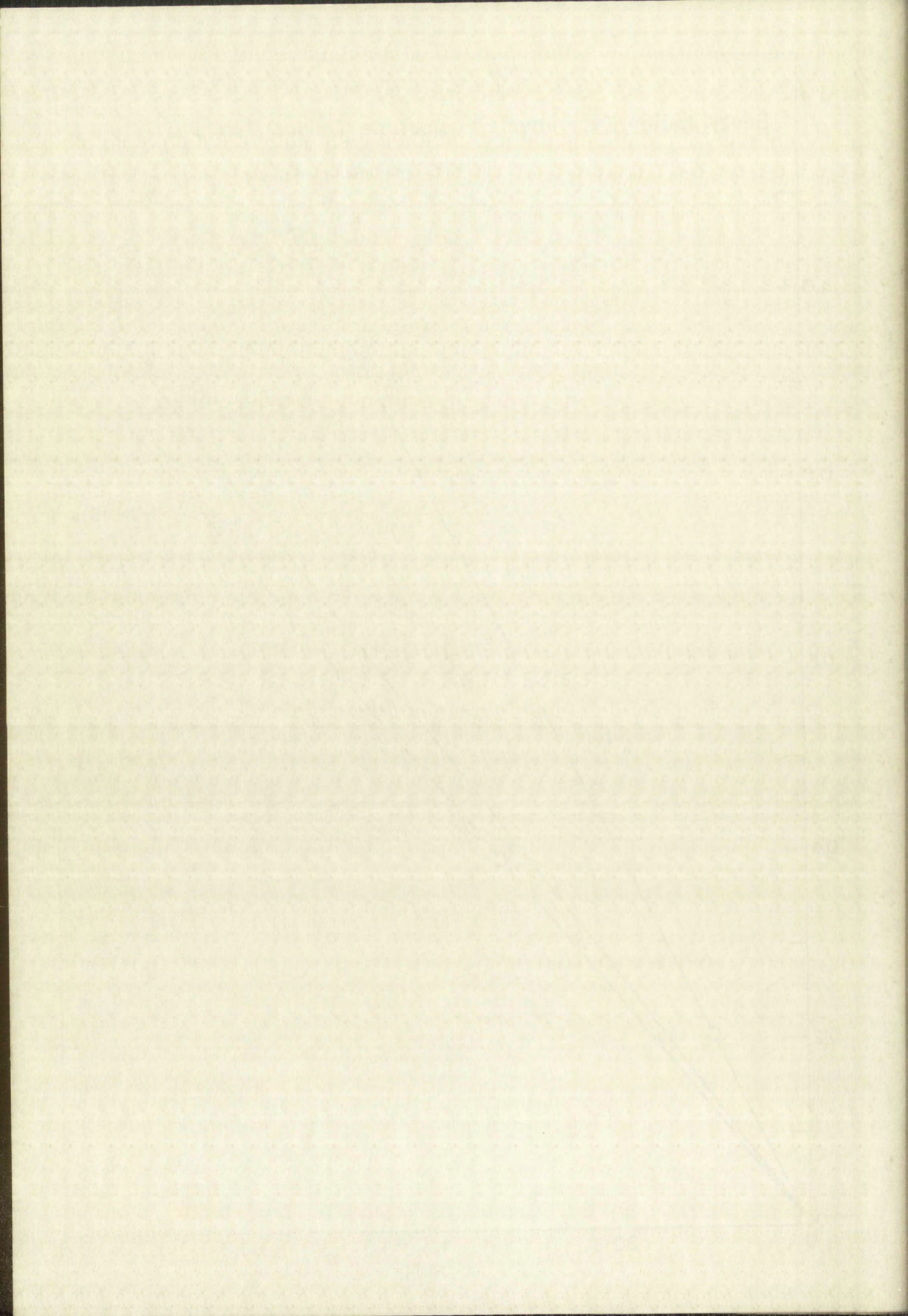


Table XX

Experimental Data for Run No. 17

Solvent composition: 7.01M Acetone

8.75M Ethanol

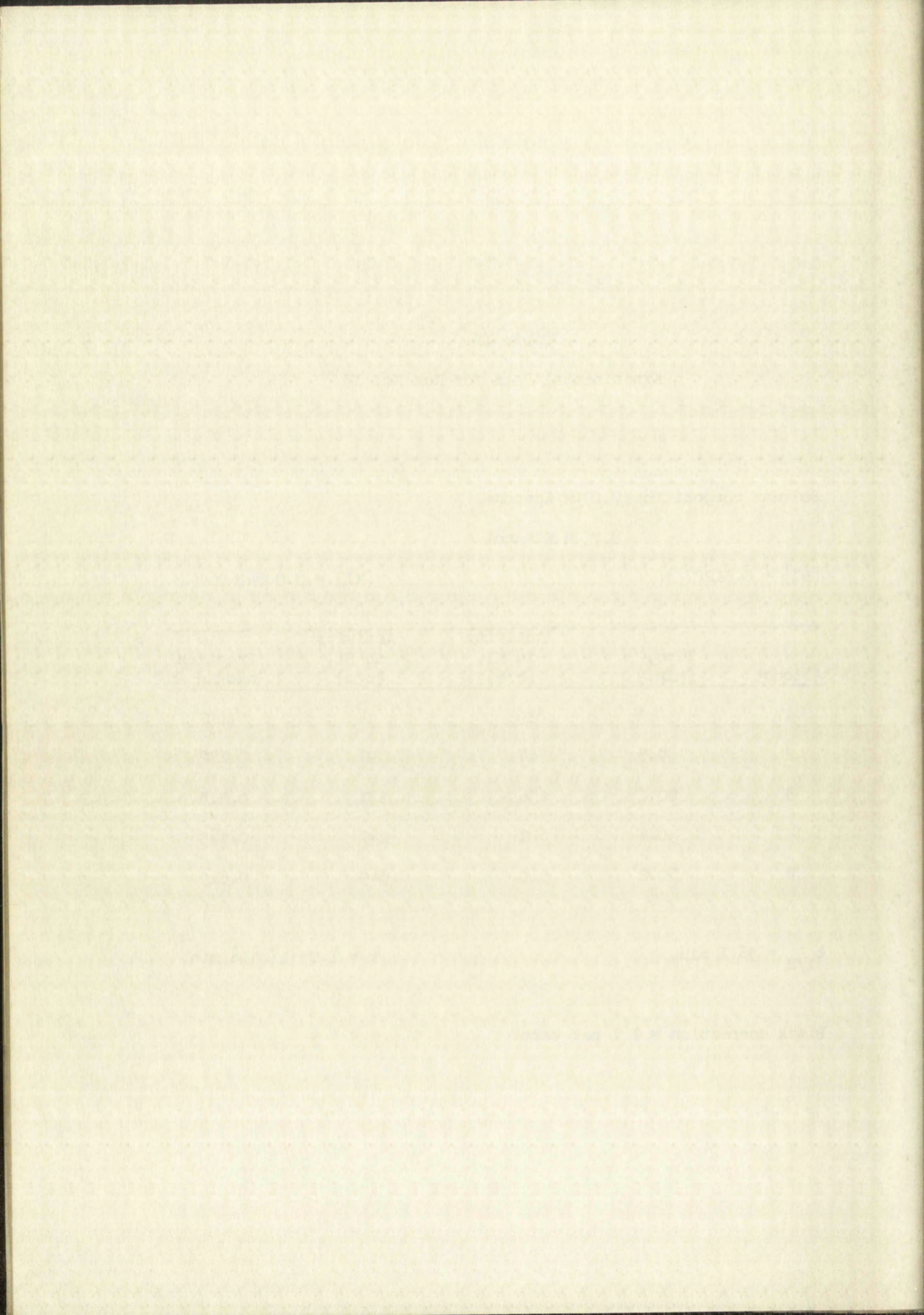
(BI) = 0.01227 M

(KI) = 0.00643 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	0.3	819	4	0.007
2	9.5	764	97	0.172
3	20.7	656	171	0.315
4	30.4	602	247	0.443
5	50.2	510	349	0.619

 $t_{1/2} = 36.1 \text{ min.}$ $k = 1.03 \text{ l./mole/min.}$

Blank correction = 1.1 per cent



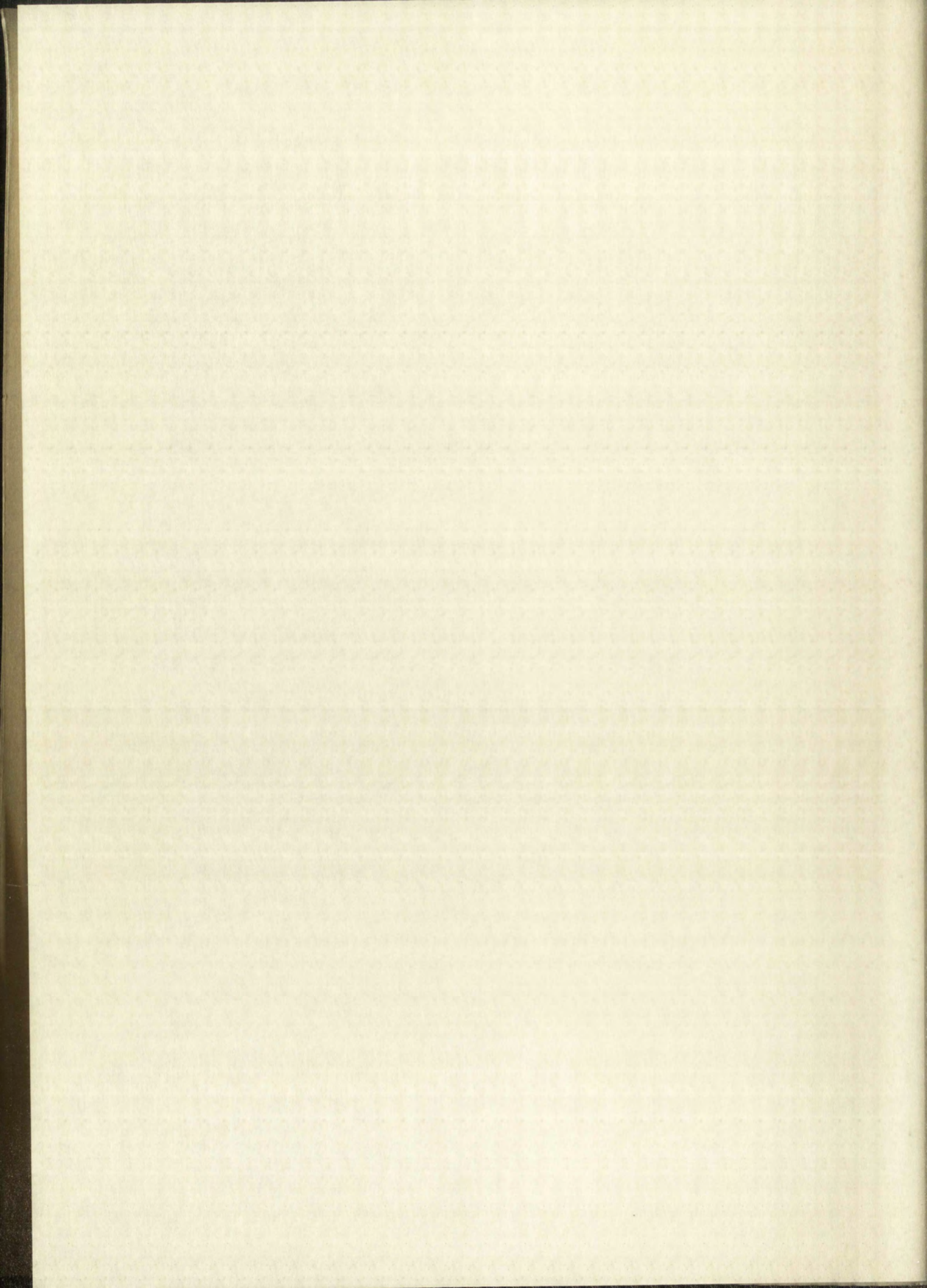
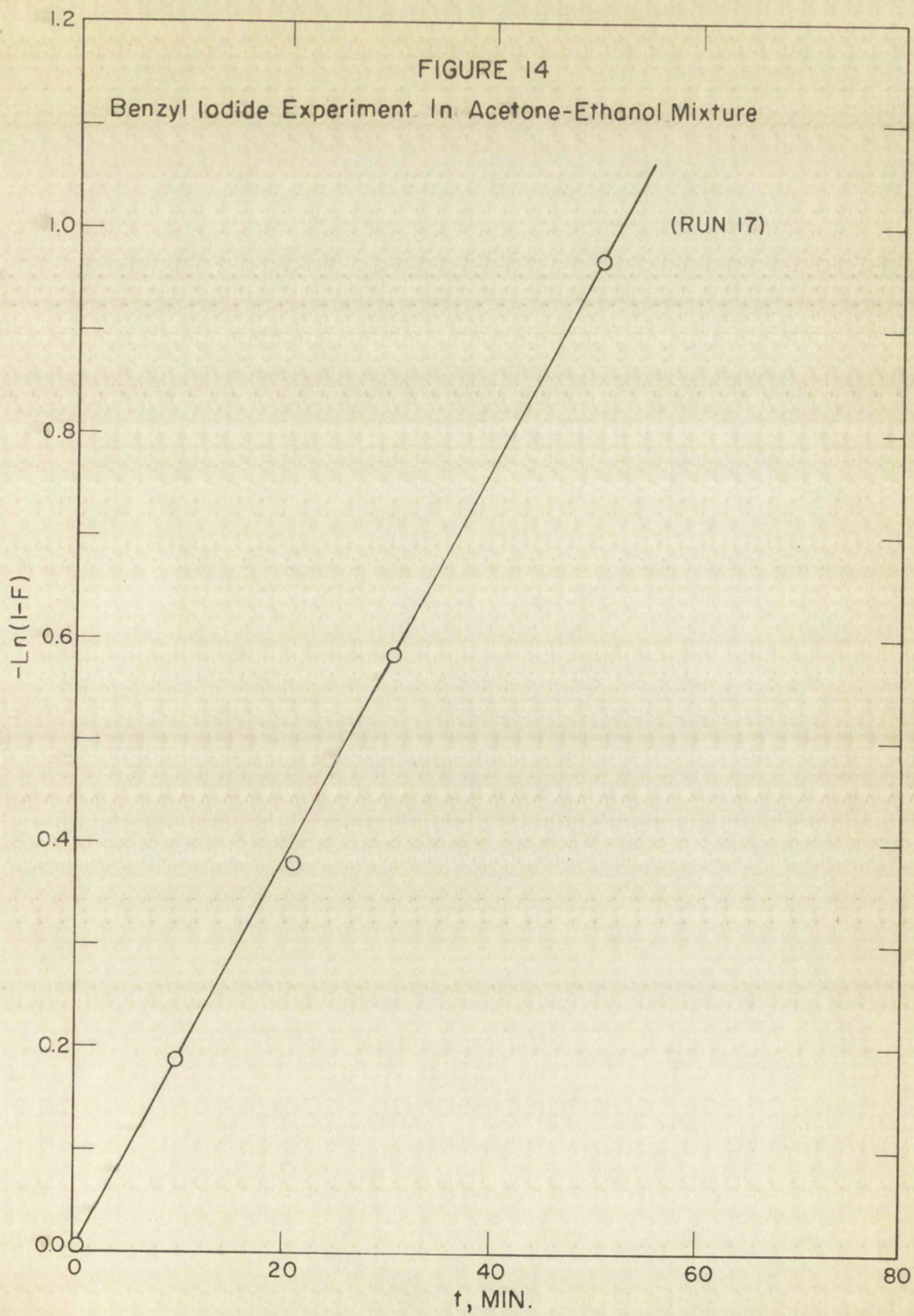


FIGURE 14

Benzyl Iodide Experiment In Acetone-Ethanol Mixture



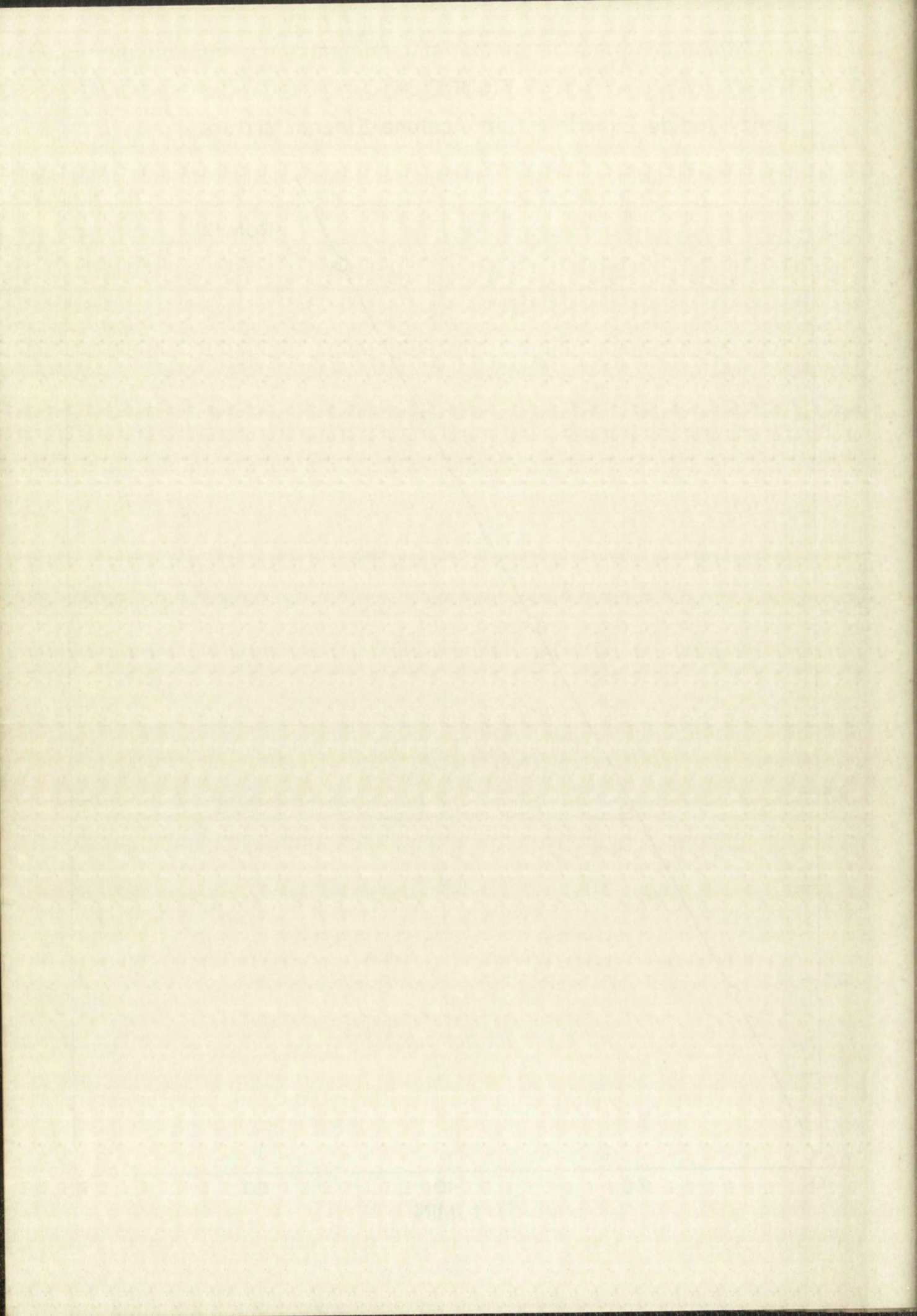


Table XXI

Experimental Data for Run No. 18

Solvent composition: 7.01 M Acetone

8.75 M Ethanol

(BI) = 0.01208 M

(KI) = 0.00641 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	11.3	2396	361	0.200
2	21.5	1985	597	0.353
3	32.2	1910	810	0.454

 $t_{1/2} = 35.3 \text{ min.}$ $k = 1.06 \text{ l./mole/min.}$

Blank correction = 1.2 per cent

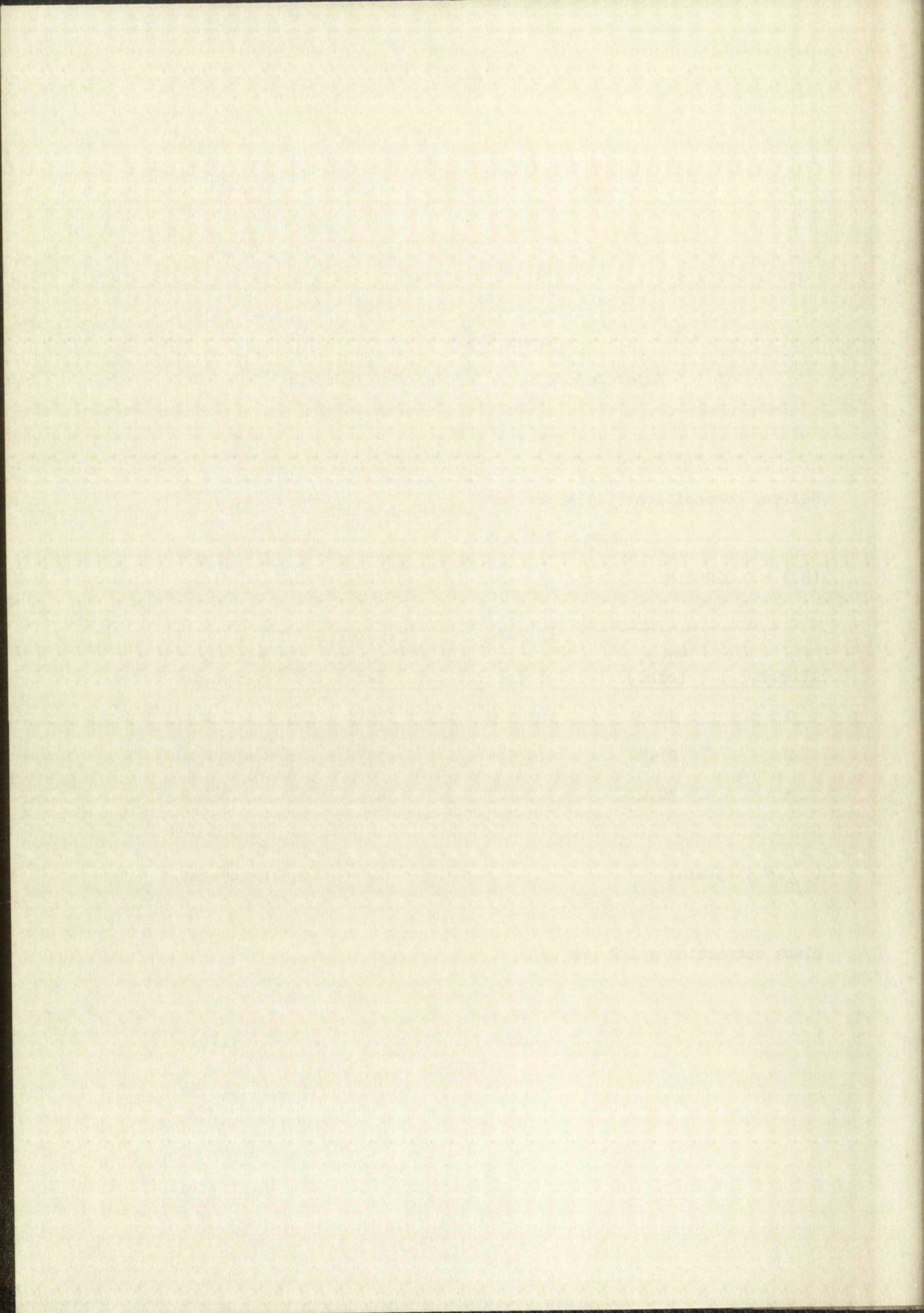


Table XXII

Experimental Data for Run No. 19

Solvent composition: 5.60 M Acetone

10.50 M Ethanol

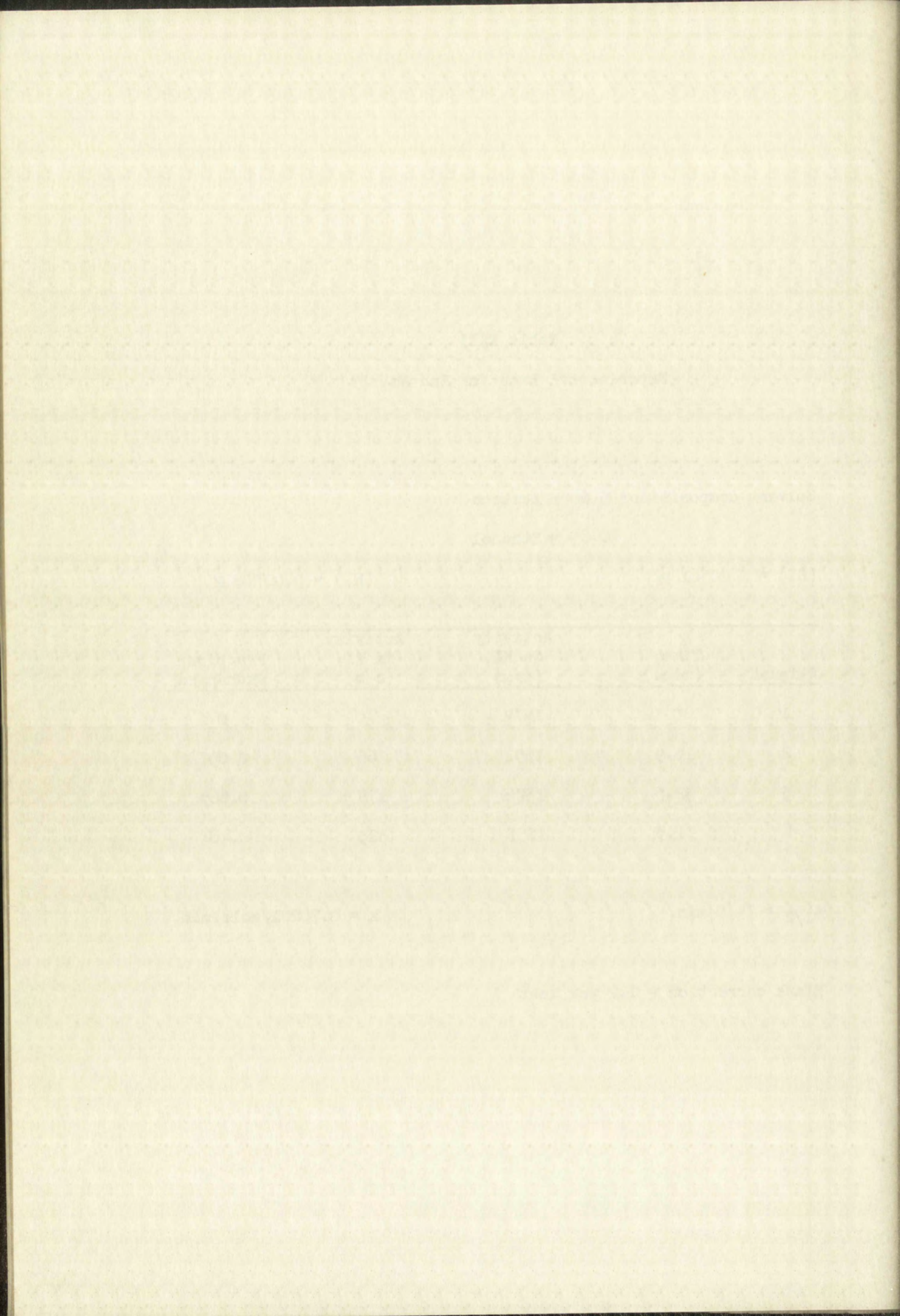
(BI) = 0.00561 M

(KI) = 0.00772 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	0	1572	0	0
2	10.9	1551	66	0.097
3	32.5	1396	175	0.265
4	71.5	1257	323	0.487

 $t_{1/2} = 74.0$ min. $k = 0.702$ l./mole/min.

Blank correction = 1.2 per cent



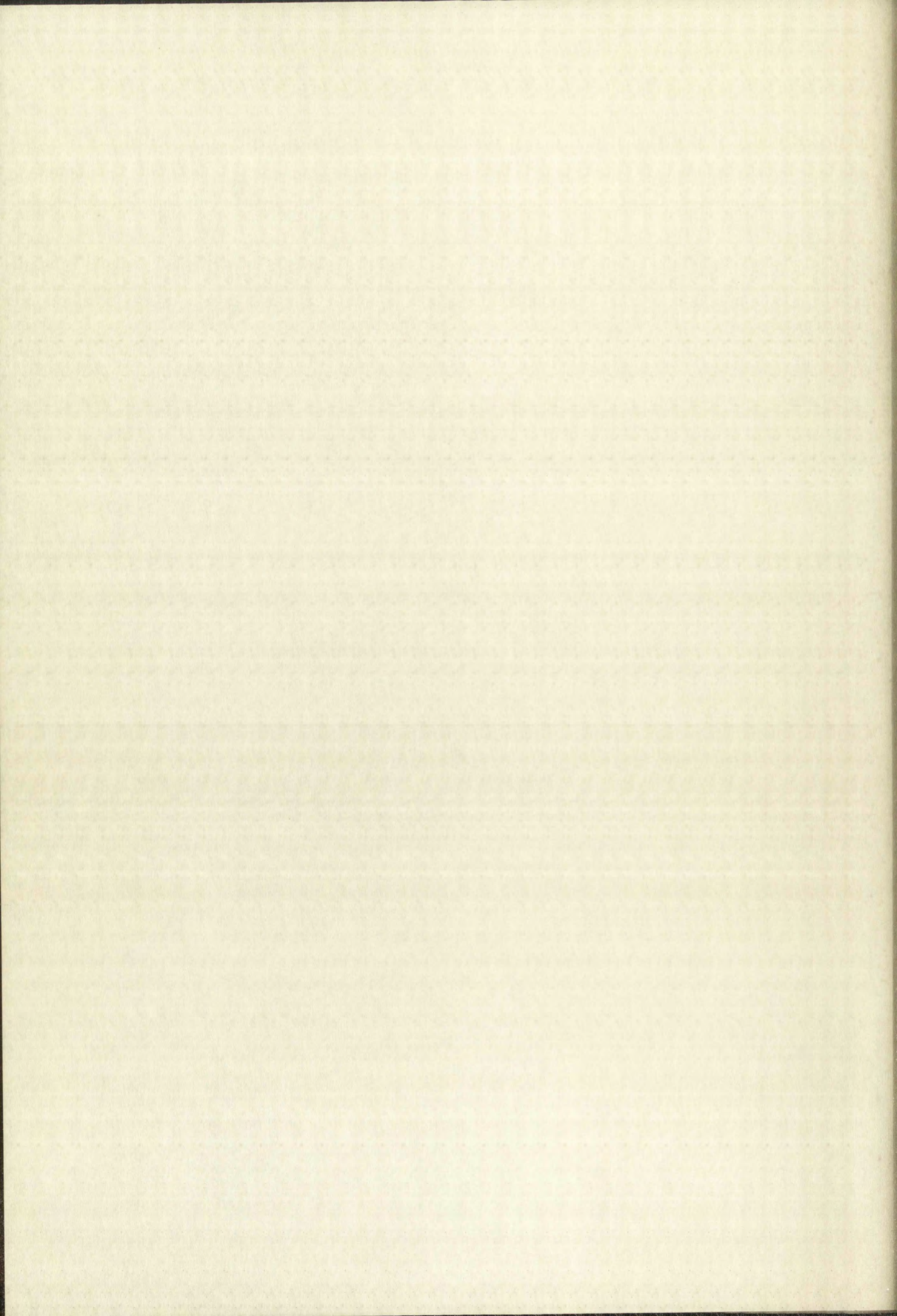
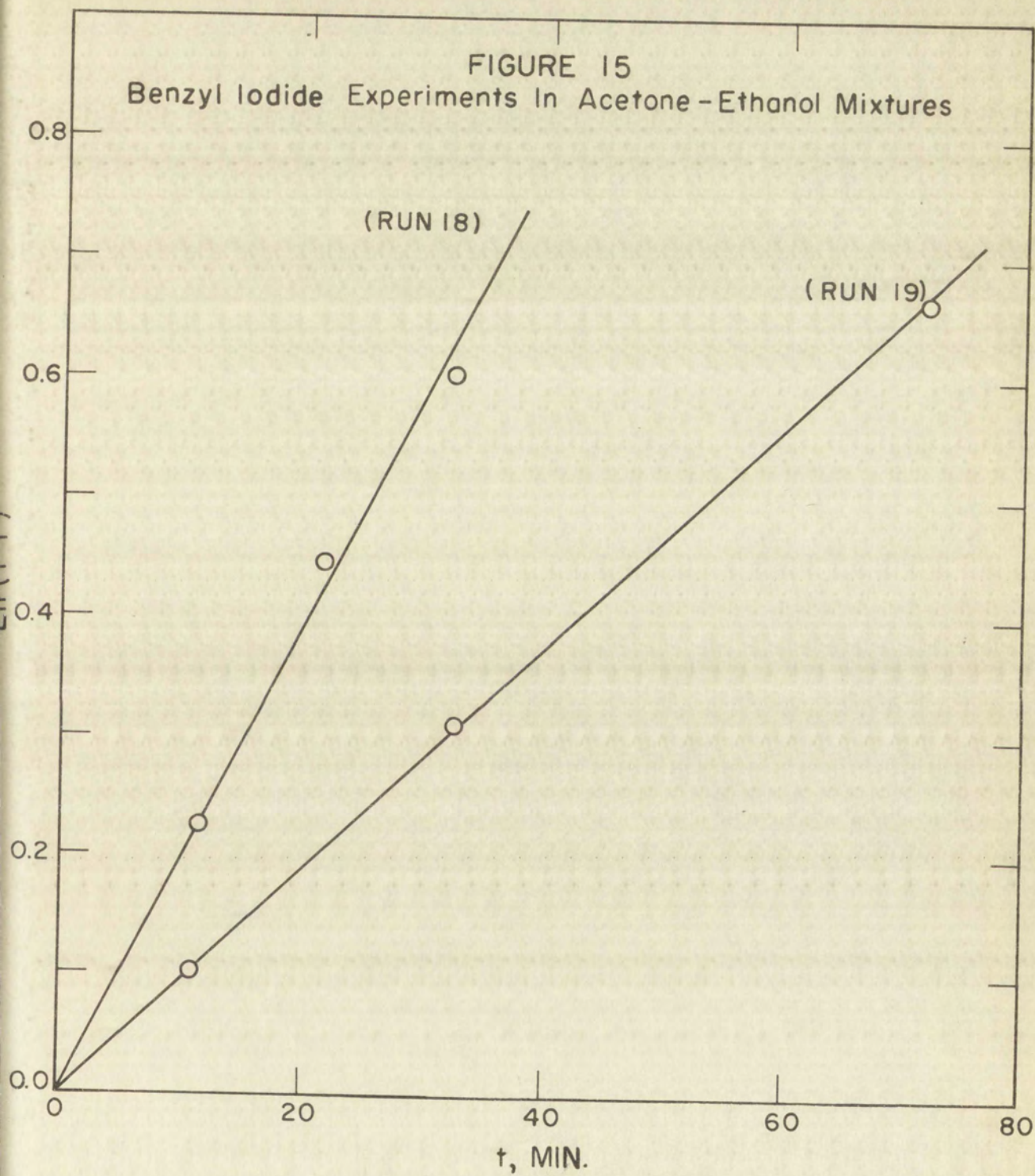


FIGURE 15
Benzyl Iodide Experiments In Acetone-Ethanol Mixtures



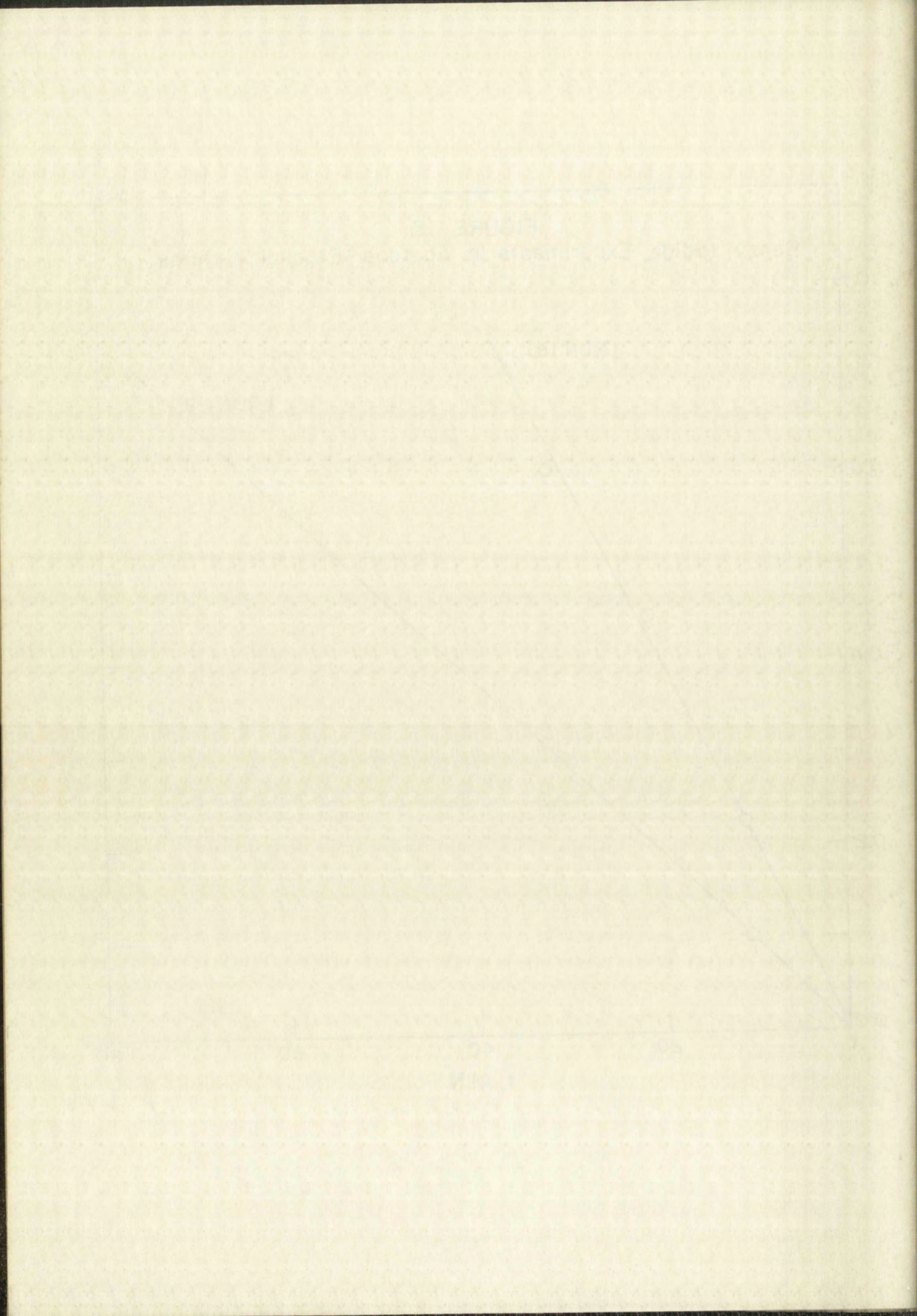


Table XXIII

Experimental Data for Run No. 20

Solvent composition: 4.67 M Acetone

11.67 M Ethanol

(BI) = 0.00806 M

(KI) = 0.00854 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	16.4	2725	200	0.141
2	29.7	2521	316	0.230
3	57.8	2254	543	0.400
4	96.8	2018	816	0.593

 $t_{1/2} = 78.3$ min. $k = 0.532$ l/mole/min.

