SOLVENT EFFECT ON IODIDE EXCHANGE

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by

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INTRODUCTION

EXCHANGE REACTIONS

When an inorganic and an organic compound containing a common halogen atom are mixed, they may, under certain conditions, exchange halogen atoms with each other. If one of the compounds contains a radioactive halogen isotope, it is possible to follow this exchange by observing the distribution of the active isotope between the organic and inorganic compounds.

Such an exchange may be represented by the equation

$$MX^* + RX \rightleftharpoons RX^* + MX$$
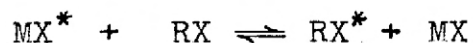
where MX and RX represent the inorganic and organic halides respectively, and the asterisk is used to denote the radioactive halogen. Since there is no change in the concentration of the chemically distinct components MX and RX, exchange is not a chemical reaction in the ordinary sense, but is simply the distribution of isotopes on a statistical basis among the halides present.

It follows that exchange reactions are not accompanied by a change in free energy, but are equilibrium reactions with an equilibrium constant equal to unity. It is also evident that the activation energy associated with the forward

reaction is identical with that associated with the reverse action. In the language of the theory of absolute reaction rates, the energy barrier is symmetrical about the reaction coordinate.

The earlier studies on halogen interchange between inorganic and organic halides were qualitative in nature, and served only to establish which compounds would or would not exchange under certain limited conditions. Recently the mathematics of exchange reactions have been developed, notably by McKay (1) and by Norris (2), permitting the quantitative interpretation of exchange data. Numerous quantitative investigations have been made on various aspects of these reactions, as a result of which they are now well established as an integral part of reaction kinetics.

Since this thesis is concerned only with solvent effects in exchange reactions, investigations on inorganic - organic halide exchange in the vapor phase (3) will not be reviewed here.

In studies on exchange reactions in solution, attention has usually been focused on the mechanism of the exchange in respect of one of the reactants, i.e. either the organic or the inorganic halide. When the inorganic halide has been the

subject of attention, the polarity of the solvent molecules
has been found to play an important role in the reaction
mechanism. It is therefore convenient to classify these in-
vestigations according to the polarity of the medium.

The Role of the Inorganic Halide in Exchange Mechanisms

Exchange in non-polar solvents

It was established by early qualitative studies that
exchange between the halides of the light metals (i.e. the
alkali metal and alkaline earth halides) or the halogens them-
selves with paraffinic halides either did not take place or
was immeasurably slow in non-polar solvents at moderate tem-
peratures (4). However, exchange of the halogens with alkyl
halides in such solvents has been effected both photochemically
at moderate temperatures and thermally at elevated temperatures.

Miller and Willard studied the exchange of bromine be-
tween the halogen and bromotrichloromethane in the liquid phase
and with carbon tetrachloride as a solvent (5). At tempera-
tures between 100° and 170°C. the rate of exchange was propor-
tional to the organic bromide concentration and the square
root of the bromine concentration, indicating that exchange
occurred between bromine atoms and the organic halide. This
was completely analogous to the reaction in the vapor phase.
These authors estimated the activation energy for exchange to

be of the order of seven kilocalories per mole.

A similar study in the same temperature range on the exchange between bromine and carbon tetrabromide in the liquid phase was made by Hodges and Miceli with identical conclusions (6). The activation energy for this exchange was estimated to be three kilocalories per mole. It is interesting to note that Hodges and Miceli observed no variation in exchange rate with change in the quantity of radioactive bromine present. This work settled the question of the effect of self-radiation on such exchange reactions, a possibility which enjoyed considerable discussion at that time.

Qualitative studies by Noyes (7) and by Wilson and Dickinson (8) indicated that exchange solvents of low dielectric constant may be promoted photochemically. Noyes found that iodine exchanged with ethylenic, paraffinic and aromatic iodides in the liquid phase under radiation from a tungsten lamp at room temperature. Wilson and Dickinson had previously promoted exchange between bromine and aliphatic bromides by irradiating carbon disulfide solutions of these reactants with green light (5000-6100 $\overset{o}{A}$). It was presumed that these exchanges involved atoms produced photochemically, although the possibility of concurrent dark reactions in exchange with unsaturated aliphatic hydrocarbons was not excluded.

Noyes and his co-workers found that exchange between iodine and cis - and trans-diiodoethylene proceeded both thermally and photochemically at moderate temperatures in hexane (9). The kinetics of both the thermal and the photo-chemical reactions indicated the iodine atoms are involved in these reactions. These structural isomers were slowly isomerized by iodine both thermally and photochemically, but the rate of isomerization was less than one percent of the exchange under the same conditions. These authors suggested that this discrepancy was due to the lower activation energy for exchange rather than a greater number of collisions in which the configuration was more favorable to exchange than to isomerization.

Ethyl iodide did not undergo photochemical or thermal exchange with iodine in hexane at these temperatures. It was decided that a carbon-carbon double bond adjacent to the carbon iodine bond was necessary for exchange under these conditions.

While exchange of the light metal halides with alkyl halides has not been successful, exchange has been obtained with several polyvalent metal halides. Fairbrother found the thermal exchange of aluminum tribromide with aliphatic bromides to be rapid in carbon disulfide, while aromatic

bromides exchanged more slowly (10). The reaction with stannous bromide was observed to be slower than that of the aluminum halide. Other metal halides, such as those of antimony, gold and zinc, showed some power of exchange. Similar observations on exchange with aluminum trihalides, have been made by Brezhneva et al (11) and by Rumpf and Pullman (12), although the latter obtained no exchange between cuprous bromide or antimony tribromide and liquid n-decyl bromide, even at 200°C. Reactions of this type are presumed to occur through the formation of complex ions, such as $AlCl_4^-$, similar to those postulated for the Friedel-Crafts reaction.

In studying the exchange of solid aluminum trichloride with carbon tetrachloride, Wallace and Willard concluded that the formation of any complex ion would require an activation energy greater than that observed (13). As an alternative, they have suggested that the exchange was heterogeneous and was the result of the induction of dipoles in the organic molecule and the adsorption of these dipoles by the solid inorganic halide.

Exchange in polar solvents

The halogens, alkali metal and alkaline earth halides have been found to undergo thermal exchange with paraffinic halides at moderate temperatures only in the presence of polar

solvents (4). These inorganic halides were at least partially ionized in solution, from which it was inferred that exchange under these conditions involved neutral organic molecules and ions supplied by the inorganic halide. Two experimental schemes have been used to verify this conclusion, one involving variation of the halide ion source and the other variation of the solvent medium.

Almost without exception, exchange under these conditions has been first order in respect of both the organic and inorganic halide concentrations, and the over-all reaction obeyed the second order exchange equation. The second order rate constant for the exchange of bromine with n-butyl bromide in 90% acetone was found to be independent of bromine concentrations less than 0.15 molar. Above this concentration the rate constant decreased (14). A similar decrease in the rate constant with increasing inorganic halide concentration has been reported by Evans and Sugden for the exchange of lithium bromide with sec-octyl bromide in anhydrous acetone (15). With constant organic halide concentration the rate constant decreased seven-fold for lithium bromide concentrations between 10^{-4} and 10^{-2} molar. On the other hand, the concentration of sodium iodide had no effect on the rate constant for the exchange of sodium iodide with ethyl iodide in methyl alcohol.

Since the conductance of sodium iodide in methyl alcohol indicated that this solute was completely ionized, no variation of rate constant with halide concentration was expected. Lithium bromide in acetone, however, was partially associated. Using conductance data, Sugden computed the fraction of this solute existing as ions at the various concentrations used in the exchange experiments. When the second order rate constants were calculated on the basis of the bromide ion concentration the values obtained for the rate constant were numerically equal within experimental error.

In this treatment of exchange with a partially associated inorganic halide, it was assumed that the inorganic exchange reaction involved (here the exchange of bromide ion with lithium bromide) was much faster than the ion-organic molecule reation. Since exchange between halide ions and the corresponding halides in aqueous solution has been found to be immeasurably fast (16), this assumption was regarded as valid.

If halide ions are involved in these reactions, the rate of exchange should be independent of the source of the halide ion, provided that the inorganic reactant is completely ionized. Hodgson, Evans and Winkler showed this to be true for the exchange of n-butyl iodide with lithium, sodium and

caesium iodides in acetonitrile (17). Cryoscopic and conductance experiments indicated that these salts were completely dissociated in this solvent, and the second order rate constants, as well as the activation energies for exchange with these salts, were essentially identical.

In studying the exchange of sodium iodide with ethyl iodide in ethanol, MacKay observed a two-fold increase in the second order rate constant with a hundred-fold increase in sodium iodide concentration (1). MacKay attributed this decrease to the deviation of the solution from ideality. It is interesting to note that Hodgson's values of the rate constant for exchange with the three alkali halides invariably showed a similar decrease over the small concentration ranges investigated.

The kinetics of exchange of cadmium and zinc iodides with butyl iodide in acetonitrile have been explained on the basis of exchange between the organic molecule and complex ions such as ZnI_3^- and $CdI_4^=$ (17). The presence of such ions in acetonitrile was supported by consideration of cryoscopic data. It appeared that complex ions were also involved in the exchange of iodine with organic iodides in this solvent.

Another mechanism has been proposed for exchange in polar solvents at high dilution. If the organic halide were

considered to be slightly dissociated in such solvents to yield halide ion of concentration comparable with that resulting from dissociation of the inorganic halide, exchange might be expected to proceed via the equilibrium established between the organic halide and its ions. Tuck found the exchange of 10^{-5} molar iodide ion with 0.2 molar tertiary butyl iodide in liquid sulfur dioxide to be independent of the iodide ion concentration (18). By following the initial exchange, during which it was assumed that the active iodide ion removed from solution remained in the organic molecule, Tuck estimated the rate of dissociation to be $2 \times 10^{-4} \text{secs}^{-1}$.

Preliminary investigations indicated the degree of dissociation of tert.-butyl iodide to be several hundred times smaller in methanol and ethanol than in sulfur dioxide.

The Role of the Organic Halide in Exchange Mechanisms

It has been established that inorganic-organic halide exchange in polar solvents involves an ion from the inorganic reactant. If the exchange proceeds by the reaction of this ion with the neutral organic molecule, it is reasonable to suppose that the exchange should be accompanied by a Walden inversion about the reaction center. Hughes and his co-workers found experimentally that such an inversion does occur (19).

The rates of racemization of two optically active organic compounds, α-bromopropionic acid and phenylmethylbromomethane, were compared with the rates of exchange of the bromine with lithium bromide under the same conditions. In both studies, the rate constant for exchange agreed, within experimental error, with that for inversion.

Several investigations have been made on the variation in rates of exchange with homologous and isomeric aliphatic halides. Elliot and Sugden found an increase in activation energy for the exchange of bromide ion with alkyl bromides in the order n-propyl<isobutyl<isopropyl (20). On the other hand, McKay's investigation of the exchange of iodide ion with normal, secondary and tertiary aliphatic iodides showed no significant variation in activation energy for compounds with two to five carbon atoms (1). However McKay observed that the rate of exchange decreased when the chain length of the normal iodides was increased, and that the rate of exchange with structural isomers decreased in the order primary > tertiary>secondary. This trend for isomeric halides has also been observed by Seelig and Hull (21).

Neiman and Protsenko have corroborated McKay's data on the exchange of iodide ion with ethyl iodide in alcoholic solutions (22).

The exchange of the alicyclic iodides of five, six, seven, eight and fifteen carbon atoms with sodium iodide in ethanol has been investigated by Van Straten, Nicholls and Winkler (23). It was found that the activation energies for exchange with these compounds agreed favorably with those reported by McKay for the aliphatic series (20-22 Kcal/mole) with the exception of cyclohexyl iodide (25.6 Kcal/mole). These authors have suggested that the height of the energy barrier in these exchange reactions was independent of the size of the ring, and they have attributed the larger activation energy of exchange with the six carbon compound to the lower initial potential energy of this ring.

When the logarithm of the frequency or entropy term of the Arrhenius equation (i.e. the non-exponential parameter) representing the exchange of amyl and n-heptyl iodide and of the alicyclic iodides with sodium iodide was plotted against the reciprocal of the number of carbon atoms in the molecule, a linear relation was obtained except for cyclopentyl iodide. It has been suggested that the change in entropy of activation observed was a function of the possible configurations that the organic molecule could assume. On this basis, the failure of the cyclic five carbon molecule to conform with the log PZ versus 1/N relation was explained by reference to the rigidity

of this ring.

Although exchange may proceed with inversion in aliphatic and alicyclic molecules, it is structurally impossible for the exchange of a halide ion with an aromatic halide to be accompanied by rearrangement of the carbon atom configuration.

The effect of the position of the nitro group in the exchange of iodide ion with the isomeric nitroidobenzenes and iodobenzene itself has been studied by Kristjanson and Winkler (24). At high temperatures (180° - 240°C.) the exchange of the ortho and para isomers in acetonitrile was similar and second order. At lower temperatures, these exchange reactions appeared to become independent of the iodide ion concentration. In contrast, the exchange with the meta isomer and with iodobenzene conformed to a first order expression throughout the temperature range of the investigations. No satisfactory mechanism has yet been proposed for these exchange reactions.

If the solvent is not inert, it is possible for an exchange to proceed by a mechanism other than those discussed above. It was found that the exchange of tert.-butyl chloride with lithium chloride in formic acid proceeded via the equilibrium between the organic chloride, the product of the hydrolysis of the organic halide by the solvent (isobutylene), and

the chloride ion (25). It appeared that the contribution to this reaction by direct ion- neutral molecule exchange was negligible.

Summary

The mechanisms of inorganic - organic halide exchange reactions may be summarized as follows:

1. In polar solvents, thermal exchange occurs at moderate temperatures by the reaction of the neutral organic molecule with an ion supplied by the inorganic halide. The ion may be simple or complex depending on the nature of the solvent and the inorganic halide.

2. Exchange of the halogens with organic halides in non-polar solvents occurs thermally at elevated temperatures and photochemically at moderate temperatures. An atomic mechanism is indicated.

3. Aluminum trihalides and some heavy metal halides will exchange with organic halides in non-polar solvents. Mechanisms involving complex formation have been proposed.

4. Exchange has not been possible between the alkali metal or alkaline earth halides and aliphatic halides in non-polar solvents.

5. Exchange of a halide ion with aliphatic halides is accompanied by Walden inversion about the seat of exchange.

6. Aromatic halides undergo exchange in polar solvents at elevated temperatures. No mechanisms have been proposed for these reactions.

THEORETICAL ASPECTS OF ION-NEUTRAL MOLECULE REACTIONS

It has been shown conclusively that ions and neutral molecules are involved in organic - inorganic halide exchange reactions in polar solvents. Since this thesis is concerned with such systems, it is relevant to review recent theories on ion-neutral molecule reactions with special reference to exchange reactions.

The Effect of Ionic Strength on the Specific Rate Constant

It has long been postulated that chemical reactions proceed by the formation of an activated complex which is in equilibrium with the reactants (26,27). Thus the reaction of A with B has been written

$$A + B \rightleftharpoons X^{\ddagger} \longrightarrow Products$$
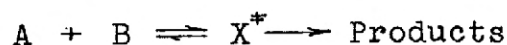
where $X^{\ddagger}$ represents the reaction complex.

The thermodynamic equilibrium constant $K^{\ddagger}$ for the equilibrium between the reactants and the complex has been defined by the equation

$$K^{\ddagger} = \frac{(fc)^{\ddagger}}{(fc)_A (fc)_B} \qquad (1)$$

where f_A f_B and $f^{\ddagger}$, the activity coefficients of A, B and the reaction complex respectively, refer to the solution at

infinite dilution. The term c, as usual, represents concentration.

According to the theory of absolute reaction rates developed by Glasstone, Laidler and Eyring (27) the velocity of a reaction will depend on the frequency of vibration of the activated complex in that direction which leads to its decomposition into products. By statistical mechanical considerations, they have derived the following expression for this frequency,

$$\nu = P \frac{k\ T}{h} \quad , \qquad (2)$$

where k and h are the Boltzman and Planck constants respectively, and T is the absolute temperature. The transmission coefficient, P, was introduced to account for the possibility that decomposition will not occur with each vibration.[1]

Following the treatment given by Glasstone, Laidler and Eyring, the velocity of the reaction is given by the product of the frequency and the concentration of the activated complex. Consequently the specific rate constant, k, for a simple bimolecular reaction is given by

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1. Since, for exchange reactions, the complex is symmetrical, there is an equal probability that decomposition will lead to exchange or to the return to the reactants. Hence P will have the value 0.5.

$$k = P \frac{\nu \, c^{\ddagger}}{c_A \cdot c_B} \quad . \tag{3}$$

Combining equations (1), (2) and (3),

$$k = P \frac{\hbar T}{h} K^{\ddagger} \frac{f_A \, f_B}{f^{\ddagger}} \quad . \tag{4}$$

Since the activity term in this equation becomes equal to unity at infinite dilution,

$$k = k_0 \frac{f_A \, f_B}{f^{\ddagger}} \quad , \tag{5}$$

where k_0 is the specific rate constant at infinite dilution.