Blank correction = 1.1 per cent

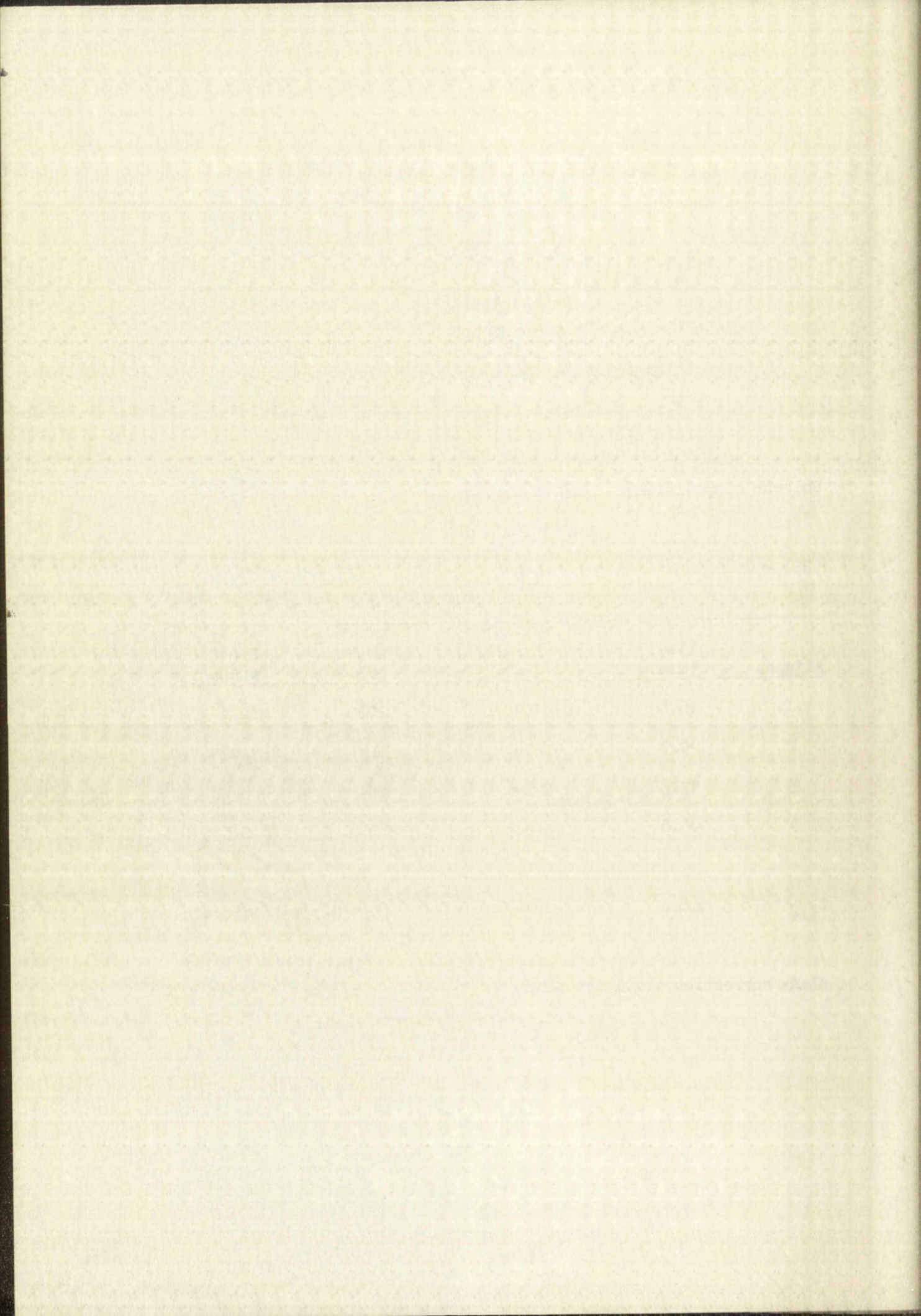


Table XXIV

Experimental Data for Run No. 21

Solvent: Absolute ethanol

 $(BI) = 0.02245 M$ $(KI) = 0.01286 M$

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	21.8	1442	74	0.077
2	60.9	1362	200	0.201
3	103.1	1249	308	0.311
4	142.5	1160	415	0.415

 $t_{1/2} = 188 \text{ min.}$ $k = 0.104 \text{ l./mole/min.}$

Blank correction = 0.6 per cent

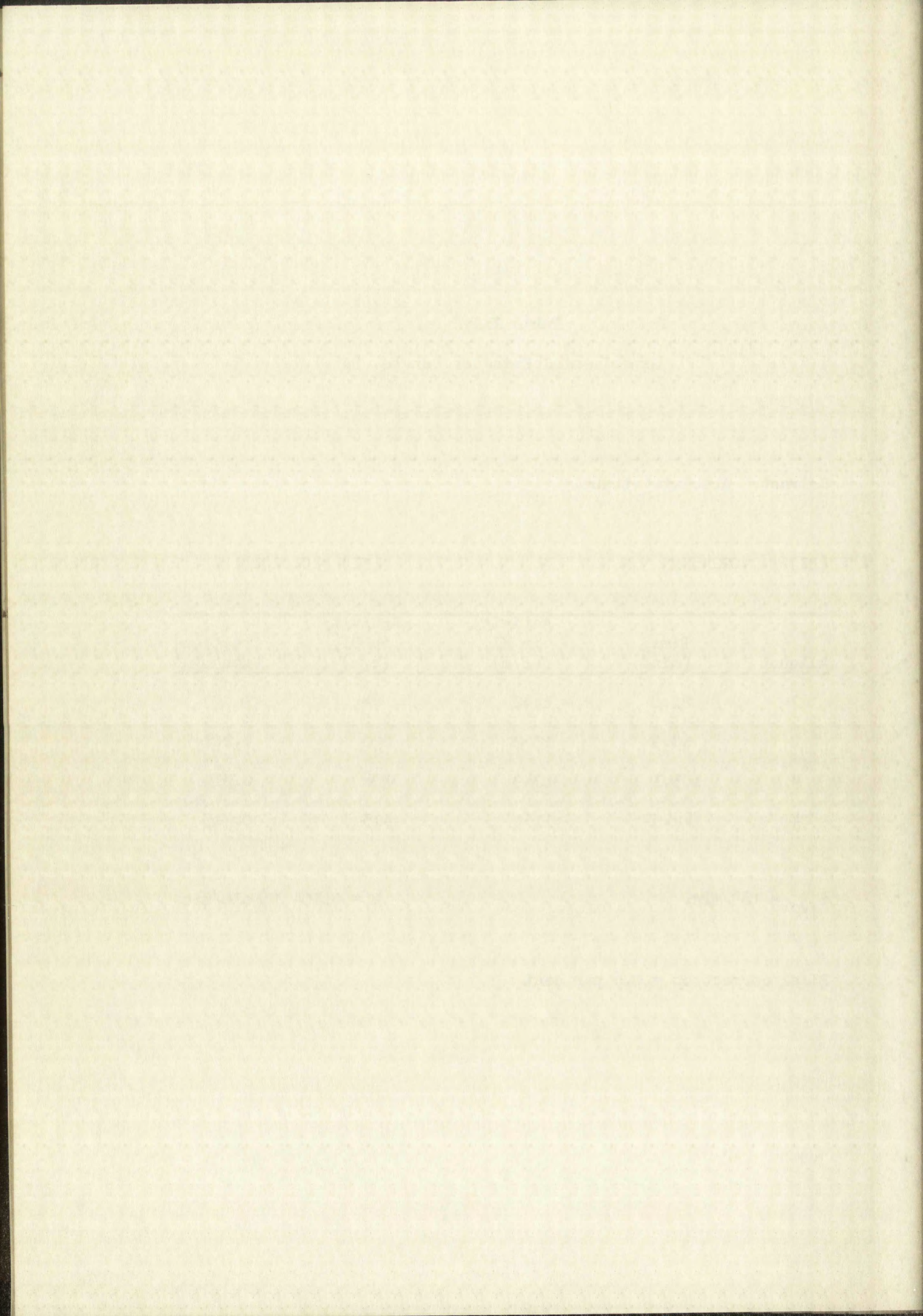


Table XXV

Experimental Data for Run No. 22

Solvent: Absolute ethanol

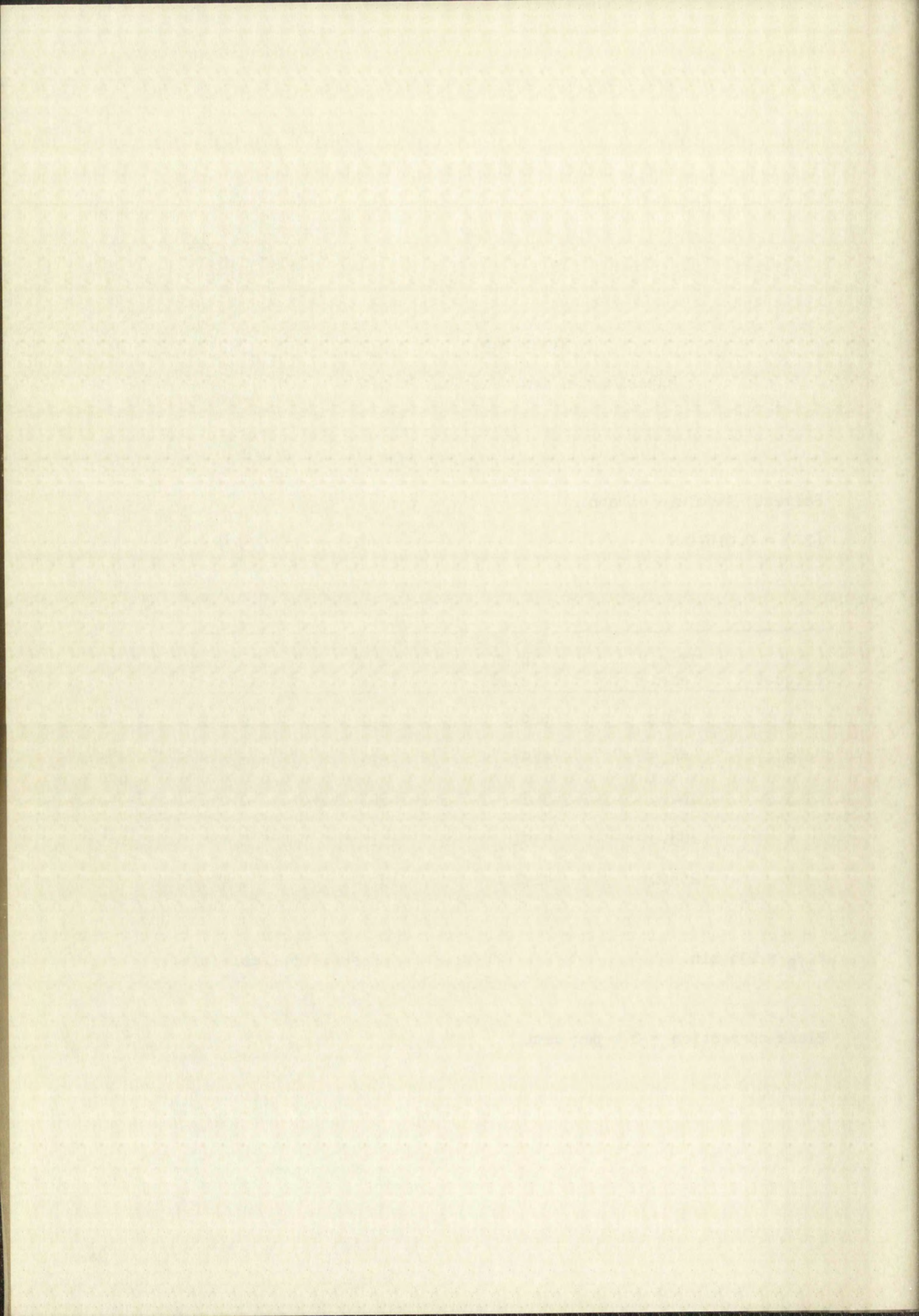
(BI) = 0.01570 M

(KI) = 0.01279 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	18.0	5897	191	0.057
2	56.5	5485	521	0.157
3	104.3	5082	823	0.253
4	183.0	4391	1313	0.418
5	235.0	4177	1571	0.496

 $t_{1/2} = 236$ min. $k = 0.103$ l/mole/min.

Blank correction = 0.4 per cent



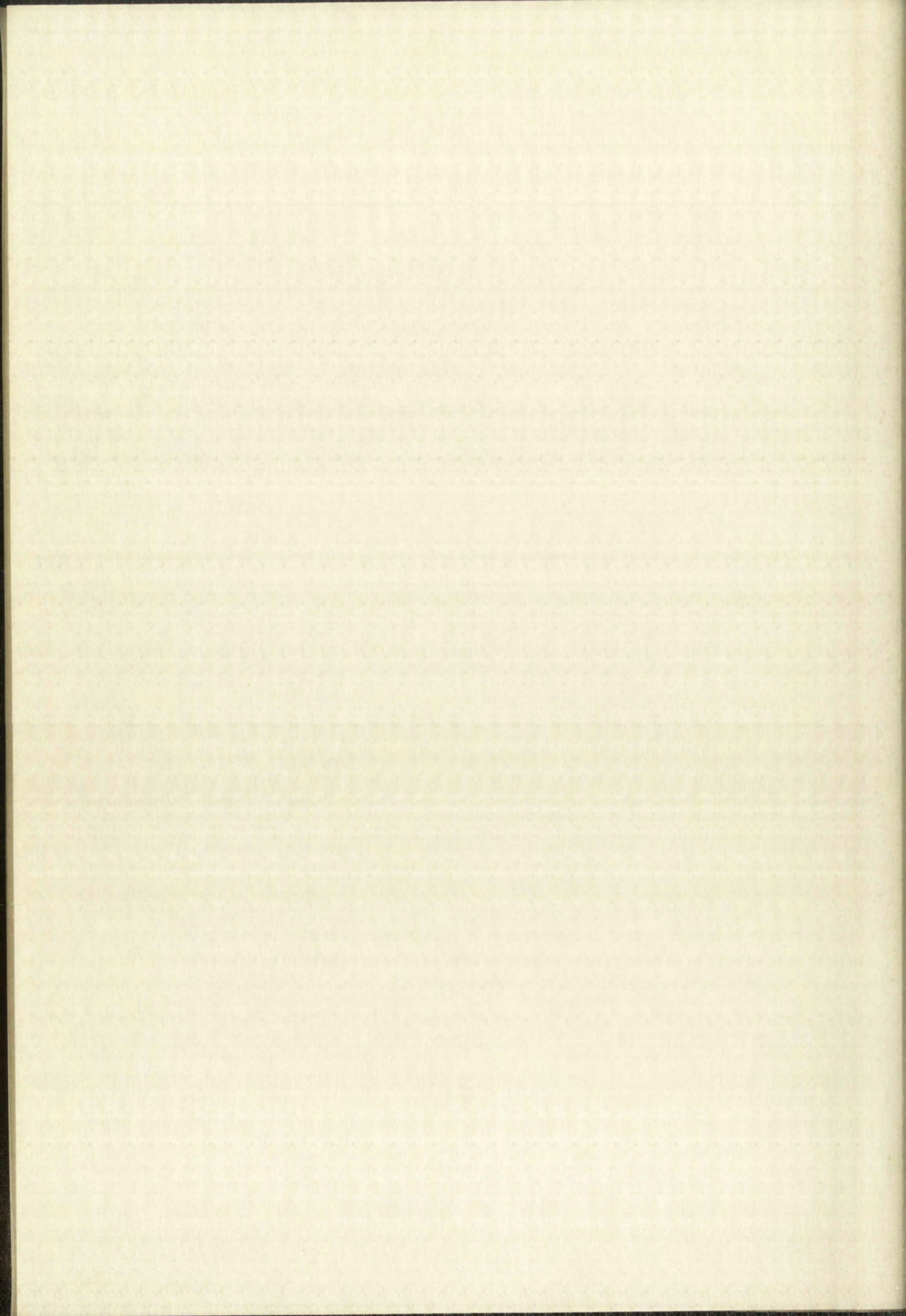
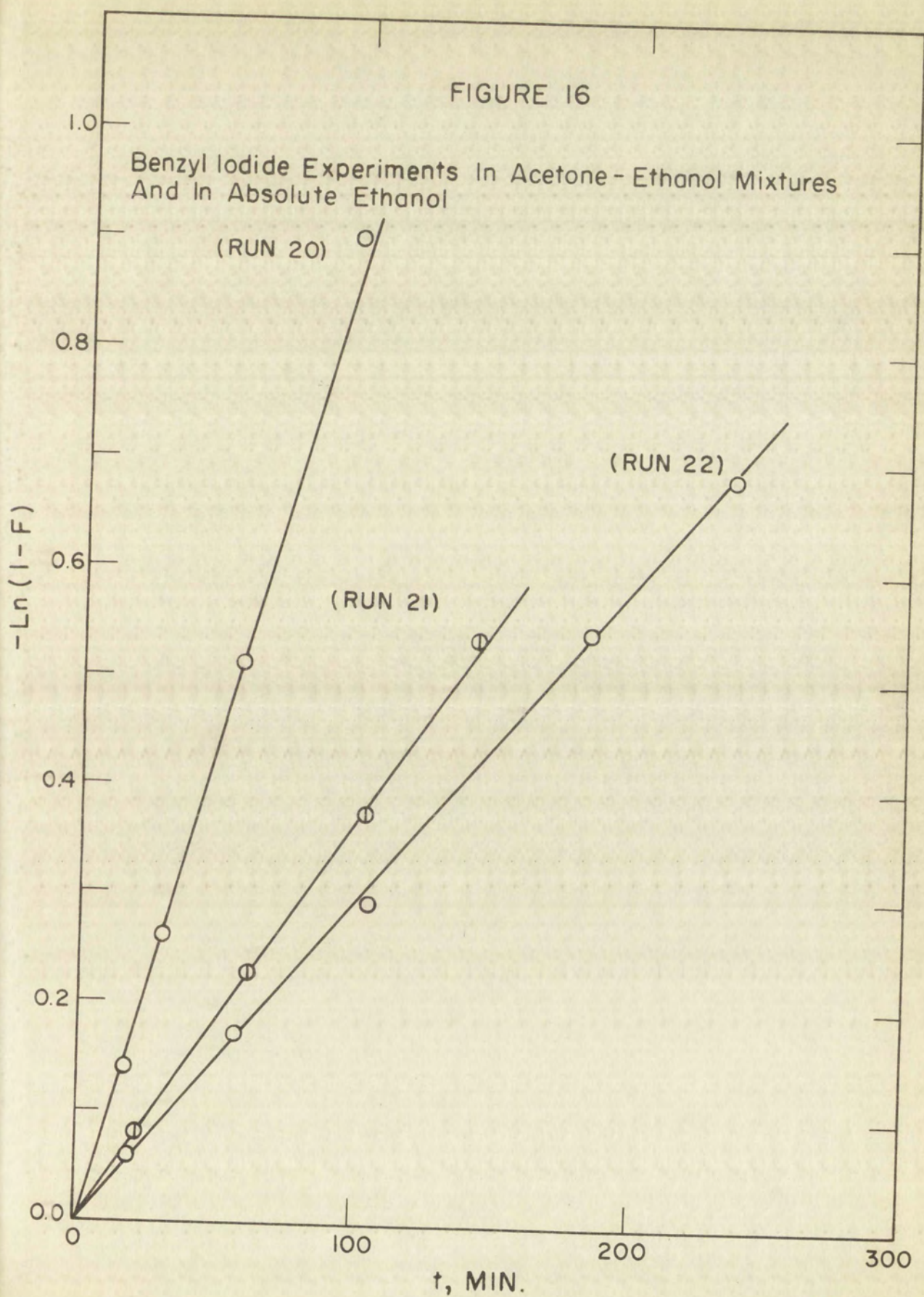
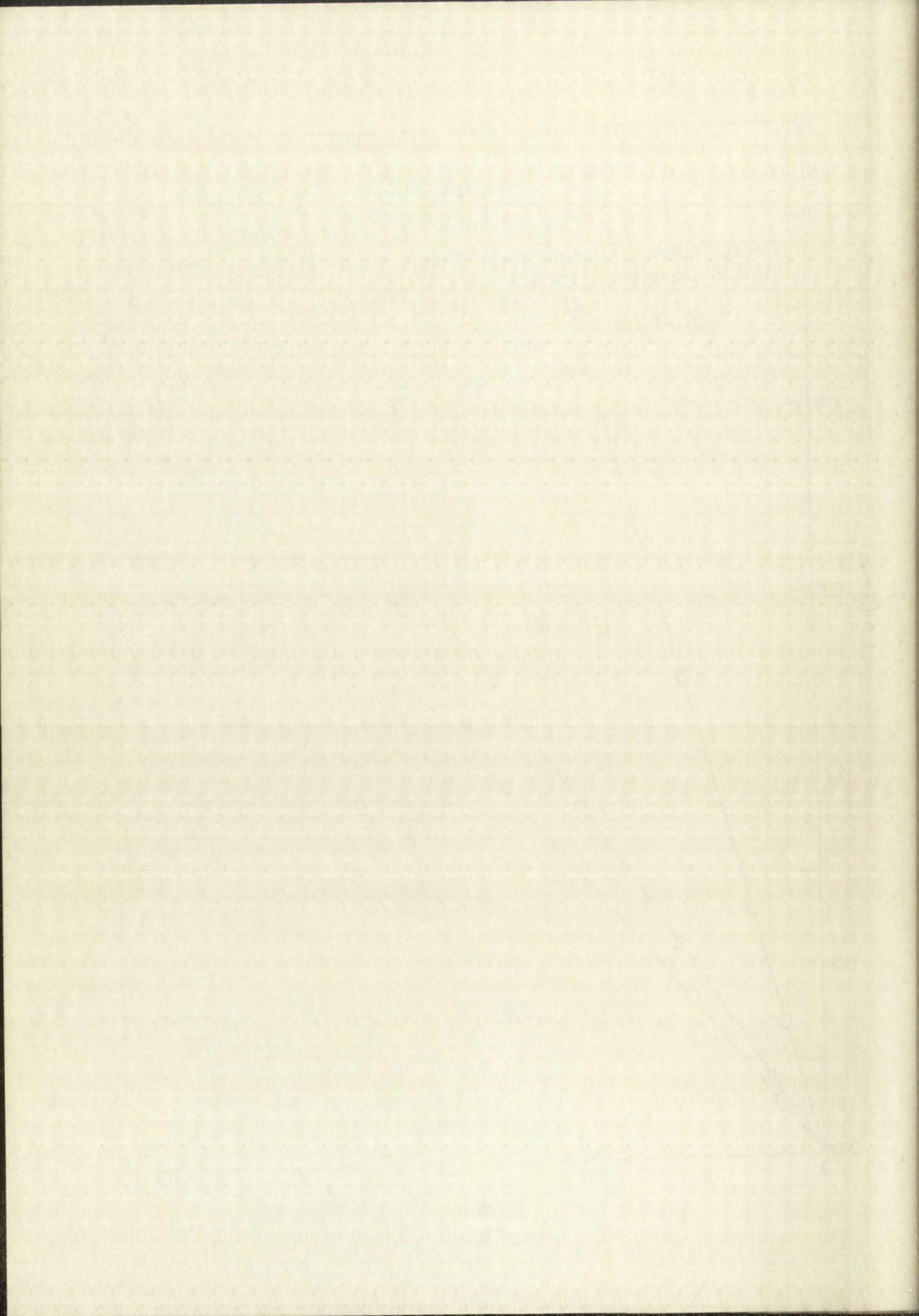


FIGURE 16

Benzyl Iodide Experiments In Acetone - Ethanol Mixtures
And In Absolute Ethanol





Experimental Data for p-Nitrobenzyl Iodide
Exchange Experiments in Acetone-Ethanol Mixtures
at 0.0°

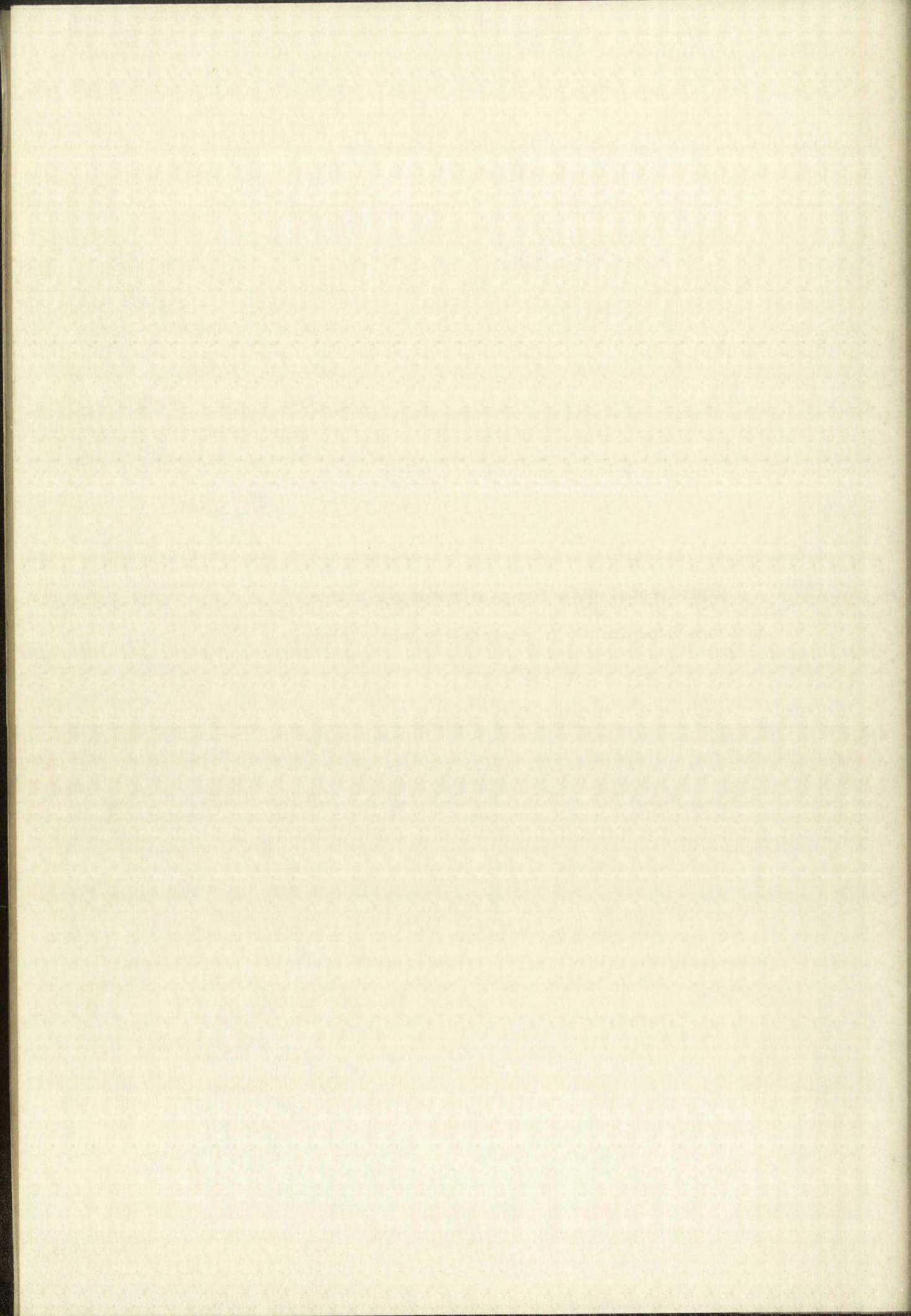


Table XXVI

Summary of p-Nitrobenzyl Iodide Exchange Experiments at 0.0° in
Acetone-Ethanol Solvent Mixtures

Run No.	$((\text{CH}_3)_2\text{CO}),$ M	$(\text{C}_2\text{H}_5\text{OH}),$ M	$(\text{PNBI}),$ $\text{M} \times 10^3$	$(\text{KI}),$ $\text{M} \times 10^3$	$t_{1/2},$ min.	$k,$ l./mole/min.
(avg.)	14.00	0	-	-	-	372.
23	13.66	0.416	0.0825	0.02132	31.9	211.
24	13.31	0.833	0.0619	0.0426	49.0	135.
25	12.60	1.75	0.03934	0.0635	99.7	67.7

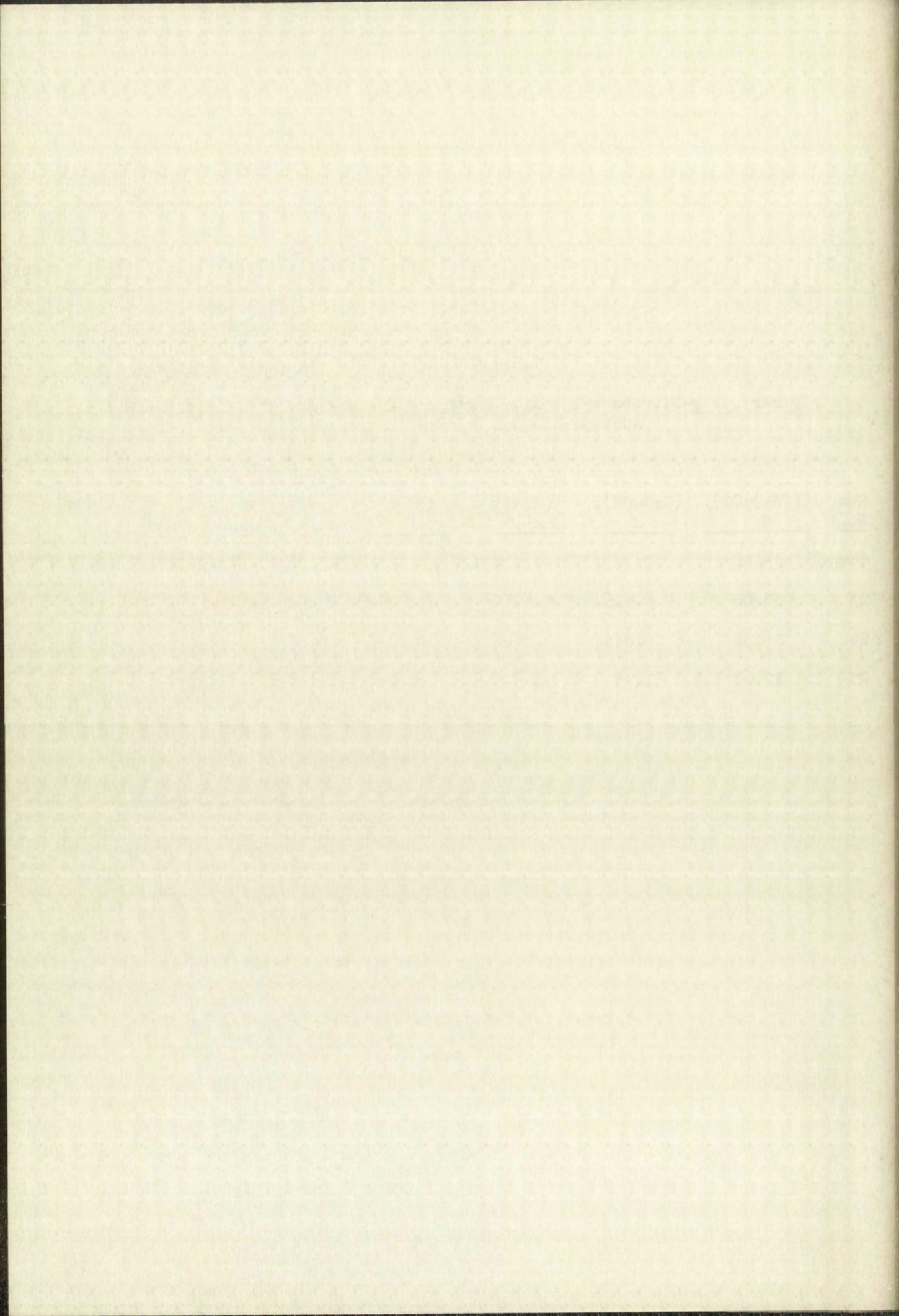


Table XXVII

Experimental Data for Run No. 23

Solvent composition: 13.66 M Acetone

0.416 M Ethanol

(PNBI) = 0.0000825 M

(KI) = 0.00002132 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in PNBI, (c/m)	Fraction exchanged
1	10.1	13,770	2626	0.202
2	19.9	11,790	4576	0.352
3	28.7	10,370	6041	0.463

 $t_{1/2} = 31.9$ min. $k = 211$ l/mole/min.

Blank correction = 0.6 per cent

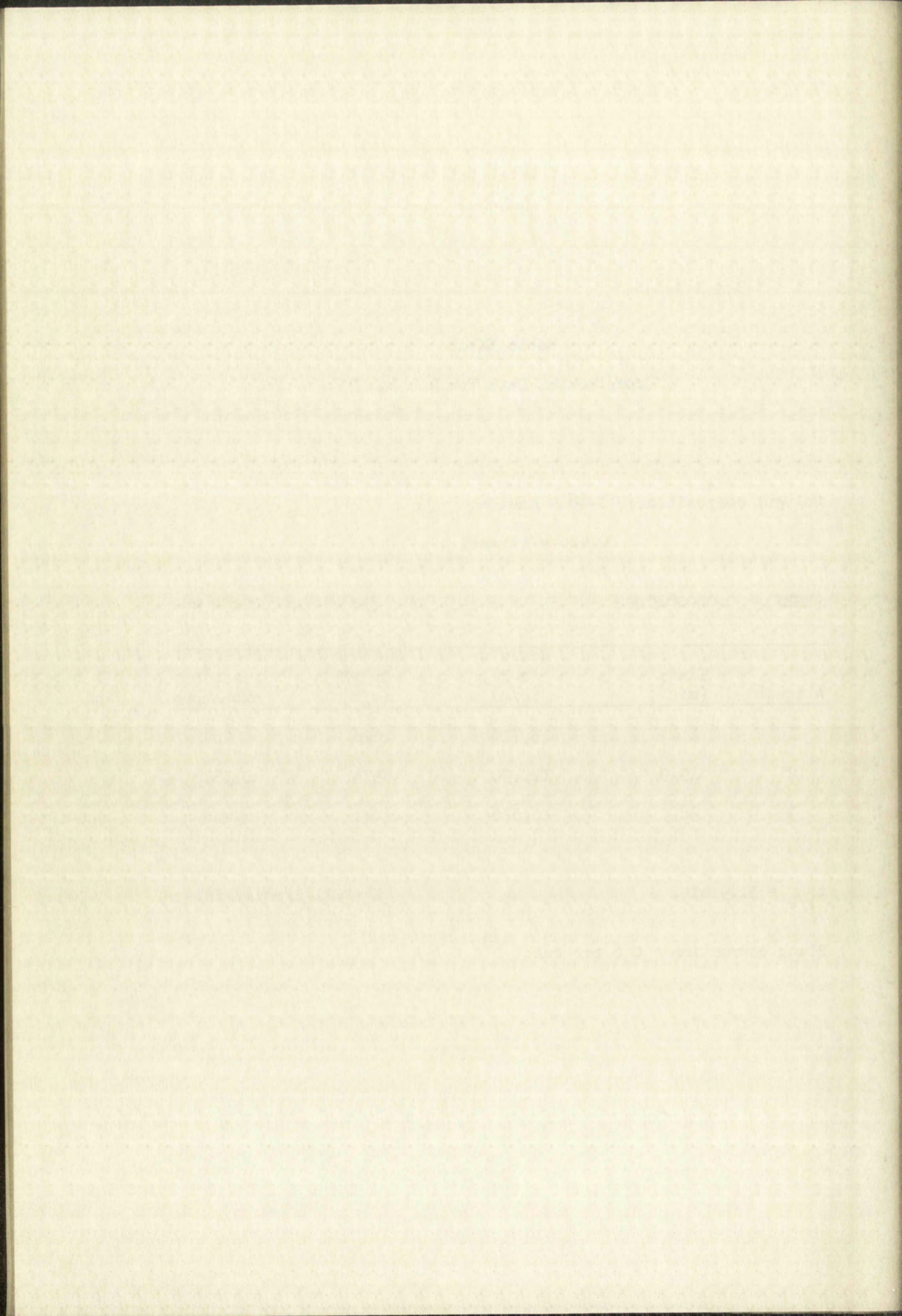


Table XXVIII

Experimental Data for Run No. 24

Solvent composition: 13.31 M Acetone

0.833 M Ethanol

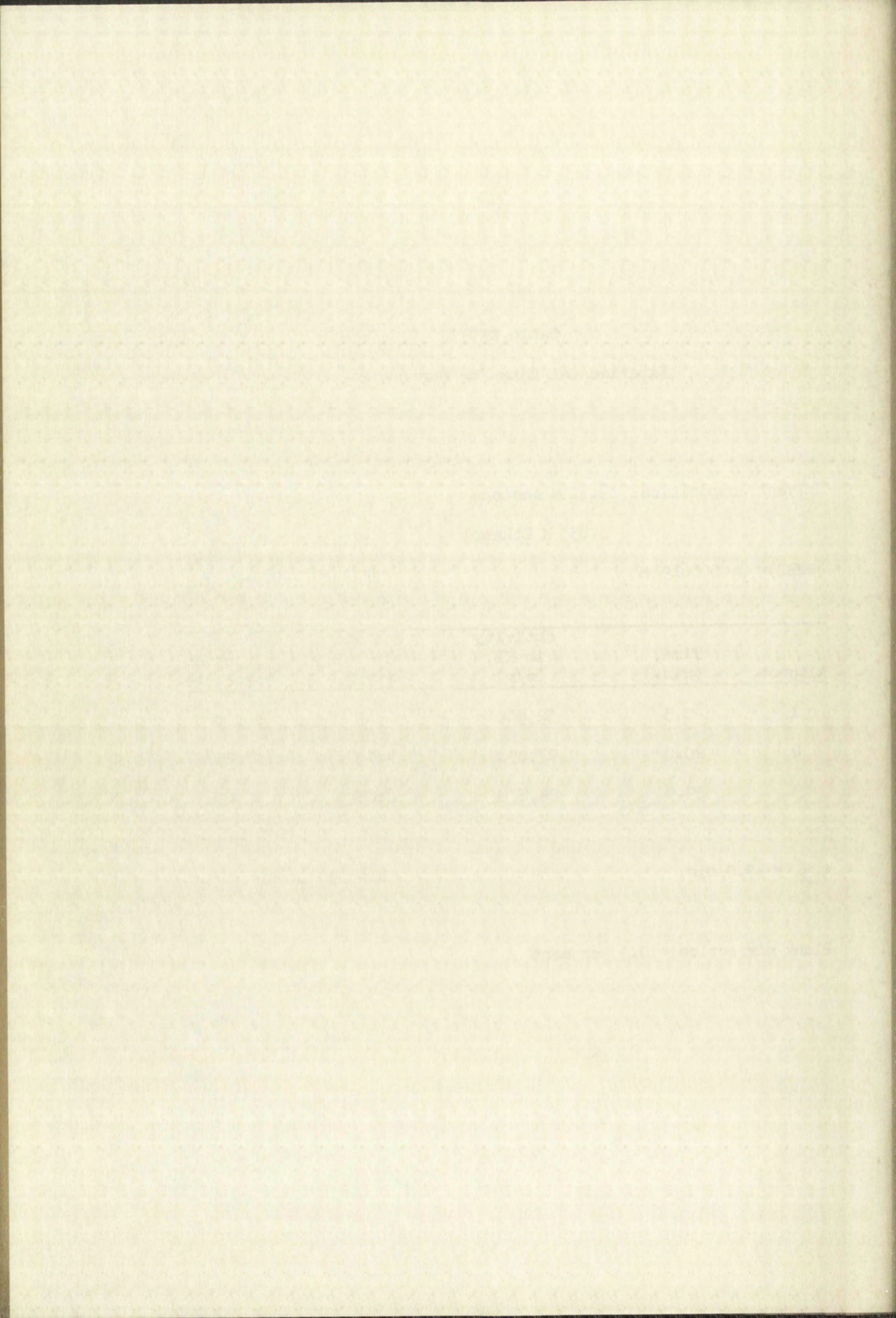
(PNBI) = 0.0000619 M

(KI) = 0.0000426 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in PNBI, (c/m)	Fraction exchanged
1	0.3	32,500	42	0.002
2	20.0	27,090	4743	0.252
3	39.9	24,270	8183	0.426

 $t_{1/2} = 49.0$ min. $k = 135$ l./mole/min.

Blank correction = 0.3 per cent



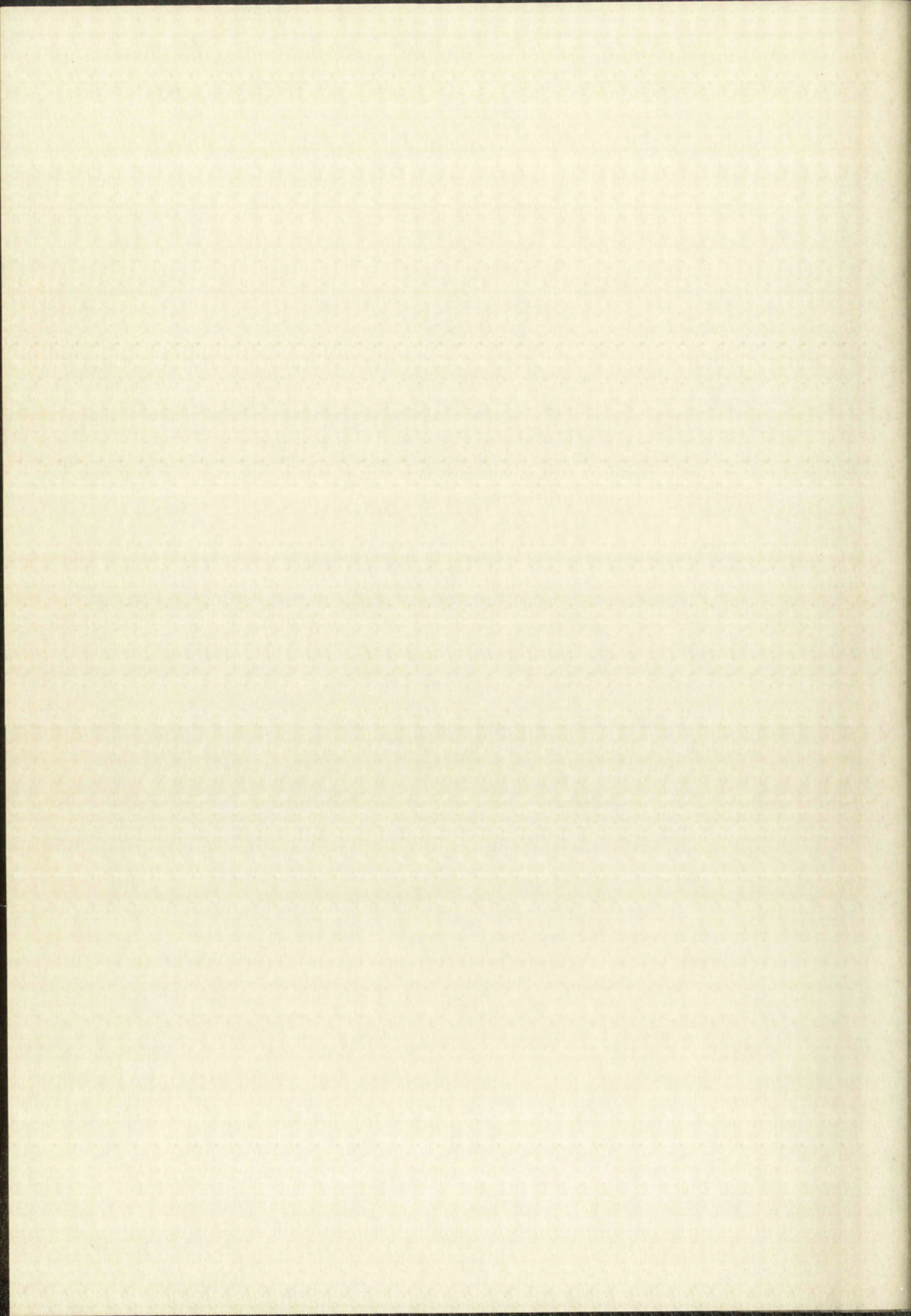
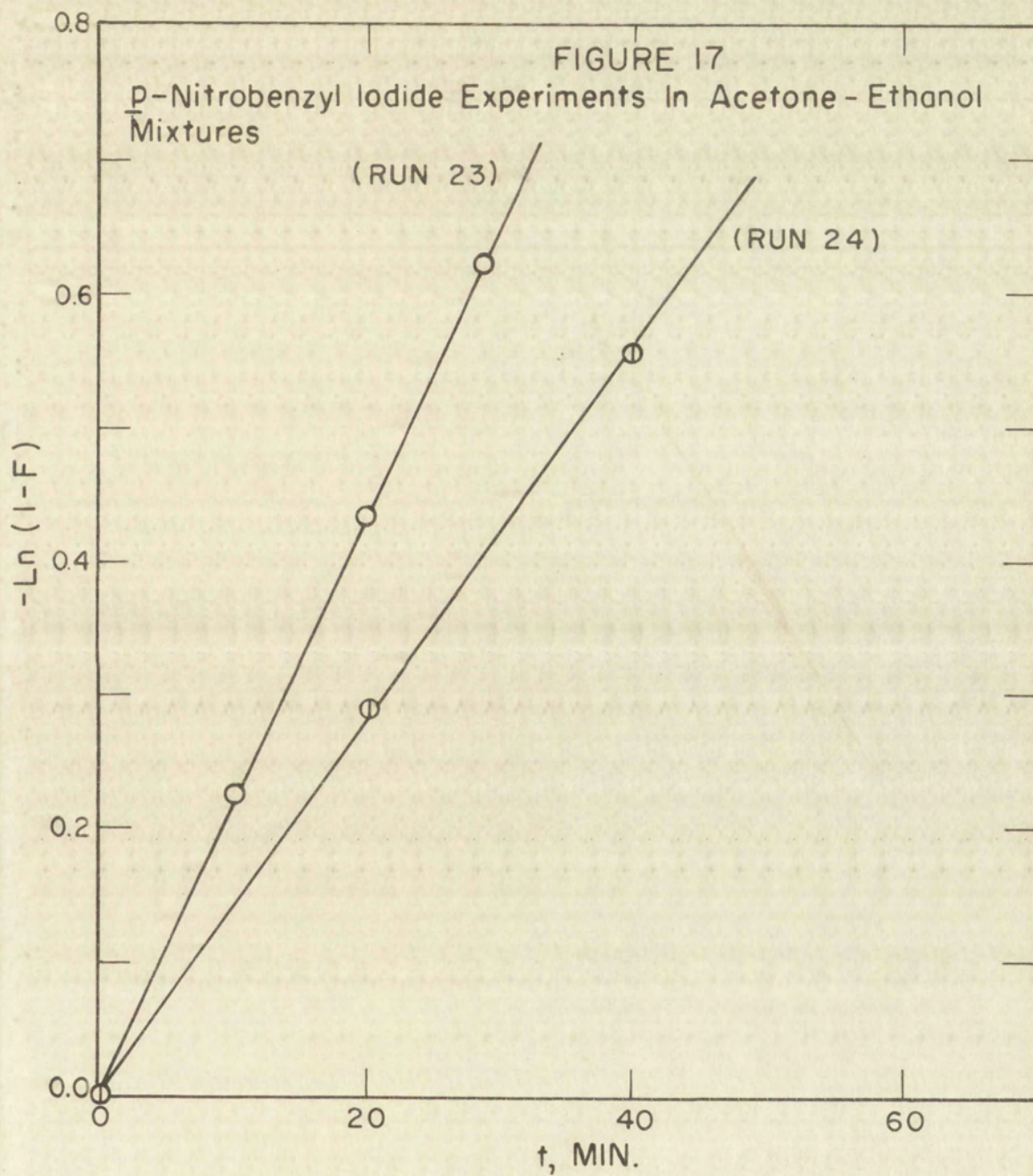


FIGURE 17
p-Nitrobenzyl Iodide Experiments In Acetone - Ethanol
Mixtures



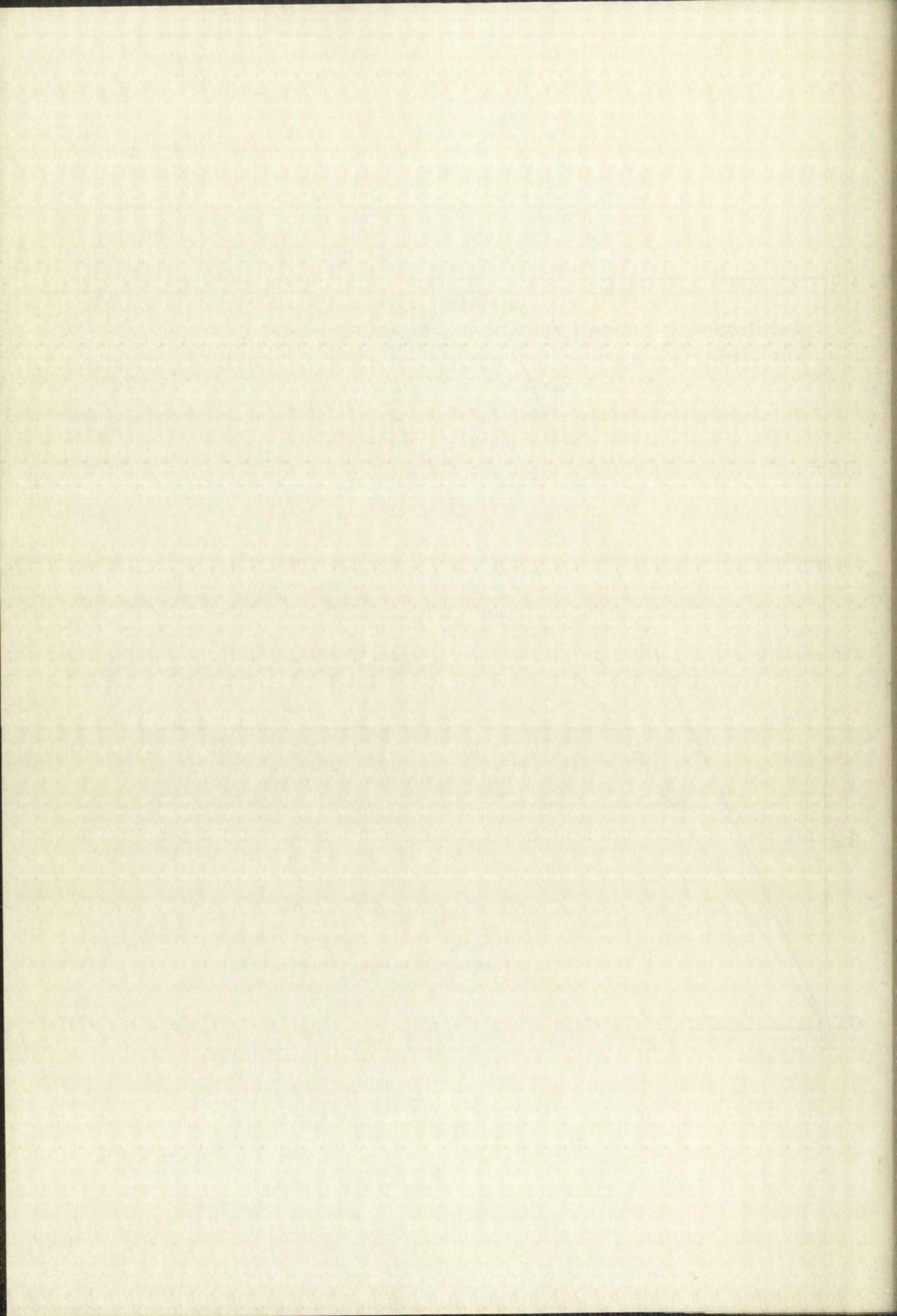


Table XXIX

Experimental Data for Run No. 25

Solvent composition: 12.60 M Acetone

1.75 M Ethanol

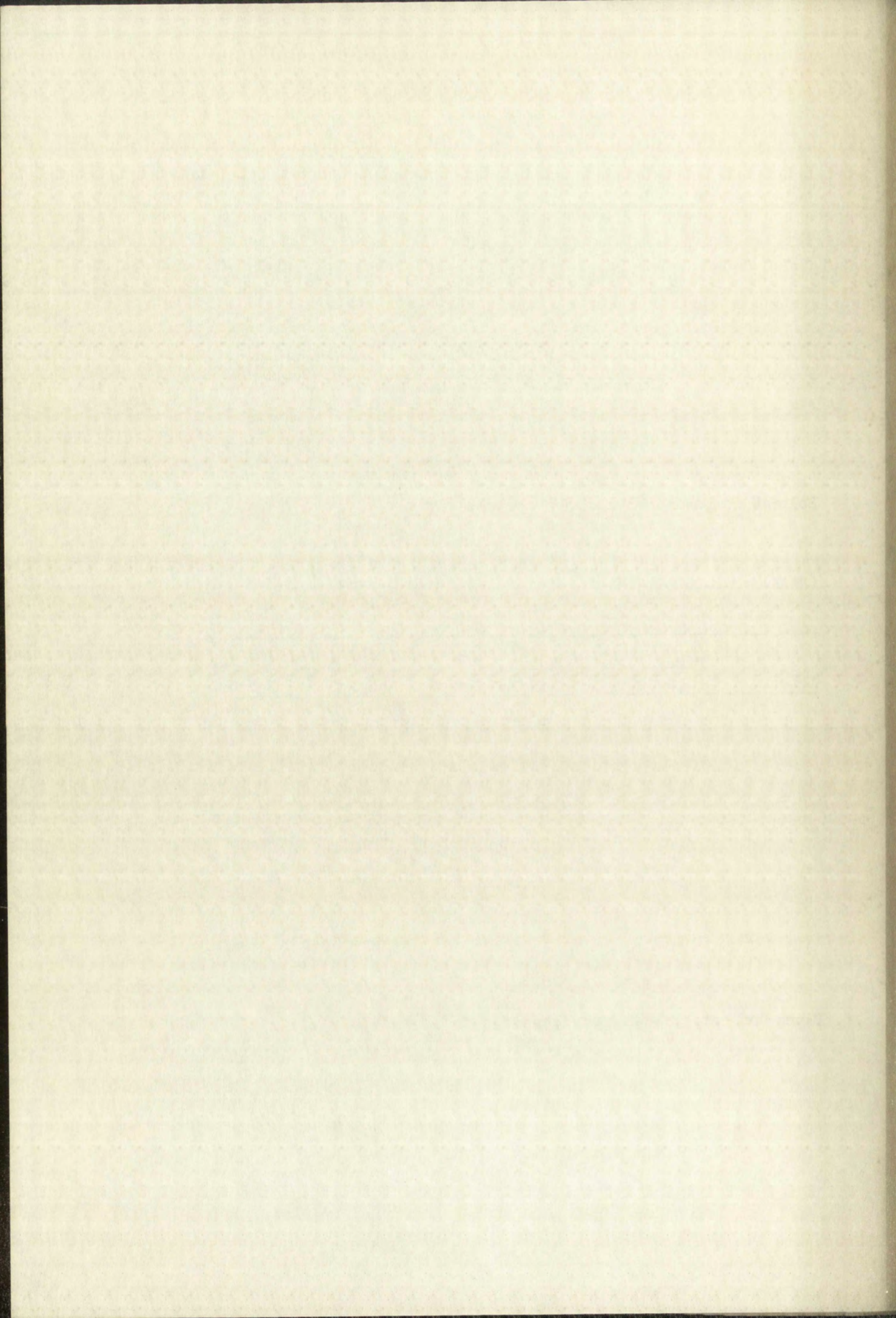
(PNBI) = 0.00003934 M

(KI) = 0.0000635 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in PNBI, (c/m)	Fraction exchanged
1	0.3	28,870	0	0
2	30.5	25,780	2341	0.218
3	60.5	24,280	3763	0.351
4	92.8	23,180	5166	0.477
5	130.4	22,840	6730	0.595

 $t_{1/2} = 99.7 \text{ min.}$ $k = 67.7 \text{ l/mole/min.}$

Blank correction = 2.6 per cent



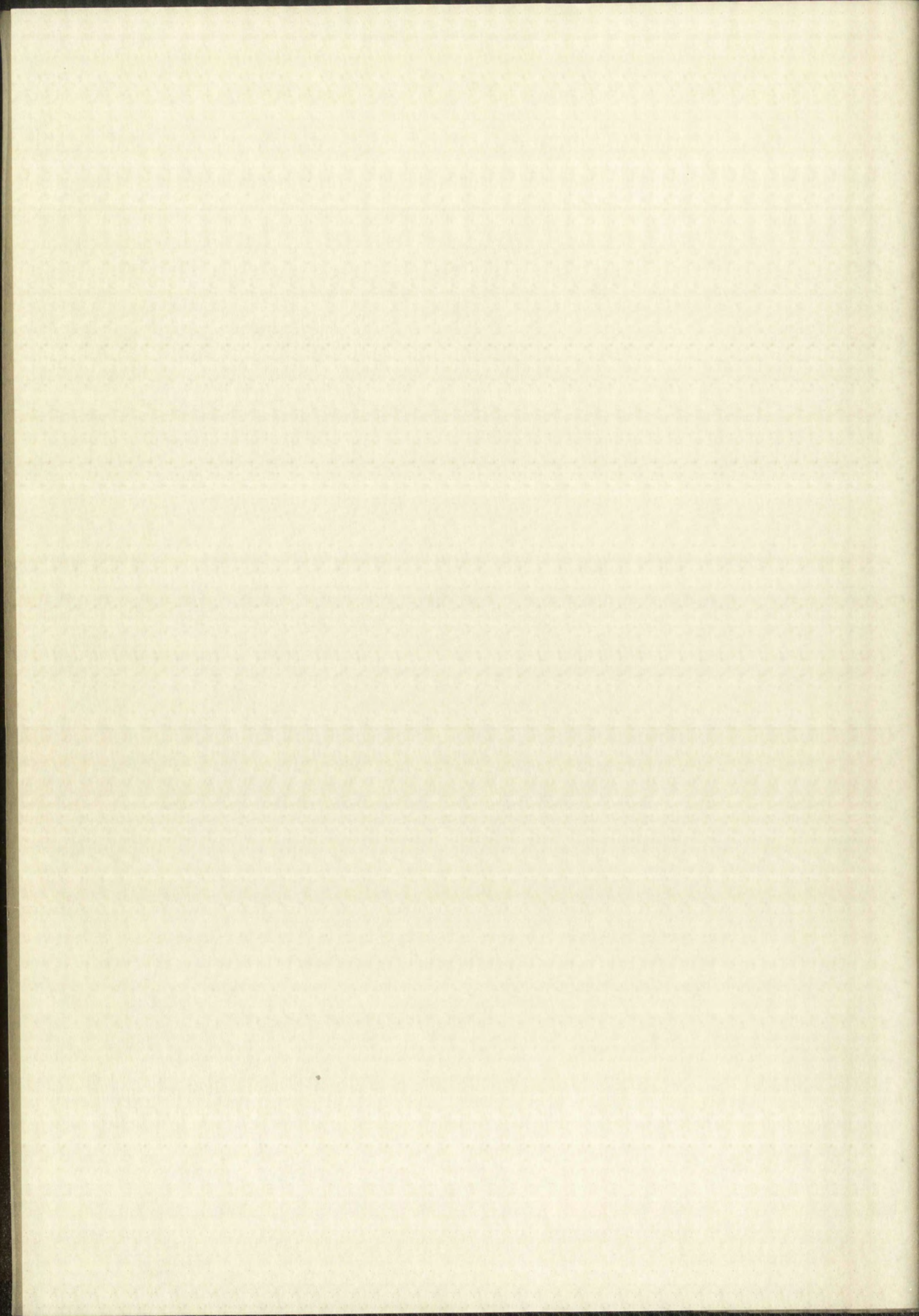
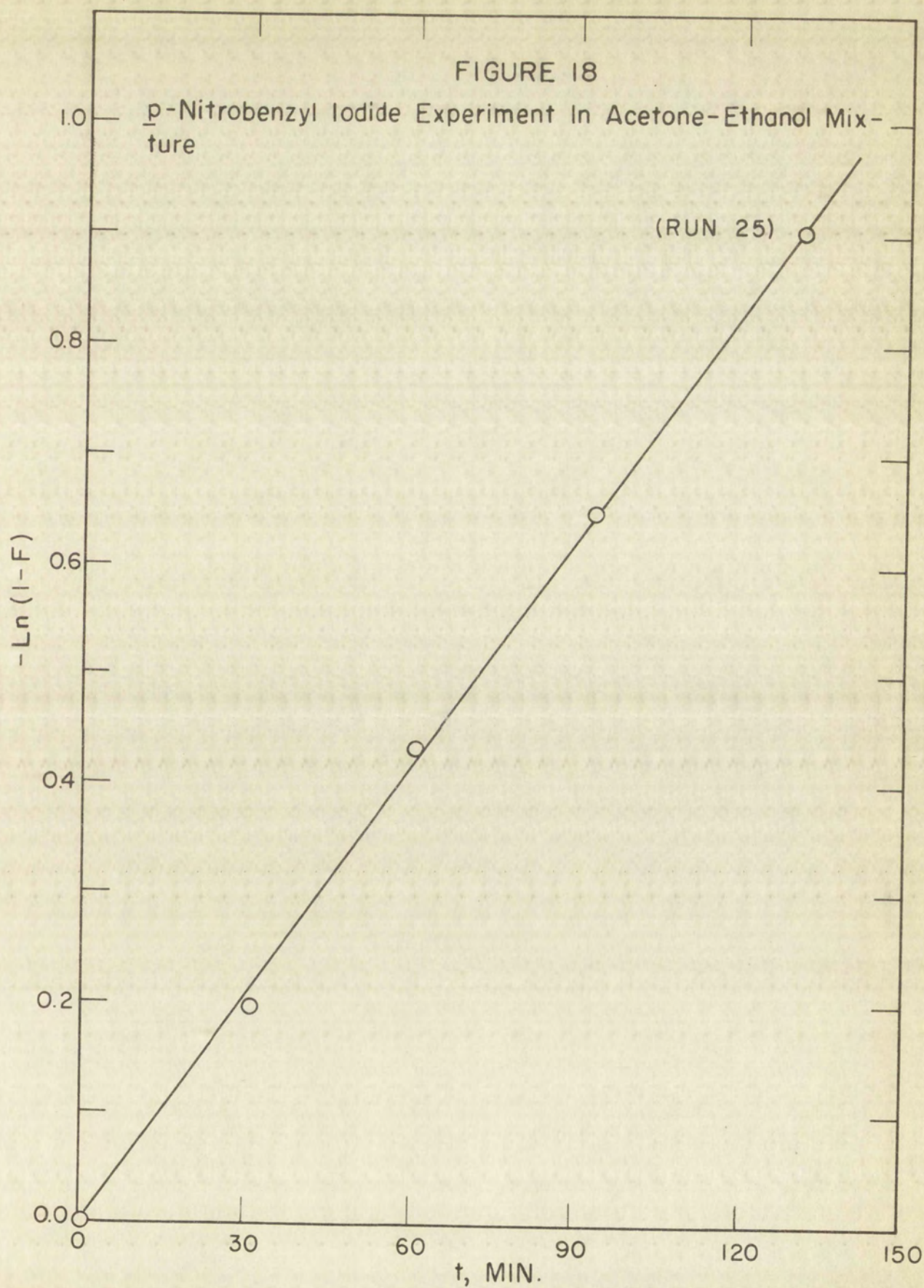
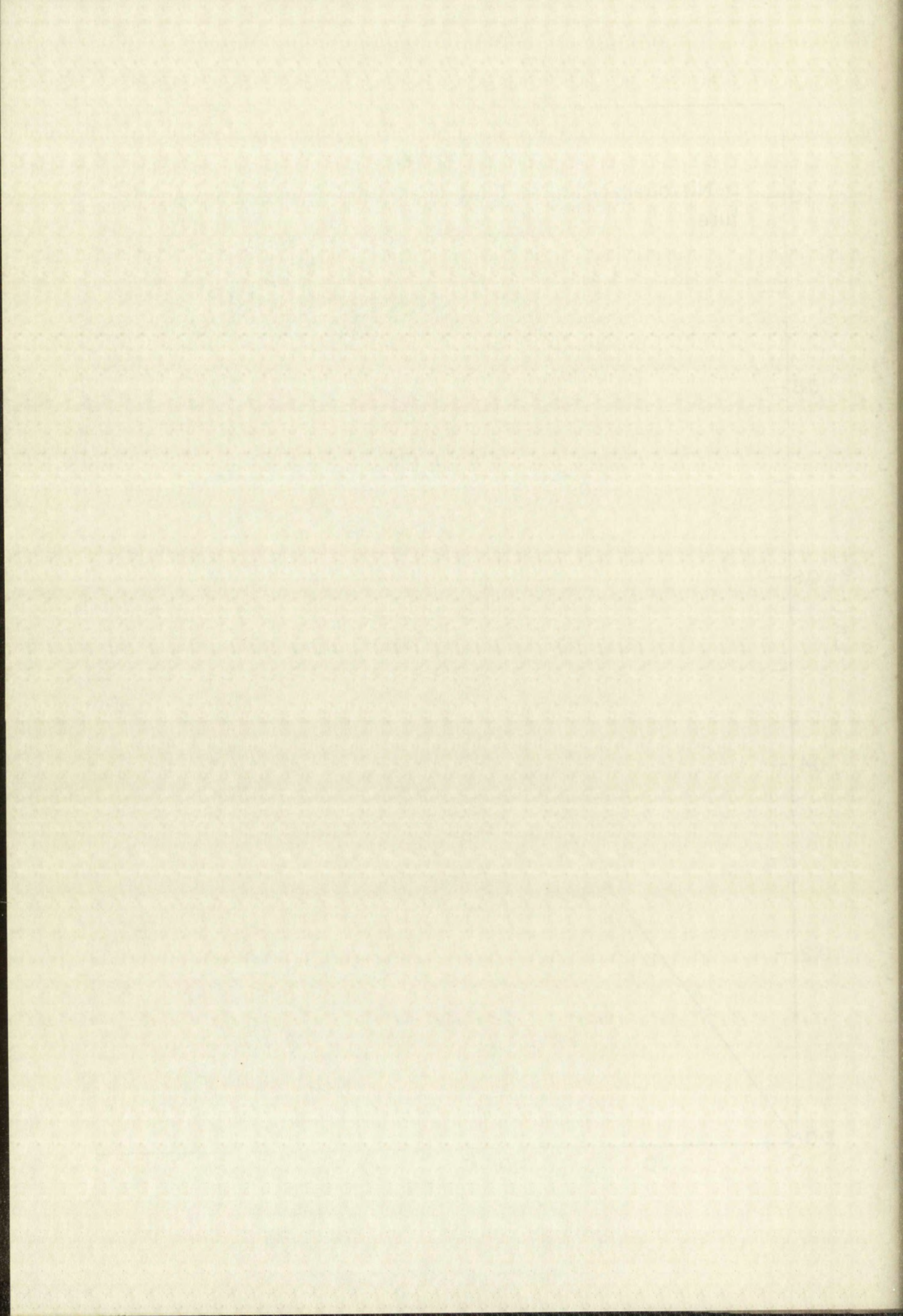


FIGURE 18

p-Nitrobenzyl Iodide Experiment In Acetone-Ethanol Mixture





Experimental Data for Benzyl Iodide

Exchange Experiments in Acetone-Carbon Tetrachloride

Mixtures at 0.0°

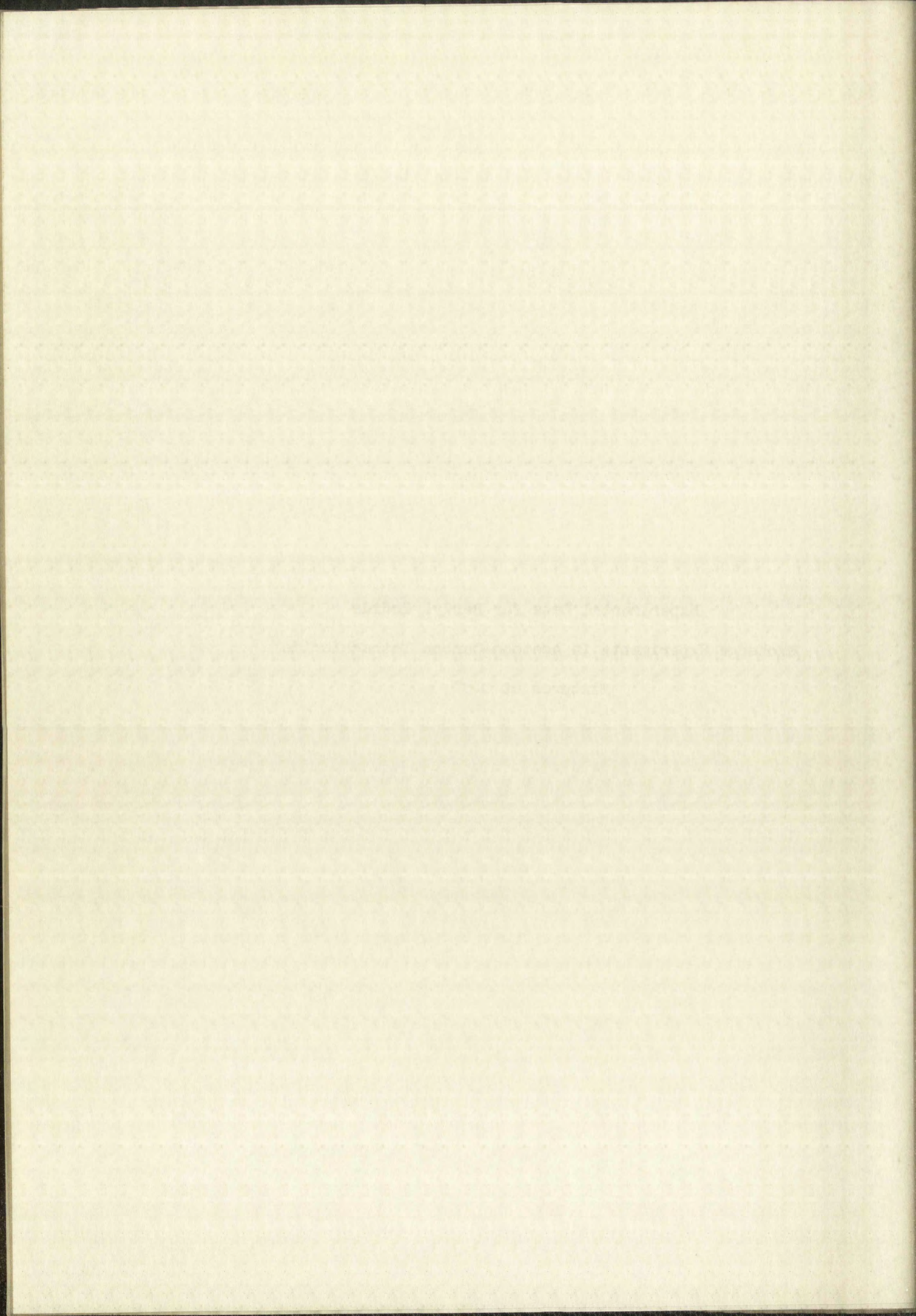


Table XXX

Summary of Benzyl Iodide Exchange Experiments at 0.0° in Acetone-
Carbon Tetrachloride Solvent Mixtures

Run No.	$((\text{CH}_3)_2\text{CO}),$ M	$(\text{CCl}_4),$ M	$(\text{BI}),_3$ $\text{M} \times 10^3$	$(\text{KI}),$ $\text{M} \times 10^3$	$t_{1/2},$ min.	$k,$ l./mole/min.
(avg.)	14.00	0	-	-	-	59.6
26	13.29	0.531	0.2532	0.2592	22.3	60.6
27	12.60	1.063	0.373	0.2580	18.0	61.0
28	11.20	2.12	0.1688	0.2592	29.2	55.5

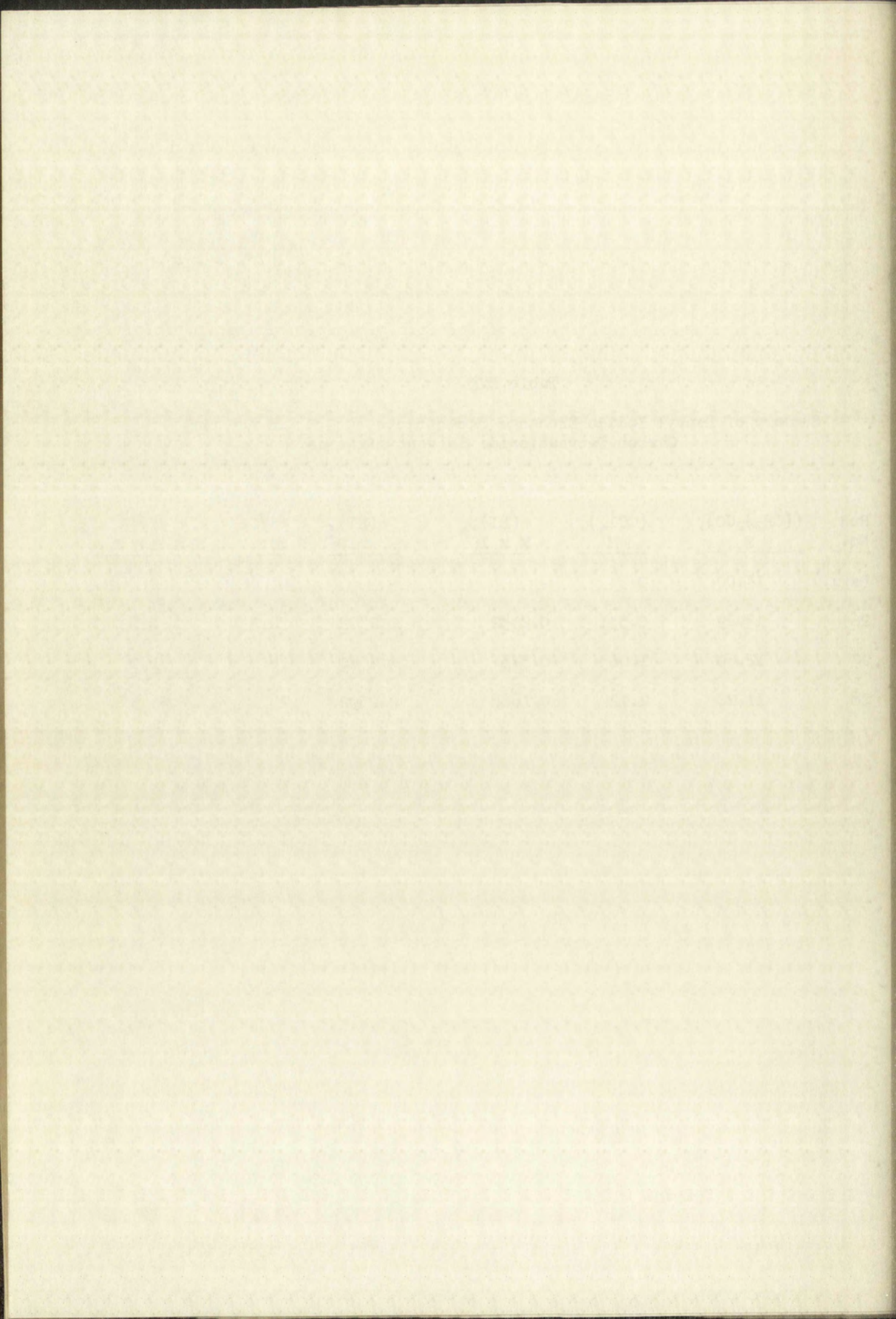


Table XXXI

Experimental Data for Run No. 26

Solvent composition: 13.29 M Acetone

0.531 M Carbon tetrachloride

(BI) = 0.0002532 M

(KI) = 0.0002592 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	6.1	3685	276	0.141
2	14.5	3317	726	0.374
3	27.6	2880	1127	0.578

 $t_{1/2} = 22.3$ min. $k = 60.6$ l/mole/min.