Glasstone, Laidler and Eyring assumed a spherical activated complex which in reactions involving ions was assigned a charge equal to the algebraic sum of the charges on the reacting species. Hence in the reaction of an ion $A_{\pm}$ with a neutral molecule B the activated complex $X^{\ddagger}$ is assumed to have the same charge as the ion. The Debye-Hückel expression was used for the activity of the ion and complex and the approximate Debye-McAulay expression for the activity of the neutral molecule.

According to the Debye-Hückel theory of interionic attraction at appreciable concentrations, the activity f_i of the ionic species i is given by (28).

$$\log f_i = -\frac{A'z_i^2\sqrt{\mu}}{1+a_i B'\sqrt{\mu}} \quad , \qquad (6)$$

where A' and B' are constants for any given solvent, a_i is the mean distance of approach of other ions to $\underline{i}$, z_i is the number of electronic charges on $\underline{i}$ and μ is the ionic strength of the solution:

$$\mu = \frac{1}{2}\sum_i c_i z_i^2 \quad . \qquad (7)$$

Hückel added a correction term to equation (6) to account for polarization of solvent molecules by the ion. This effect was considered to be proportional to the ionic strength, hence

$$\log f_i = -\frac{A' z_i^2\sqrt{\mu}}{1+a_i B'\sqrt{\mu}} + C_i\mu \quad , \qquad (8)$$

where C_i is an arbitrary constant.

An expression was derived by Debye and McAulay for the activity of a neutral molecule in a solution of ionic strength μ (29). This is, in its approximate form,

$$\log f_B = C_B\mu \quad . \qquad (9)$$

Using equation (8) to evaluate the activity coefficients of the ion and activated complex, equation (9) for the activity coefficient of the neutral molecule, and assuming

the mean distance of approach, a_1 , to be the same for both ion and activated complex, Glasstone, Laidler and Eyring obtained

$$\log \frac{f_A\, f_B}{f^{\ddagger}} = \frac{A'\sqrt{\mu}}{1 + aB'\sqrt{\mu}}\, (z_{X^{\ddagger}} - z_{A_\pm}) + (C_{A_\pm} + C_B - C_{X^{\ddagger}}). \quad (10)$$

Since the charge on the complex is assumed equal to that on the ion, the first term on the right hand side of equation (10) vanishes, leaving

$$\log \frac{f_A\, f_B}{f^{\ddagger}} = (C_{A_\pm} + C_B - C_{X^{\ddagger}})\mu = C\mu . \quad (11)$$

Taking logarithms of both sides of equation (5)

$$\log k = \log k_O + \log \frac{f_A\, f_B}{f^{\ddagger}} , \quad (5a)$$

and substituting for the activity coefficient term as given by equation (11),

$$\log k = \log k_O + C\mu . \quad (12)$$

As Glasstone, Laidler and Eyring have pointed out, this equation implies that the logarithm of the rate constant for a reaction between a molecule and an ion should vary with the first power of the ionic strength. Since the experimental constant C has been found to be small, the correction term is negligible in dilute solutions.

Moelwyn-Hughes has discussed the variation in rate constant with ionic strength from a completely different standpoint (30). This author considered the experimental activation energy, E, defined by the Arrhenius equation

$$k = A e^{-E/RT} ,$$
(13)

to be the sum of an electrostatic energy increment E_e and a non-electrostatic energy increment E_n. That is,

$$E = E_n + E_e .$$
(14)

For inversion to occur in the reaction of an ion and a polar organic molecule, Moelwyn-Hughes has demonstrated that the ion must approach the end of the molecular dipole bearing opposite charge to that of the ion. It was possible to estimate the electrostatic energy term E_e in terms of the electrostatic effect between the ion and the dipole. For this energy term,

$$E_e = Nz_A \varepsilon \bar{\Phi} ,$$
(15)

where $z_A \varepsilon$ is the total electronic charge, N is Avogadro's number, and $\bar{\Phi}$ is some function of the dipole moment of B, the dielectric constant of the medium, the angle of approach, and the ionic strength of the solution.

Combining equations (13), (14) and (15),

$$K = A e^{-E_n} e^{-Nz_A \varepsilon \Phi} ,$$ (16)

whence

$$\ln k = -E_n + \ln A - Nz_A \varepsilon \Phi .$$ (17)

Moelwyn-Hughes considered E_n to be constant, and by grouping this term with $\ln A$ and setting the sum equal to a constant $\underline{a}$, he obtained

$$\ln k = a - Nz_A \varepsilon \Phi .$$ (18)

Debye (28) and Spong (31) have developed expressions for Φ, both which were used by Moelwyn-Hughes in his discussion. It is not necessary to discuss these equations here, other than to note that according to Spong, Φ for any given solvent and reactants is a function of the ionic strength alone. Thus

$$Nz_A \varepsilon \Phi = -b\mu$$ (19)

Substituting equation (19) in equation (18),

$$\ln k = a + b\mu .$$ (20)

Comparing this equation with equation (12) developed by Glasstone, Laidler and Eyring,

$$\log k = \log k_0 + C\mu ,$$ (12)

it may be noted that although the constants do not have the same significance, the equations have the same form and predict similar variation in the observed rate constant, k, with ionic strength.

The linear relation implied in these equations has been observed by Bronsted and his co-workers in the hydrolysis of acetals by mineral acids (32). The observed rate constant was found to increase with increasing hydronium ion concentration as well as with increasing concentration of neutral salts.

The Effect of Dielectric Constant on the Specific Rate Constant

To discuss the effect of change in the dielectric strength of the solution on the rate of a reaction, Laidler and Eyring have related the activity coefficient at infinite dilution to the activity coefficient in an ideal gas (33). This was done by defining an activity coefficient β by the equation

$$\alpha = \beta f , \qquad (21)$$

where α and f are the activity coefficients referred to an ideal gas and to infinite dilution respectively. Since the observed rate constant k is related to the rate constant k_o at infinite dilution by the expression

$$k = k_0 \frac{f_A f_B}{f^{\ddagger}} \quad , \tag{5}$$

it follows from equations (21) and (5) that the rate constant at infinite dilution and the rate constant in an ideal gas k_g are related by the equation

$$k_0 = k_g \frac{\beta_A \beta_B}{\beta^{\ddagger}} \tag{22}$$

whence

$$\ln k_0 = \ln k_g + \ln \frac{\beta_A \beta_B}{\beta^{\ddagger}} \tag{22a}$$

A relation between the rate constant of an ion-neutral molecule reaction and the dielectric constant of the solvent has been developed by Laidler and Eyring in the following manner (33). It was assumed that the activated complex is a sphere of radius $r^{\ddagger}$ and with a charge equal to that of the reacting ion $A_{\pm}$. The free energy change $\Delta G^{\ddagger}$ accompanying the transfer of the charged complex from a vacuum (dielectric constant unity) to a solvent of dielectric constant D was considered to be the sum of the free energy changes of four distinct steps.

a. The ion is discharged in a vacuum with free energy change ΔG_1 given by $- (z\epsilon)^2/2r$, where $z\epsilon$ is the total charge on the complex.

b. The uncharged particle is transferred to an infinitely

dilute solution with a small non-electrostatic free energy change ΔG_2 equal to some constant I_1. This free energy change is due to van der Waals type forces between the uncharged particle and the solvent molecules.

c. The particle is re-charged with a resulting free energy change ΔG_3 equal to $(z\epsilon)^2/2Dr$.

d. A second non-electrostatic term I_2 is introduced to account for the polarization and orientation of the solvent molecules surrounding the charged complex.

Hence

$$\Delta G^{\ddagger} = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 \qquad ,$$

and

$$\Delta G^{\ddagger} = \frac{(z\epsilon)^2}{2r^{\ddagger}} \left(\frac{1}{D} - 1 \right) + I_1 + I_2 . \qquad (23)$$

Since

$$\Delta G^{\ddagger} = kT \ln \beta^{\ddagger} , \qquad (24)$$

combining equations (23) and (24) yields

$$\ln \beta^{\ddagger} = \frac{(z\epsilon)^2}{2kTr^{\ddagger}} \left(\frac{1}{D} - 1 \right) + \Sigma I . \qquad (25)$$

A similar expression was obtained for the logarithm of the activity coefficient of the ion, $A_{\pm}$.

Laidler and Eyring accounted for the small free energy change associated with the transfer of the neutral

molecule from the vapor state to the infinitely dilute solution. For this discussion it will be assumed that this free energy change can be neglected and that $\ln \beta_\theta$ is equal to unity.

When these authors substituted the appropriate expressions for this activity of the ion and the reaction complex in the rate constant equation (22a), the following expression was obtained:

$$\ln \ k_0 = \ln k_g + \frac{(z\varepsilon)^2}{2 \ \pmb{\mathbb{k}} \ T} \left(\frac{1}{D} - 1 \right) \left(\frac{1}{r_A} - \frac{1}{r^*} \right) , \qquad (26)$$

in which $\pmb{\mathbb{k}}$ is the Boltzman constant, D is the dielectric constant of the solvent, and r_A and r^* are the radii of the ion and the reaction complex respectively. In deriving this equation, it was assumed that the non-electrostatic terms were small and could be neglected.

Differentiation of equation (25) with respect to the dielectric constant resulted in the expression

$$\frac{d(\ln \ k_0)}{d \ (1/D)} = \frac{(z\varepsilon)^2}{2 \ \pmb{\mathbb{k}} \ T} \left(\frac{1}{r_A} - \frac{1}{r^*} \right) \qquad . \qquad (27)$$

Accordingly, a plot of $\log k_0$, the specific rate constant at infinite dilution, versus the reciprocal of the dielectric constant should yield a straight line with slope equal to the right hand side of equation (27). Laidler and Eyring have pointed out that the radius of the complex will

normally be greater than that of the ion, so that the line should have a positive slope. This is equivalent to saying that the specific rate constant should decrease with increasing dielectric constant.

Scatchard has pointed out that this relation for ion-molecule reactions was inferred in his development for the effect of dielectric constant on reactions between ions (34). He assumed the reaction complex to be two spheres, the direct opposite of the spherical model adopted by Laidler and Eyring.

Several ion-neutral molecule reactions, for example the decomposition of sulfonium salts in mixed water-alcohol solvents (35), have been found to exhibit the behavior predicted by equation (27).

In comparing the effect of water, methanol and acetone on the forward and reverse exchanges of iodide ion with methyl bromide, Moelwyn-Hughes observed that the parameter A of the Arrhenius equation (13) was essentially constant in these solvents (36). The corresponding activation energies however decreased sharply with decreasing dielectric constant. He concluded that the primary effect of change of solvent in these reactions was to alter the activation energy.

The Effect of Solvent on Activation Energy

According to Moelwyn-Hughes, the activation energy for the reaction between an ion and a neutral molecule may be regarded as the sum of a non-electrostatic energy term E_n and a corresponding electrostatic term E_e (30). Thus, as was shown in equation (14),

$$E = E_n + E_e \ . \tag{14}$$

This author has pointed out that, since the electrostatic energy term is dependent on the dielectric constant, which in turn is temperature dependent, the activation energy should be temperature dependent.

Introducing the dependence of dielectric constant on the temperature, Moelwyn-Hughes obtained

$$E = E_n + (1 - LT)E_e \ , \tag{28}$$

where L is defined by the equation

$$- \left(\frac{d \ln D}{dT} \right)_P = L \ . \tag{29}$$

He calculated the magnitude of the electrostatic energy term for aqueous solutions and obtained a value of E_e which was less than 0.1 kilocalories per mole. Since the term L in equation (29) is small, (for methanol, L is equal to 2.34×10^{-3}),

it was concluded that the influence of the temperature dependent term in equation (28) will be negligible. Therefore, no detectable change in the observed activation energy due to the temperature dependence of the dielectric constant is to be expected.

Ogg and Polanyi considered the activation energy of halide ion-organic halide exchange or interchange to be the sum of four distinct energy increments (37). The first of these increments involved the electrostatic interaction of the ion and the molecule as the charge of the former approached the dipole of the latter. This term is therefore essentially equal to the E_e term in the Moelwyn-Hughes treatment. Secondly, in the activated complex, the halide atom will be displaced from its stable position and energy E_d must be supplied to distort the carbon-halide bond. Furthermore, since these reactions are accompanied by inversion, a third term E_p was introduced to allow for the energy required to shift the carbon bonds from the tetrahedral to a planar configuration. Finally, the energy required to overcome any solvation barrier, E_s, was included. From these considerations then, the activation energy for reaction between an ion and a neutral molecule is given by

$$E = E_e + E_d + E_p + E_s \qquad (30)$$

The Effect of Solvent on the Heat and Entropy of Activation

The equilibrium constant $K^{\ddagger}$ has been defined as the constant for the equilibrium between the reactants and the activated complex:

$$A + B \rightleftharpoons X^{\ddagger} \longrightarrow products.$$
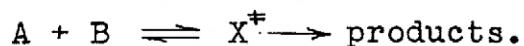
It has been repeatedly demonstrated that, as in any equilibrium process, thermodynamic functions can be associated with this equilibrium (26,27).

Thus a free energy of activation, $\Delta G^{\ddagger}$, has been defined in terms of $K^{\ddagger}$ in the usual manner:

$$K^{\ddagger} = e^{-\Delta G^{\ddagger}/RT} . \tag{31}$$

Similarly the heat and entropy of activation have been defined by the relation

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} . \tag{32}$$

It has been observed that heats and entropies of solution are often related by an expression of this type:

$$T\Delta S = \beta \Delta H - \delta \tag{33}$$

where β and δ are constants. Since equation (33) should apply equally well to the reactants and to the complex, Evans

and Polanyi have suggested that the following relation should hold for reactions in various solvents (38):

$$T \Delta S^{\ddagger} = \beta \Delta H^{\ddagger} + \gamma \; . \qquad (34)$$

Accordingly, there should be a linear relation between the heat and entropy of activation. This has been found to be true for several reactions in solution.

Laidler and Eyring have pointed out that exceptions to this general equation are invariably exceptions to the expected rate constant-dielectric constant relation (33). They attribute these discrepancies to solvation of the reactants or of the activation complex.

Solvent Effects and Exchange Reactions

These theoretical considerations of ion-neutral molecule reactions may be briefly summarized as follows.

(a) Increasing ionic strength at appreciable concentrations should result in a small linear increase in the observed specific rate constant according to equation (12) and (20). By the development of the former,

$$\log k = \log k_o + C\mu \; , \qquad (12)$$

where k is the observed rate constant at ionic strength μ,

k_o is the rate constant at infinite dilution, and C is a constant.

(b)   Increase in the dielectric constant of the medium should result in the decrease of the specific rate constant at infinite dilution according to equation (27).

$$\frac{d(\ln k_o)}{d\,(1/D)} = \frac{(z\varepsilon)^2}{2\,k\,T} \left(\frac{1}{r_{A_\pm}} - \frac{1}{r^{\ddagger}} \right) \tag{27}$$

where $z\varepsilon$ is the charge on the ion, D is the dielectric constant of the solvent, k is the Boltzman constant and $r_{A_\pm}$ and $r^{\ddagger}$ are the radii of the ion and complex respectively.   Failure of the rate constants to obey this reaction may be due in part to solvation effects.

(c)   According to Ogg and Polanyi, the activation energy of a reaction involving an ion and a neutral organic molecule may be considered to be the sum of four energy terms:

$$E = E_e + E_d + E_p + E_s \tag{30}$$

where E_e is an electrostatic energy term, E_d and E_p are derived by structural considerations, and E_s represents the energy necessary to overcome solvation effects.

In the study of halide exchange reactions in polar solvents, it has been found, almost without exception, that the specific rate constant decreased with increasing halide

ion concentration, contrary to the behavior predicted in (a) above. In one exchange (lithium bromide with octyl bromide in acetone (15)), this decrease was attributed to the association of the inorganic halide. It would appear that in this instance the connection term in equation (12) was not sufficiently large to be evident in the specific rate constant.

There are not sufficient exchange data in the literature to permit a fair comparison between experimental results and the expression developed by Laidler and Eyring relating the dielectric constant and the rate constant (equation (12)). The need for a comprehensive study of an exchange reaction in various solvents is evident. It is interesting to note that for such a study involving given organic and inorganic halides, all of the terms in the Ogg-Polanyi energy equation (30) will be constant save for the solvation term. Hence any variation in activation energy from solvent to solvent would be due, according to this theory, to solvent effects.