Blank correction = 0.6 per cent

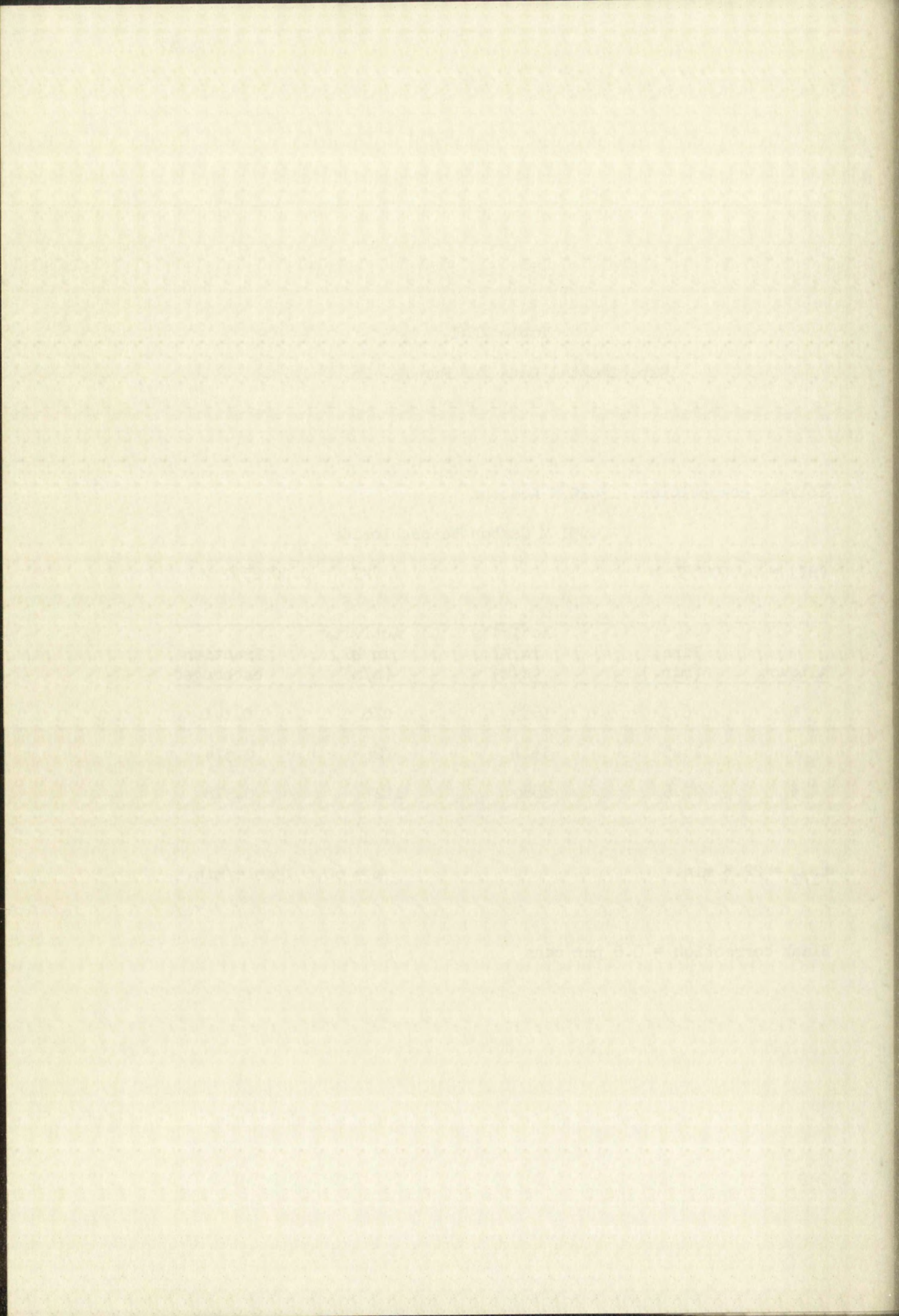


Table XXXII

Experimental Data for Run No. 27

Solvent composition: 12.60 M Acetone

1.063 M Carbon tetrachloride

(BI) = 0.000373 M

(KI) = 0.0002580 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	0.3	4499	25	0.009
2	10.8	3604	896	0.337
3	21.2	3024	1473	0.554
4	40.3	2416	2146	0.796

 $t_{1/2} = 18.0 \text{ min.}$ $k = 61.0 \text{ l./mole/min.}$

Blank correction = 0.7 per cent

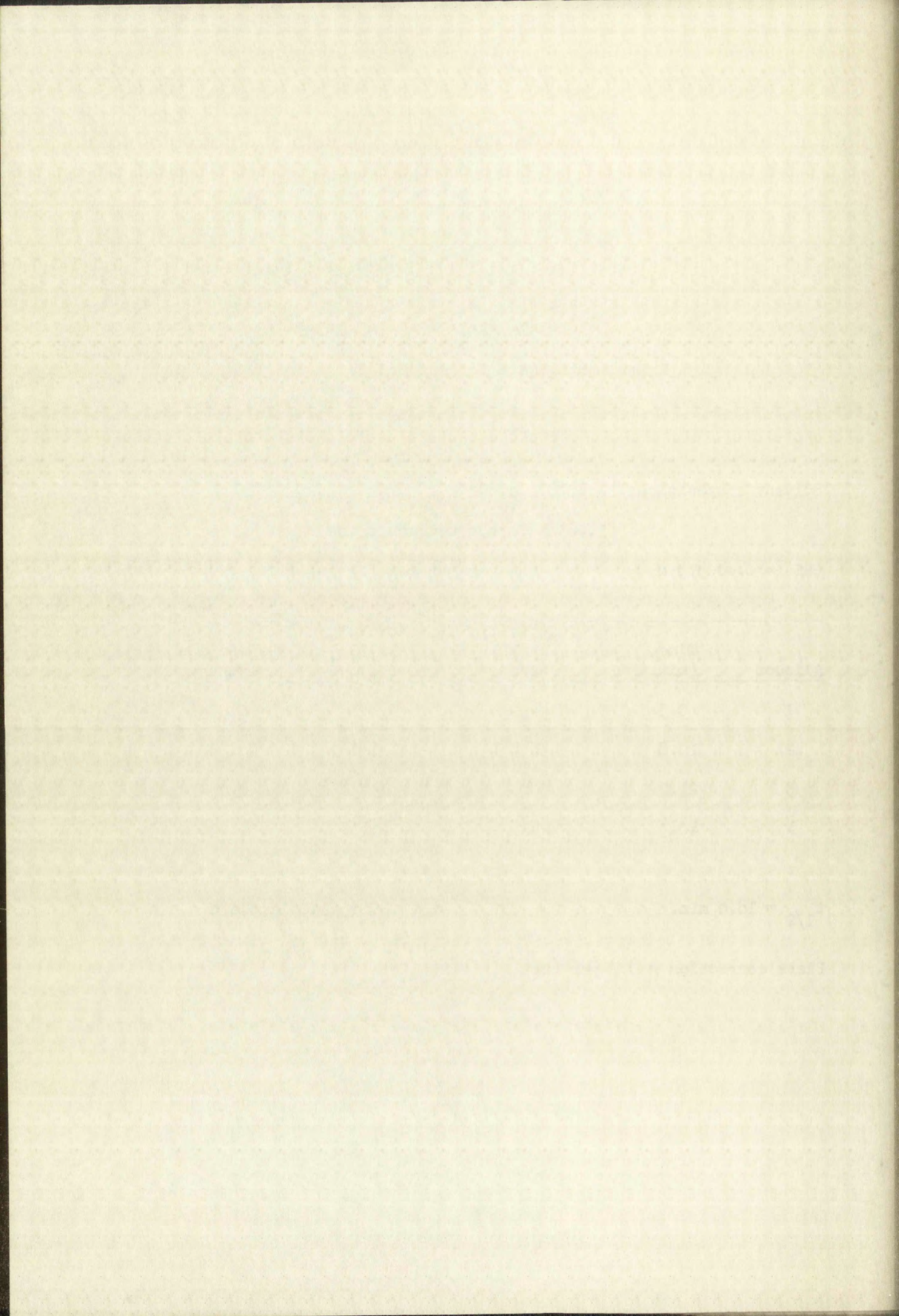


Table XXXIII

Experimental Data for Run No. 28

Solvent composition: 11.20 M Acetone

2.12 M Carbon tetrachloride

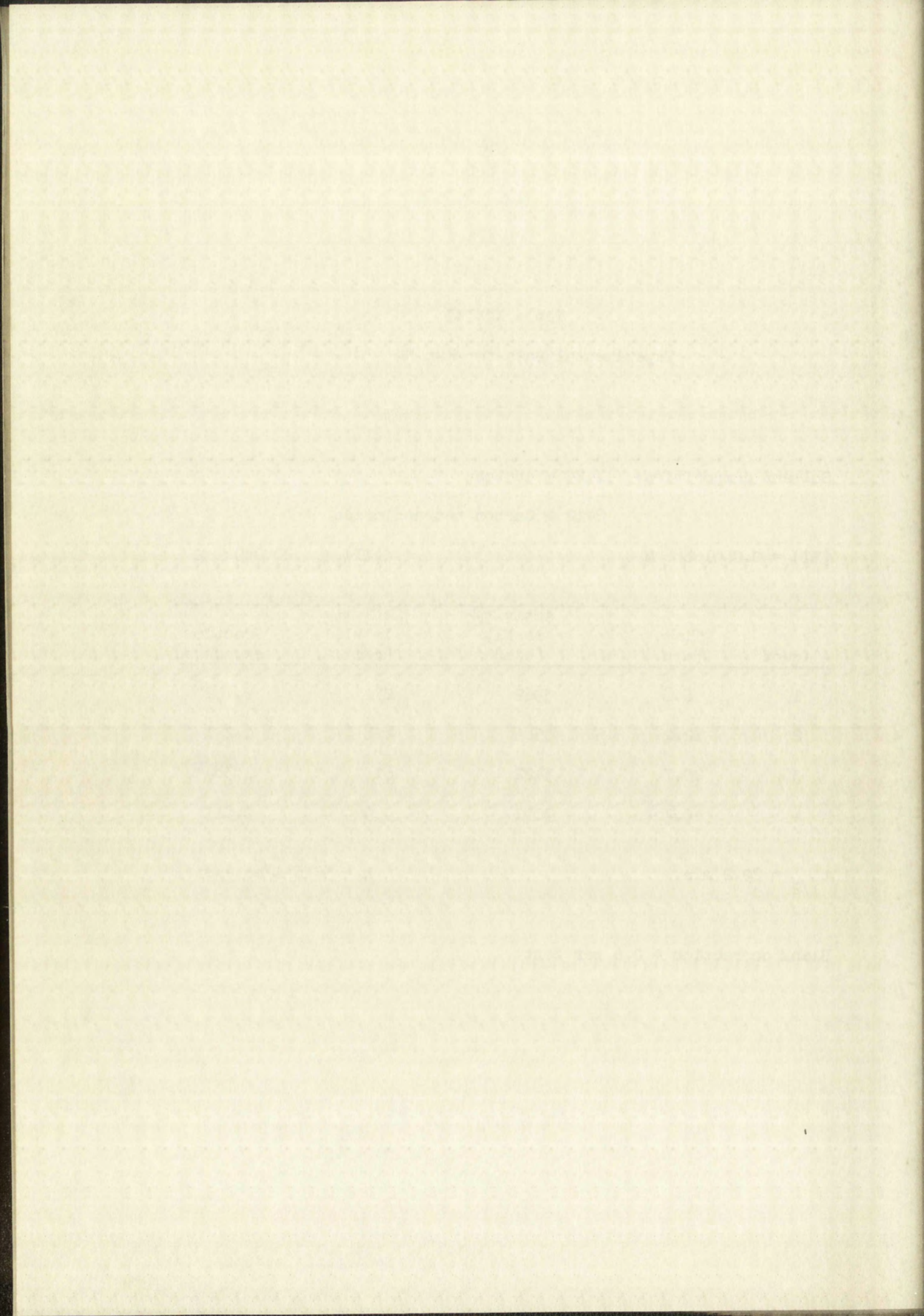
(BI) = 0.0001688 M

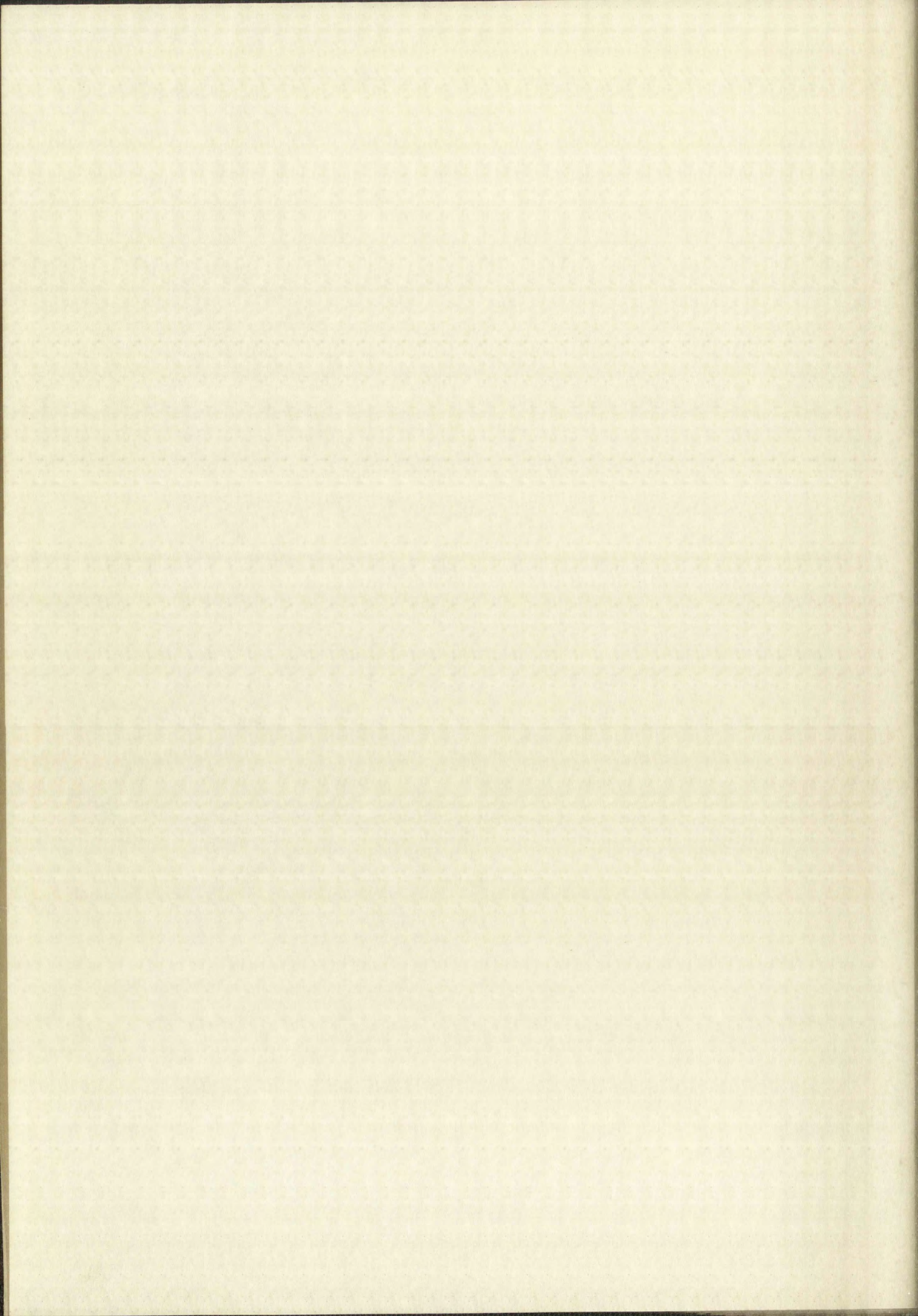
(KI) = 0.0002592 M

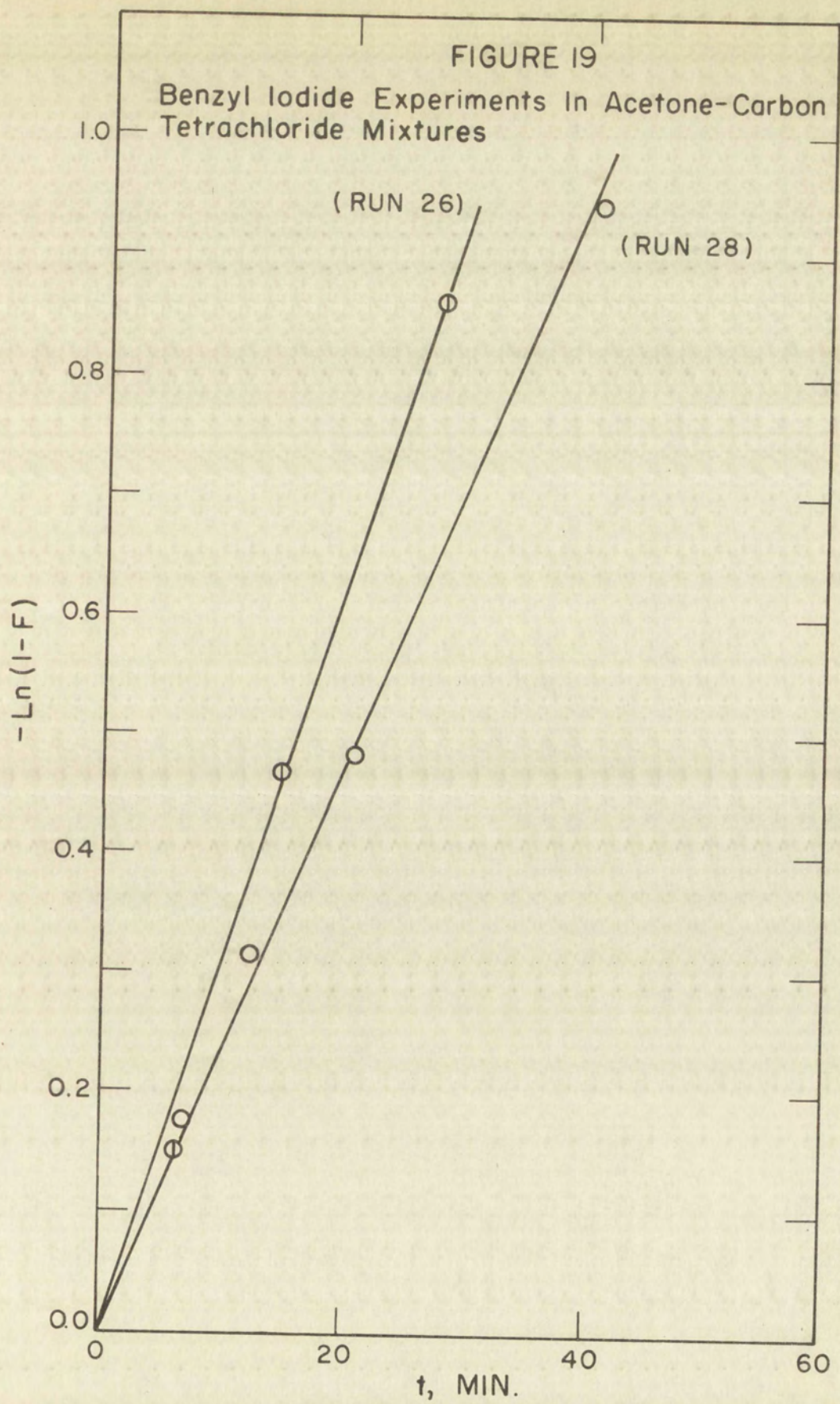
Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	6.8	3962	271	0.162
2	12.2	3581	428	0.271
3	20.7	3422	610	0.384
4	40.6	3051	969	0.611

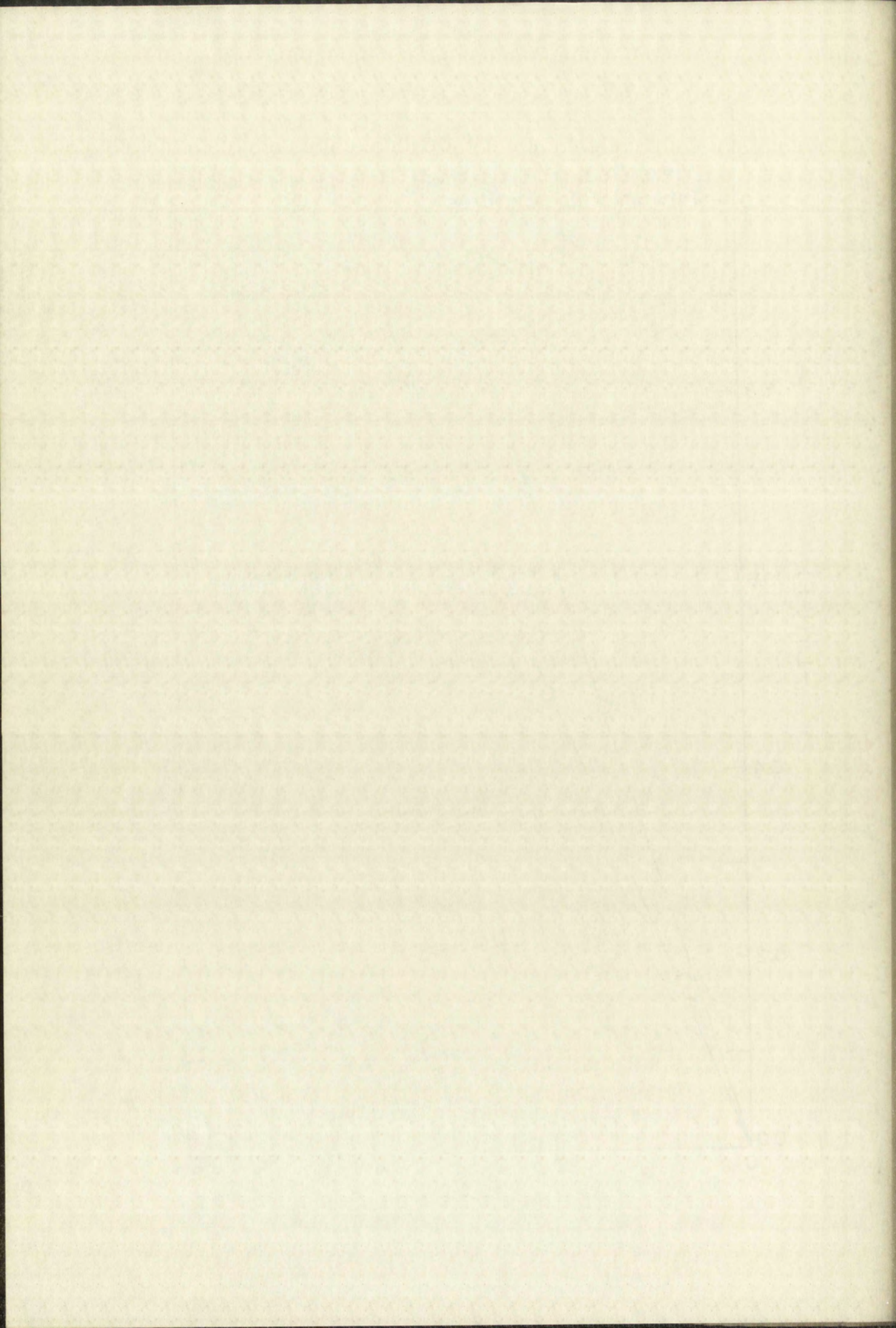
 $t_{1/2} = 29.2$ min. $k = 55.5$ l./mole/min.

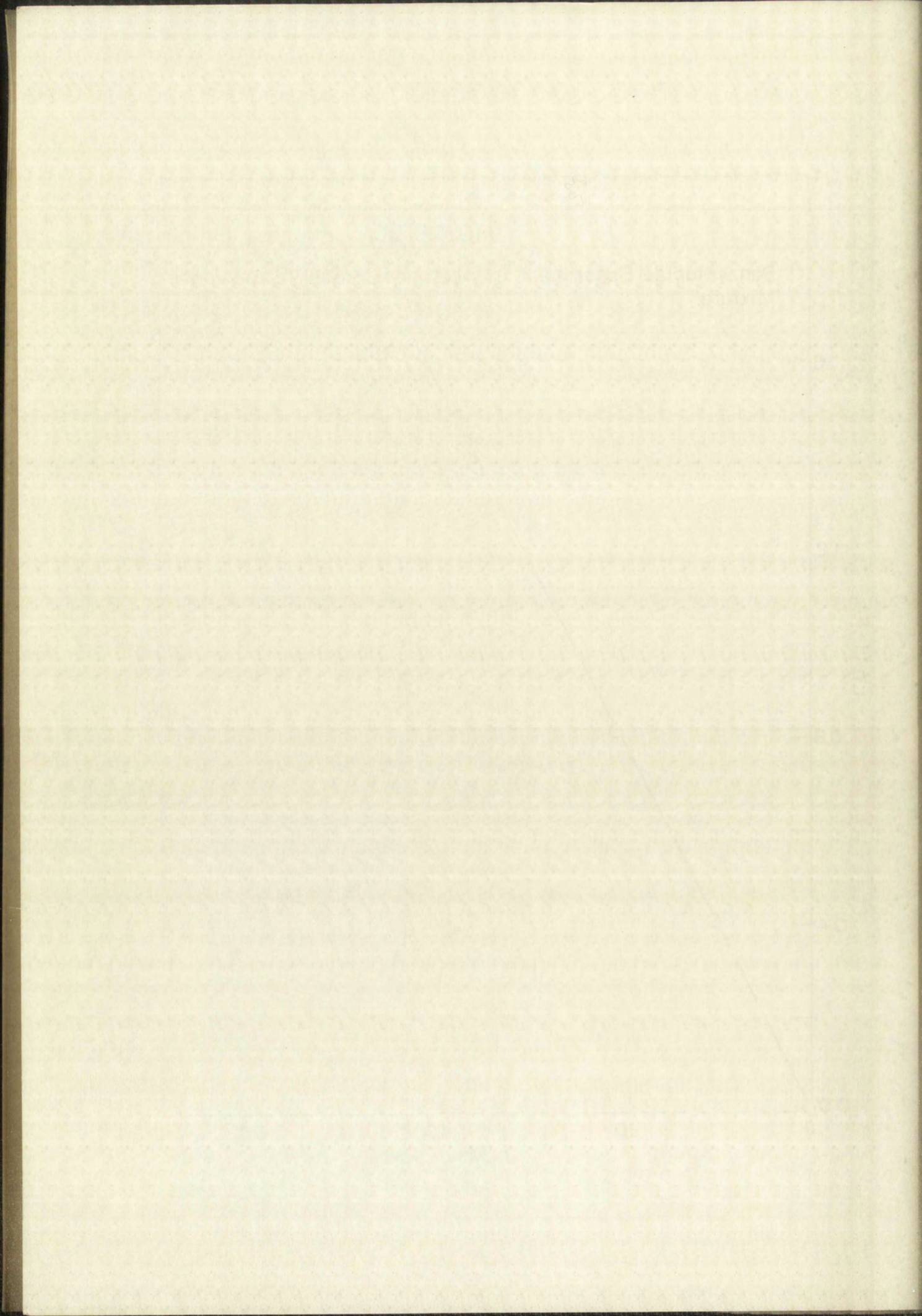
Blank correction = 0.6 per cent











Experimental Data for Benzyl Iodide
Exchange Reactions in Acetone-Water Mixtures
at 0.0°

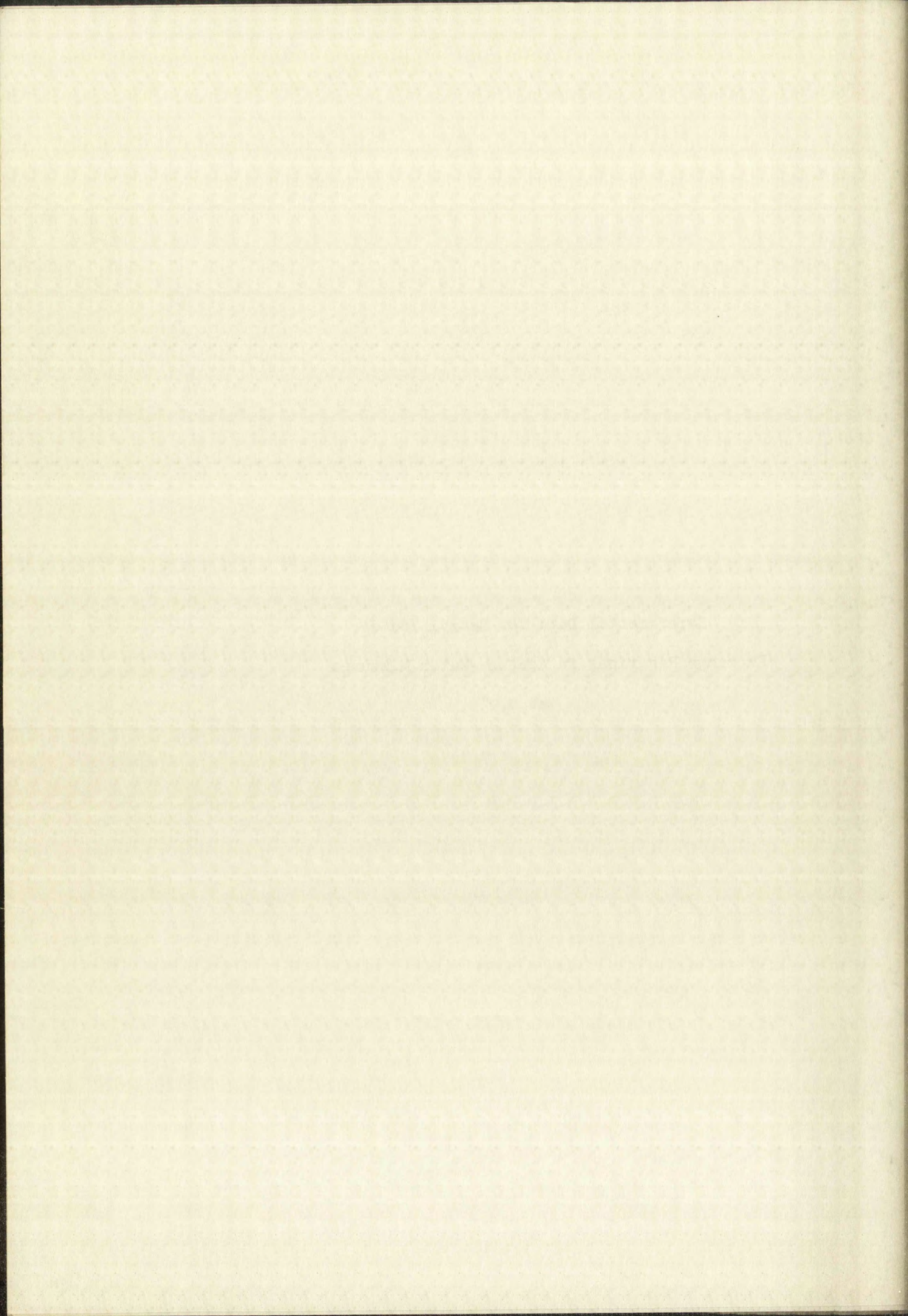


Table XXXIV

Summary of Benzyl Iodide Exchange Experiments at 0.0° in Acetone-Water Solvent Mixtures

Run No.	$((\text{CH}_3)_2\text{CO}),$ M	$(\text{H}_2\text{O}),$ M	$(\text{BI}),$ M $\times 10^3$	$(\text{KI}),$ M $\times 10^3$	$t_{1/2},$ min.	$k,$ l./mole/min.
(avg.)	14.00	0	-	-	-	59.6
29	13.95	0.256	0.1244	0.3120	35.3	45.0
30	13.82	0.648	0.3838	0.1501	37.3	34.8
31	13.70	1.296	0.2558	0.3002	52.5	23.7

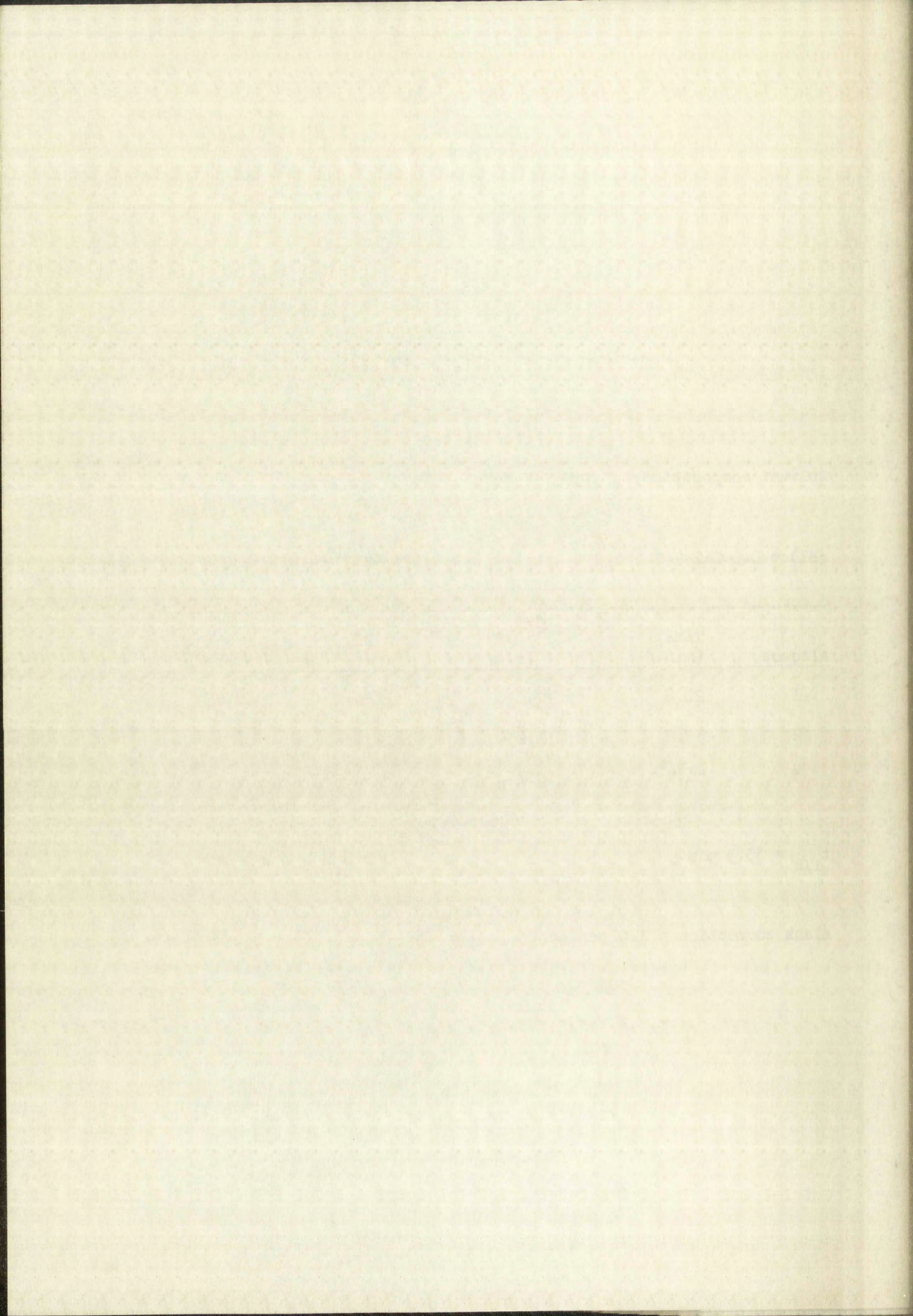


Table XXXVI

Experimental Data for Run No. 30

Solvent composition: 13.82 M Acetone

0.648 M Water

(BI) = 0.0003838 M

(KI) = 0.0001501 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	19.7	2264	632	0.304
2	48.4	1688	1255	0.593
3	78.8	1328	1614	0.763

 $t_{1/2} = 37.3 \text{ min.}$ $k = 34.8 \text{ l./mole/min.}$

Blank correction = 1.4 per cent

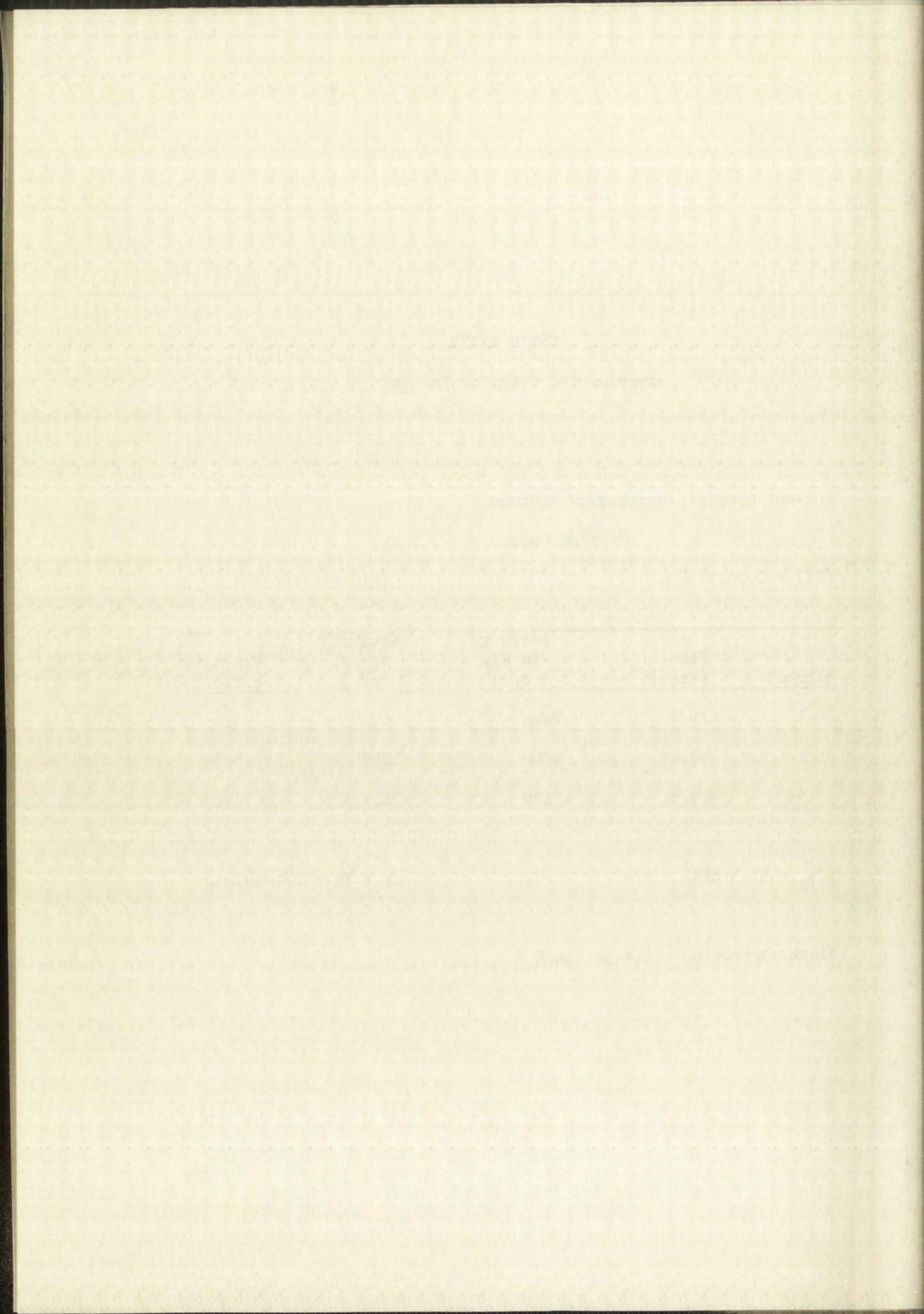


Table XXXVII

Experimental Data for Run No. 31

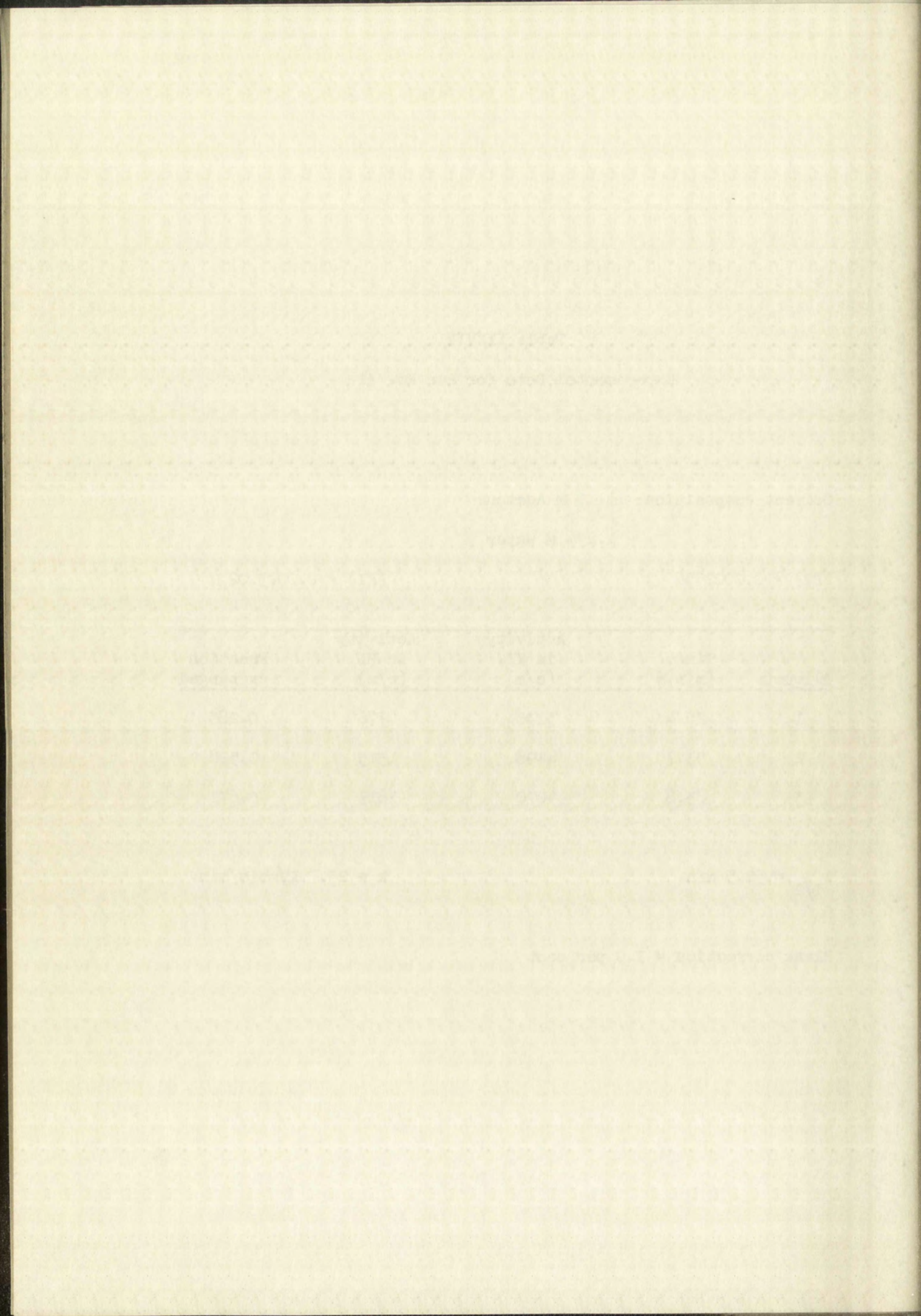
Solvent composition: 13.70 M Acetone

1.296 M Water

 $(BI) = 0.0002558 \text{ M}$ $(KI) = 0.0003002 \text{ M}$

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	25.4	5136	776	0.285
2	53.7	4498	1373	0.508
3	83.8	4070	1817	0.671

 $t_{1/2} = 52.5 \text{ min.}$ $k = 23.7 \text{ l./mole/min.}$ Blank correction ≈ 1.0 per cent



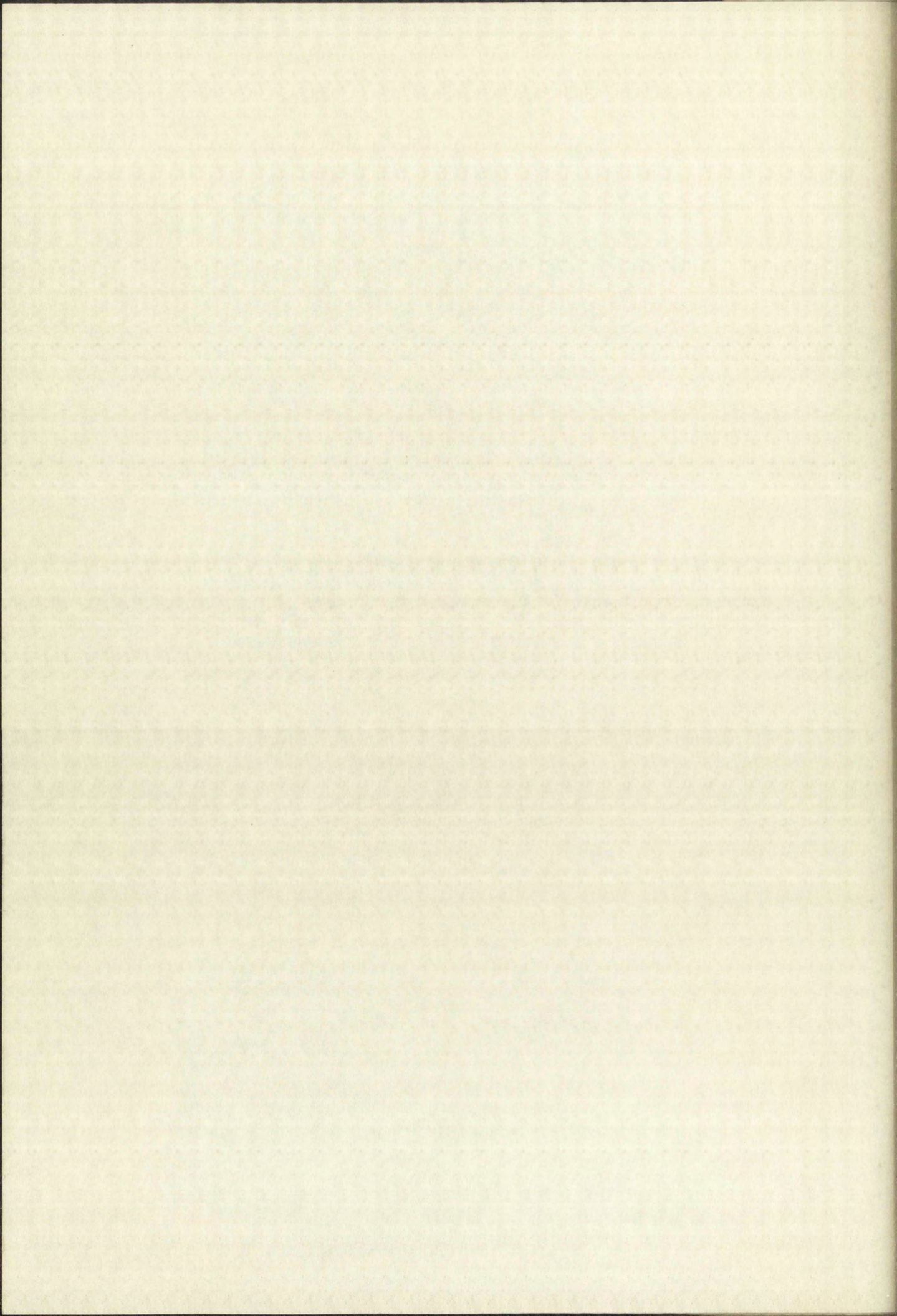


Table XXXVIII

Summary of Benzyl Iodide Exchange Experiments at 0.0° in Acetone-
Phenol Solvent Mixtures

Run No.	$((\text{CH}_3)_2\text{CO}),$ M	$(\text{C}_6\text{H}_5\text{OH}),$ M	$(\text{BI}),$ $\text{M} \times 10^3$	$(\text{KI}),$ $\text{M} \times 10^3$	$t_{1/2},$ min.	$k,$ l/mole/min.
(Avg.)	14.00	0.0	-	-	-	59.6
32	13.92	0.0661	0.2557	0.0610	51.9	42.2
33	13.86	0.1136	0.2046	0.0976	64.2	35.8
34	13.60	0.336	0.3846	0.1384	62.5	21.2
35	13.20	0.672	0.2563	0.2768	115.	11.3
36	12.38	1.345	0.529	0.2412	211.	4.27

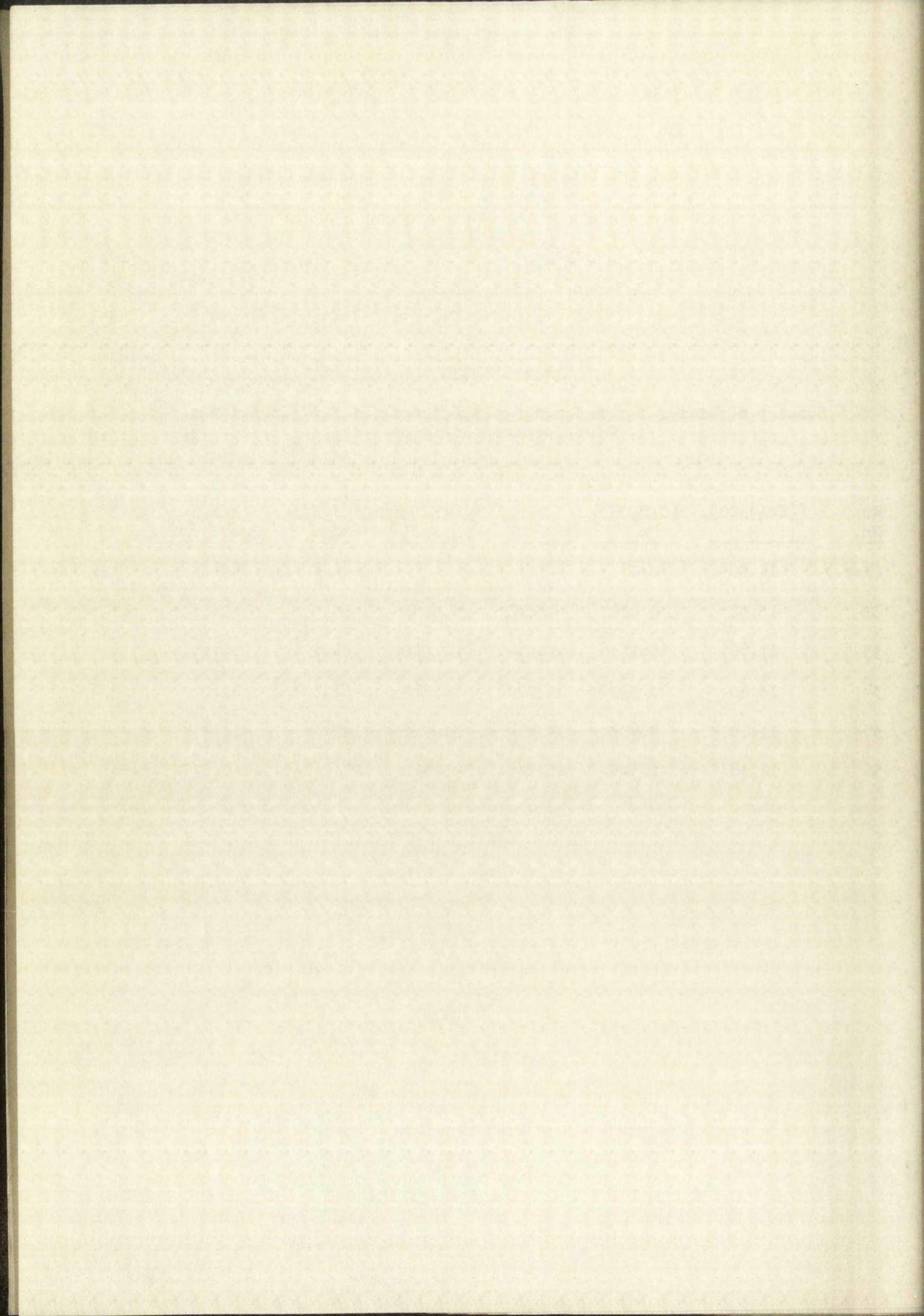


Table XXXIX

Experimental Data for Run No. 32

Solvent composition: 13.92 M Acetone

0.0661 M Phenol

(BI) = 0.0002557 M

(KI) = 0.0000610 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	28.7	3224	1104	0.316
2	54.5	2476	1792	0.520
3	80.5	1986	2250	0.658

 $t_{1/2} = 51.9$ min. $k = 42.2$ l/mole/min.

Blank correction = 2.3 per cent

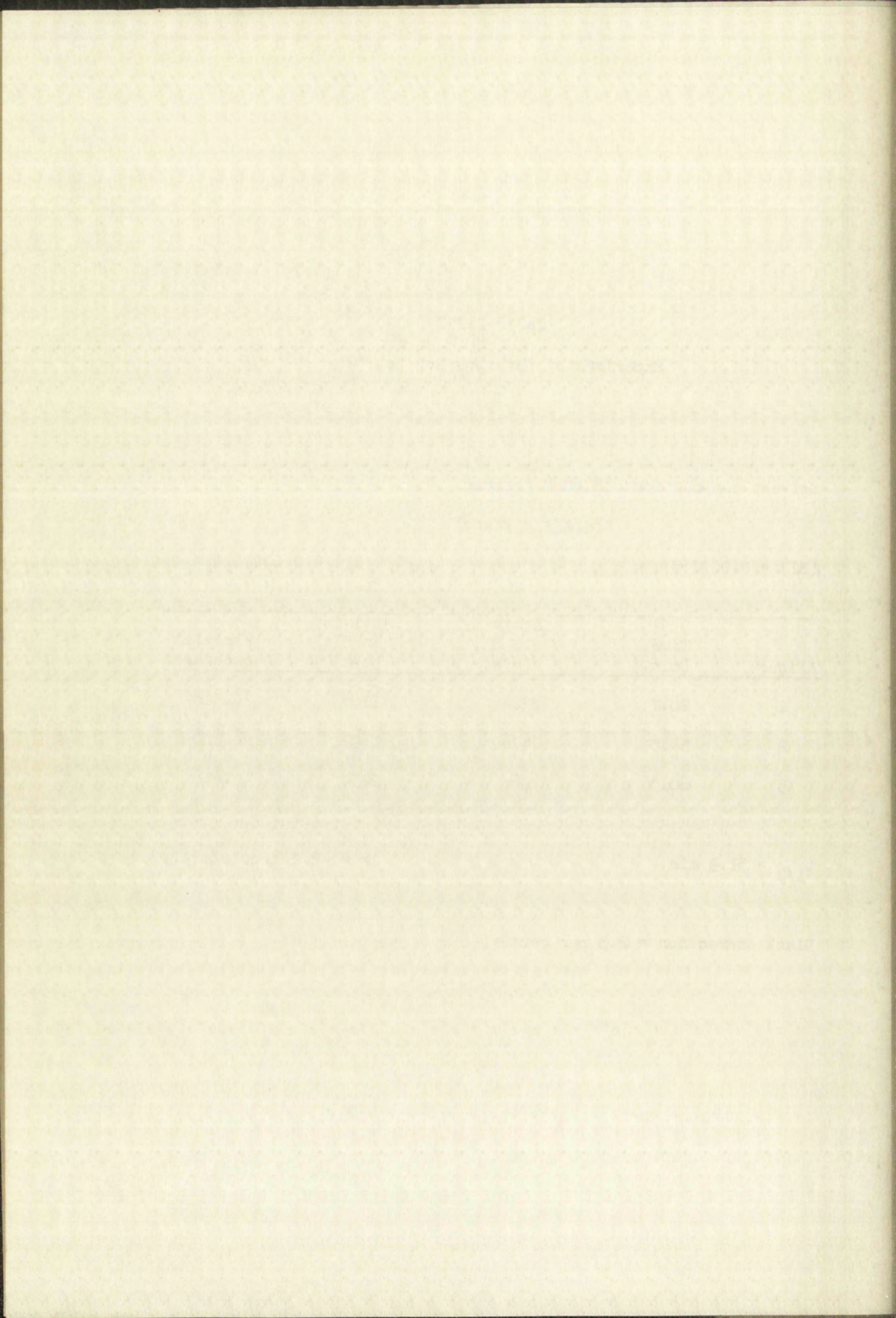


Table XXXX

Experimental Data for Run No. 33

Solvent composition: 13.86 M Acetone

0.1136 M Phenol

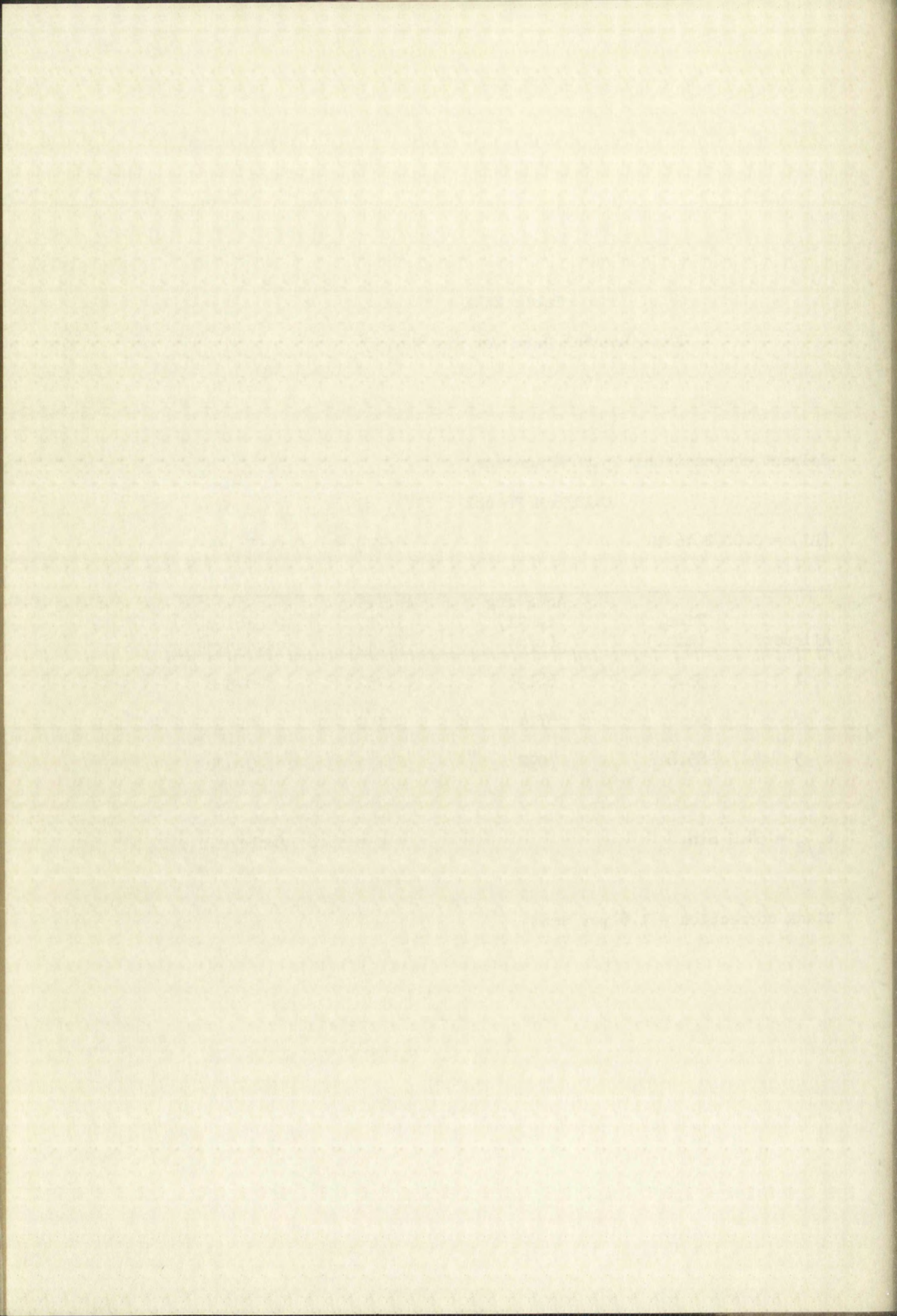
(BI) = 0.0002046 M

(KI) = 0.0000976 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	33.3	6819	1752	0.302
2	60.0	5714	2792	0.485
3	85.8	5092	3479	0.600

 $t_{1/2} = 64.2$ min. $k = 35.8$ l/mole/min.

Blank correction = 1.6 per cent



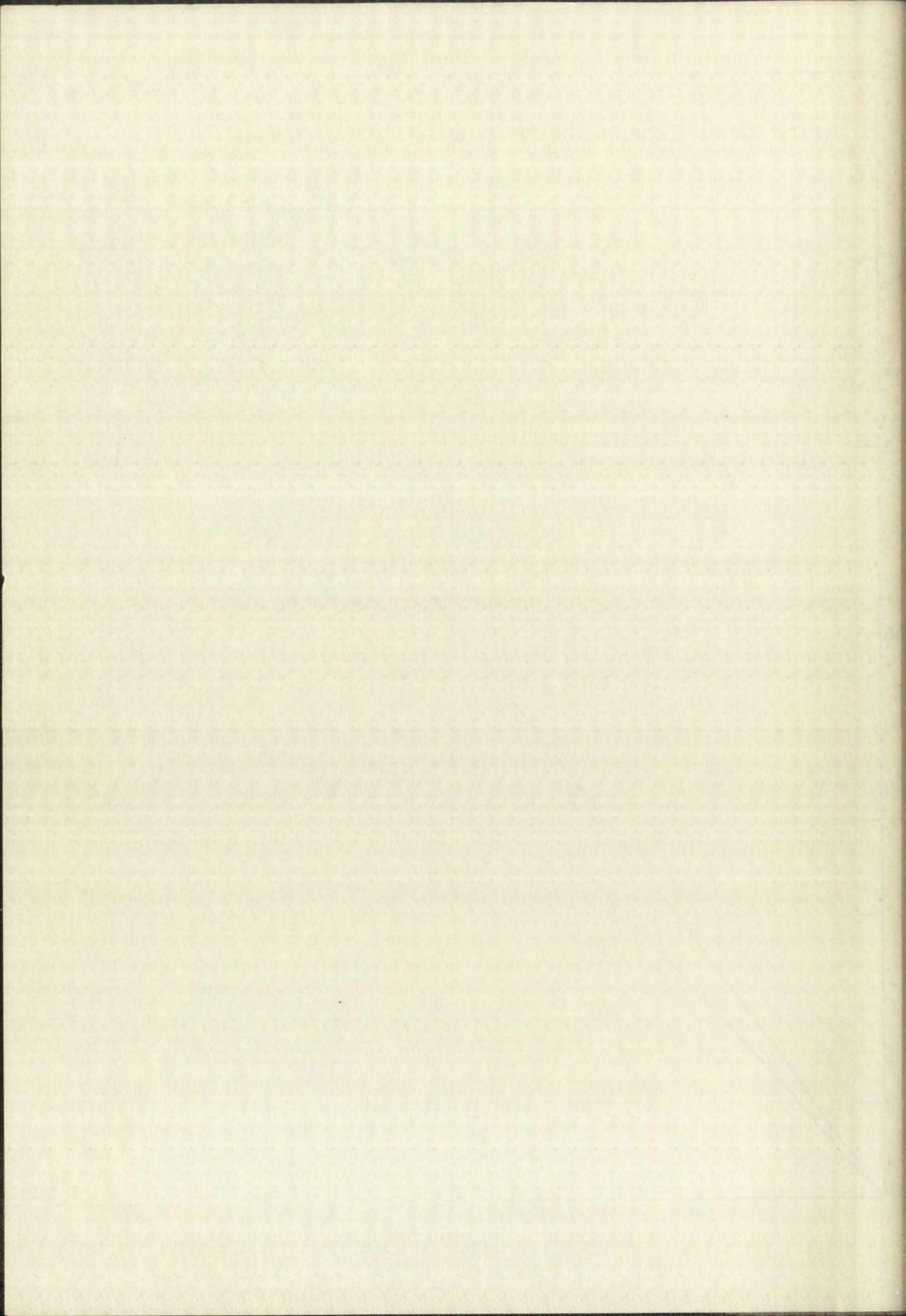


Table XXXXI

Experimental Data for Run No. 34

Solvent composition: 13.60 M Acetone

0.336 M Phenol

(BI) = 0.0003846 M

(KI) = 0.0001384 M

Aliquot	Time, (min)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	20.0	16,270	3017	0.213
2	43.7	13,830	5279	0.376
3	62.5	11,870	6899	0.500

 $t_{1/2} = 62.5$ min. $k = 21.2$ l./mole/min.

Blank correction = 2.3 per cent



Table XXXXII

Experimental Data for Run No. 35

Solvent composition: 13.20 M Acetone

0.672 M Phenol

(BI) = 0.0002563 M

(KI) = 0.0002768 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	27.4	35,000	2879	0.158
2	65.5	31,550	5877	0.327
3	91.5	29,980	7586	0.420

 $t_{1/2} = 115$ min. $k = 11.3$ l./mole/min.

Blank correction = 2.3 per cent

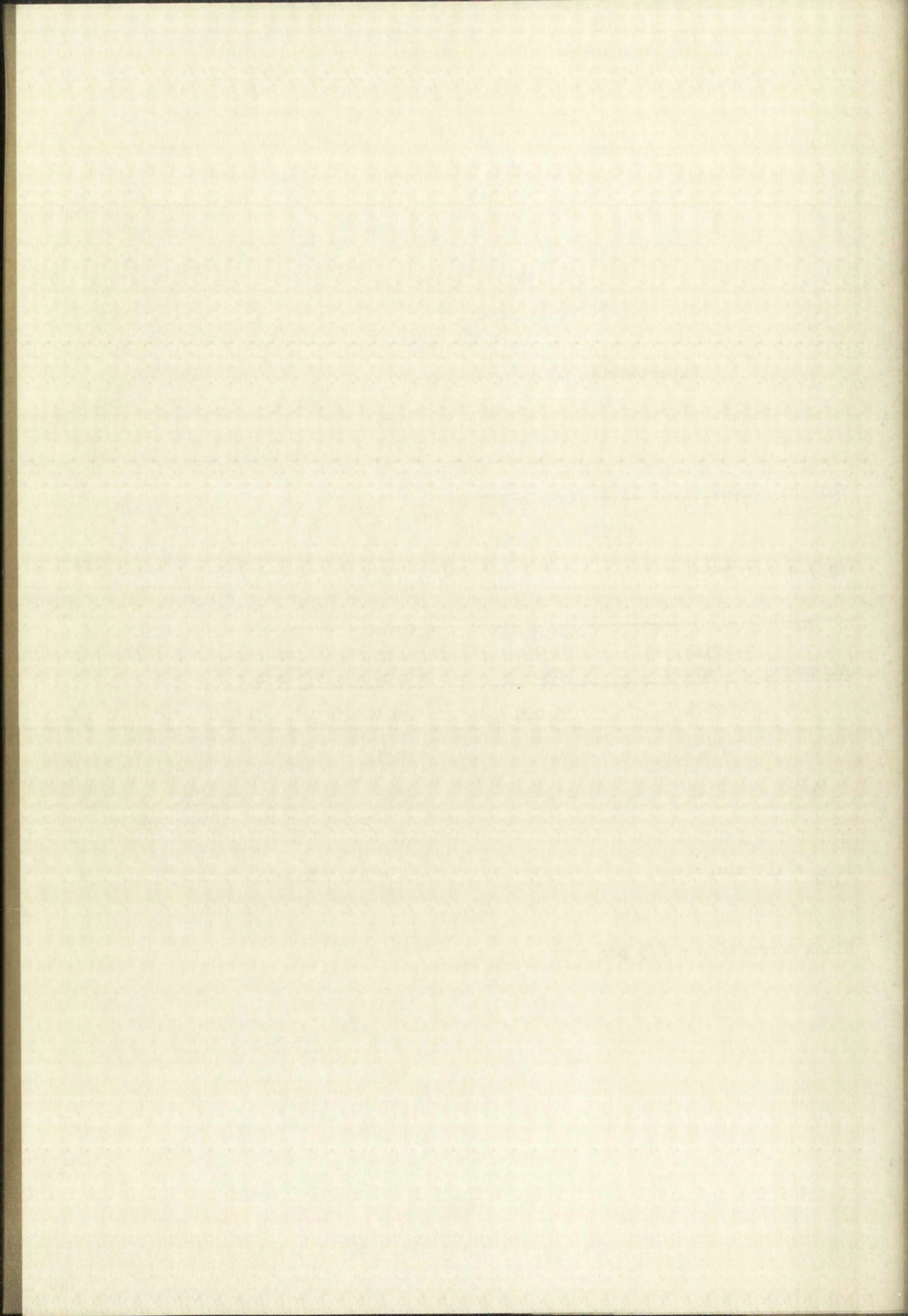


Table XXXXIII

Experimental Data for Run No. 36

Solvent composition: 12.38 M Acetone

1.345 M Phenol

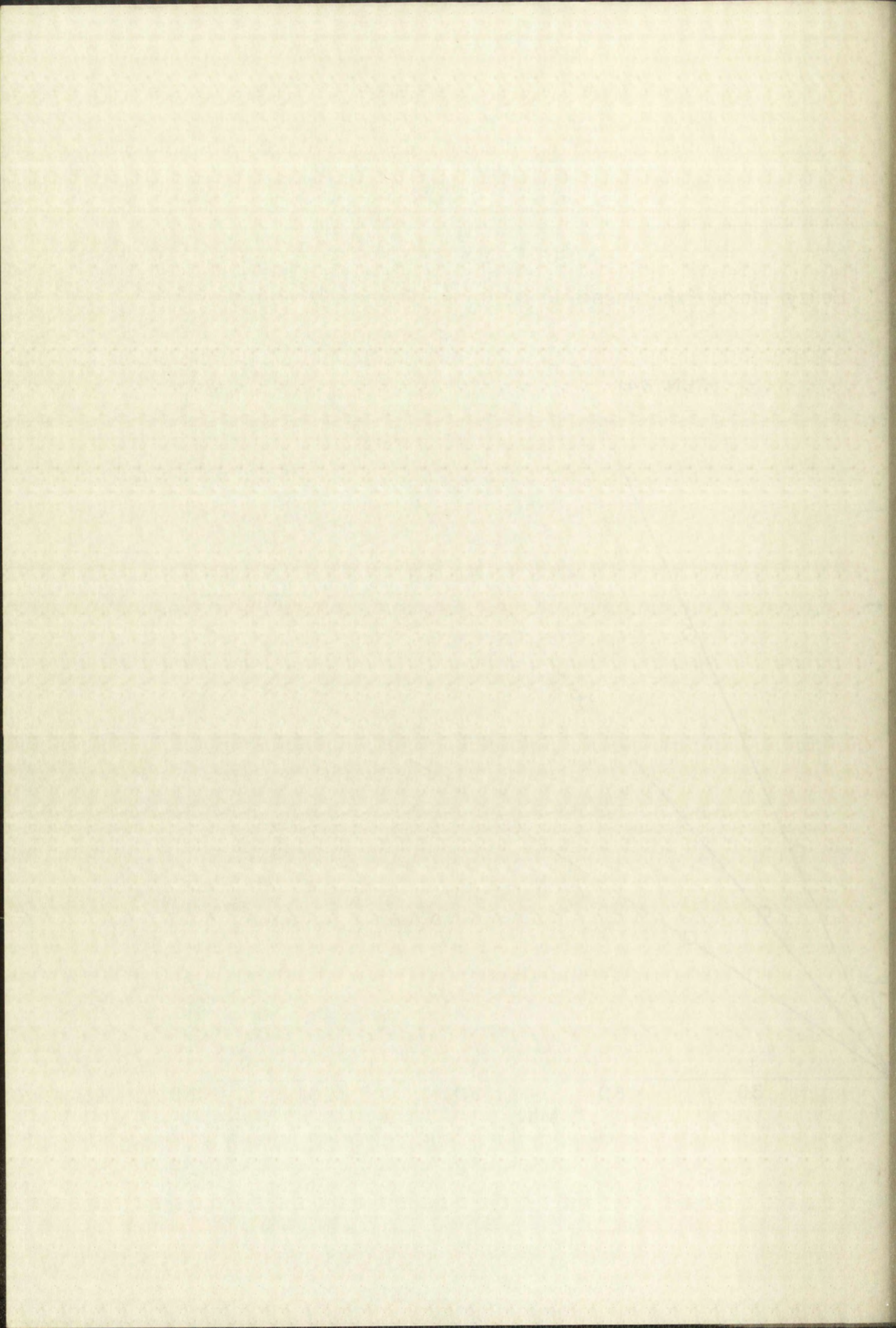
(BI) = 0.000529 M

(KI) = 0.0002412 M

Aliquot	Time, (min.)	Activity in KI, (c/m)	Activity in BI, (c/m)	Fraction exchanged
1	43.8	13,110	1373	0.138
2	81.0	11,940	2282	0.234
3	122.6	10,890	3238	0.334

 $t_{1/2} = 211$ min. $k = 4.27$ l./mole/min.