The present study was made to obtain information about one exchange reaction in a series of solvents, and to determine, if possible,

   (a) the effect of ionic strength on the rate constants,

   (b) the solvent effect on the rate constants, and

   (c) the solvent effect on the activation energy.

Using this information, it was hoped to have some test of the various theoretical conclusions as they might be applied to exchange reactions.

EXPERIMENTAL PROCEDURE AND RESULTS

Of the halogen isotopes, the radioactive iodine isotope I^{131} is the most satisfactory for exchange studies. Owing to its moderate half life (8 days), radioactive decay of this isotope is insignificant during normal counting periods, yet for millicurie amounts is sufficiently rapid to simplify the disposal of radioactive waste products. Its radiation can easily be detected by end-window Geiger tubes. Since this isotope could be obtained from the Atomic Energy Project of the National Research Council, the exchange of iodine between an inorganic and organic iodide was selected as the reaction to be studied in this investigation of solvent effects.

REACTANTS AND SOLVENTS

Organic Iodide

Normal butyl iodide was used as the organic halide in the exchange reactions. This compound has a relatively low vapor pressure at room temperature and was therefore easily handled. Moreover, choice of the same organic halide as that used by Hodgson et.al. in exchange studies in acetonitrile (17) made it possible to include their data in an examination of solvent effects.

The n-butyl iodide was supplied by Brickman and Co., Montreal. As received, it contained some free iodine, which was removed by shaking the liquid with a small amount of mercury. It was filtered and freshly distilled as required to avoid the recurrence of iodine due to decomposition. The fraction in the boiling range 129.8°-130°C. was taken for these experiments.

Inorganic Iodide

For this study it was essential that the inorganic halide have an appreciable solubility in solvents of low as well as high dielectric constant. Several possible inorganic halides were considered.

The alkali and alkaline earth halides did not satisfy the solubility requirements. Although phosphorus and arsenic triiodides were soluble to some extent in solvents of low dielectric constant, their tendency to decompose in the presence of oxygen and of moisture would have imposed serious experimental difficulties. Hydrogen iodide and iodine itself were suitable from the standpoint of solubility. However, the former, being a powerful reducing agent, does not form stable solutions. On the other hand, iodine has been observed to form complex ions in many solvents (39), and difficulties in interpretation of exchange data with this halide were forseen.

Consequently, in spite of its ease of oxidation, hydrogen iodide was chosen as the inorganic reactant.

It was found that hydrogen iodide could be most conveniently handled as a stock solution prepared by the addition of gaseous hydrogen iodide to the solvent. Gaseous hydrogen iodide was prepared by the action of water on reagent grade phosphorus and iodine (40). The equation for the overall reaction is

$$2P + 5I_2 + 8H_2O \longrightarrow \overline{10HI} + 2H_3PO_4 \quad .$$
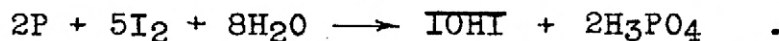
The apparatus used in the generation and purification of hydrogen iodide is illustrated in Fig. 1. The generator consisted of a 200 ml. roundbottom flask fitted with a dropping funnel and a delivery tube to the purification train of a small U-tube and two 24 mm. traps, and finally the hydrogen iodide storage trap. With the exception of the rubber stopper holding the dropping funnel, standard taper ground-glass joints were used throughout the apparatus. It could be completely dismantled for cleaning purposes. Apiezon "M" grease was found to be only slightly susceptible to attack by hydrogen iodide, and was used to lubricate the stopcocks and ground joints. The system was swept with dry nitrogen prior to the generation of hydrogen iodide.

Fig. 1.

Hydrogen Iodide Generator and

Purification Train.

A. Hydrogen Iodide Generator
B. Red phosphorous absorption tube
C. Trap at 0°C.
D. Trap at -34°C.
E. Storage Trap, -76°C.
F. Nitrogen Inlet
G. Outlet to fume hood
H. Stock solution flask
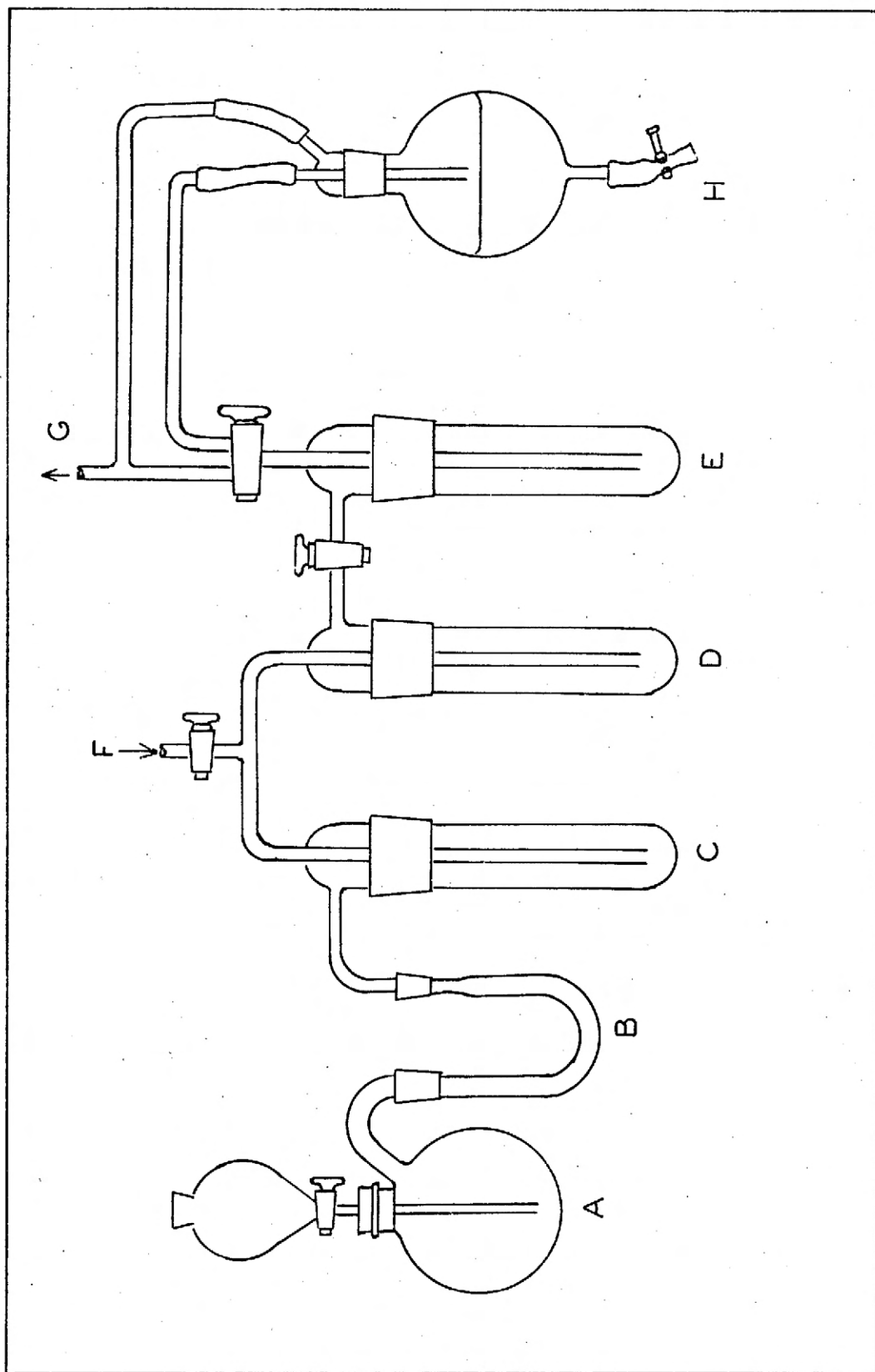
Water was added dropwise to a mixture of twenty parts iodine to one of red phosphorous by weight. The reaction was initially exothermic and the reaction flask was cooled during this period to prevent undue sublimation of iodine. The gas evolved was purified by passing it over red phosphorous, through the first trap which was maintained at $0^{\circ}C.$, and the second trap, maintained slightly above the boiling point of hydrogen iodide $(-35^{\circ}C.)$. The last trap, cooled to $-76^{\circ}C.$ by a dry ice - acetone mixture, served to collect the hydrogen iodide. The product obtained was pure white, with a melting point of $-51^{\circ}C.$ as compared with $-50.8^{\circ}C.$ reported in the literature (40).

Solvents

Preparation of the Solvents

Hydrogen iodide was found to react with many common organic solvents. In preliminary solubility studies, it was found that it was immediately oxidized to iodine by nitrobenzene and nitromethane. Similar effects were observed in aldehydes and ketones. After a short initiation period, long white needles were formed when gaseous hydrogen iodide was added to acetonitrile. (This compound, which slowly decomposed in contact with the air, may be ethyl iodimide or ethyl diiodamide). Furthermore, there is reason to believe that complex ions are formed between basic organic solvents, such as aniline, and

this acid (41).

Hydrogen iodide does not react with paraffinic and aromatic hydrocarbons, nor with the simple aliphatic alcohols and carboxylic acids. In this study, toluene, glacial acetic acid, methanol, ethanol, n-butanol, n-hexanol, and n-dodecanol were employed. Since it is believed that ions will attract the more polar molecules in mixed solvents and thereby cause non-uniformity in the dielectric strength of the medium (27), no attempt was made to use mixed solvents in these investigations.

The source and preparation of the solvents were:

Methanol (A.C.S. Reagent Grade Acetone Free; supplied by Brickman and Co., Montreal). This solvent was dried with magnesium methylate according to the procedure outlined by Fieser (42) and distilled. On redistillation, the fraction boiling between 64.5° and 64.7°C. was retained.

Ethanol (Industrial Absolute, 99.5%, supplied by Commercial Alcohols Inc.). Aldehydes and ketones were reduced by refluxing the alcohol with powdered zinc and potassium hydroxide. The distillate from this treatment was dried with magnesium ethylate (42), and the fraction boiling at 78.3°C. was recovered by redistillation.

n-Butanol (Supplied by Brickman and Co., Montreal). The butanol was purified by distillation only, and the fraction

boiling between 117.2° and 117.5°C. collected for use.

n-Hexanol (Supplied by Brickman and Co., Montreal). The fraction of this solvent boiling between 156° and 157°C. was taken for these investigations.

n-Dodecanol (Supplied by Brickman and Co., Montreal). Normal dodecyl alcohol (lauryl alcohol) has a freezing point of 24°C. and a boiling point of 258°C. at 760 mm. pressure. The alcohol supplied was found to have a freezing point of 17°C. This was distilled at 30 mm. pressure, and the first 25% and the last 15% discarded. The product from this distillation, with a melting point of 20°C. was redistilled under nitrogen and the fraction boiling between 160°-162°C./30 mm. was collected. This fraction, with a melting point of 21°C., was considered sufficiently pure for present purposes.

Glacial Acetic Acid (Reagent Grade, Nichols Chemical Co.). The fraction boiling between 116.5° and 116.7°C. was used in these experiments. The melting point of this fraction was 16.2°C., indicating the presence of traces of water. No attempt was made to remove this water.

Toluene (Mallinkrodt Reagent Grade). This solvent was dried by distillation from sodium. The fraction boiling from 110.5° to 110.8°C. was retained.

Benzene (A.C.S. Reagent Grade, Thiophene Free, supplied by Brickman and Co., Montreal). Benzene was distilled from

from sodium to yield a fraction with a boiling point of 80.1°C. This material was used in the dielectric constant determinations.

It has been observed that hydrogen iodide reacts slowly with dissolved oxygen (40). Consequently the solvents, with the exception of the dodecanol (see above), were refluxed with nitrogen following purification. They were subsequently stored under nitrogen in all-glass flasks designed to permit transfer of the solvent by nitrogen pressure.

The tank nitrogen used in these experiments contained about 0.2% oxygen which was removed by passing the gas over copper turnings at 500°C. Moisture in the nitrogen was removed by anhydrous calcium chloride.

Dielectric constants of the solvents

The effect of the solvent on the rate of reactions between ions and molecules has been expressed by Laidler and Eyring in terms of the dielectric constant of the solvent (equation 12). The dielectric constants of methanol, ethanol and toluene at 25°C. were available in the literature, but the values for the other solvents have not been reported. Consequently they were determined experimentally for n-butanol, n-hexanol, n-dodecanol and acetic acid.

An experimental condenser consisting of two concentric brass cylinders was constructed following a design described by Funt (43). The larger of the cylinders was closed at one end by a hard rubber plug and formed the container for the liquid under investigation. The position of the inner electrode was maintained at one end by the plug and at the other by a similar hard rubber lid to which it was attached. In using this condenser, the outer electrode was filled so that the liquid overflowed when the inner electrode was lowered into position. By this procedure the performance of the condenser was completely reproducible.

The measurements were made with a General Radio Co. capacitance bridge (type T-716c, Schering circuit), using a Clough Brengle oscillator as the high frequency source and a Royal Canadian Navy radio receiver as the detector.

The capacity of the experimental condenser when filled with the various solvents was determined by the substitution method. In the procedure, the capacitance bridge was balanced with a precision variable condenser of known capacitance, contained in one arm of the Schering bridge, at some capacity C'. The experimental condenser containing the liquid $\underline{x}$ as a dielectric medium was connected to the bridge in parallel with the precision condenser, and the bridge again

balanced by reducing the capacity of the precision condenser to some value C. Since the capacities of parallel condensers are additive, this procedure in effect substituted the unknown capacity for part of the precision condenser. Hence

$$C_x = C' - C. \tag{35}$$

The unknown capacity C_x is the sum of the capacity of the experimental condenser and the stray capacitance effects, C_o. That is,

$$C_x = C_o + D_x C_g, \tag{36}$$

where D_x is the dielectric constant of the liquid $\underline{x}$ and C_g is the capacity of the experimental condenser in air.

Theoretically, it was possible to calculate the constant C_g from the geometry of the experimental condenser. However, it was more convenient to determine C_x for substances of known dielectric constant, substitute for C_x and D_x in equation (36) and solve the two simultaneous equations obtained for C_o and C_g. Air and benzene were used for this purpose.

The experimental condenser was placed in a thermostat at $25° \pm 0.05°C$. with oil as the liquid medium, and the capacities determined at 100 kilocycles. The results have been summarized in Table I.

TABLE I

Determination of Capacitance by the Substitution Method

Temperature: $25° \pm 0.05°C$.
Frequency: 100 Kilocycles

Capacity of Standard Condenser at bridge balance:
$C' = 997.0$ picofarads $(\mu\mu f)$
$d' = 0.0005$

Solvent	C picofarads	$d \times 10^4$	C_x picofarads
Air	962.8	6.5	34.2
Benzene	932.8	6.6	64.2
Ethanol	394.5	1455	582
n-Butanol	578.5	315	419
n-Hexanol	685.3	95.0	311.7
n-Dodecanol	841.2	0.5	155.8
Acetic Acid	838.3	24.0	158.7

A power loss is associated with all condensers which, if it is large, must be taken into account in the determination of the capacity of the condenser. In this bridge, the power loss was expressed in terms of the dissipation factor, d. When this factor was less than 0.1, no correction to equation (35) was required, but with the condenser filled with ethanol the dissipation factor exceeded 0.1, and the unknown capacity C_x was obtained using the equation.

$$C = \frac{(C'-C) - C(d-d')^2}{1 - (d-d')^2}, \quad (0.1 < d < 1.0) \quad (37)$$

where the terms d and d' correspond to the power loss during the determination of capacities C and C' respectively (44).

Taking the dielectric constant of benzene at 25^OC. to be 2.273 (45), the constants C_O and C_g were found to be 10.6 and 23.6 $\mu\mu$f (picofarads) respectively. An equation for D_x in terms of C_x was obtained by substituting these numerical values in equation (36) and rearranging. Hence

$$D_x = \frac{C_x - 10.6}{23.6} \quad . \tag{38}$$

The experimentally determined dielectric constants are given in table II, along with the dielectric constants of acetonitrile, methanol and ethanol as reported in the literature.

TABLE II

Dielectric Constants at 25^OC.

Solvent	D (exp.)	D Literature	Reference
Acetonitrile		36.7	(45)
Methanol		32.66	(46)
Ethanol	24.2	24.26	(45)
n-Butanol	17.3		
n-Hexanol	12.8		
n-Dodecanol	6.15		
Acetic Acid	6.27		

The Standardization and Stability of Hydrogen Iodide Solutions

Stock solutions of hydrogen iodide were prepared by distillation of hydrogen iodide into the solvent, with the temperature of the storage trap increased to -35°C. (see Fig.1). The first and last fifteen percent of the hydrogen iodide in the trap were discarded. No lubricant was used on the ground glass joint of the flask containing the stock solution.

The concentrations of the stock solutions were determined by titration of aliquots with standard silver nitrate solution, using eosin as an indicator (47). The determinations were made in the presence of the solvent. Methanol was added to those solvents which were insoluble in water so that a homogeneous solution was maintained during addition of the silver nitrate solution. It was found that eosin did not behave as an adsorption indicator in the presence of the higher alcohols, and these solutions were titrated to the floc-point, i.e. the point at which the silver iodide precipitate coagulated.

The silver nitrate solution was standardized for each determination with reagent grade potassium iodide. The solvent used to dissolve the potassium iodide contained the same quantity of organic solvent as the hydrogen iodide solution, and

was acidified with acetic acid so that the conditions would be essentially identical. The value obtained for the normality of the silver nitrate was not influenced by the nature of the organic solvent involved. In all titrations, precision of better than 0.5% was observed, and where eosin was effective as an indicator, the precision was better than 0.2%

Decomposition of the stock solution, even during their preparation, was made evident by the pink color of free iodine. Some of this decomposition was undoubtedly due to trace amounts of oxygen remaining in the solvent, in spite of the precautions taken to remove and exclude it. In addition, the instability of hydrogen iodide in the presence of aldehydes and ketones was demonstrated in the preliminary solubility studies, and much of the decomposition may be attributed to these and other easily reduced impurities in the solvents. Unfortunately, impurities of this type were difficult to remove. For example, although the ethanol was rigorously purified, the absortion spectrum of a 10^{-4} molar solution in this solvent showed that a large part of the hydrogen iodide had been oxidized to iodine. Therefore stock solutions diluted to low concentrations were of doubtful composition and were avoided.

The degree of decomposition was estimated by

colorimetric comparison with solutions of iodine in the same solvent. Decomposition of 0.5% of the hydrogen iodide was tolerated. In most of the solvents the stock solution could be used for four to five days after its preparation before this arbitrary limit was exceeded.

DISSOCIATION CONSTANTS OF HYDROGEN IODIDE

It is well known that the ions of strong electrolytes show a decreasing tendency for dissociation, i.e. an increasing tendency to form ion pairs, as the dielectric constant of the solvent decreases (28). In fact, it has been suggested that in solvents of low dielectric strength, ion triplets as well as ion pairs may be formed. Such association of hydrogen and iodide ions might be expected to be greater, for example, in dodecanol ($D_{25}o$, 6.15) than in methanol ($D_{25}o$, 32.7).

The observed rate of reaction between an ion and a neutral molecule, in this instance iodide ion and butyl iodide, will depend on the concentration of the ion in the solution. Consequently, before proceeding to the exchange results, it is necessary to discuss the electrolytic dissociation of hydrogen iodide in the solvents used in the exchange experiments, with a view to estimating the dissociation constants.

Conductance of Hydrogen Iodide Solutions

Conductance experiments were made to obtain information on the association of hydrogen iodide in methanol, ethanol, butanol, hexanol, dodecanol and acetic acid. These measurements were made with a portable conductance bridge (Industrial Instruments Co., Model RC-1), and a small conductance cell (capacity 12ml., dead space about 12ml.; cell constant 0.318), maintained at $25^{\circ} \pm 0.02^{\circ}$C. in an oil bath. The conductance data are given in Tables III and IV.

At concentrations greater than 5×10^{-3} molar, decomposition of the hydrogen iodide solutions was maintained below 1% and the accuracy of the conductance data was considered to be defined by the accuracy of the bridge ($\pm 2\%$). However, at concentrations below 10^{-3} molar the decomposition of the solution became the predominating factor and the accuracy could no longer be estimated. No conductance measurements were made at concentrations less than 5×10^{-4} molar.

In Fig.2, the logarithm of the equivalent conductance Λ has been plotted against the logarithm of the hydrogen iodide concentration, in accordance with the method adopted by Fuoss and Kraus to show the variation in conductance with the dielectric constant of the solvent (28).

TABLE III

The Conductance of Hydrogen Iodide

in Methanol, Ethanol and n-Butanol at 25°C.

Solvent, Dielectric Constant	a_o (conc. HI) Moles/liter	$L \times 10^4$ Specific Conductance	Λ Equivalent Conductance
Methanol	0.200	231	116
	0.100	127.3	127
D = 32.7	0.0500	69.1	138
	0.0250	36.9	148
	0.0125	19.8	159
	0.00625	11.8	169
	0.00312	5.51	177
	0.00156	2.86	183
	0.00078	1.46	187
Ethanol	0.388	147	37.9
	0.194	81.3	41.9
D = 24.2	0.0970	44.6	46.0
	0.0485	24.9	52.4
	0.0243	13.7	56.3
	0.01215	7.52	61.9
	0.00607	4.03	66.5
	0.00304	2.15	70.8
	0.00152	1.13	74.4
	0.00076	0.594	78.0
n-Butanol	0.216	23.6	10.9
	0.108	13.5	12.5
D = 17.3	0.0540	7.50	13.9
	0.0270	4.13	15.3
	0.0135	2.29	17.0
	0.00675	1.24	18.4
	0.00337	0.675	19.9
	0.00168	0.378	22.5
	0.00084	0.212	25.5

TABLE IV

The Conductance of Hydrogen Iodide

in n-Hexanol, n-Dodecanol and Glacial Acetic Acid at 25°C.

Solvent, Dielectric Constant	a_0 (conc. HI) moles/liter	$L \times 10^{-4}$ Specific Conductance	Λ Equivalent Conductance
n-Hexanol	0.289	9.94	3.44
	0.145	4.82	3.33
D = 12.8	0.0722	2.23	3.09
	0.0361	1.04	2.89
	0.0181	0.540	2.99
	0.00902	0.288	3.29
	0.00451	0.164	3.64
	0.00226	0.0863	3.82
	0.00057	0.0250	4.40
n-Dodecanol	0.396	1.89	0.477
	0.198	0.732	0.370
D = 6.15	0.0990	0.255	0.258
	0.0495	0.0652	0.132
	0.0248	0.0204	0.0823
	0.0124	0.00974	0.0906
	0.0062	0.00621	0.100
	0.0031	0.00333	0.107
Acetic Acid	0.273	9.72	3.56
	0.136	2.75	2.02
D = 6.27	0.0680	0.743	1.09
	0.0340	0.253	0.745
	0.0170	0.109	0.642
	0.00850	0.0567	0.668
	0.00425	0.0337	0.793
	0.00212	0.0209	0.985
	0.00106	0.0131	1.235

Fig. 2.

Effect of Dielectric Constant on

Hydrogen Iodide Conductance.

A.   Methanol
B.   Ethanol
C.   n-Butanol
D.   n-Hexanol
E.   Acetic Acid
F.   n-Dodecanol
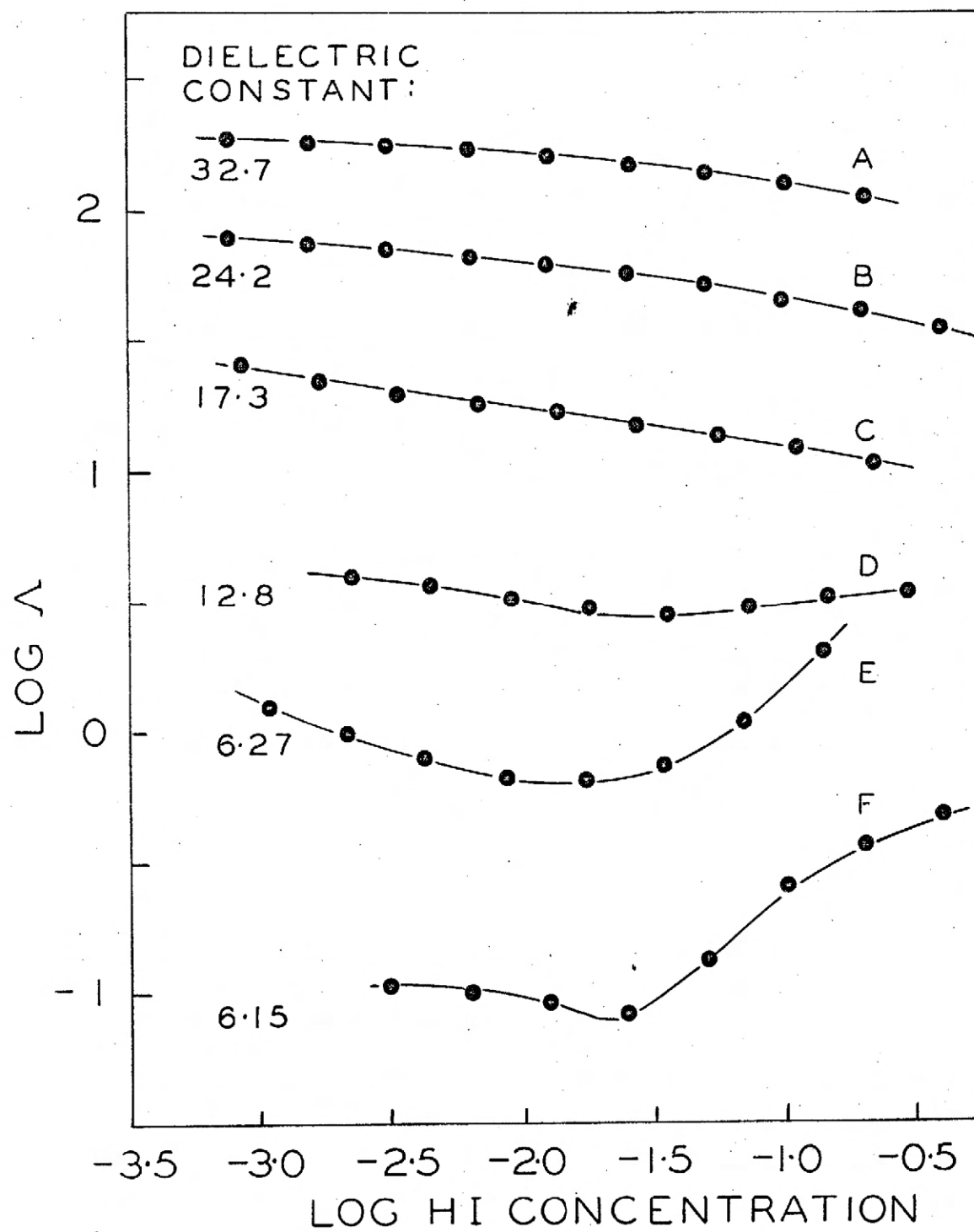
It is evident that the equivalent conductance in n-hexanol, n-dodecanol and acetic acid exhibited a minimum in the concentration range studied, and the electrolytic dissociation of hydrogen iodide in these solvents will therefore be discussed separately.

Dissociation of Hydrogen Iodide in Methanol, Ethanol and Butanol

Kraus and Bray showed that a number of strong electrolytes in solvents of low dielectric constants obeyed the Ostwald dilution law (28):

$$K = \frac{\Lambda^2 c}{\Lambda^0 (\Lambda^0 - \Lambda)} \quad , \tag{39}$$

where K is the dissociation constant, Λ is the equivalent conductance at concentration c and Λ^0 is the conductance at infinite dilution. With the introduction of the theory of interionic attraction it became apparent that even in dilute solutions the calculation of dissociation constants from conductance data should be based not on Λ^0, but on Λ', the conductance of the electrolyte at finite concentrations in the absence of ionic association. Using the Debye-Hückel limiting law, Fuoss and Kraus (48) and later, Shedlovsky (49), devised graphical methods for the simultaneous determination of Λ^0 and the dissociation constant K using conductance data alone.

Theoretically, then, it should be possible to determine the dissociation constants of hydrogen iodide in methanol, ethanol and butanol using the conductance data recorded in Table III. However, these methods require conductance information at low concentrations, and in view of the uncertainty associated with the results obtained for concentrations less than 5×10^{-3} molar, use of the Fuoss and Kraus or the Shedlovsky treatment could not be justified.

It was shown (50) that the Fuoss and Kraus method of successive approximations could be applied with satisfactory results to the conductance data obtained by Goldschmidt and Dahl for hydrogen chloride, bromide and iodide in ethanol (51). The dissociation constants given by these calculations are recorded in Table V. Ogston obtained essentially the same figure for the dissociation constant of hydrogen chloride in this solvent (52). Moreover, the activity coefficient of hydrogen chloride in ethanol was found by E.M.F. measurements to be represented by

$$- \log f = A \sqrt{c} \quad , \tag{40}$$

but the parameter A was greater than that predicted by the Debye-Hückel limiting law, indicating the formation of associated ion pairs (53).

TABLE V

Dissociation Constants of
the Hydrogen Halides at 25°C.

Solvent	Hydrogen Halide	K MacInnes (50)	K Ogston (52)
Methanol	HCl		0.118
Ethanol	HCl	0.015	0.0189
	HBr	0.022	
	HI	0.020	

Ogston found dissociation constant of hydrogen chloride in methanol to be 0.118 (52). The dissociation constant for hydrogen iodide in methanol has not been reported in the literature. However, in view of the similarity in dissociation constants reported for the hydrogen halides in ethanol (see Table V), it is reasonable to assume that the dissociation constants for HCl and HI in methanol will be of the same order. For the purpose of the present investigation, then, the dissociation constant of hydrogen iodide in methanol may be assumed to be 0.1.

Dissociation of Hydrogen Iodide in Hexanol, Dodecanol and Acetic Acid

The conductance minimum observed for hydrogen iodide in hexanol, dodecanol and acetic acid is characteristic of

electrolytes in solvents of low dielectric constant. An explanation of this behavior has been proposed by Fuoss and Kraus, based on the formation of triple ions (28, 54). Their argument will be discussed here using hydrogen iodide as the model.

Fuoss and Kraus assumed that in the addition to the formation of ion pairs in solution,

$$H^+ + I^- \rightleftharpoons HI \quad ,$$
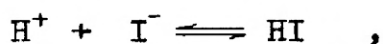
the solute ions and ion pairs may associate to form triple ions,

$$HI + I^- \rightleftharpoons IHI^- \ ,$$
$$H^+ + HI \rightleftharpoons HIH^+ \ .$$
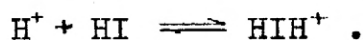
To avoid the complication of considering two different triple ion constants, they assumed the triple ions to be formed to the same extent[1]. The instability constant, K_3, associated with triple ion formation and assumed to be the same for both ions, was expressed in terms of the concentrations of the ions, ion pairs and triple ions by

$$K_3 = \frac{ai}{j} \quad , \tag{41}$$

---

1. Although this assumption may be valid for simple ions of approximately the same size, it is not likely to be true for the hydrogen and iodide ions. It has been accepted here as a first approximation.

where on this model $\underline{a}$, $\underline{i}$ and $\underline{j}$ represent the concentration of hydrogen iodide, the simple ions and the triple ions, respectively. Similarly the dissociation constant K of the ion pair was given by

$$K = \frac{i^2}{a} \ .\qquad (42)$$

$\propto$ and δ were defined as the fraction of the total electrolyte existing as simple and triple ions respectively, and were assumed to be small compared with unity. Thus, $\underline{a}$, the concentration of the ion pairs was taken to be equal to the total concentration of the electrolyte a_0. $\propto$ and δ were then expressed in terms of the total concentration and the equilibrium constants by the equations

$$\propto \ = (K/a_0)^{\frac{1}{2}} \ ,\qquad (43)$$

$$\text{and} \qquad \delta \ = (Ka_0)^{\frac{1}{2}}/K_3 \ .\qquad (44)$$

Fuoss and Kraus pointed out that, unlike the ion pairs, the triple ions will be capable of conducting electricity, and that the conductance Λ of a solution containing both simple and triple ions will be given by the sum of the contributions of the simple and triple ions. Hence

$$\Lambda \ = \ \propto \Lambda^o \ + \ \delta \Lambda^o_3 \ ,\qquad (45)$$

where Λ^o and Λ^o_3 are the sum of the limiting ionic conductances of the two simple ions and the two triple ions respectively. In this expression the terms correcting for interionic sttraction have been discarded.

Combining equations (43), (44) and (45), they obtained

$$\Lambda = \left(\frac{K}{a_o}\right)^{\frac{1}{2}}\Lambda^o + \frac{(Ka_o)^{\frac{1}{2}}}{K_3} \Lambda^o_3 \quad . \tag{46}$$

It was immediately evident from equation (46) that if triple ions are formed in solution, the conductance must pass through a minimum. At low concentration, the conductance will be due to simple ions alone and will decrease with increasing concentration according to the first term. At higher concentrations, however, the absolute value of the second term (i.e. the conductance due to the triple ions) will exceed that of the first term and the observed conductance will increase.