Blank correction = 2.8 per cent



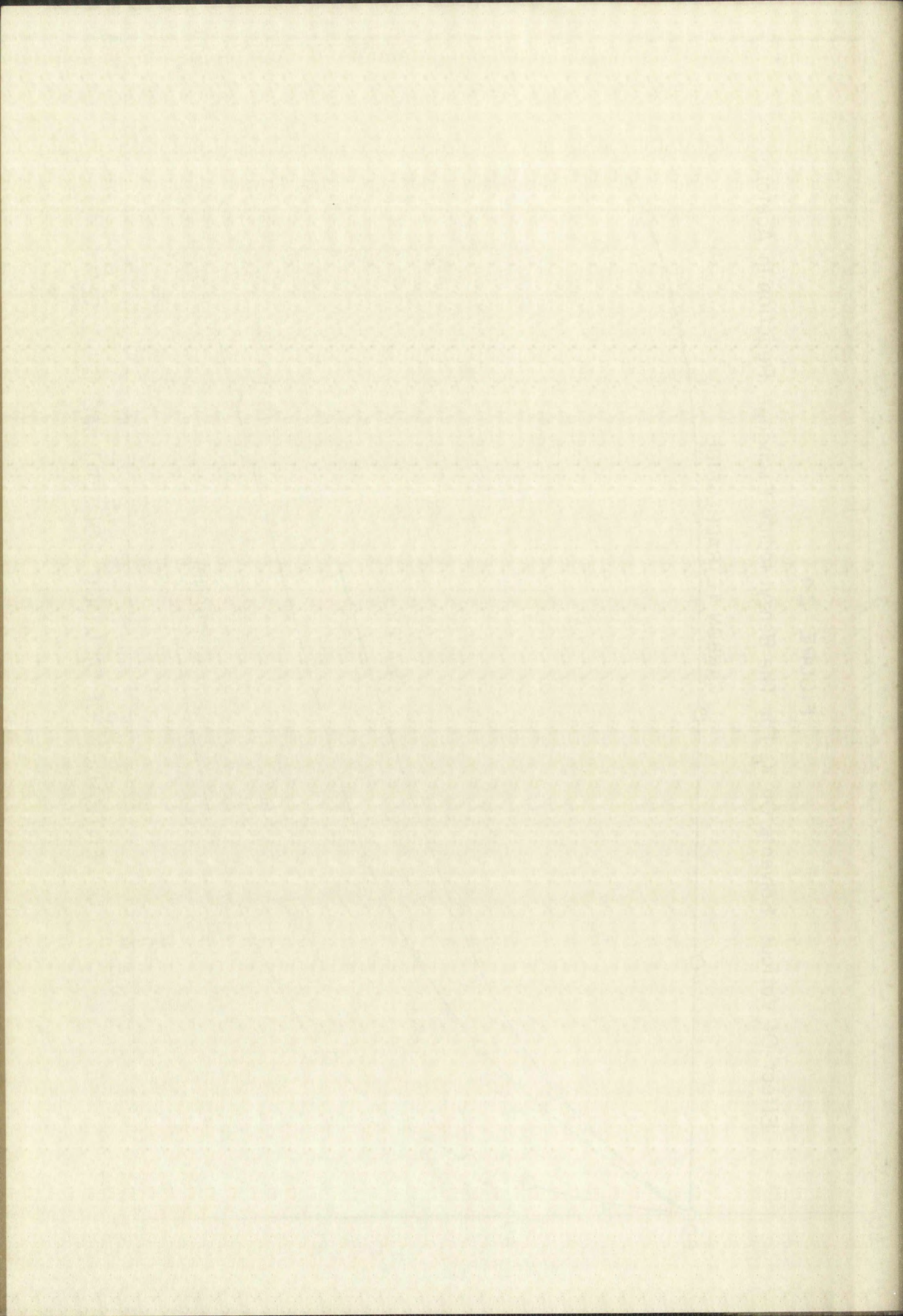


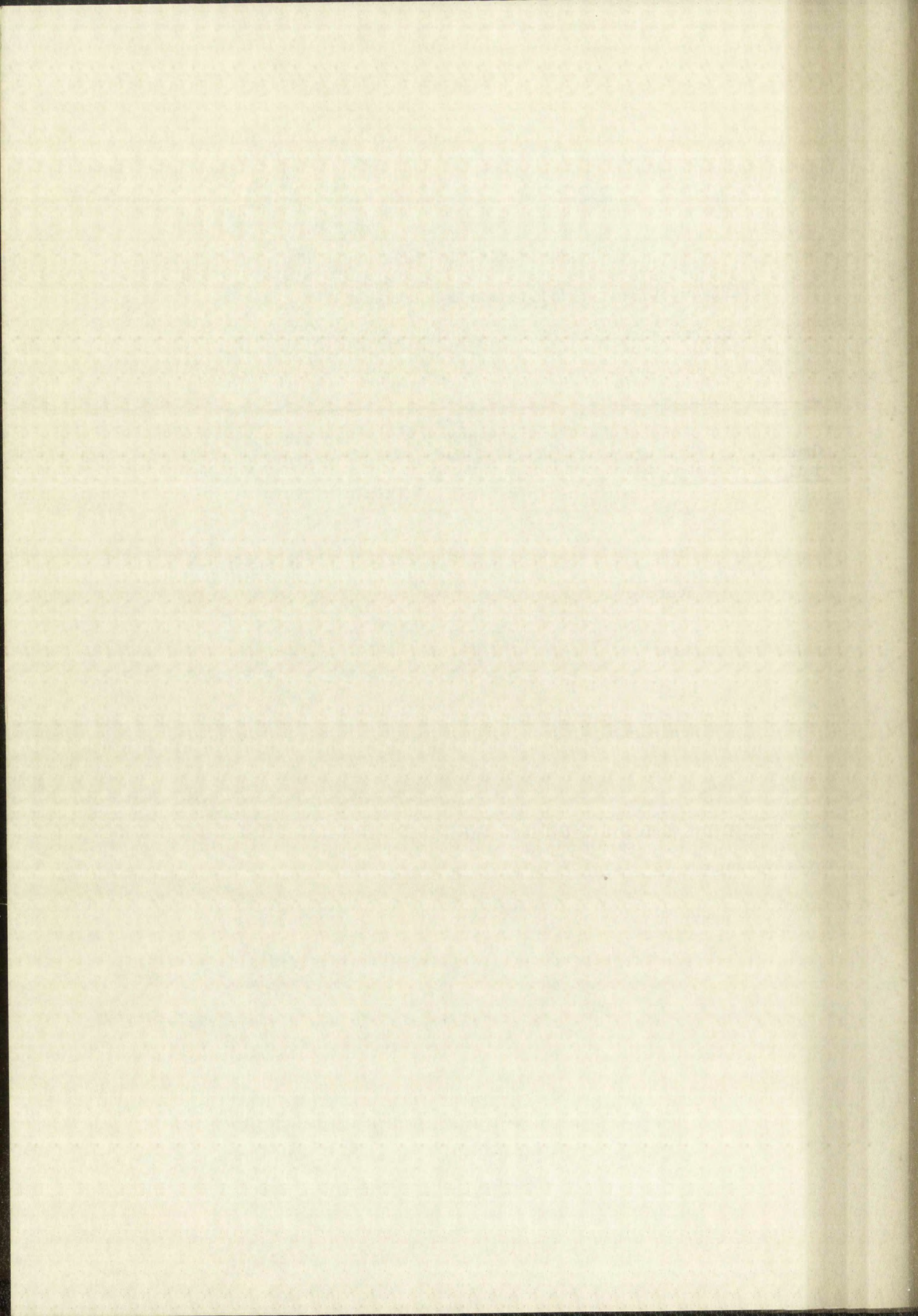
Table XXXIV

Comparison of Benzyl Iodide and p-Nitrobenzyl
Iodide Exchange Results in Various Absolute Solvents

Organic iodide	Absolute solvent*	Collision frequency,		Activation energy, Kcal/mole
		-1 min.	-12 x 10	
BI	MeOH	0.2		15.65
	EtOH	5.0		17.15
	Acetone	5.7		13.72
PNBI	MeOH	0.54		15.76
	EtOH	8.13		16.69
	Acetone	120.		14.35

*Data for BI in alcohols from reference 15.

Data for PNBI in alcohols from reference 16.

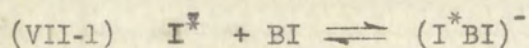


Part VII

Discussion

Exchange reactions in absolute acetone. -

The results of the benzyl iodide exchange reactions in absolute acetone are consistent with the following mechanism:



The benzyl iodide results can be summarized by the rate law

$$(VII-3) \quad R = 5.7 \times 10^{12} e^{-13,720/RT} (KI) (BI)$$

The results obtained with p-nitrobenzyl iodide, can be expressed by a similar rate law:

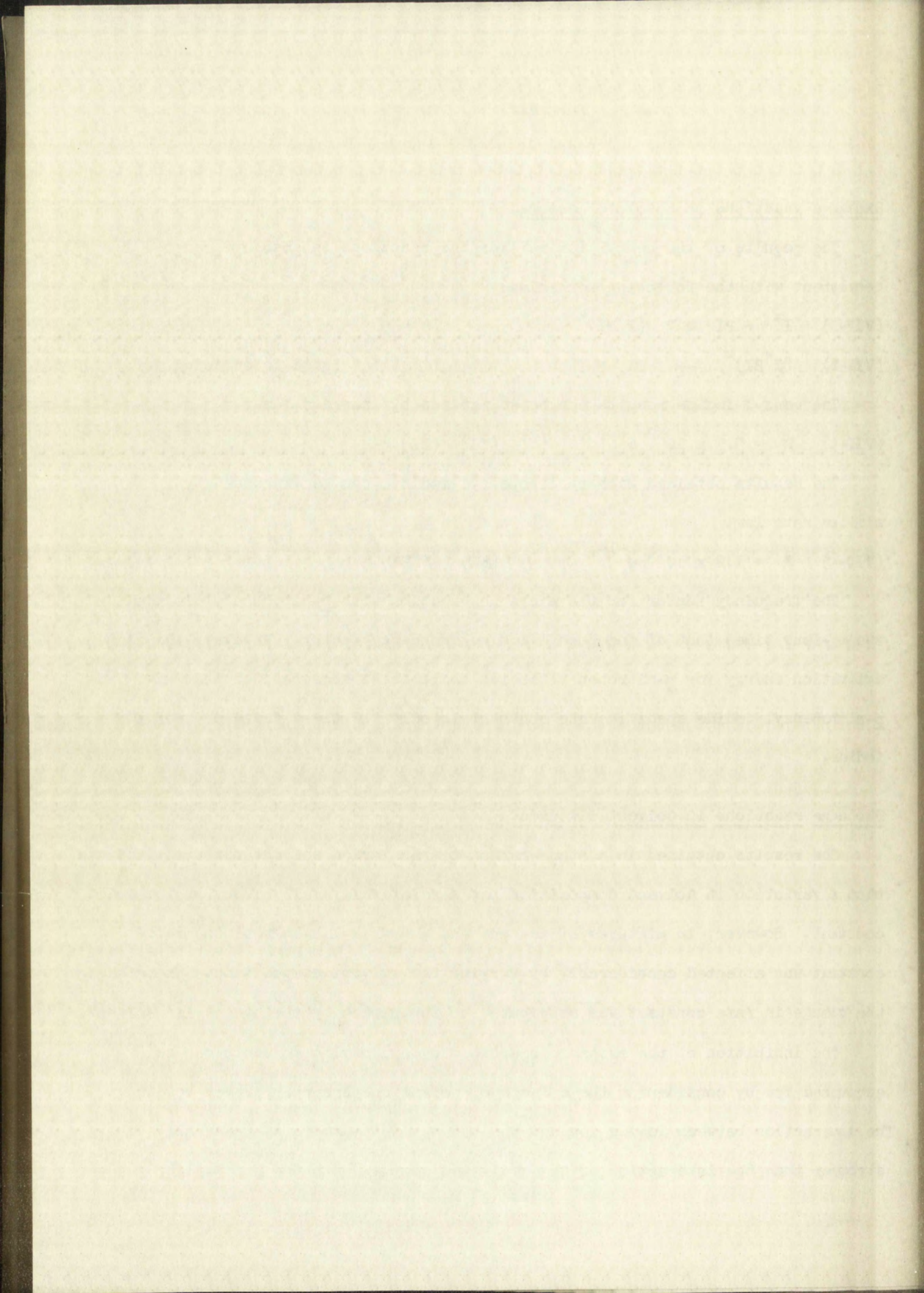
$$(VII-4) \quad R = 1.2 \times 10^{14} e^{-14,350/RT} (KI) (PNBI)$$

The frequency factor for the exchange reaction with p-nitrobenzyl iodide is twenty-four times that of the benzyl-iodide frequency factor. However, the higher activation energy for p-nitrobenzyl iodide compensates somewhat, so that at 0° the p-nitrobenzyl iodide specific rate constant is only 6.2 times that for benzyl iodide.

Exchange reactions in solvent mixtures. -

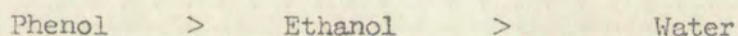
The results obtained in acetone-carbon tetrachloride solvent mixtures indicate that a variation in solvent composition has a relatively small effect on the rate constant. However, in mixtures of acetone and a hydroxylic solvent the rate constant was affected considerably by varying the solvent composition. Therefore, the change in rate constant was attributed to inhibition by the hydroxylic solvent.

The inhibition of the exchange reactions by hydroxylic solvents can be accounted for by considering the effects of solvation through hydrogen bonding. The interaction between iodide ion and the hydroxylic hydrogen is presumably stronger than the interaction of the activated complex with the hydroxylic



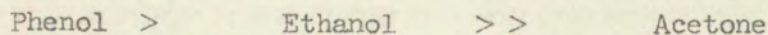
hydrogen, because the iodide ion has the greater charge density. Consequently if a solvating acetone molecule is replaced by a hydroxylic molecule, the energy of the solvated iodide ion would be lowered relative to that of the activated complex. If this energy is of the order of one-half the normal ethanol hydrogen bond energy (~ 6.5 kcal./mole), the ethanol-solvated species would have a much higher activation energy. An increase of 3 kcal./mole in the activation energy would cause a 250-fold decrease in the specific rate constant. Therefore the net result of displacing an acetone molecule by an ethanol molecule on an iodide ion would be to reduce the abundance of rapidly-reacting acetonated species, thereby reducing the reaction rate.

The results of this investigation suggest the following order of increasing effectiveness as inhibitors for the exchange reaction:

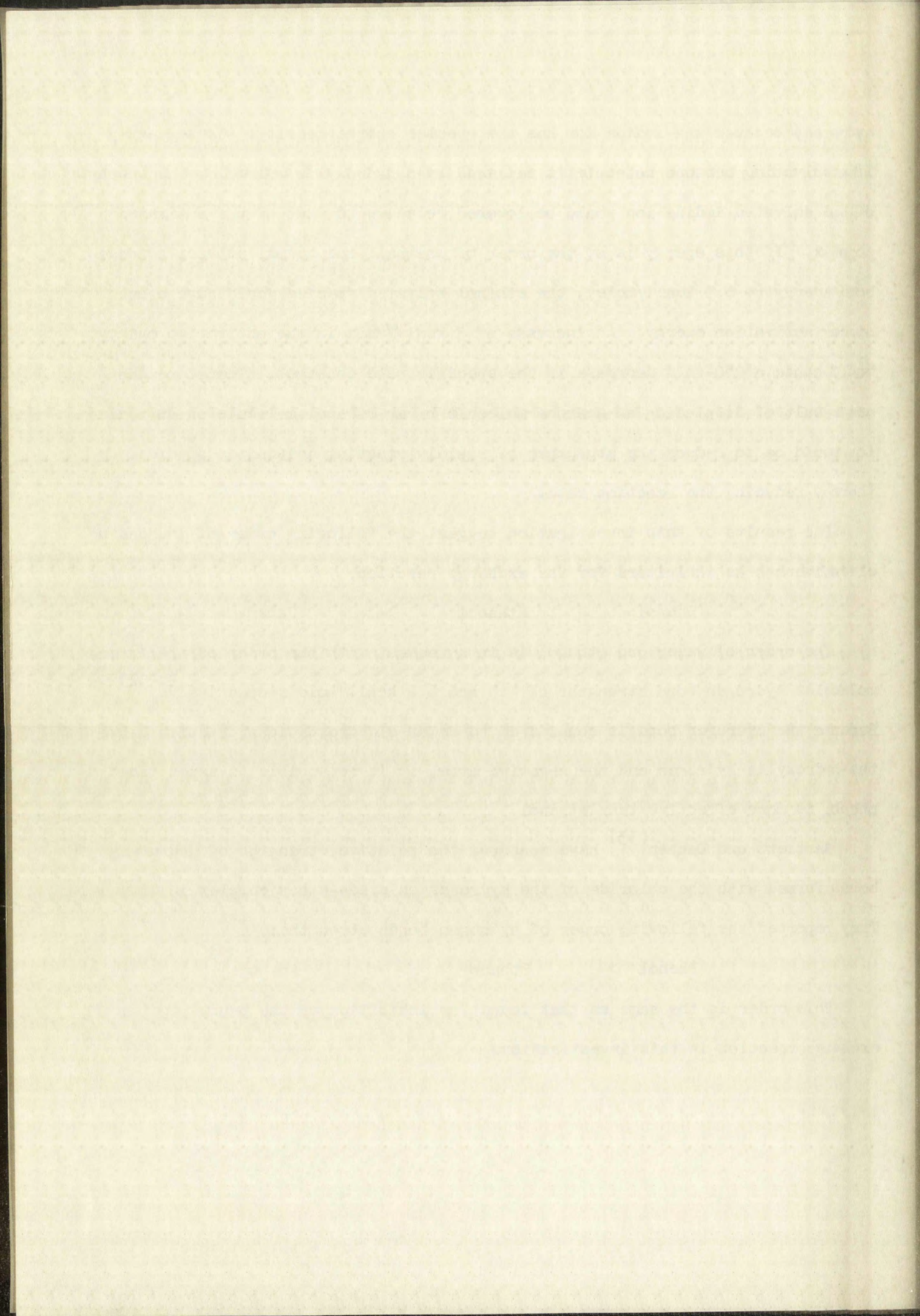


The order of water and ethanol is in agreement with the order of the inter-molecular hydrogen bond strengths of 4.5 and 6.2 kcal./mole respectively.⁽³²⁾ Because the hydrogen bond is considered to be an electrostatic attraction between the hydroxylic hydrogen and the negative atom, it is reasonable to expect that phenol is more effective than ethanol.

Bartlett and Dauben⁽³³⁾ have measured the relative strengths of hydrogen bonds formed with the chloride of the hydrogen chloride-ether complex in dioxane. They reported the following order of hydrogen bonds strengths:

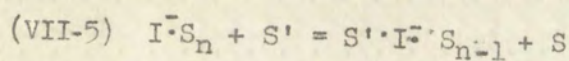


This order is the same as that found for inhibition of the benzyl iodide exchange reaction in this investigation.



Quantitative treatment of results in solvent mixtures. -

In the previous section it has been proposed that inhibition of the exchange reaction is caused by a reduction in the number of rapidly-reacting iodide ions that are solvated by acetone only. From equation (VIII-3), this would decrease the reaction rate proportionately. Therefore, if one knew the proportion of iodide ions that are hydrogen-bonded at a given concentration of hydroxylic solvent, it would be possible to predict the experimentally observed reaction rate, or what is equivalent, the experimentally observed rate constant. Consider the following equilibrium:



where $I^- \cdot S_n$ = an iodide ion solvated by n molecules of acetone

S' = one molecule of hydroxylic solvent

$S' \cdot I^- \cdot S_{n-1}$ = a solvated iodide ion that has been hydrogen-bonded by S'

S = the molecule of acetone displaced

S_n = an undefined number of solvating acetone molecules

The equilibrium constant K_1 can be defined for equation (VIII-5):

$$(VII-6) \quad K_1 = \frac{[S' \cdot I^- \cdot S_{n-1}][S]}{[I^- \cdot S_n][S']}$$

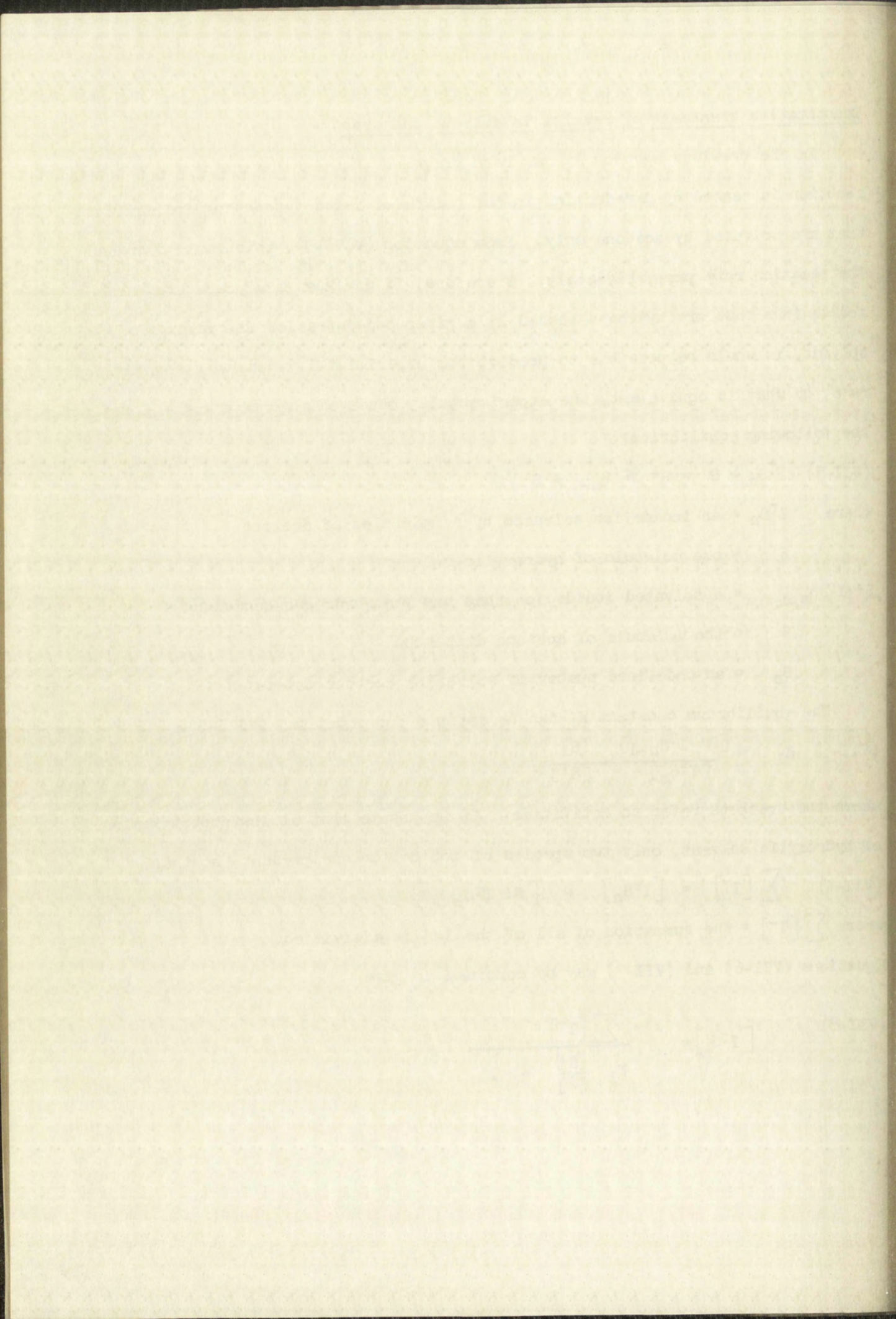
where the brackets refer to activities. If we assume that at low concentrations of hydroxylic solvent, only two species of iodide ion are present, so that

$$(VII-7) \quad \sum [I^-] = [I^- \cdot S_n] + [S' \cdot I^- \cdot S_{n-1}]$$

where $\sum [I^-]$ = the summation of all of the iodide activities.

Equations (VII-6) and (VII-7) may be combined to give

$$(VII-8) \quad [I^- \cdot S_n] = \frac{\sum [I^-]}{K_1 \frac{[S']}{[S]} + 1}$$



For the bimolecular benzyl iodide exchange mechanism the reaction rate for the rapidly-reacting species can be expressed as

$$(VII-9) \quad R = k_2 [I^{\cdot}S_n] \left(\sum [BI] \right)$$

where $\sum [BI]$ = the summation of all of the benzyl iodide activities,

k_2 = the experimental rate constant in absolute acetone.

The concentration of rapidly-reacting species of benzyl iodide is assumed to be constantly proportional to the total benzyl iodide activity, $\sum [BI]$.

Substitution of equation (VII-8) into (VII-9) gives

$$(VII-10) \quad R = \frac{k_2}{K_1 \frac{[S']}{[S]} + 1} \left(\sum [I^{\cdot}] \right) \left(\sum [BI] \right)$$

However, in measuring the experimentally observed second-order rate constant, k_o , the total concentrations have been used in the expression

$$(VII-11) \quad R = k_o (KI) (BI) = k_o \left(\sum [I^{\cdot}] \right) \left(\sum [BI] \right)$$

Therefore, by comparison of equations (VII-10) and (VII-11) it can be seen that

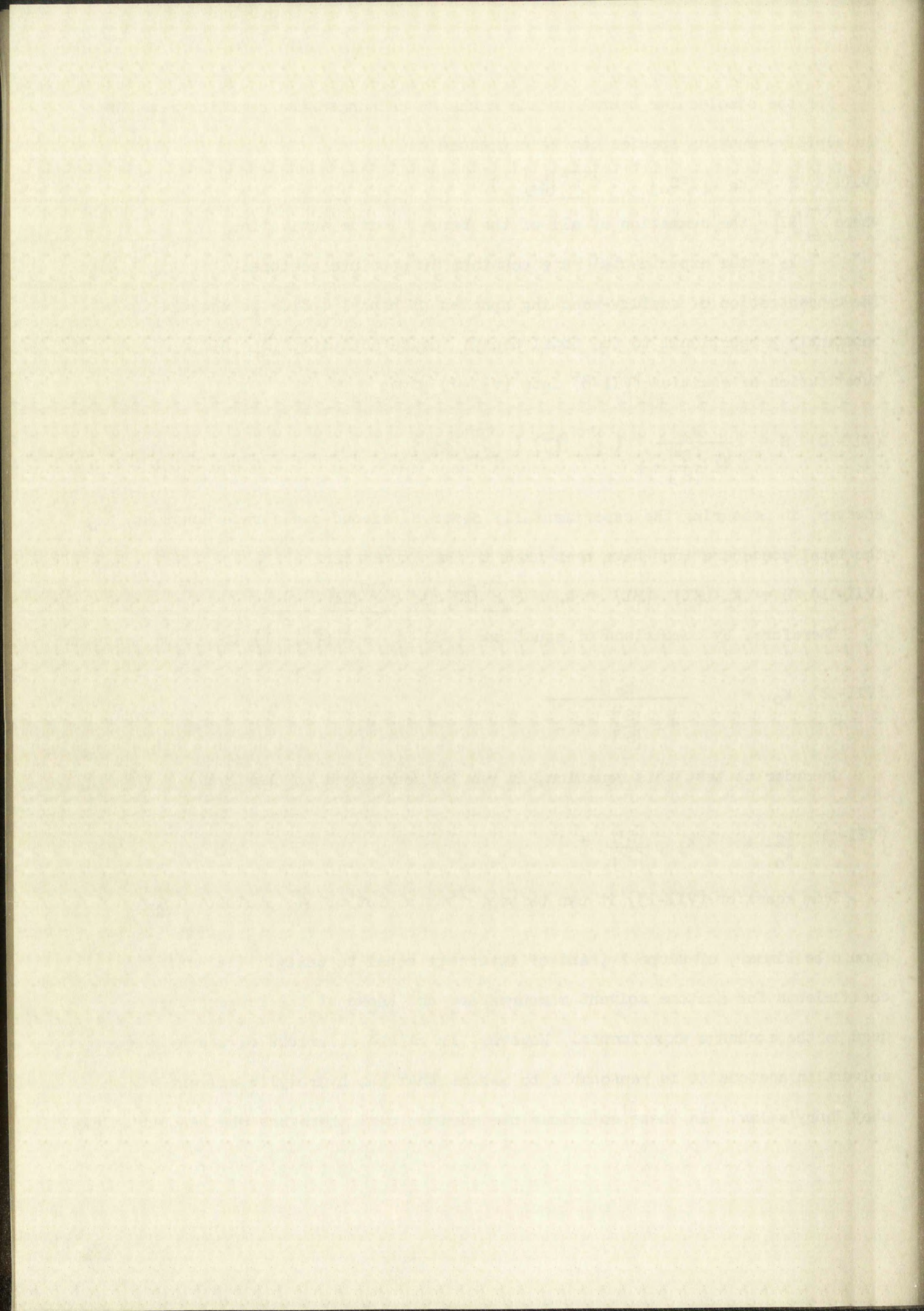
$$(VII-12) \quad k_o = \frac{k_2}{K_1 \frac{[S']}{[S]} + 1}$$

In order to test this equation, it can be rearranged to the form

$$(VII-13) \quad \frac{k_2}{k_o} = K_1 \frac{[S']}{[S]} + 1$$

From equation (VII-13) it can be seen that a plot of $\frac{k_2}{k_o}$ against $\frac{[S']}{[S]}$

should be linear, of slope K_1 , and of intercept equal to unity. The activity coefficients for acetone solvent mixtures are not known at the temperatures used in the exchange experiments. However, in dilute solutions of the hydroxylic solvent in acetone it is reasonable to assume that the hydroxylic solvent will obey Henry's law. In these solutions the acetone must therefore obey Raoult's law,



and the activity coefficients for each solvent must be constant. Therefore since $[S] = \gamma X_S$, where γ = the rational activity coefficient and X_S is the mole fraction of acetone in the solvent mixture, equation (VII-13) may be rewritten as

$$(VII-14) \quad \frac{k_2}{k_0} = K_1 \frac{\gamma' X_S'}{\gamma X_S} + 1 = K_2 \frac{X_S'}{X_S} + 1$$

$$\text{where } K_2 = K_1 \frac{\gamma'}{\gamma}$$

It should be noted that

$$(VII-15) \quad \frac{X_S'}{X_S} = \frac{(S')}{(S)}$$

where parentheses refer to molar concentrations. Therefore a plot of k_2/k_0 against $(S')/(S)$ is the same as a plot against X_S'/X_S . The mole fraction basis has been chosen for convenience.

In the above derivation it has been assumed that (1) the amounts of solvent associated with the exchange reactants is negligible in comparison to the total solvent present, and (2) that the activity coefficients of the exchange reactants are both unity. Both assumptions are based on the low concentrations of exchange reactants used in this investigation.

In Figure 25, k_2/k_0 has been plotted against X_S'/X_S for the solvent mixtures used in the exchange experiments. It can be seen that equation (VII-14) represents the data fairly well at low values of X_S'/X_S . The slopes of the lines in Figure 25 give the values of K_2 shown in Table XXXV for the benzyl iodide data.

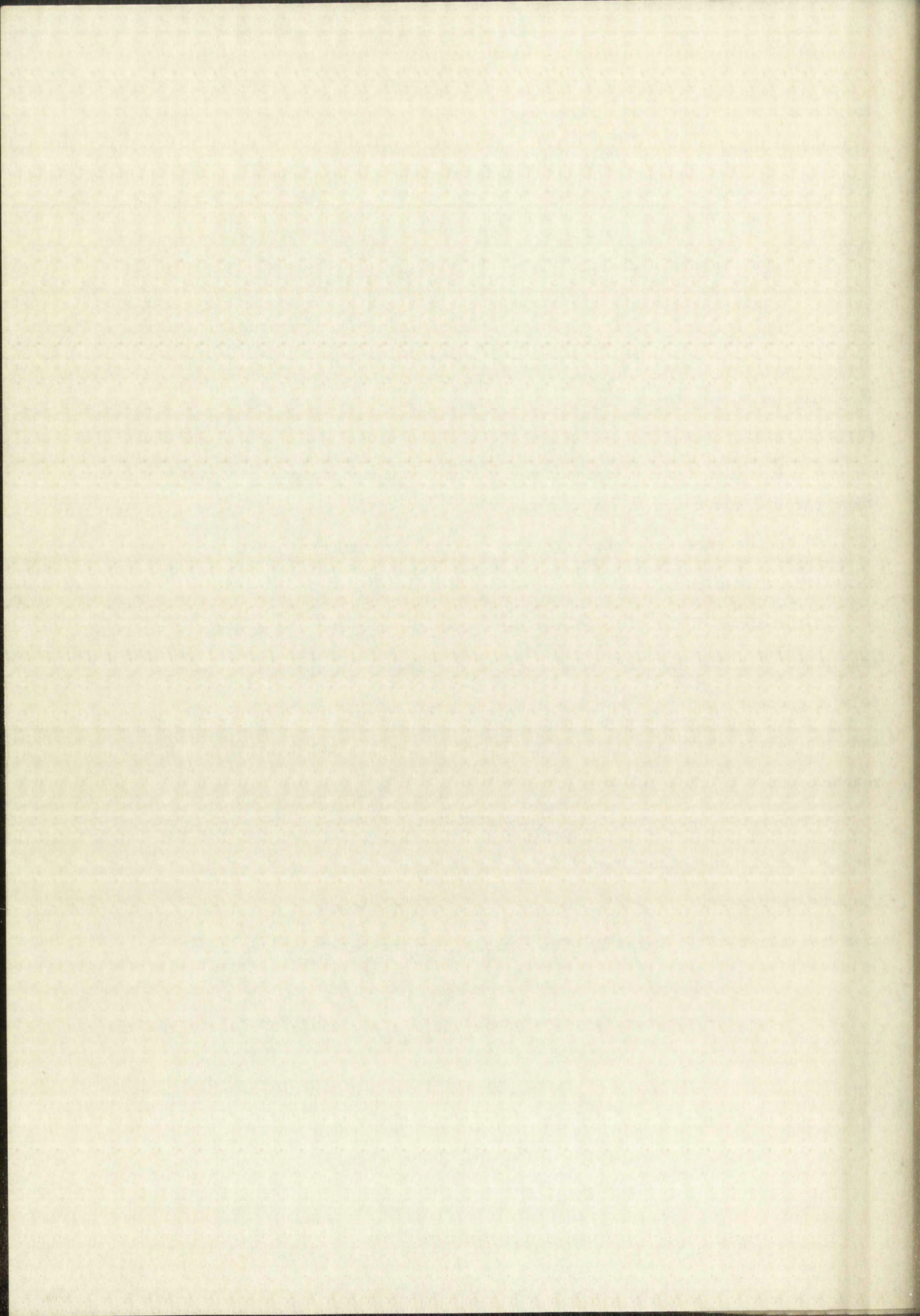


Table XXXV

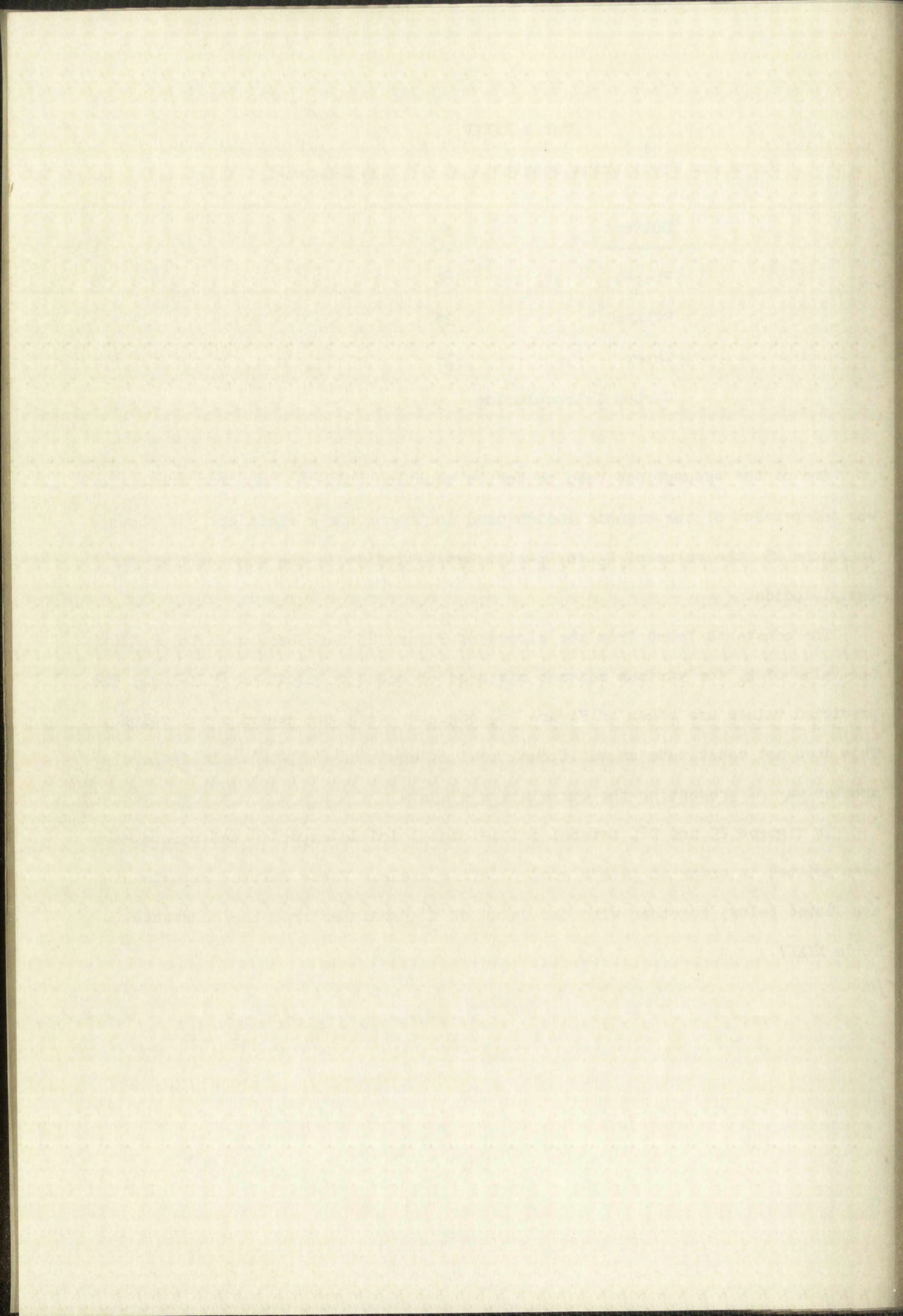
Solvation Equilibrium Constants at 0° from Figure 25

<u>Solvent</u>	<u>K₂</u>
Phenol	80
Ethanol	25
Water	15
Carbon Tetrachloride	0

One of the assumptions used to derive equation (VII-14) was that inhibition was independent of the organic iodide used in the exchange reaction. As shown in Figure 25, the value of K_2 for p-nitrobenzyl iodide is the same as that for benzyl iodide.