By rearranging equation (46), they obtained

$$\Lambda a_o^{\frac{1}{2}} = K^{\frac{1}{2}} \Lambda^o + \frac{K^{\frac{1}{2}}}{K_3} \Lambda^o_3 a_o \quad . \tag{47}$$

These authors showed that a plot of $\Lambda a_o^{\frac{1}{2}}$ versus a_o should result in a straight line with slope equal to $K^{\frac{1}{2}}\Lambda^o_3/K_3$ and intercept equal to $K^{\frac{1}{2}}\Lambda^o$.

The conditions for minimum conductance were obtained by differentiating equation (46) with respect to the concentration and setting the result equal to zero. Hence

$$ K_3 = \Lambda_3^{\circ} a_m / \Lambda^{\circ} \quad , \tag{48} $$

where a_m is the concentration of the electrolyte at minimum conductance. By restricting equation (46) to the conditions existing at the minimum point and substituting for K_3 in terms of equation (48), they obtained

$$ K^{\frac{1}{2}} = \frac{\Lambda_m a_m^{\frac{1}{2}}}{2 \Lambda^{\circ}} \quad , \tag{49} $$

where Λ_m is the minimum conductance.

Values of K and K_3 have been calculated from conductance data by the graphical analysis of equation (47) and by the substitution of concentration and conductance at the minimum point in equations (48) and (49). It has been the practice to use values for the limiting conductance, Λ° , obtained by extrapolation of the conductance data to infinite dilution. When the limiting conductance could not be obtained directly, as has often been found in solvents of very low dielectric constant, Walden's rule has been employed to obtain an estimate of Λ° . The limiting conductance of the triple ions cannot be obtained

experimentally and can only be assigned some reasonable value, usually one-half or one-third of the limiting conductance of the simple ions.

In view of the conductance minima observed for hydrogen iodide in hexanol, dodecanol and acetic acid, it appears that triple ions were formed in these solvents. According to equation (47), then, a plot of $\Lambda a_0^{\frac{1}{2}}$ versus the concentration of the electrolyte a_0 should result in a straight line. While this was observed for the solute in acetic acid, the data for conductance in the two alcohols did not give a linear plot. The graphs for acetic acid and hexanol are illustrated in Fig. 3.

The failure of the conductance data for the alcohols to satisfy equation (47) may be due in part to the assumptions made in the derivation of the equation. However the error in the conductance data introduced by the deterioration of the solution is believed to be primarily responsible for these discrepancies.

Because of the uncertainty in the conductance data in dilute solutions, graphical analysis and equation (47) were used to estimate K and K_3 only for the solute in acetic acid. Furthermore, these limitations made the direct deter-

Fig. 3.

Conductance of Hydrogen Iodide

in Hexanol and Acetic Acid.

$\Lambda a_0^{\frac{1}{2}}$ versus a_0
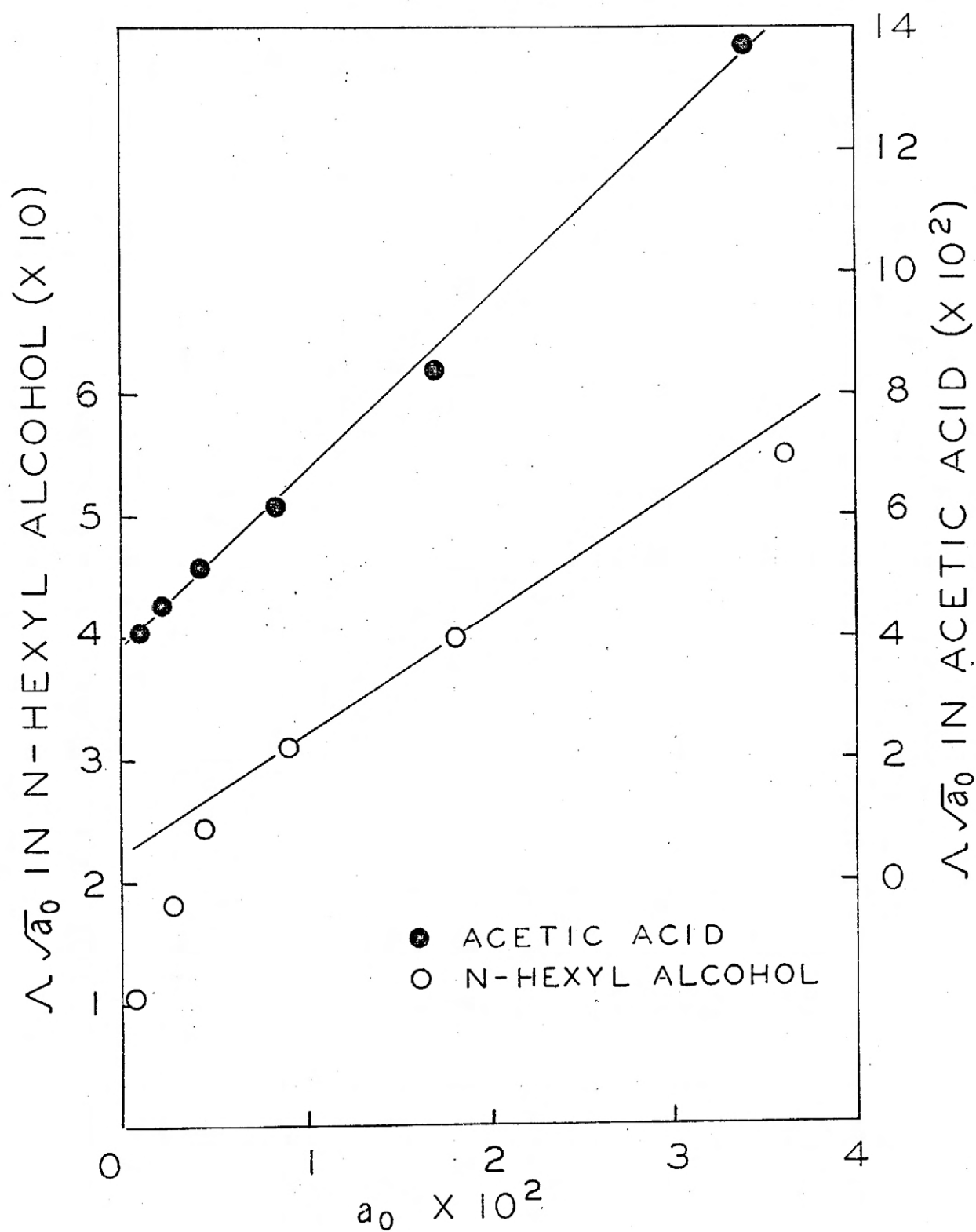
mination of the limiting conductance Λ^o impractical. However the decomposition of hydrogen iodide was negligible at the concentrations corresponding to the conductance minima, hence the constants K and K_3 could be estimated by equations (48) and (49).

Walden's rule was used to estimate the limiting conductance Λ^o required in the solution of equation (49). The ionic conductance of the hydrogen and iodide ions in methanol and ethanol was obtained from the Landolt-Bornstein tables (45) and used to establish the conductance-viscosity constant. The data used in these calculations are given in Table VI. The available information on hydrogen chloride are included in this table to indicate the constancy of the conductance-viscosity product in the aliphatic alcohols.

The conductance-viscosity product for hydrogen chloride was found to decrease from methanol to propanol, and the same trend was evident for hydrogen iodide. As a first approximation, the Walden constant was assumed to be 100 mho poise per equivalent for hydrogen iodide, and values for Λ^o in hexanol, dodecanol and acetic acid were obtained (see Table VI).

The calculation of K_3 using equation (48) is independent of the absolute value assigned to Λ^o. In

keeping with the usual practice, the limiting conductance of the triple ions was assumed to be half the limiting conductance of the simple ions, i.e. $\Lambda^{\circ}_3/\Lambda^{\circ}$ was assigned the value 0.5.

TABLE VI

The Conductance-Viscosity Product
for HCl and HI in Various Solvents at 25°C.
(from the "Landolt-Bornstein Tabellen" (45))

HX	Solvent	Viscosity η (poise)	Λ°	$\eta\Lambda^{\circ}$
HCl	Methanol	0.547	197	108
	Ethanol	1.15	83.8	96.4
	n-Propanol	1.97	46.6	91.9
HI	Methanol	0.547	207	119
	Ethanol	1.15	89.7	103
	n-Hexanol	4.37[a]	(23)	
	n-Dodecanol	18.8[b]	(5.3)	(100)
	Acetic Acid	1.17	(85)	

a. Reference 55
b. Reference 56 This value is reported for 20°C., i.e. four degrees below the melting point of pure n-dodecanol.

The results of these calculations are given in Table VII. The accuracy of the values obtained for K is primarily dependent on the validity of Walden's rule in these solvents. It is evident in equation (49) that an error of 50% in the estimated value of Λ° will only alter K by a factor of four, hence it can be assumed that the values obtained for K are of the correct order.

TABLE VII

Estimation of K and K_3 by
Equations (48) and (49)
$(\Lambda_3^\circ/\Lambda^\circ = 0.5)$

Solvent	Λ_m	$a_m^{\frac{1}{2}}$	Λ°	K	K_3
n-Hexanol	2.9	0.19	23	1×10^{-4}	2×10^{-2}
n-Dodecanol	0.080	0.14	5.3	4×10^{-6}	1×10^{-2}
Acetic Acid	0.66	0.11	85	7×10^{-7} 2×10^{-7}	6×10^{-3} 7×10^{-3} (a)

(a). Obtained by graphical solution (Fig. 3) of equation
(47)

The values of K and K_3 for hydrogen iodide in acetic
acid were also calculated by substituting the slope and inter-
cept for Fig. 3 in equation (47). Good agreement was obtained
by the two methods (see Table VII). The intercept and slope
of the line drawn in Fig. 3 to represent the solute in hexanol
were determined by substitution of Λ°, K and K_3 from
Table VII in the constant terms of equation (47). The failure
of the experimental points to fall on this line indicates
the effect on the conductance of the decomposition of the
solution at concentrations below 5×10^{-3} molar.

The dissociation constants of hydrogen iodide in
methanol, ethanol, hexanol, dodecanol and acetic acid have

been reviewed in Table VIII. The expected increase in ion association with increasing dielectric constant is evident in the regular decrease in the dissociation constant in the alcohols. If it is assumed that these values are of the correct order of magnitude, a value of 10^{-3} may be assigned to the dissociation constant of hydrogen iodide in n-butanol.

TABLE VIII

The Dissociation Constant K for HI and the Instability Constant K_3 for H_2I and HI_2 in Various Solvents at $25^{\circ}C$.

Solvent	Dielectric Constant	K	K_3
Methanol	36.7	1×10^{-1}	-
Ethanol	24.2	2×10^{-2}	-
n-Butanol	17.3	(1×10^{-3})	-
n-Hexanol	12.8	1×10^{-4}	2×10^{-2}
n-Dodecanol	6.15	4×10^{-6}	1×10^{-2}
Acetic Acid	6.27	7×10^{-7}	6×10^{-3}

It must be emphasized that of the constants given in Table VIII, only the value for the solute in ethanol can be regarded as correct. The broad assumption made in the estimation of the other constants render them quite uncertain, but it seems reasonable to assume that they are of the correct order of magnitude.

THE EXCHANGE EXPERIMENTS

Mathematics of Exchange Reactions

The mathematics of organic-inorganic halide exchange reactions were developed by McKay for inorganic halides containing one halogen atom per molecule (1). Hodgson, Evans and Winkler later expanded this treatment to include exchange with inorganic molecules containing $\underline{n}$ halogen atoms per molecule (17). Their development is discussed here using hydrogen iodide and n-butyl iodide as particular models.

For the exchange of hydrogen iodide (HI) with n-Butyl iodide (BuI) according to the equation

$$\underset{c-x}{\text{HI}^*} + \underset{b}{\text{BuI}} \rightleftharpoons \underset{a_0}{\text{HI}} + \underset{x}{\text{BuI}^*}$$

the rate of formation of active organic species is given by

$$\frac{dx}{dt} = V\left(\frac{c-x}{a_0} - \frac{x}{b}\right) \tag{50}$$

where V is the velocity constant or the number of exchanges taking place in unit time, a_0 and b are the concentrations of hydrogen iodide and butyl iodide, c is the initial concentration of radioactive hydrogen iodide, and x is the concentration of radioactive butyl iodide at time $\underline{t}$.

Integration of the differential equation (50) with the boundary condition that the concentration of radioactive organic halide is zero at zero time yields

$$V = \frac{a_0 b}{(a_0 + b)\, t} \ln \frac{1}{1 - (x/c)\,(1 + a_0/b)} \quad . \qquad (51)$$

It has been pointed out that the experimental determination of $\underline{x}$ and $\underline{c}$ is neither practical nor necessary since the results can be expressed in terms of the specific activity, i.e. the number of disintegrations per unit time per unit weight of the sample analysed. If A_0 and A_t represent the specific activity of HI at zero time and at time $\underline{t}$ respectively, then

$$\frac{A_t}{A_0} = \frac{c - x}{c} = 1 - \frac{x}{c} \quad . \qquad (52)$$

Substitution of equation (52) in equation (51) replaces the term in $\underline{x}$ and $\underline{c}$ for one in A_t and A_0 .

Equation (51) may also be expressed in terms of σ_t, the degree of exchange which is defined as the fraction of the total exchange which has taken place at time $\underline{t}$. That is,

$$\sigma_t = \frac{A_0 - A_t}{A_0 - A_\infty} \quad , \qquad (53)$$

where A_∞ is the activity at infinite time.

When the exchange is complete, the radioactive

halogen will be distributed on a statistical basis between the iodides present. Hence

$$A_\infty = \frac{a_0}{a_0 + b} A_0 .$$ (54)

Therefore the velocity constant V may be expressed in terms of the concentrations a_0 and b, and the degree of exchange σ, by the substitution of the last three equations in equation (51). Hence

$$V = \frac{a_0 b}{(a_0 + b)t} \ln \frac{1}{(1 - \sigma)} .$$ (55)

This equation illustrates a characteristic property of exchange reactions. It has been repeatedly shown, both experimentally and mathematically, that for any given exchange reaction there is a simple logarithmic relation between the degree of exchange and the time. Consequently all exchange reactions taken singly appear to be first order. To ascertain the true order it is necessary to determine velocity constants for different concentrations of the reactants. The specific rate constant k will be the product of the velocity constant and some function of the concentrations a_0, and b, depending on the order of the reaction. For example, for a first order reaction,

$$k = V/a_0 \quad \text{or} \quad V/b_0 ,$$

and for a second order reaction

$$k = V/a_0 b \quad .$$

Consequently an exchange reaction which is first order with respect to a_0 and b will obey the second order exchange equation

$$k = \frac{2.303}{(a_0 + b)t} \log \frac{1}{(1 - \sigma)} \quad . \qquad (56)$$

Preparation of Radioactive Hydrogen Iodide

The iodide isotope was supplied as carrier-free sodium iodide dissolved in a small quantity of water. The half-life of the dissolved solids was determined, and the figure of 8.02 days obtained showed the solution to be free of radioactive impurities.

The hydrogen iodide was activated in the preliminary exchange experiments by adding a sufficient quantity of the aqueous NaI^{131} solution to the stock hydrogen iodide solution and allowing the exchange to proceed to completion. This procedure had two serious disadvantages. First, it introduced a small quantity of water into the organic solvent. Second, there was no means of knowing whether or not the sodium and hydrogen iodides had exchanged, particularly in the less polar solvents. Consequently this procedure was discarded.

The possibility of activating the hydrogen iodide during its preparation was considered. However, since the quantity of iodide used in its preparation was several times greater than the hydrogen iodide withdrawn from the generator, considerable radioiodine would have been wasted by such a procedure.

These disadvantages could be avoided with almost total recovery of the radioactive isotope if the hydrogen iodide could be activated by exchange after preparation and before distillation into the solvent. Hence the exchange of iodine between sodium iodide and liquid hydrogen iodide was investigated. A small quantity of the active sodium iodide solution was evaporated to dryness in the bottom of the hydrogen iodide storage trap (see Fig. 1). The product subsequently collected in this trap was liquefied and maintained at -45°C. It was found that in one to two hours at this temperature the exchange was complete, i.e. the residue in the trap following distillation of the hydrogen iodide contained no activity. This exchange was adopted as the method of activating the hydrogen iodide.

Experimental Procedure

The exchange of hydrogen iodide with n-butyl iodide

in methanol, ethanol, butanol, hexanol and acetic acid was studied at 0°, 25°, 36.2° and 48.6°C.[1]. The reaction was studied at only one temperature in toluene and in dodecanol, 48.6°C. for the former and 25°C. for the latter.

The thermostat at 0°C. consisted of a mixture of crushed ice and distilled water contained in a dewar and stirred by an air jet. The other thermostats were the usual constant temperature baths, controlled by mercury thermoregulators to within $\pm 0.02^{\circ}$C. Water was used as the liquid medium in the 25° and 36.2° baths, and a light oil was employed at 48.6°C.

Erlenmeyers were used as reaction flasks in the majority of the exchange reactions. To exclude oxygen from the system, the stoppers in these flasks were designed to permit the introduction of nitrogen. Thus the flasks were flushed with nitrogen prior to the experiments and a nitrogen pressure of a few inches of water was maintained in the flasks during the exchange reaction. The quantity of reaction solution and the size of the flask were selected to give a negligible dead space.

The butyl iodide and active hydrogen iodide solutions

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1. The exchange in ethanol was studied at 34.7°C. rather than 36.2°C.

were brought to bath temperature in separate erlenmeyers, removed from the bath and quickly mixed. Zero time samples were removed immediately after the reaction mixture was returned to the bath. Samples were removed from the erlenmeyers with rapid delivery pipettes.

The exchange reactions at zero degrees were found to be slow for the reactant concentrations used. Rather than attempt to exclude oxygen by nitrogen over the period of time required, the reactions at this temperature were conducted in sealed tubes. Since hydrogen iodide was found to have an appreciable vapor pressure over toluene and acetic acid, sealed tubes were used for these solvents at all four temperatures to minimize the dead space and to avoid the loss of hydrogen iodide when samples were taken. For these relatively slow exchanges, the error introduced by initiating the reaction at room temperature rather than at bath temperature was negligible.

In all the experiments the reaction flasks and tubes were wrapped in aluminum foil to preclude the possibility of exchange by a photochemical mechanism.

The reaction was stopped by separation of the inorganic and organic halides. The sample removed from the

reaction flask was shaken with equal volumes of water and benzene in a separatory funnel and the aqueous layer withdrawn immediately. This portion containing the hydrogen iodide, was washed twice with benzene and transferred to a standard 50 ml. centrifuge tube.

The iodide was precipitated with silver nitrate and counted as the silver salt. A procedure developed by Hodgson, Evans and Winkler (17) was used in the preparation of the silver iodide for counting. The procedure consisted of the following steps:

(a) The hydrogen iodide was precipitated from the aqueous solution by an excess of aqueous silver nitrate and centrifuged.

(b) The residue was washed once with water to remove excess silver nitrate, once with ethanol to remove traces of benzene, then once again with water to remove the alcohol. The slurry formed was centrifuged and the liquid decanted after each washing. Loss of part of the silver iodide was of no consequence since the precipitate was analysed in terms of activity per unit weight.

(c) Five to ten milliliters of concentrated nitric acid was added to the precipitate and the mixture heated

at 100°C. for fifteen to thirty minutes depending on the quantity of solid present. In addition to destroying any remaining organic material, this treatment appeared to change the residue from a floc to finely divided particles, essential in the preparation of uniform counting samples.

(d) The acid was decanted and the precipitate washed twice with water and once with ethanol (or methanol).

(e) The precipitate was washed with dry, acetone-free methanol, following which it was slurried in five to ten milliliters of this solvent. Part of the slurry was transferred by means of a five milliliter graduated pipette and syringe to a glass collar and a tared glass counting slide. The methanol was evaporated slowly with the aid of a 150 watt spot lamp, leaving a fine grained silver iodide precipitate.

The slides used were standard 4x4 cm. glass specimen slides. The collars were made by cutting 34 mm. pyrex tubing into two centimeter lengths and polishing one face optically flat. This surface when moistened with methanol and pressed firmly onto the slide formed a methanol-tight container for the silver iodide slurry.

To obtain a smooth uniform halide deposit, it was

essential that the methanol be free of water and acetone.
In fact, there appeared to be some correlation between the
quality of the plate and the relative humidity, better
precipitates being obtained when the humidity was low.
Acetone-free A.C.S. grade methanol, dried with magnesium
methylate and distilled, was found to give precipitates of
the required uniformity.

The collar was removed after drying and the slide
cooled in a desiccator and weighed. After the activity of
the precipitate had been determined, the slide was cleaned
in hot concentrated sulfuric acid for subsequent use.

Since two to three hours were required in the evap-
oration of the methanol from the slides, maximum efficiency
in the plating procedure was attained when as many slides
as possible were dried simultaneously. Thirty glass collars
were made for this purpose.

The activity of the silver iodide was determined
using end-window Geiger-Müller tubes supplied by the Atomic
Energy Project, and scalers manufactured by the Atomic
Instrument Co, (Model 101A, scale of 64).

Sources and Control of Experimental Error

Deterioration of hydrogen iodide solutions resulting

in the formation of iodine was mentioned previously. Since Hodgson et. al. found the exchange of n-butyl iodide with iodine to be 10^3 times slower than the exchange with sodium iodide in acetonitrile (17), the contribution to the exchange of hydrogen iodide with butyl iodide by the small quantity of iodine present was considered to be negligible.

The efficiency of the organic-inorganic iodide separation was checked in each experiment by comparing the activity of the zero time sample with that of the stock hydrogen iodide solution. In none of these checks was the difference in activities greater than the counting error.

It was evident that the greatest errors in these experiments were associated with the determination of the specific activity of the silver iodide. The sources of error discussed here are inherent in all analyses requiring the use of a Geiger counter.

(i) Self-absorption. The absorption of radiation by the precipitate itself results in an apparent activity less than the true specific activity. The effect of precipitate weight on the observed activity of a particular stock solution was determined, with the results recorded in Table IX. It was found that self-absorption occurs in silver iodide precipitates of 30 mm. diameter weighing over 45 milligrams.

This was in agreement with results previously obtained in a similar investigation (17).

TABLE IX

Self-absorption by AgI^{131}
(plated discs, 30mm. diameter)

Weight mg.	Counts/ minute	A*
23.3	5216	224
34.8	7744	220
35.6	7936	222
41.6	9280	223
45.7	10048	220
56.2	11744	209
62.3	12352	198

* A is the specific activity in counts per milligram-minute.

The lower weight limit for acceptable deposits of silver iodide was determined by the accuracy with which they could be weighed ($\pm$ 0.2 mg.). Hence attempts were made to plate out precipitates weighing between 20 and 40 mg., although the specific activities of a few deposits weighing as little as 14 mg. and as much as 46 mg. were accepted.

(ii) Geometry. It was also evident from the study reported in Table IX that the precipitates prepared in this manner were sufficiently uniform and the position of the slide under the Geiger tube was sufficiently reproducible to make the

errors due to geometry effects negligible.

(iii) <u>Coincidence and background</u>. The number of disintegrations registered by a counting tube is inversely proportional to the square of the distance between the tube and the source. Using this law and a Ag^{110} source, it was found that the Geiger tubes would respond to 14,000 counts per minute without coincidence. Consequently, the specific activity of the samples could be as high as 500 counts per mg. per min. for 20 mg. samples, or 300 counts per mg. per min. for 40 mg. samples, without introducing any detectable error due to coincidence counting.

The background count of the tubes protected by a lead castle was below 25 counts per minute, and the activity of samples having less than 3000 counts per minute were corrected accordingly. Activities as low as 400 counts could be determined without appreciable error due to fluctuation in background count.

(iv) <u>Statistical fluctuations</u>. The disintegration of an unstable isotope is a purely random phenomenon, consequently statistical fluctuations are inherent in the determination of the activity of a sample. Equations have been developed which permit calculation of the relative error which can be

expected when a given number of disintegrations are observed over a short time interval (57). These equations indicate that 10^4 disintegrations recorded in a one minute observation will have a probable error of 0.67% , while the probable error in 10^3 counts in the same time interval will be 2%. Accordingly, in these experiments the counting interval was selected to give at least 10^4 counts.

(v) Stability of Geiger tube voltage. Geiger tubes have a characteristic voltage range (plateau) in which the effect of voltage fluctuations on the count registered is a minimum. The count registered by new tubes used in these experiments was found to increase two to four percent per 100 volt increase. This dependence increased as the tubes 'aged'. Since counting samples with low activity required several minutes, the necessity of having good voltage stabilization was evident. A power pack was built for this purpose by reference to the circuit contained in a scaler manufactured by Instrument Development Laboratories. The wiring diagram in its final form is given in Fig. 4.

The voltage supplied by this unit in the 900-1400 volt range was independent of the input voltage between 100 and 120 volts. Its use permitted all the precipitates obtained in an exchange reaction to be counted with only

Fig. 4.

Wiring Diagram

Geiger Tube Power Pack.

POWER PACK WIRING DIAGRAM
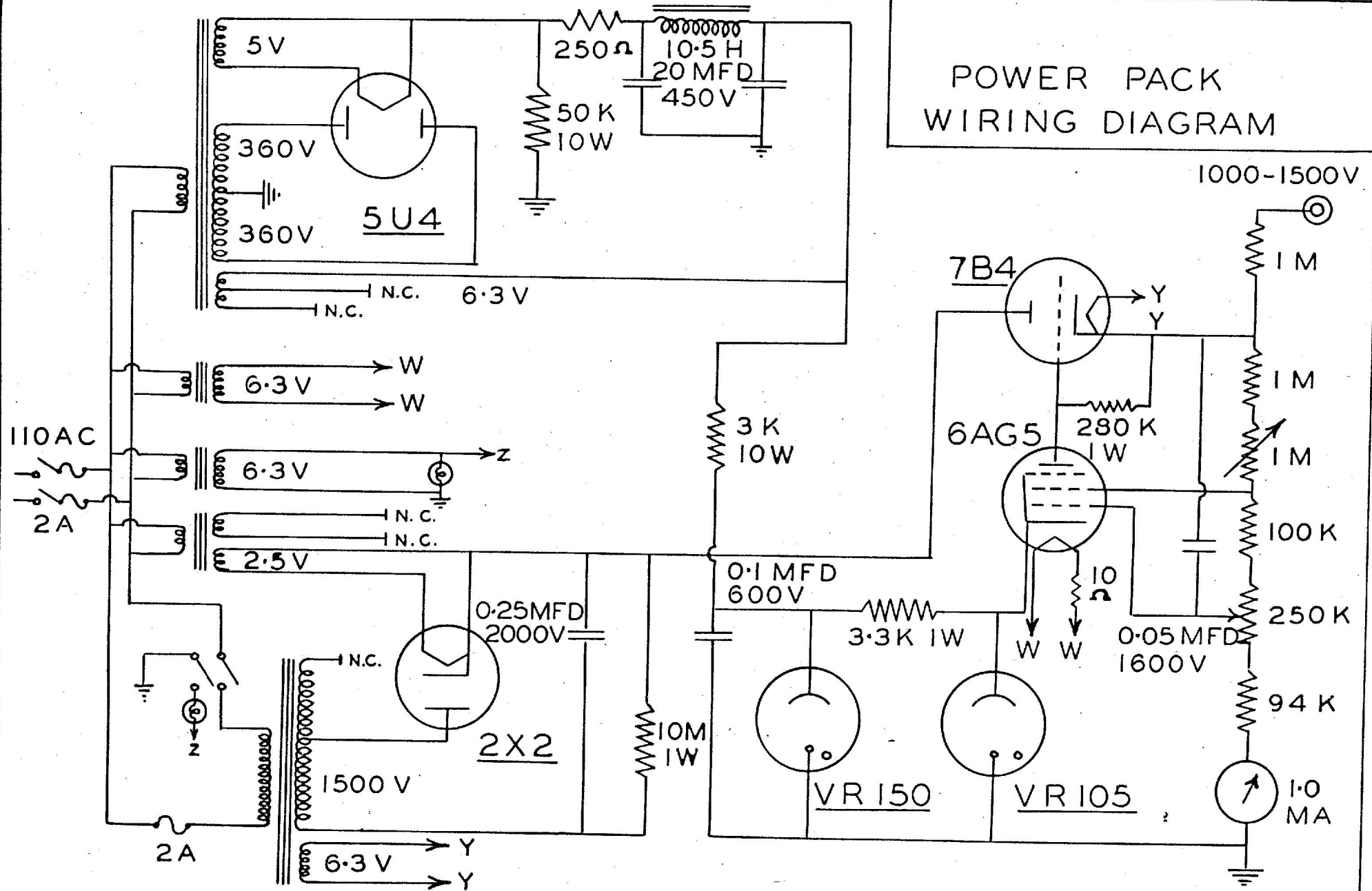
occasional reference to a standard or zero time sample, provided the Geiger tube was in good operating condition.

Since all of the calculations involved the initial specific activity of the hydrogen iodide, it was essential that this figure be known with as much certainty as possible. At least four of these precipitates were prepared, two from zero time samples and two from the stock hydrogen iodide solution. Duplicate precipitates were prepared for the other samples, with the exception of the solutions less than 0.03 molar in hydrogen iodide. The difference in activities of the duplicate samples seldom exceeded three percent.

The curves in Fig. 5 were constructed for a hypothetical exchange to show the error introduced in the rate constant by two percent error in the specific activity. At high degrees of exchange, the specific activity is low and the uncertainty is therefore greater than two percent, hence these curves do not accurately represent the error to be expected above 80% exchange. It was evident however that the greatest accuracy could be expected in samples withdrawn when the exchange was 30 to 80% complete. These curves also indicated the advantage in maintaining low hydrogen iodide-butyl iodide concentration ratios.

Fig. 5.

Error Introduced in Rate Constant

by 2% Error in Specific Activity.

HI/BuI Concentration Ratios:
        A.   0.01
        B.   0.10
        C.   1.00
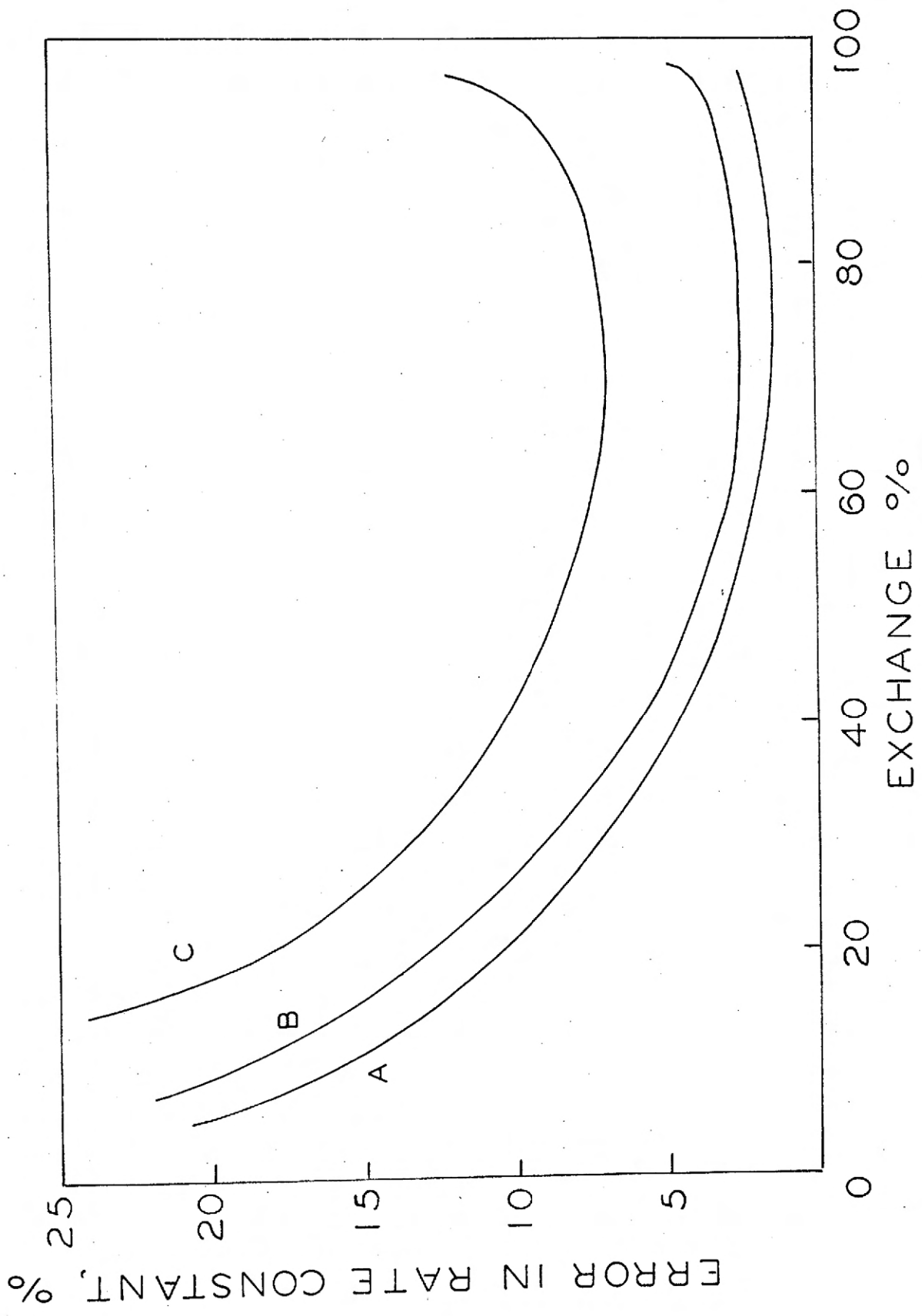
The Exchange Results

The results recorded in Table X for the exchange of butyl iodide with hydrogen iodide in ethanol at 25°C. are typical of the results obtained in these experiments.