The constants found from the slopes of Figure 25 have been used to predict the value of k_0 for various solvent mixtures by means of equation (VII-14). The predicted values are shown in Figure 26, together with the experimental values. This does not constitute an additional test of equation (VII-14). It is merely another way of presenting the correlation of data.

In figures 25 and 26, several of the benzyl iodide experimental points have been omitted in order to give a good plotting scale. These omitted experiments are listed below, together with the value of k_0 predicted from the constants in Table XXXV.



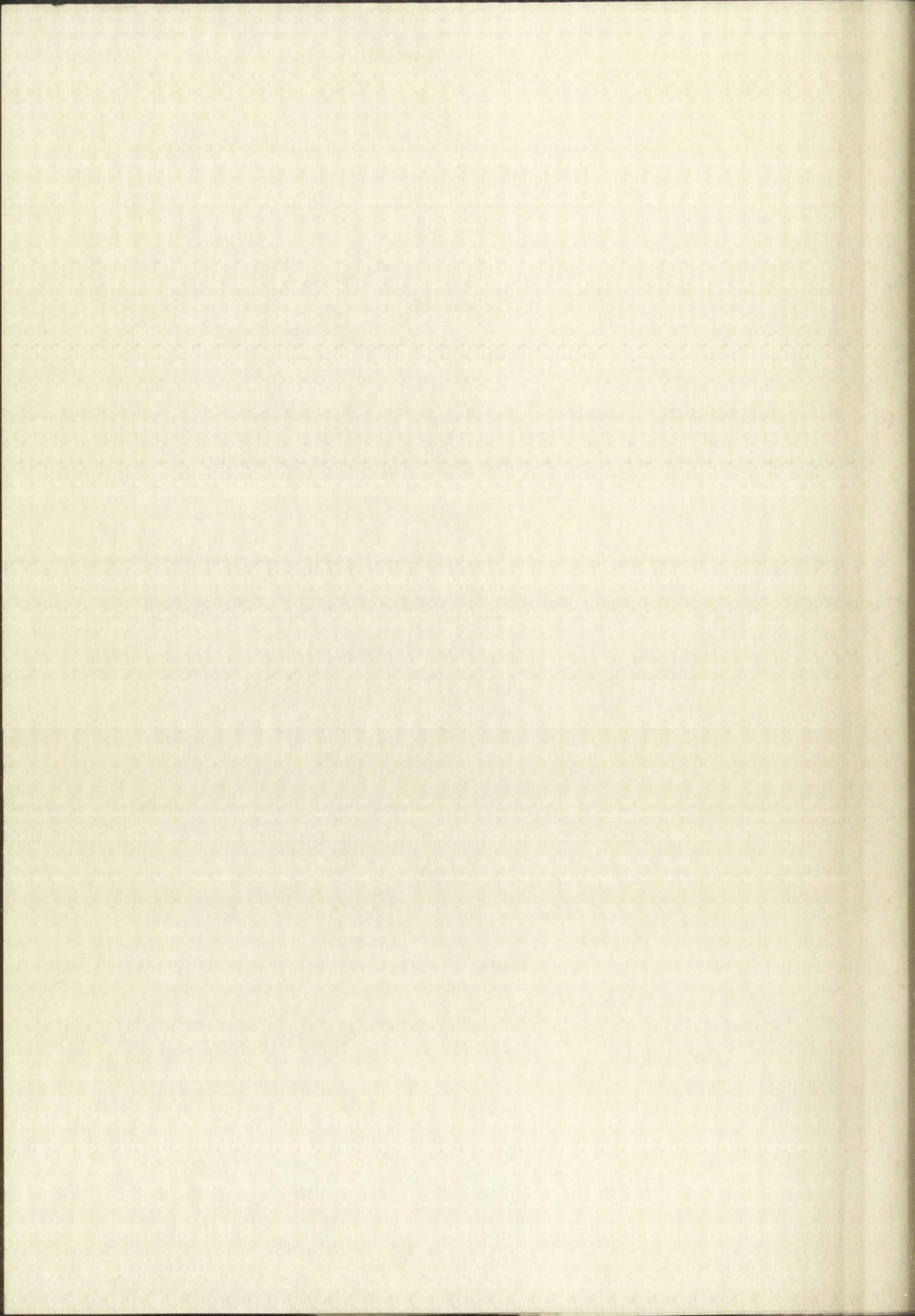
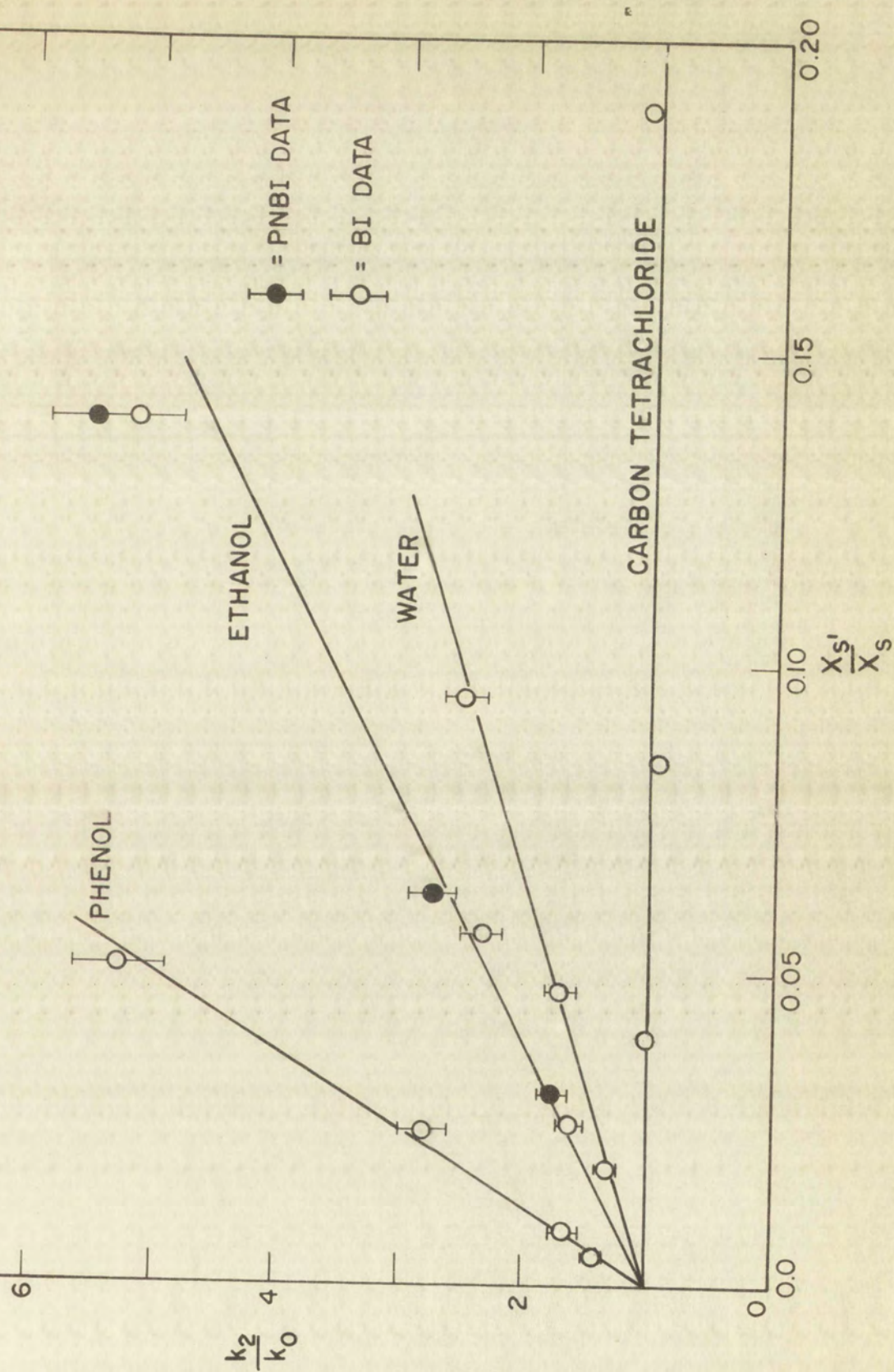


FIGURE 25
 Plot Of $\frac{k_2}{k_0}$ Against $\frac{X_{S'}}{X_S}$ For Experiments In Solvent Mixtures At 0°



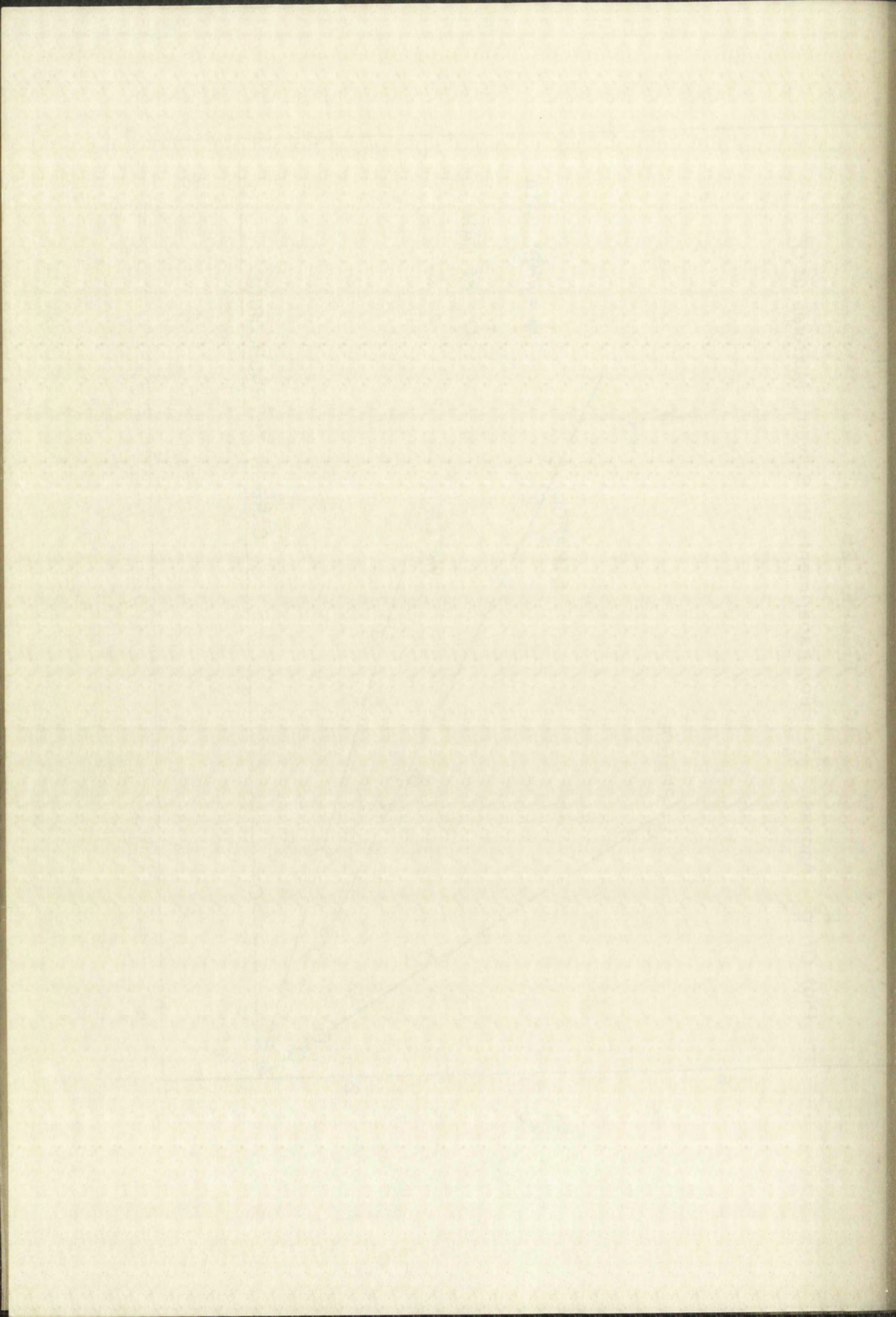


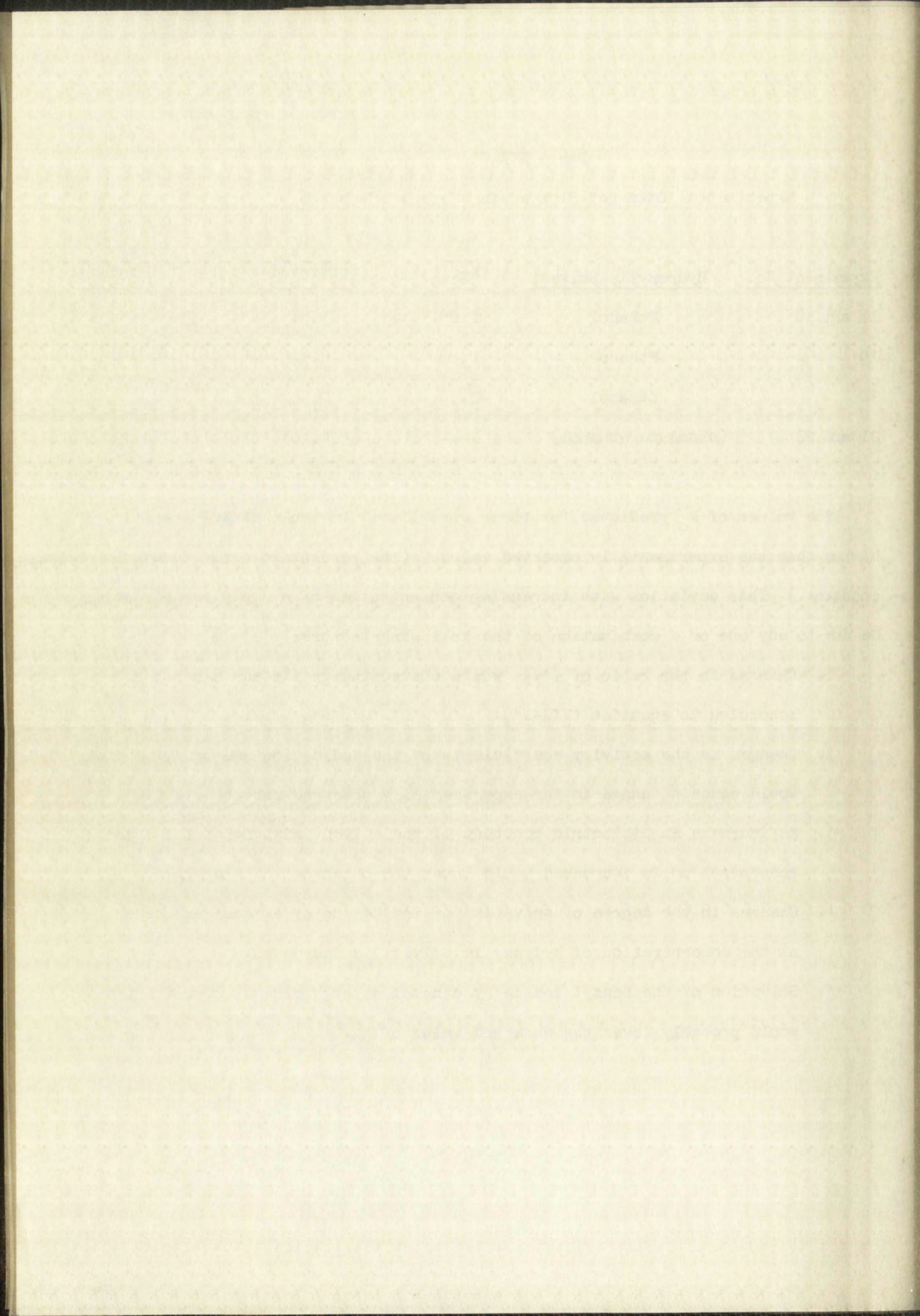
Table XXXVI

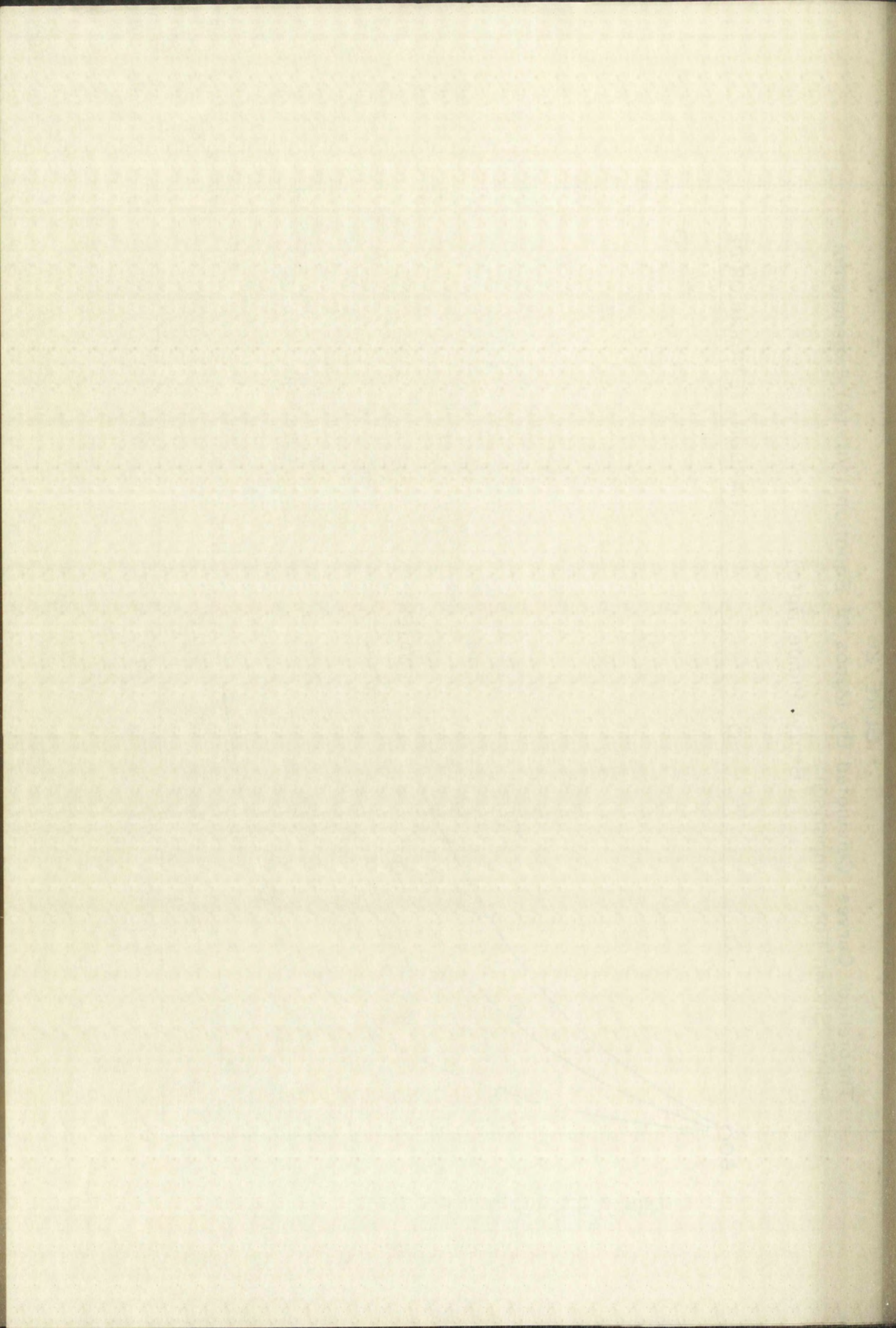
Experimental Data not Plotted in Figures 25 and 26

Experiment No.	Hydroxylic Solvent	X_S'	k_O , l./mole/min.	
		X_S	Observed	Predicted
17 and 18	Ethanol	1.25	1.04	1.8
19	Ethanol	1.88	0.702	1.2
20	Ethanol	2.50	0.532	0.94
21 and 22	(absolute ethanol)	----	0.104	0

The values of k_O predicted for those runs listed in Table XXXVI are all higher than the experimentally observed value. (The percentage error is nearly constant.) This deviation with increasing concentration of hydroxylic solvent may be due to any one or a combination of the following factors:

1. Changes in the ratio of γ'/γ would change the predicted value of k_O according to equation (VII-14).
2. Changes in the activity coefficients of the iodide ion and benzyl iodide would cause a change in the experimentally observed rate constant.
3. An increase in dielectric constant of the solvent mixture as the ethanol concentration is increased would lower the observed value of k_O .
4. Changes in the degree of solvation of iodide ion by ethanol may occur as the concentration of hydroxylic solvent is increased.
5. Solvation of the benzyl iodide by ethanol at high ethanol concentrations would probably lower the observed value of k_O .





Effect of solvent activity coefficients on the quantitative treatment of the exchange data. -

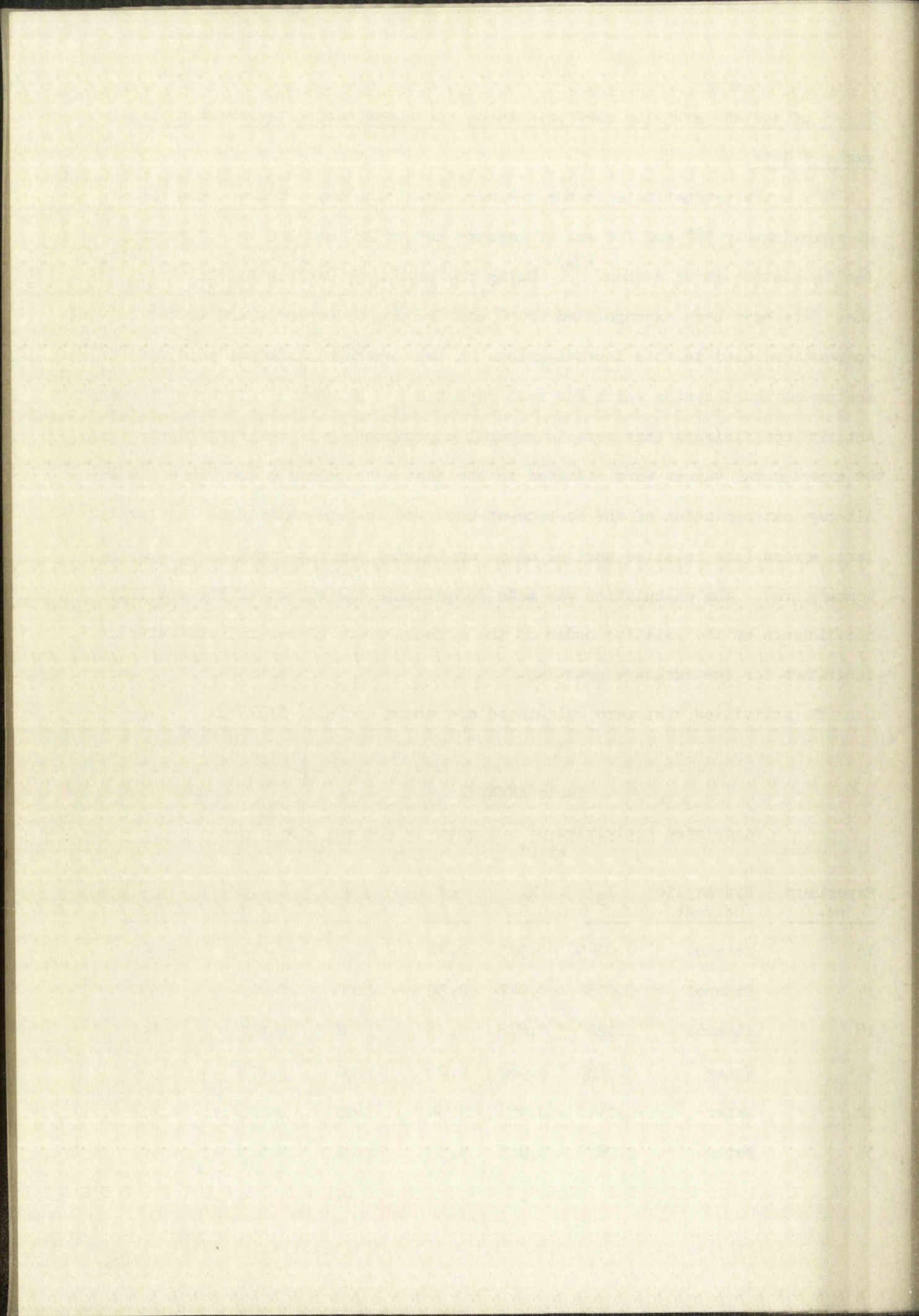
The activity coefficients for the acetone-ethanol system have been reported⁽³⁴⁾ at approximately 58° and 760 mm. of mercury and at 22° and 200 mm. of mercury for the acetone-water system.⁽³⁸⁾ Using the method of Carlson and Colburn,^(35,36) these data have been extrapolated to 0° and 760 mm. of mercury, and to the solvent compositions used in this investigation. A test extrapolation was made for the acetone-methanol system which has been reported⁽³⁷⁾ at several different temperatures. Activity coefficients that were in general approximately 10 per cent higher than the experimental values were obtained in the test extrapolation (see Appendix). Although extrapolation of the acetone-ethanol and acetone-water data may involve large errors (the relative partial molal enthalpies are not known as a function of temperature), the calculation was made to estimate the effect of the activity coefficients on the relative order of the effectiveness of ethanol and water as inhibitors for the exchange reaction.

The activities that were calculated are shown in Table XXXXVII.

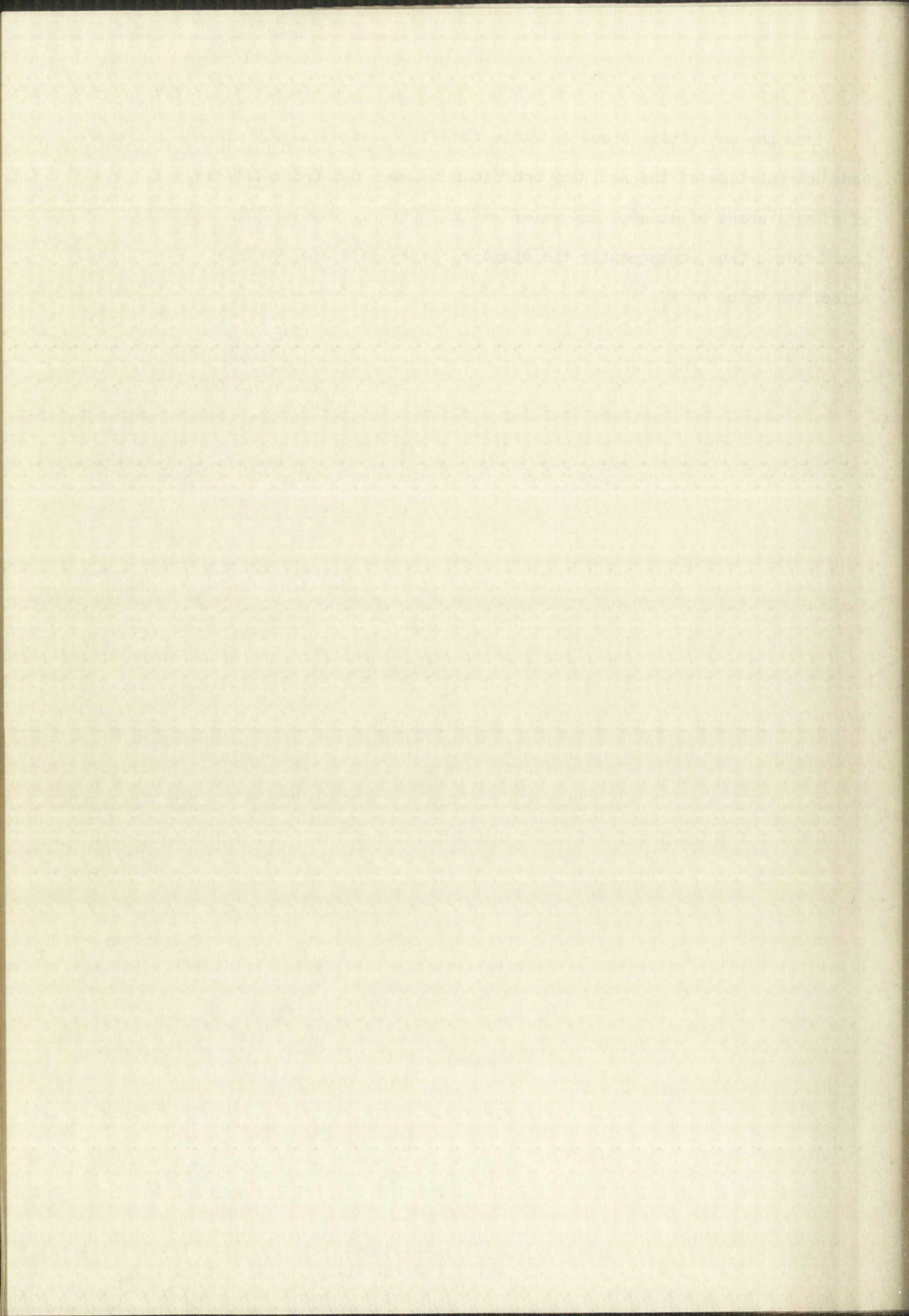
Table XXXXVII

Calculated Activities of Solvents in Solvent Mixtures
at 0°

Experiment No.	Hydroxylic Solvent	X_S'	X_S	γ'	γ	$\frac{[S']}{M}$	$\frac{[S]}{M}$
16	Ethanol	0.0249	0.975	2.42	1.00	0.0603	0.975
17	Ethanol	0.0532	0.947	2.32	1.00	0.123	0.947
18	Ethanol	0.122	0.878	2.15	1.02	0.262	0.897
31	Water	0.0180	0.982	4.20	1.00	0.0757	0.982
32	Water	0.0448	0.955	3.94	1.00	0.177	0.955
33	Water	0.0867	0.913	3.57	1.01	0.310	0.923



From the activities shown in Table XXXXVII, plotted in Figure 27, it appears that introduction of the activity coefficients does not change the relative order of effectiveness of ethanol and water as inhibitors. However, the activity coefficients (and consequently the standard state selected for each solvent) will affect the value of K_1 .



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Part VIII

Appendix

Extrapolation of Activity Coefficient Data for Binary Systems

The general procedure for the extrapolation of data given at one set of concentrations and at a fixed temperature to the desired concentrations at a different temperature (in this case 0°) is given in references 35 and 36. Three basic steps are involved:

1. An equation involving the mole-fraction composition and activity coefficients was found for the given data at the given temperature. This curve also involves arbitrary constants which can be evaluated from the data. Two sets of equations may be used.

(a) The Margules equations:

$$\text{(VIII-1a)} \quad \log \gamma_2 = (2A_1 - A_2) X_1^2 + 2(A_2 - A_1) X_1^3$$

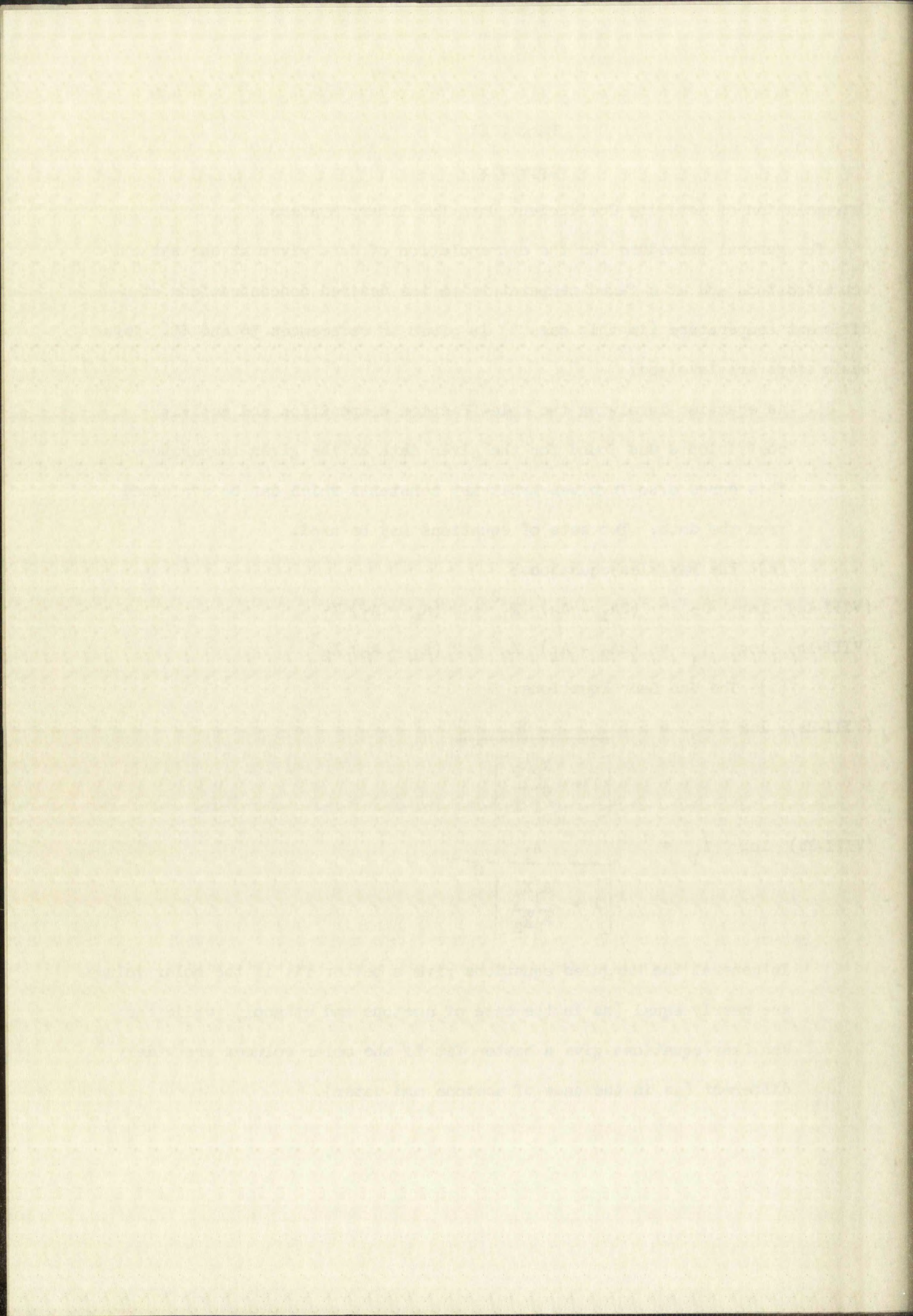
$$\text{(VIII-1b)} \quad \log \gamma_1 = (2A_2 - A_1) X_2^2 + 2(A_1 - A_2) X_2^3$$

(b) The Van Laar Equations:

$$\text{(VIII-2a)} \quad \log \gamma_2 = \frac{A_2}{\left[1 + \frac{X_2 A_2}{X_1 A_1} \right]^2}$$

$$\text{(VIII-2b)} \quad \log \gamma_1 = \frac{A_1}{\left[1 + \frac{A_1 X_1}{A_2 X_2} \right]^2}$$

In general the Margules equations give a better fit if the molar volumes are nearly equal (as in the case of acetone and ethanol), while the Van Laar equations give a better fit if the molar volumes are widely different (as in the case of acetone and water).



2. The constants A_1 and A_2 were extrapolated from the given temperature to the desired temperature by means of the following equations:

$$(VIII-3a) \quad \frac{dA_1}{dT} = \frac{-L_1^\circ}{2.3RT^2}$$

$$(VIII-3b) \quad \frac{dA_2}{dT} = \frac{-L_2^\circ}{2.3RT^2}$$

where L_1° and L_2° are the relative partial molal enthalpies for the infinitely dilute solutions. Both L_1° and L_2° are also temperature-dependent, but in general this dependence is not known over the full temperature range involved in the extrapolation. If the relative partial molal heat capacities are known, L_1° and L_2° can be computed from the equations

$$(VIII-4a) \quad \frac{dL_1^\circ}{dT} = (MC)_1^\circ - (MC)_1$$

$$(VIII-4b) \quad \frac{dL_2^\circ}{dT} = (MC)_2^\circ - (MC)_2$$

where $(MC)_1^\circ$ and $(MC)_2^\circ$ are the molal heat capacities at infinite dilution. They are also temperature-dependent.

3. The activity coefficients at the desired concentrations were then calculated by means of equations (VIII-1a) and (VIII-1b) using the constants calculated for the desired temperature.