The degree of exchange, σ, was calculated by equation (53),

$$\sigma_t = \frac{A_0 - A_t}{A_0 - A_\infty} , \qquad (53)$$

with the specific activity at infinite time obtained from

$$A_\infty = \frac{a_0}{(a_0 + b)} A_0 \qquad (54)$$

The exchange rates have been expressed here in terms of the second order rate constant, designated by the symbol k_e, and calculated by equation (56):

$$k_e = \frac{2.303}{(a_0 + b)t} \log \frac{1}{1 - \sigma} , \qquad (56)$$

where t is the time in hours, a_0 is the hydrogen iodide concentration and b is the butyl iodide concentration.

The mean value of the rate constants for each exchange was determined graphically by plotting $1/(1 - \sigma)$ versus the time as indicated by the rate curve in Fig. 6 for the exchange data in Table X. The rate constants at temperatures

TABLE X

The Exchange of Hydrogen Iodide with n-Butyl Iodide
in Ethyl Alcohol at 25°C.

HI   0.103 molar
BuI   0.600 molar

Sample (time in hrs.)	Count /min.*	Wt. (mg.)	A**	$\sigma\%$	k_e 1/mole-hr.
Stock	10624	35.6	299		
	6720	23.0	292		
Zero	8704	29.7	293		
	8128	27.4	297		
1.0	-	48.6	-	25.0	0.409
	6496	28.0	232		
2.0	5792	32.2	180	45.3	0.427
	4896	27.0	181		
2.5	5504	33.4	165	51.2	0.409
	5888	35.2	167		
3.0	5952	39.1	152	57.2	0.402
	6272	42.1	149		
3.5	4416	32.9	134	63.9	0.414
	5312	40.0	133		
4.5	2592	23.7	109	73.8	0.424
	3872	35.5	109		
∞			43		
Graphical Analysis (Fig. 6)					$0.413 \pm 2\%$

* Average of at least two determinations
** A, specific activity, counts/mg. min.

Fig. 6.

Reaction Time Curve

Exchange of 0.103 M
hydrogen iodide with
0.600 M butyl iodide
in ethanol at 25°C.
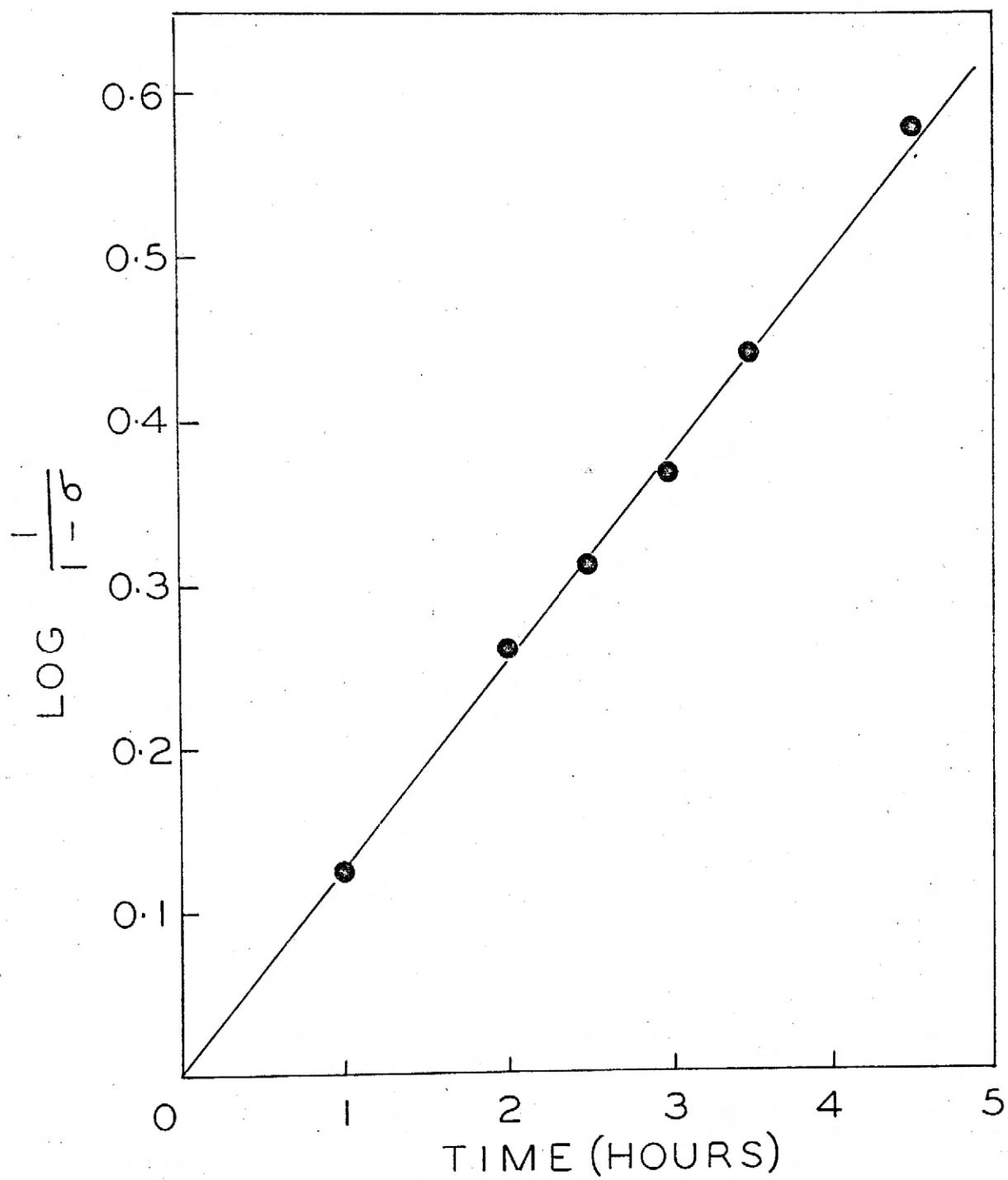
other than 25°C. have been corrected for expansion of the
solvent, using density data obtained from the Landolt-
Bornstein tables (45). The results of the exchange reactions
have been summarized in Tables XI to XIV while the details
of these experiments have been relegated to an appendix,
to avoid their intrusion into the presentation of the essen-
tial data.

The procedures in two of the exchange investigations
merit special consideration. It was observed during the
exchange studies in acetic acid that this solvent could be
readily supercooled. Six tubes were placed in the 0° ther-
mostat, 16° below the freezing point of the solvent, and
left undisturbed until the ice in the bath had to be renewed.
Two of the samples were recovered in the liquid state and
were subsequently analysed. Although the degree of exchange
was unfortunately small and the experimental error corres-
pondingly large, the results are included in Table XIV.

An attempt was made to follow the exchange of hydrogen
iodide with sodium iodide in hexanol. To separate the re-
actants, hydrogen peroxide was added to the water-benzene
mixture to oxidize the hydrogen iodide to iodine and permit
its removal in the benzene layer. As a control to this
separation, the exchange of iodine with sodium iodide in hexanol

was also investigated. The results are recorded in Table XI. It was found that the exchange of iodine and hydrogen iodide with sodium iodide at room temperature was essentially complete in the time required to separate reactants. The experimental error associated with the determination of the specific activity at such high degrees of exchange did not warrant the calculation of a rate constant for these exchange reactions.

TABLE XI

The Exchange of Hydrogen Iodide with Sodium Iodide
and of Iodine with Sodium Iodide in
n-Hexanol at 25.0°C.

HI 0.115 Moles/liter
I_2 0.115 gram ions/liter

Reagent	NaI M	Time mins.	A	$\sigma\%$
-	0.0100		401	
Iodine	0.0100	Zero	33	99.3
Hydrogen Iodide	0.0100	Zero	43	97.3
		Zero	40	98.0
		5	38	98.4
		∞	32	

TABLE XII

The Exchange of Hydrogen Iodide with n-Butyl Iodide
in Toluene at 48.6°C.

Conc. HI M	Conc. BuI M	Time hr.	A	$\sigma\%$	k_e 1/mole-hr.
0.0971	0.500	Zero	188		
		23	187		
		91	186		
		163	182	4.0	4×10^{-4}
		∞	31		

TABLE XIII

The Second Order Rate Constants (k_e) for
the Exchange of Hydrogen Iodide with n-Butyl Iodide
in Methyl, Ethyl, and n-Butyl Alcohols

Solvent	HI M	BuI M	Temp. $^{\circ}$C.	k_e 1/mole-hr.	
Methyl Alcohol	0.0751	0.500	0.0	0.00874 ± 3%	
	0.0563	0.625	25.0	0.162	1%
	0.0409	0.455	36.2	0.525	2%
	0.107	0.286		0.480	3%
	0.0751	0.200	48.6	1.49	3%
Ethyl Alcohol	0.0539	0.500	0.0	0.0215 ± 3%	
	0.0098	0.600	25.0	0.519	2%
	0.0290	0.334		0.473	1%
	0.0342	0.600		0.469	3%
	0.0866	0.200		0.382	2%
	0.1025	0.600		0.413	2%
	0.1675	0.600		0.379	1%
	0.244	0.600		0.362	1%
	0.335	0.600		0.333	2%
	0.0268	0.100	34.7	1.43	2%
	0.0356	0.267		1.27	2%
	0.0356	0.133	48.6	5.56	3%
n-Butyl Alcohol	0.102	0.625	0.0	0.0260 ± 2%	
	0.102	0.625	25.0	0.561	3%
	0.0387	0.143	36.2	1.87	1%
	0.170	0.375		1.86	2%
	0.0387	0.143	48.6	6.15	2%

TABLE XIV

The Second Order Rate Constants (k_e) for
the Exchange of Hydrogen Iodide with n-Butyl Iodide
in n-Hexyl and n-Dodecyl Alcohols and Acetic Acid

Solvent	HI M	BuI M	Temp. °C	k_e 1/mole-hr.	
n-Hexyl Alcohol	0.0993	0.625	0.0	0.0276	± 1%
	0.0247	0.800	25.0	0.364	2%
	0.0617	0.800		0.465	1%
	0.0993	0.625		0.484	2%
	0.123	0.800		0.486	1%
	0.339	0.800		0.540	2%
	0.678	0.800		0.550	2%
	0.0442	0.250	36.2	1.55	2%
	0.118	0.556		1.65	2%
	0.0756	0.214	48.6	4.63	3%
n-Dodecyl Alcohol	0.0119	1.00	25.0	0.174	± 2%
	0.0228	1.00		0.197	2%
	0.0603	1.00		0.248	2%
	0.125	1.00		0.319	3%
	0.159	0.333		0.330	2%
	0.159	1.00		0.342	2%
	0.251	1.00		0.349	2%
	0.318	1.00		0.385	2%
Glacial Acetic Acid	0.0819	1.00	0.0	0.0043	±10%
	0.0148	1.00	25.0	0.0353	3%
	0.0520	1.00		0.0521	3%
	0.0615	0.625		0.0611	2%
	0.104	1.00		0.0765	3%
	0.208	1.00		0.101	3%
	0.312	1.00		0.0980	3%
	0.0819	1.00	36.2	0.200	2%
	0.0467	0.715	48.6	0.594	3%
	0.117	0.286		0.726	2%

DISCUSSION OF RESULTS

While the exchange of hydrogen iodide with n-butyl iodide in the alcohols and acetic acid was found to be complete in less than ten hours at 50°C., the exchange in toluene was less than four percent in 160 hours at this temperature. Assuming the small decrease in activity to be the result of exchange rather than experimental error, the specific rate constant appeared to be less than 4×10^{-4} liters per mole-hour in toluene (Table XXI) as compared with 1.5 liters per mole-hour in methanol.

In view of the low dielectric constant of toluene (D 2.44)(45), it is likely that only a small fraction of the hydrogen iodide was dissociated in this solvent, while in methanol the dissociation was essentially complete. An exchange mechanism involving ions is immediately evident, on the basis of which the slow rate of exchange in toluene may be attributed to the small iodide ion concentration in this solvent. This does not exclude the possibility of some direct exchange between hydrogen iodide (i.e. the ion pair H^+I^-) and butyl iodide, nor of some exchange through an ionic complex. However, exchange by a direct mechanism could not be faster than the overall rate in toluene, and therefore the

contribution of such a mechanism to the total exchange rate in the alcohols and in acetic acid may be regarded as insignificant.

It was shown previously that the specific rate constant $\underline{k}$ for an exchange reaction is given by

$$V = ka_0^n b^m \quad ,$$

where V is the velocity constant or the number of exchanges occurring per unit time and, in these investigations, a_0 and b are the concentrations of hydrogen iodide and butyl iodide respectively. The order of the reaction was obtained by substitution of experimentally determined velocity constants in the above expression, as well as the concentrations a_0 and b raised to appropriate powers, and observing the constancy of $\underline{k}$. The results of some of these calculations are given in Table XV.

It was found that the exchange of hydrogen iodide with butyl iodide in the alcohols and in acetic acid was most closely represented by the second order rate constant,

$$k_e = V/a_0 b \quad .$$

Hence the second order rate equation,

$$k_e = \frac{2.303}{(a_o + b)t} \log \frac{1}{1 - \sigma} \quad , \qquad (56)$$

was used to calculate the experimental rate constants (k_e). This constant was found to decrease with increasing hydrogen iodide concentration in methanol, ethanol and butanol, while the opposite effect, i.e. increasing values for k_e with increasing hydrogen iodide concentration, was observed for exchange in hexanol, dodecanol and acetic acid. The exchange mechanisms in these latter solvents will be discussed separately.

TABLE XV

The Order of the Exchange Reaction
Between Hydrogen Iodide and n-Butyl Iodide

a_o HI M	b BuI M	$k =$				
		V/a_o	V/b	V/a_ob	V/a_o^2b	V/a_ob^2
Methanol 36.2°C.						
0.0409	0.455	0.234	0.0215	0.525	12.8	1.15
0.107	0.286	0.137	0.0514	0.480	4.49	1.68
Ethanol 25.0°C.						
0.0290	0.334	0.158	0.0137	0.473	16.8	1.42
0.0866	0.200	0.0765	0.033	0.382	4.4	1.90
0.335	0.600	0.200	0.112	0.333	0.99	0.55
Dodecanol 25.0°C.						
0.0119	1.00	0.174	0.00207	0.174	14.6	0.174
0.159	0.333	0.110	0.0525	0.330	2.1	1.00
0.385	1.00	0.385	0.123	0.385	1.2	0.385

EXCHANGE IN METHANOL, ETHANOL AND BUTANOL

Exchange Mechanism; Effect of Hydrogen Iodide Concentration

The direct exchange of hydrogen iodide with butyl iodide according to the equation

$$HI^* + BuI \rightleftharpoons BuI^* + HI$$
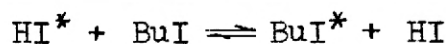
has been shown to be extremely slow compared with the exchange through an ion intermediate,

$$\begin{array}{cccc} HI^* + & I^- & \rightleftharpoons HI + & I^{*-} \\ c-x & i & a & y \end{array} \quad ,$$

$$\begin{array}{cccc} BuI + & I^{*-} & \xrightarrow{k_1} BuI^* + & I^- \\ b & y & \overleftarrow{k_{-1}} \; x & i \end{array} \quad ,$$
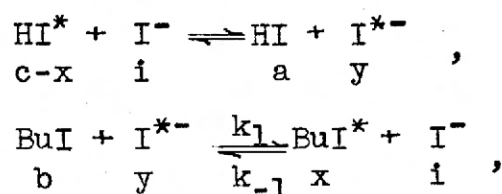
where the asterisk denotes the radioactive isotope. Moreover, since the exchange of hydrogen iodide with sodium iodide in hexanol was found to be immeasurably fast, the exchange of iodide ion with hydrogen iodide may be taken to be essentially instantaneous and the distribution of the active isotope among the inorganic species will be complete at all times. Consequently the ratio of active to inactive iodide ions will be equal to the ratio of total active inorganic species to total inactive inorganic species throughout the exchange reaction. That is,

$$\frac{c - x}{a_o} = \frac{y}{i} \quad , \tag{57}$$

where a_o is the total concentration of hydrogen iodide,

i is the iodide ion concentration,

c is the concentration of radioactive hydrogen iodide at zero time,

c-x is the concentration of radioactive hydrogen iodide at time $\underline{t}$,

and y is the concentration of active iodide ion at time $\underline{t}$.