In order to test this method, the activity coefficients for the acetone (subscript 1) and methanol (subscript 2) system at 56° were extrapolated to 8° . The data shown in Table XXXVIII have been reported by Fordyce and Simonsen. ⁽³⁷⁾

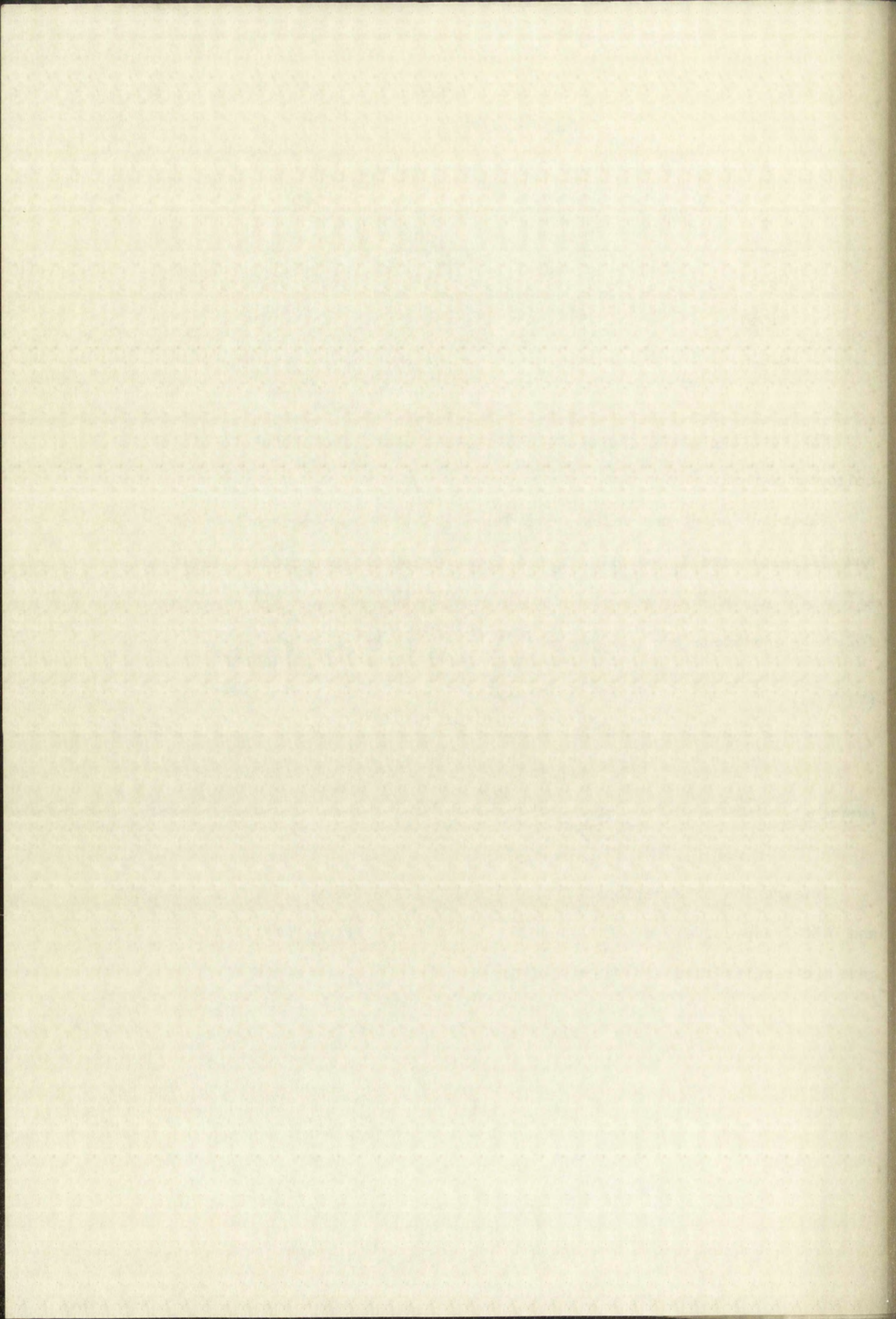


Table XXXIX

Activity Coefficients for Acetone-Methanol System at 8°

Liquid Composition		Activity Coefficients			
X_2	X_1	(Calculated)		(Experimental)	
		γ_2	γ_1	γ_2	γ_1
0.145	0.855	1.8	1.02	1.69	1.01
0.300	0.700	1.4	1.09	1.30	1.07

Because the calculation appears to give a value that is good to within less than 10 per cent, the acetone-ethanol and acetone-water systems were subjected to the same calculation.

The data in Table L have been reported for the acetone-ethanol system. (34)

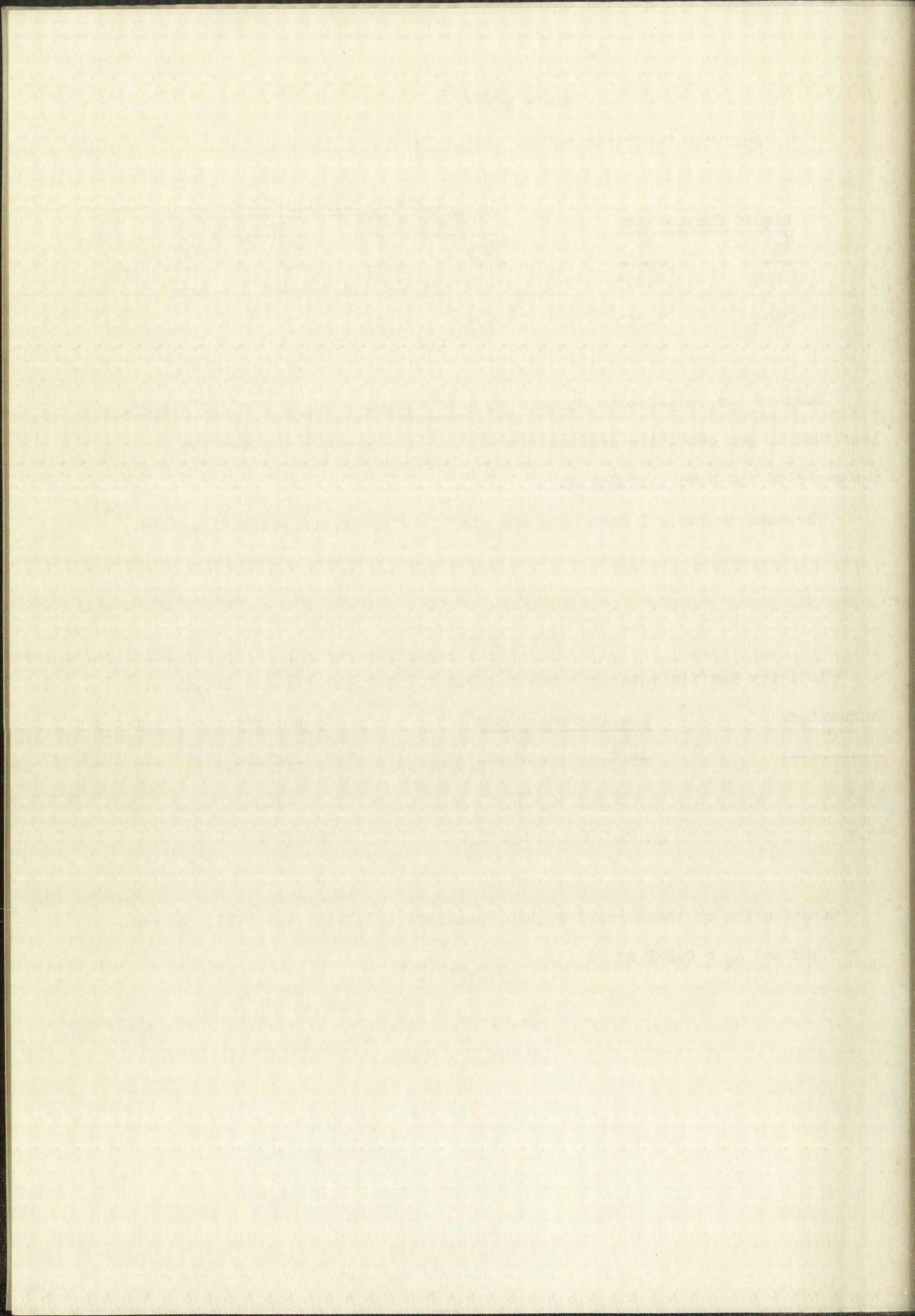
Table L

Activity Coefficients for Acetone-Ethanol System at 760 mm. Mercury

Temperature °C	Liquid Composition		Activity Coefficients	
	X_2	X_1	γ_2	γ_1
57.3	0.125	0.875	1.63	1.03
58.7	0.264	0.736	1.54	1.04

Substitution of these results into equations (VIII-1a) and (VIII-1b) gave

$$A_1 = 0.462 \text{ and } A_2 = 0.222 \text{ at } 58^\circ.$$



At 25°, $L_1^\circ = 116$, $L_2^\circ = 1250$ cal/mole⁽³⁹⁾

$$(MC)_1^\circ - (MC)_1 = 5.1, (MC)_2^\circ - (MC)_2 = 21.8 \text{ cal/mole}^\circ\text{K}$$

$$(VIII-6) \int_{116}^{L_1^\circ} (dL_1^\circ) = \int_{298^\circ}^T (5.1 \text{ dT})$$

$$(VIII-7) L_1^\circ = 5.1 T - 1520 + 116 = 5.1 T - 1404$$

$$(VIII-8) \int_{1250}^{L_2^\circ} (dL_2^\circ) = \int_{298^\circ}^T 21.8 \text{ dT}$$

$$(VIII-9) L_2^\circ = 21.8 T - 5250$$

Substitution of equations (VIII-7) and (VIII-9) into equations (VIII-3a) and (VIII-3b) gave

$$\frac{dA_1}{dT} = -\frac{1}{2.3R} \left[\frac{5.1T-1404}{T^2} \right] = - \left[\frac{1.116}{T} - \frac{307}{T^2} \right]$$

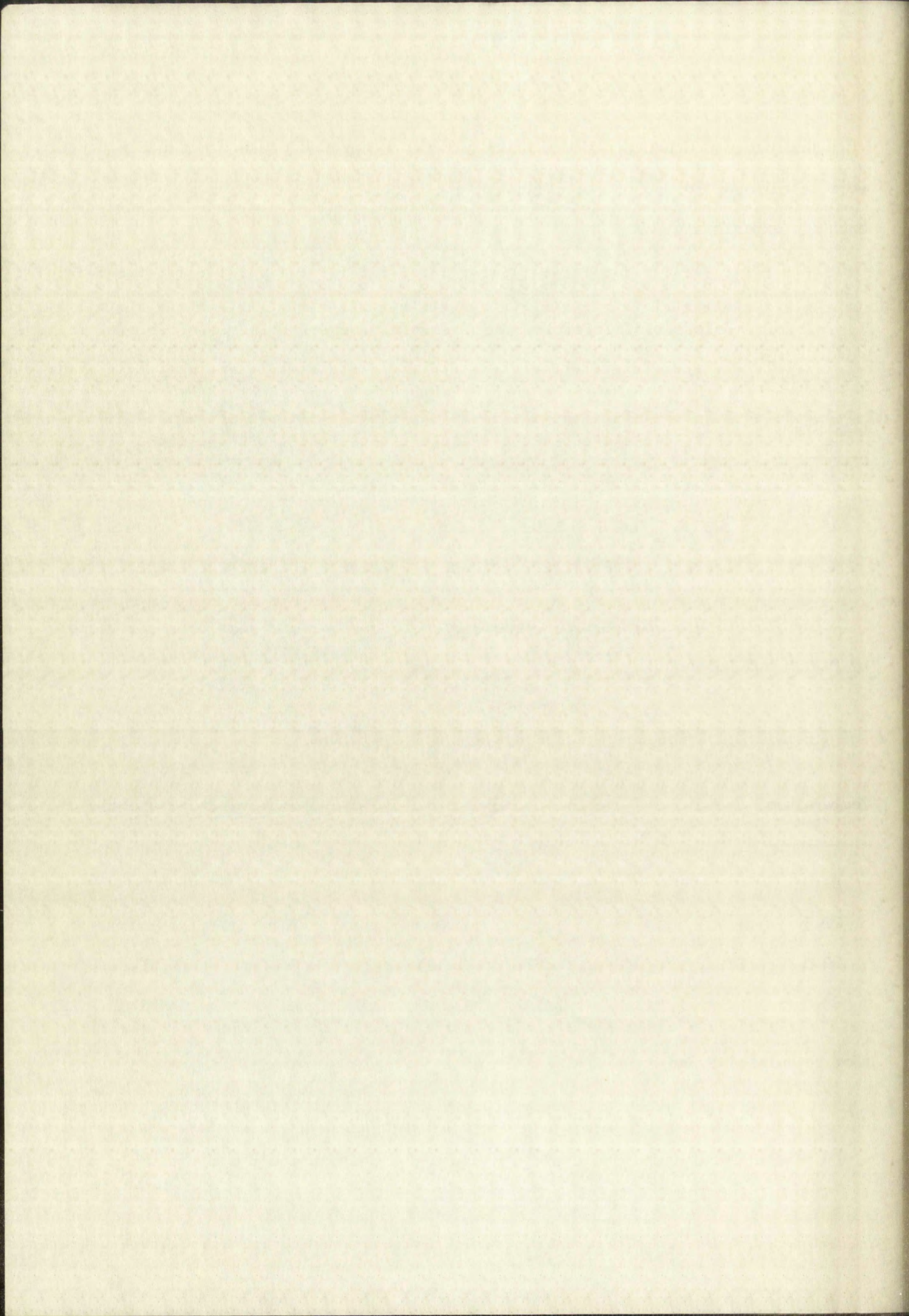
$$\frac{dA_1}{dT} = \frac{307}{T^2} - \frac{1.116}{T}$$

$$(VIII-10) \int_{0.462}^{A_1} dA_1 = \int_{331^\circ}^{273^\circ} \left[\frac{307}{T^2} - \frac{1.116}{T} \right] dT$$

Integration of equation (VIII-10) gave $A_1 = 0.476$ at 0°

By an identical calculation $A_2 = 0.402$

(Note: if the change in L_1° and L_2° with temperature had been neglected, the values of A_1 and A_2 at 0° would have been 0.478 and 0.397 respectively.)



From these data the values of A_1 and A_2 were found to be 0.946 and 0.698, respectively, at 22° by use of the Van Laar equations (VIII-2a) and (VIII-2b).

The reported⁽³⁹⁾ values for L_1° and L_2° at 15° are -2600 and -90 cal/mole, respectively. Partial molal heat capacities are unreported. Using these data, A_1 and A_2 were extrapolated to 0°, and found to be 0.785 and 0.642 respectively. Substitution of these constants into equations (VIII-2a) and (VIII-2b) gave the following activity coefficients for the concentrations used in the exchange experiments:

Table LIII

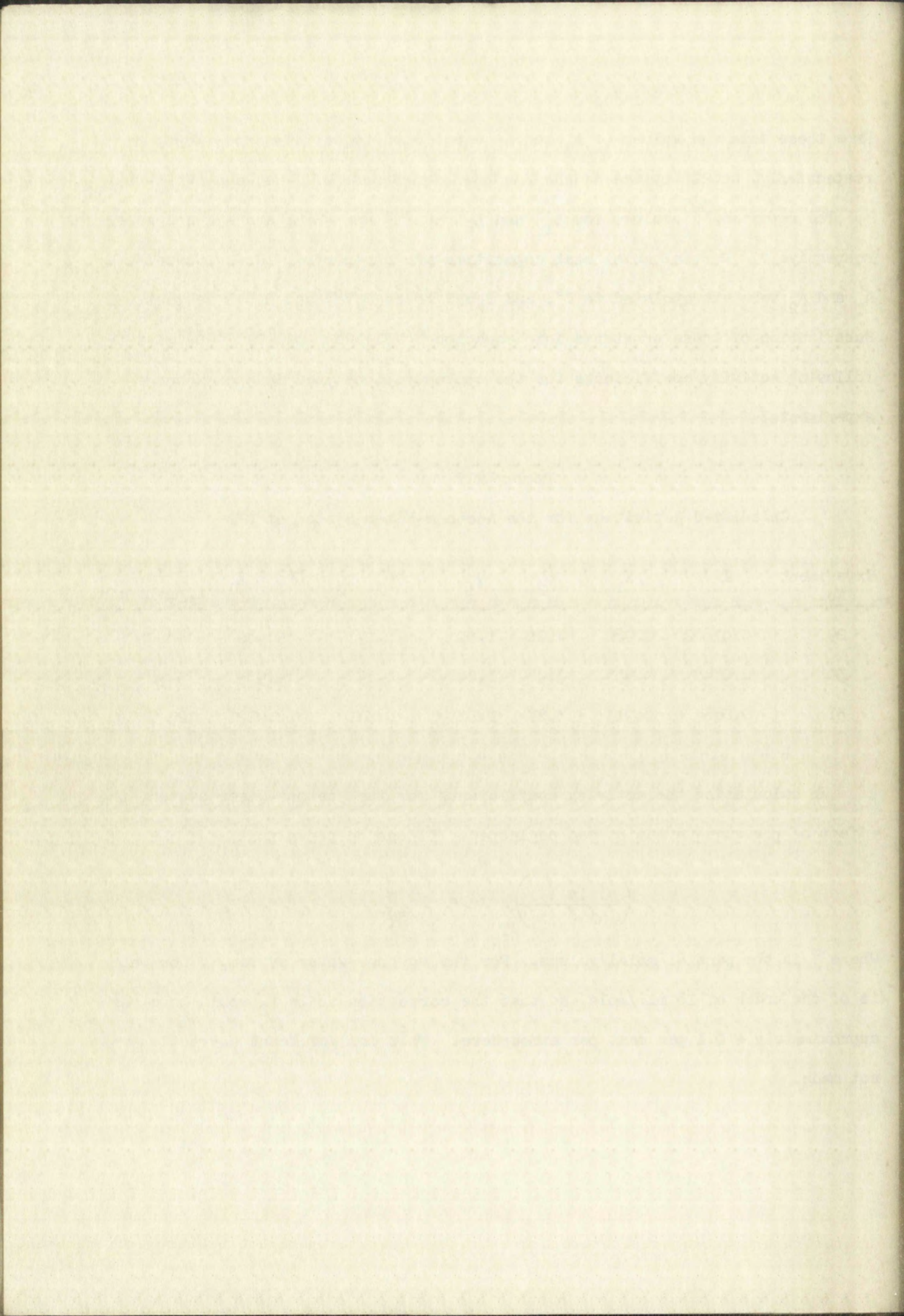
Calculated Activities for the Acetone-Water System at 0°

Experiment No.	X_2	X_1	γ_2	γ_1	$\gamma_2 X_2$	$\gamma_1 X_1$	$\frac{k_o}{l./mole/min.}$
29	0.01802	0.982	4.20	1.00	0.0757	0.982	45.0
30	0.0448	0.955	3.94	1.00	0.177	0.955	34.8
31	0.0867	0.913	3.57	1.01	0.310	0.922	23.7

In calculating the activity coefficients for the acetone-water system, the effect of pressure variation was neglected. It can be shown that

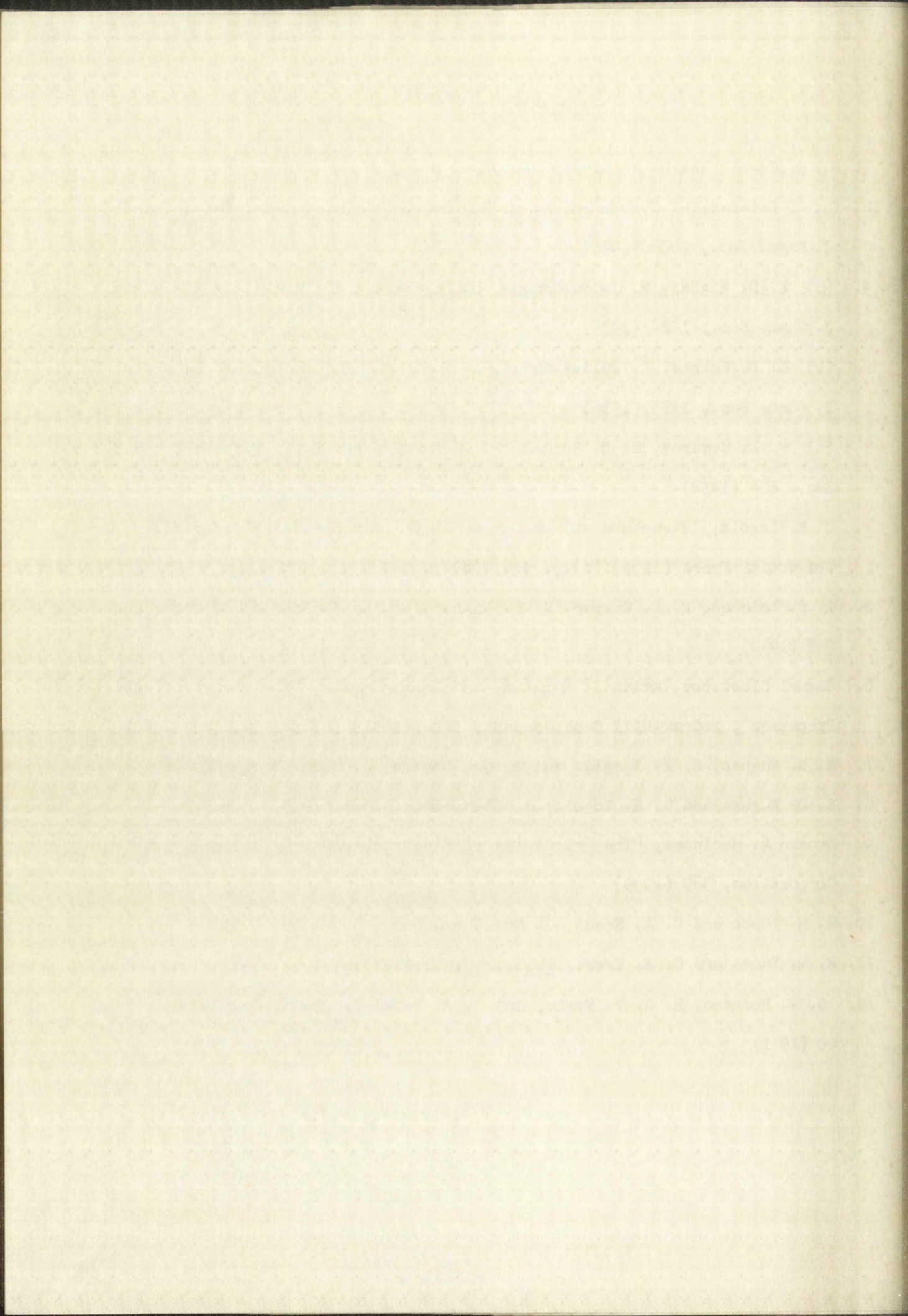
$$\left(\frac{\partial \ln \gamma}{\partial P} \right)_T = \frac{\bar{V}}{RT}$$

Where \bar{V} is the partial molal volume. For the acetone-water system, \bar{V} for water is of the order of 18 ml./mole, so that the correction to $\ln \gamma_2$ would have been approximately + 0.1 per cent per atmosphere. This insignificant correction was not made.

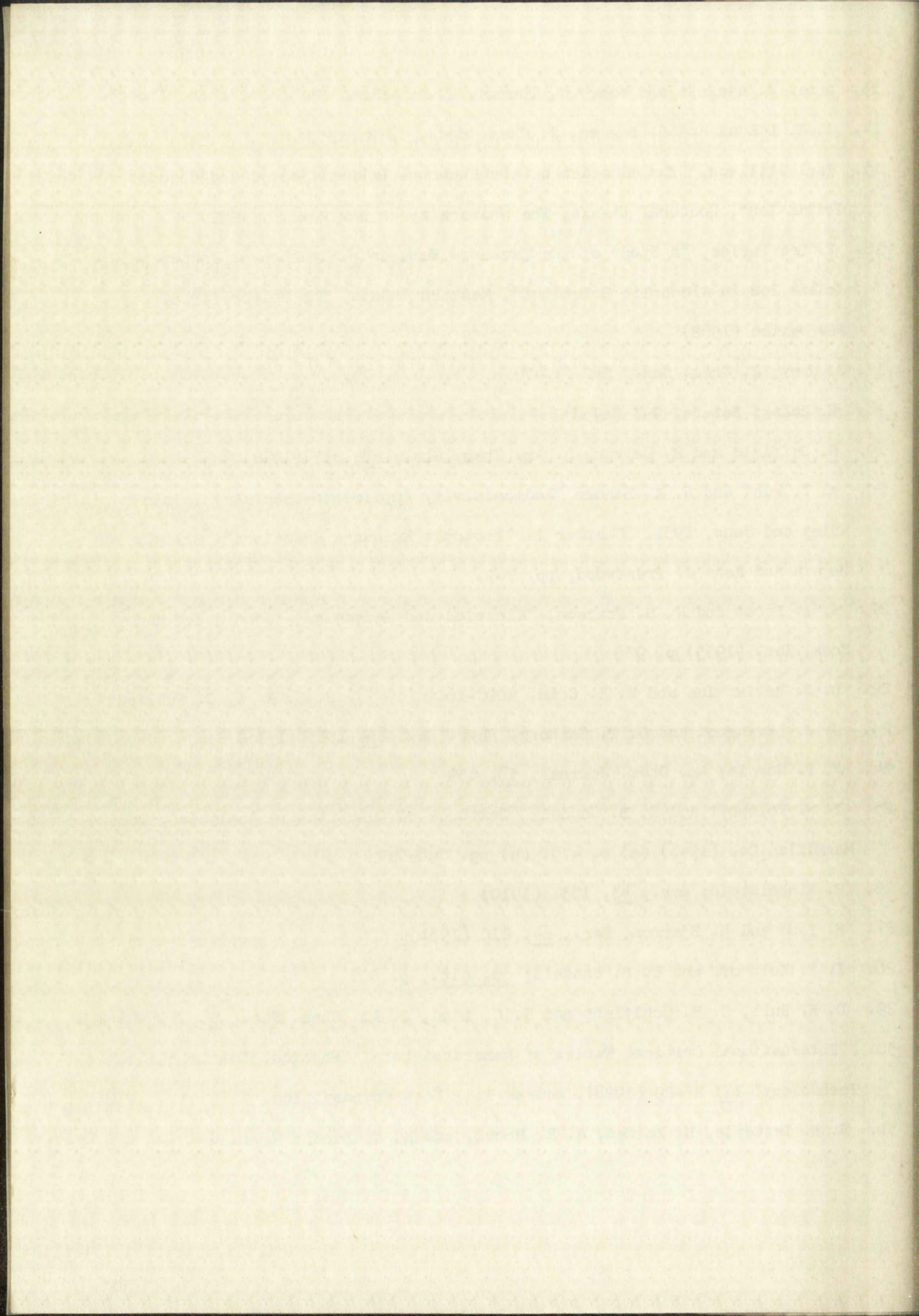


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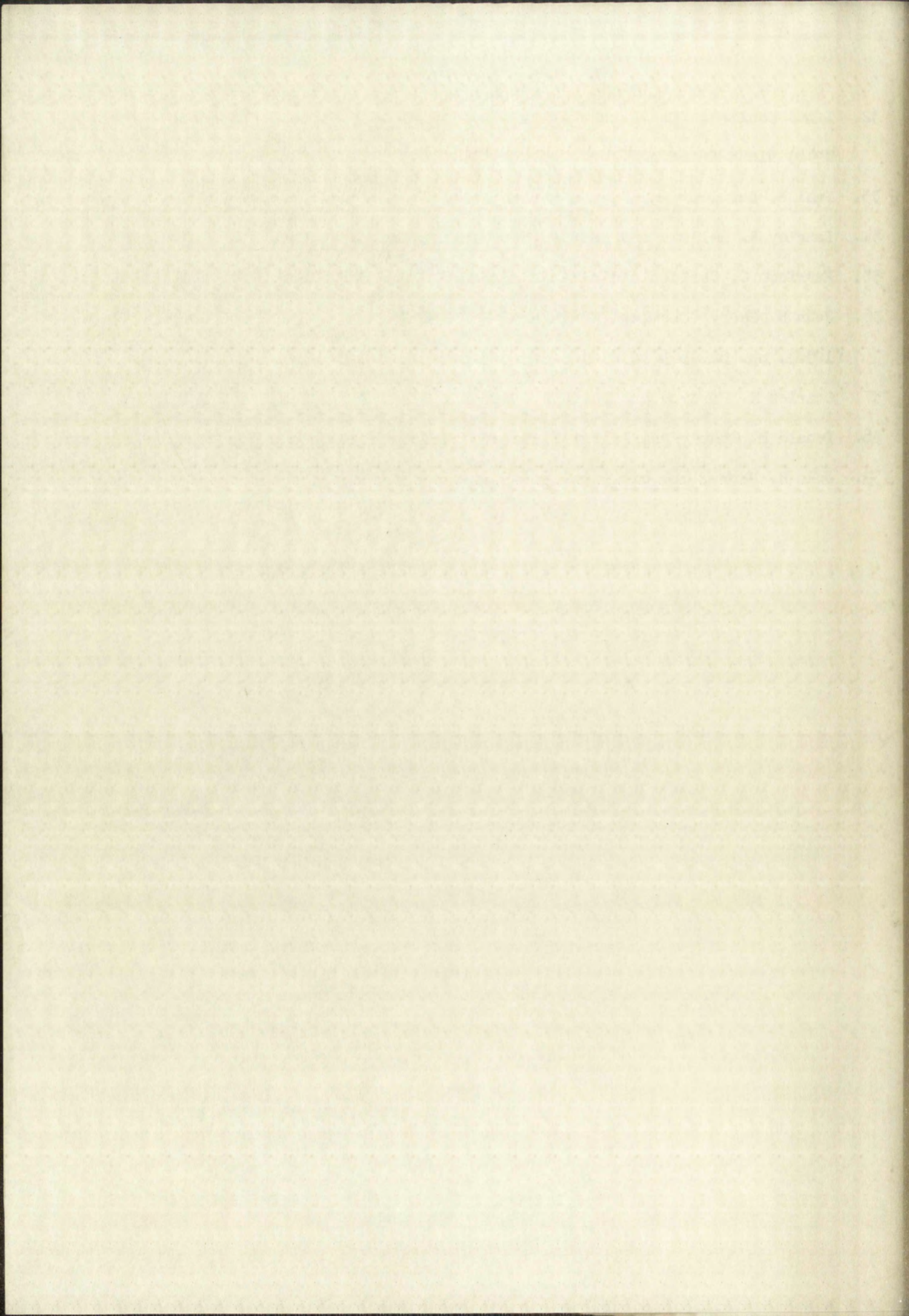
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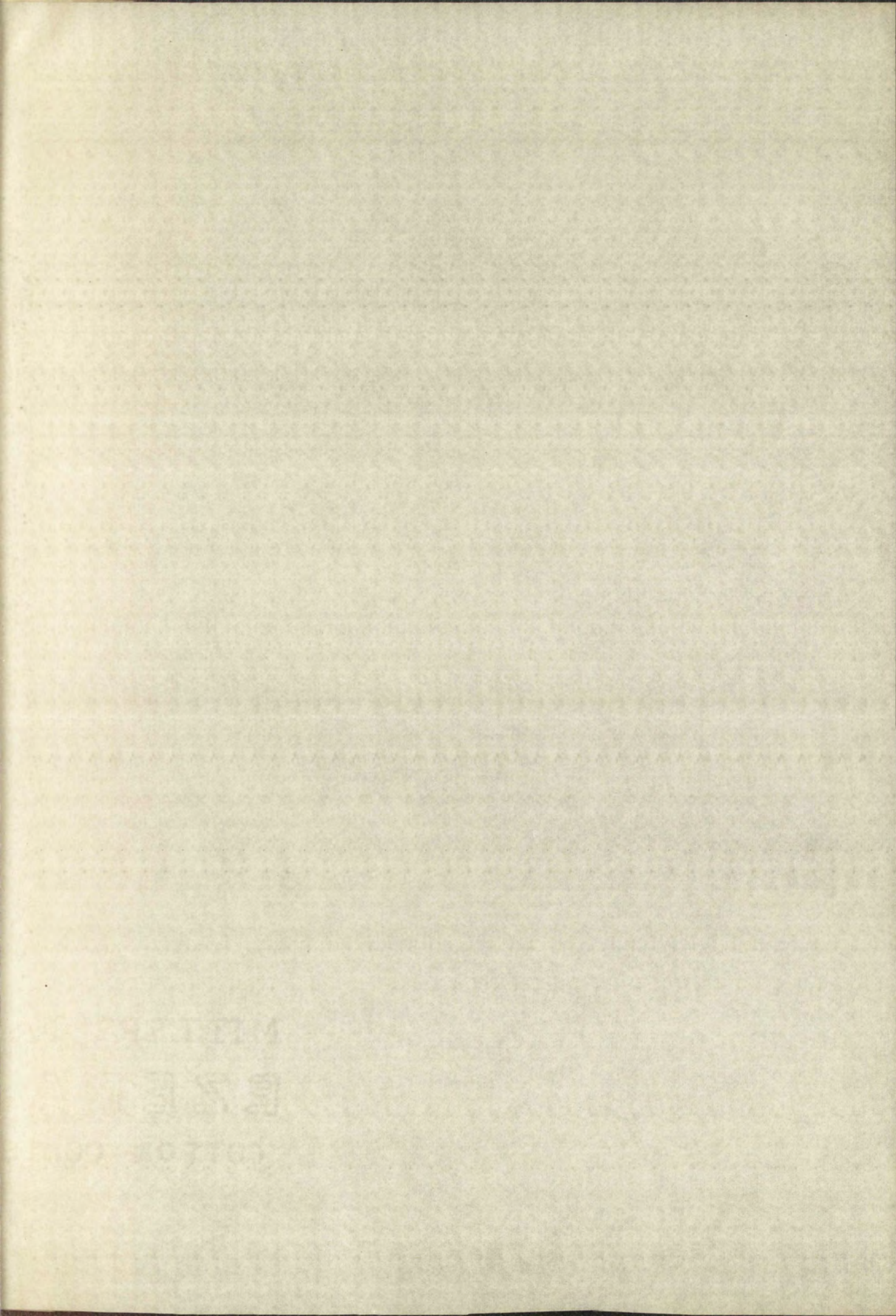


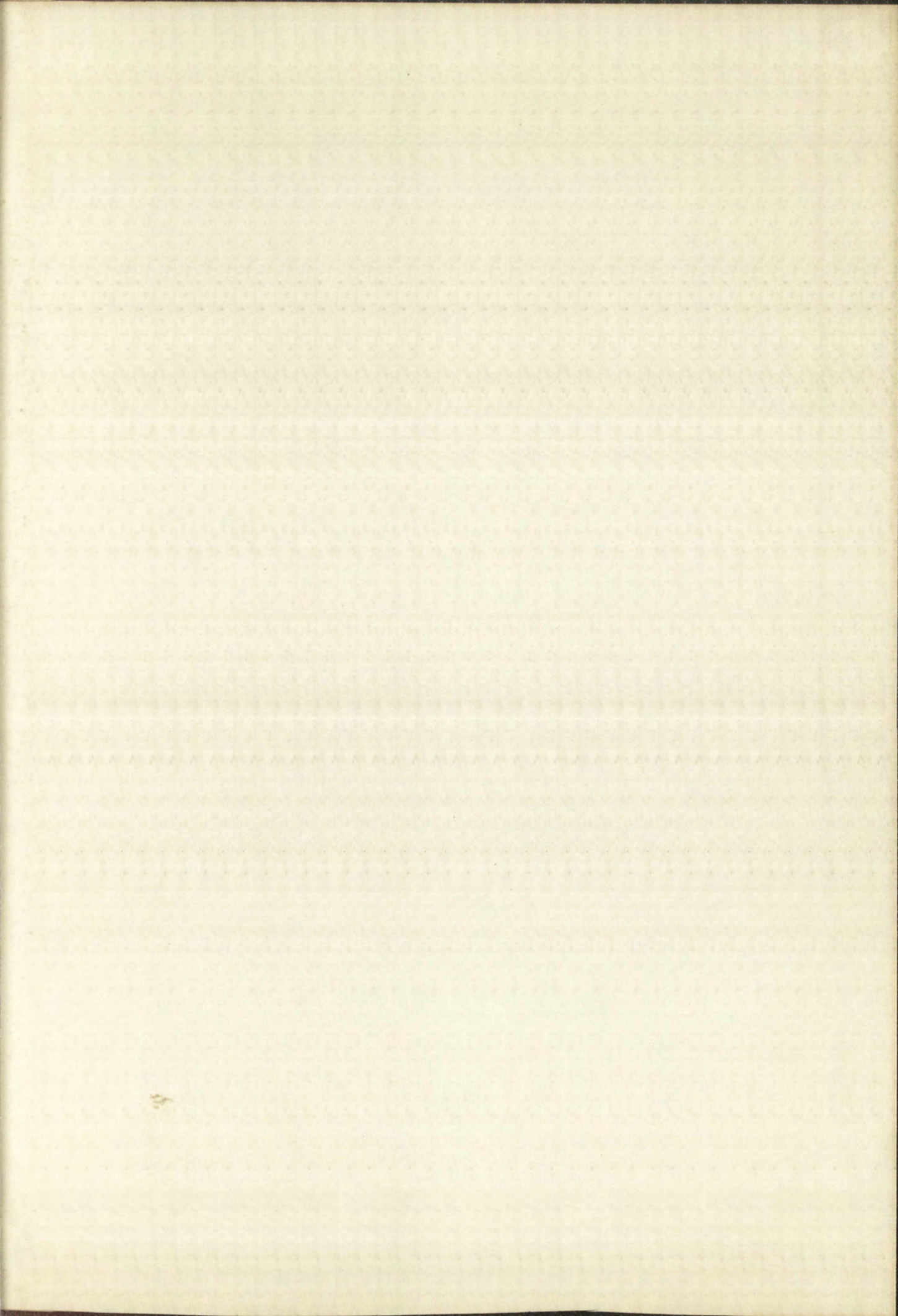
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