The rate controlling step, the exchange of iodide ion with butyl iodide, has been shown to be second order and may be represented by the differential equation

$$\frac{dx}{dt} = k_1(by) - k_{-1}(ix), \tag{58}$$

where $\underline{x}$ and $\underline{b}$ are the concentrations of radioactive and inactive butyl iodide respectively, and k_1 and k_{-1} are the specific rate constants for the forward and reverse reactions. Since this is an equilibrium reaction and the equilibrium constant is unity,

$$k_1 = k_{-1} \quad ,$$

hence

$$\frac{dx}{dt} = k_1(by - ix) \quad . \tag{59}$$

Substitution for $\underline{y}$ in equation (59) in terms of equation (57) yields

$$\frac{dx}{dt} = k_1 \left(\frac{ib(c-x)}{a_o} - ix \right), \tag{60}$$

which may be rearranged to give

$$\frac{dx}{b(c-x) - a_o x} = \frac{i}{a_o} k_1 dt \quad . \tag{61}$$

The observed second order rate constant, k_e, represents the overall reaction

$$\begin{array}{ccccc}
RI & + & HI^* & \rightleftharpoons & RI^* & + & HI \\
b & & c-x & & x & & a_o
\end{array} \quad ,$$
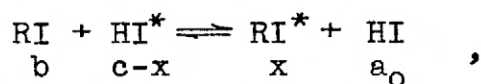
where

$$\frac{dx}{dt} = k_e \left(b(c-x) - xa_o \right) \quad , \tag{62}$$

which yields

$$\frac{dx}{b(c-x) - a_o x} = k_e dt \quad . \tag{63}$$

It is immediately evident by comparison of equation (61) with equation (63) that the true rate constant, k_1, and the experimental rate constant, k_e, are related by the expression

$$k_e = \frac{i}{a_o} k_1 \quad . \tag{64}$$

The factor i/a_o is in effect the degree of dissociation of hydrogen iodide, hence

$$k_e = \propto k_1 \quad . \tag{65}$$

Consequently a decrease in the experimental rate constant with increasing hydrogen iodide concentration is to be expected, since α will assume progressively smaller values as the concentration increases.

The true constant, k_1, may be determined in two ways. If the experimental rate constants have been measured at low concentrations, they may be extrapolated to infinite dilution where k_e will approach k_1. Alternatively, if the dissociation constant is known, the degree of dissociation may be calculated and k_1 obtained by substitution in equation (65).

The extent to which hydrogen iodide was oxidized in dilute solution limited the present investigations to concentrations greater than 0.01 molar, and extrapolation from this relatively high concentration could not be justified. Consequently it has been necessary to assume some reasonable value for the dissociation constant and estimate the true rate constant by substitution in equation (65). Unfortunately, only the dissociation constant of hydrogen iodide in ethyl alcohol is known with any measure of certainty, while the others could only be estimated by making the broad assumptions discussed previously. For this reason, the symbol k_e/α rather than k_1 will be used here for the true rate constant, to emphasize the uncertainty in the calculations arising from

the uncertainty in the dissociation constant.

The experimental rate constants obtained for exchange in ethanol at 25°C. over a thirty-fold hydrogen iodide concentration are given in Table XVI. The degrees of dissociation included in this table were calculated using the dissociation constant (0.020) recorded by MacInnes (50). Since this constant was determined directly from conductance data by the method of Fuoss and Kraus, it may be assumed to be correct. However the values of k_e/α were found to increase more than two-fold over the concentration range investigated (Table XVI).

TABLE XVI

The Effect of Hydrogen Iodide Concentration
on the Experimental Rate Constant, k_e, for
Exchange in Ethanol at 25°C.

HI M	k_e 1/mole hr.	α	k_e/α 1/mole hr.
0.0098	0.519	0.735	0.715
0.0290	0.473	0.555	0.851
0.0342	0.469	0.526	0.890
0.0866	0.382	0.378	1.01
0.103	0.413	0.354	1.17
0.168	0.379	0.290	1.31
0.244	0.362	0.248	1.49
0.335	0.333	0.214	1.55

The failure of k_e/α to be independent of concentration

does not necessarily indicate that the value assumed for the dissociation constant is incorrect or that the argument leading to equation (65) is invalid for this exchange reaction. According to Glasstone, Laidler and Eyring, the specific rate constant for the reaction of an ion with a molecule should increase with increasing ionic strength according to the equation

$$\log k = \log k_o + C\mu \quad , \qquad (12)$$

where k_o is the rate constant at infinite dilution, C is a constant, and μ is the ionic strength of the solution. Substituting the symbol adopted in the present argument, equation (12) becomes

$$\log k_e/\propto = \log k_1^o + C\mu \quad , \qquad (66)$$

where k_1^o represents the true rate constant at infinite dilution. Equation (66) may be written in the exponential form, the result expanded in a power series and the approximate equation obtained:

$$k_e/\propto = k_1^o(1 + C\mu) \quad . \qquad (67)$$

According to this hypothesis, a plot of $k_e/\propto$ against the ionic strength should result in a straight line. Assuming the product of the degree of dissociation and the

hydrogen iodide concentration to be approximately equal to the ionic strength, the linear relation obtained (Fig. 7) seems to support the contention that the increase in k_e/α with increasing concentration is due to the effect of ionic strength on the exchange rate. Moreover, extrapolation of this line to zero ionic strength indicates that the rate constant at infinite dilution, k_1^o, may be equal to 0.62 liters per mole-hour.

The exchange in methanol and in n-butanol at 25^oC. was investigated at one hydrogen iodide concentration only. The experimental rate constants and the corresponding values of k_e/α are given in Table XVII.

TABLE XVII

Estimated Values of k_e/α for
Exchange in Methanol and n-Butanol at 25^oC.

Solvent	HI M	k_e 1/mole-hr.	α	$k_e/$ 1/mole-hr.	
Methanol	0.0563	0.162	0.714	0.23	±10%
n-Butanol	0.102	0.561	0.094	6.0	±60%

The degree of dissociation in methanol was estimated using a dissociation constant of 0.1 . This constant, obtained by analogy with the dissociation constant of hydrogen chloride in methanol, is probably correct to within ±50%, hence the

Fig. 7.

Dependence of k_e/α on Ionic Strength:
Exchange of Hydrogen Iodide and Butyl
Iodide in Ethanol at 25°C.
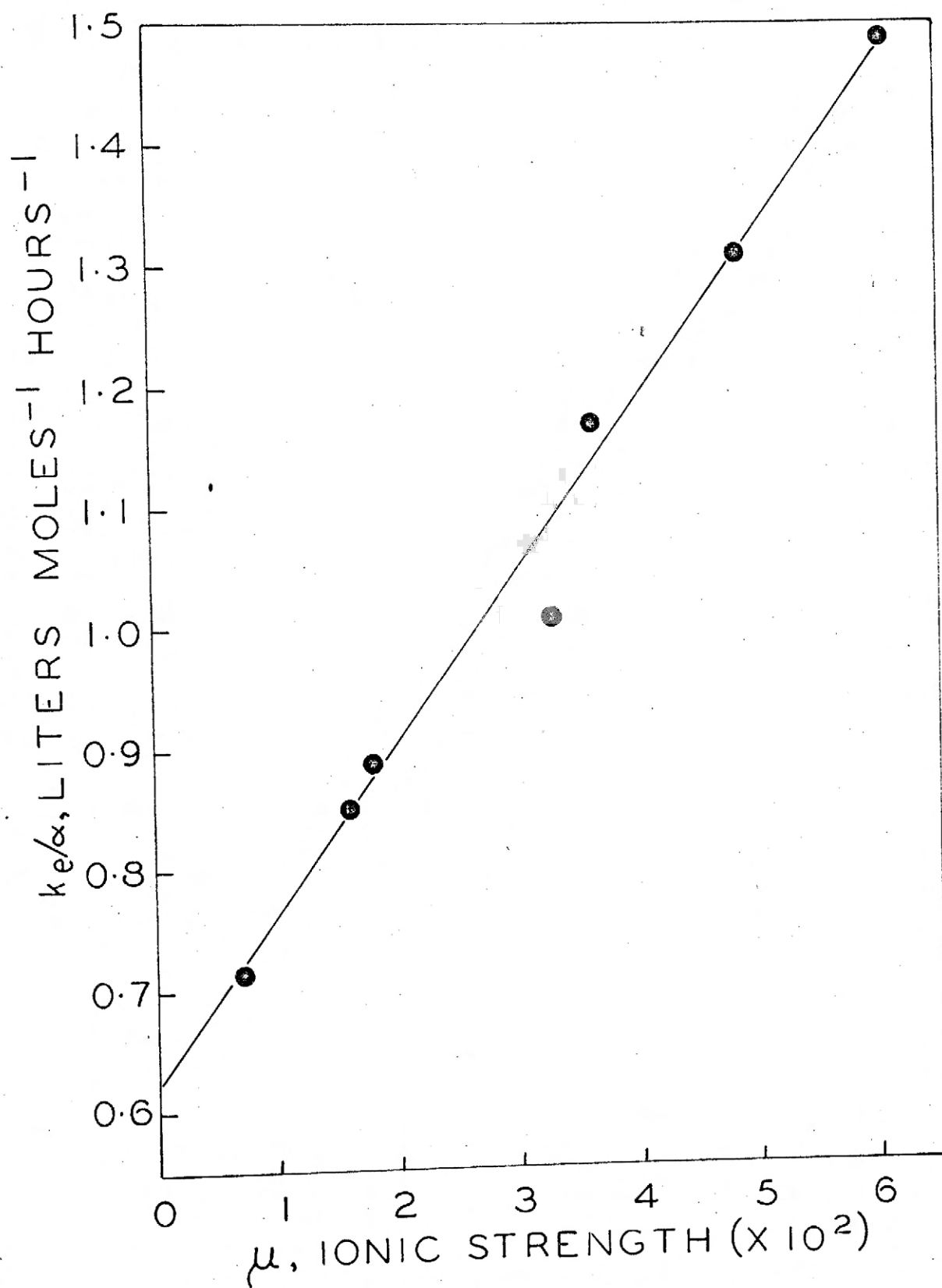
uncertainty in k_e/α should not be greater than $\pm10\%$. On the other hand, the dissociation constant for hydrogen iodide in butanol was selected by comparison of the dissociation constant in ethanol (2×10^{-2}) with the estimated dissociation constant in hexanol (10^{-4}). However, a five-fold error in this rough approximation alters the value of k_e/α by less than 60%. Consequently these estimates of the rate constant in methanol and butanol may be assumed to be of the correct order of magnitude.

Effect of Temperature

It was found that the change in the experimental rate constants with temperature in methanol, ethanol and butanol could be represented by the equation

$$k_e = Ae^{-E_e/RT} \quad , \qquad (68)$$

where E_e designates the experimental activation energy. The dependence of k_e on hydrogen iodide concentration was taken into account by comparing rate constants within a small hydrogen iodide concentration range. The values of the parameters A and E_e obtained are given in Table XVIII, and a typical activation energy curve is shown in Fig. 8.

TABLE XVIII

Arrhenius Line Parameters for
the Exchange of Hydrogen Iodide with n-Butyl Iodide
in Methanol, Ethanol and n-Butanol

Solvent	log A	E_e Kcal/mole
Methanol	12.8	18.6 0.1
Ethanol	14.0	19.5 0.1
n-Butanol	14.0	19.4 0.1

The temperature dependence of the true rate constant will be given by

$$k_1 = A_1 e^{-E_1/RT} \quad , \quad (69)$$

where E_1 is the true activation energy. Since the experimental rate constant and the true rate constant are related by the equation

$$k_e = \propto k_1 \quad , \quad (65)$$

it follows that

$$A e^{-E_e/RT} = \propto A_1 e^{-E_1/RT} \quad . \quad (70)$$

Since the degree of dissociation is temperature dependent, E_e and E_1 will not be strictly equal. However the temperature dependence of $\propto$ is slight, and in view of the

Fig. 8.

Temperature Dependence of Rate
of Exchange of Hydrogen Iodide
with Butyl Iodide in Ethanol.
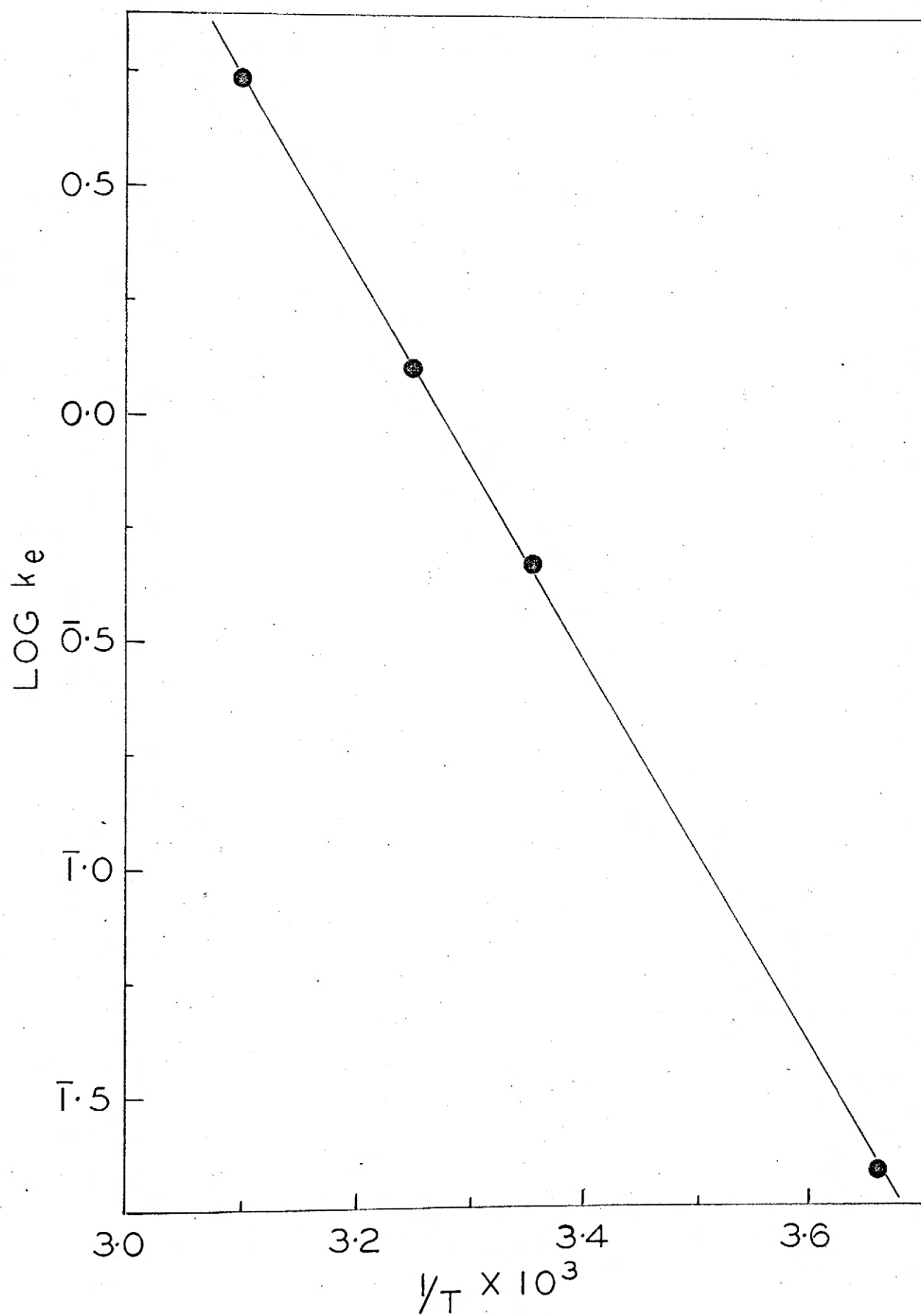
magnitude of the experimental activation energies, it is reasonable to assume that it can be neglected. Consequently the experimental activation energies will be taken to be approximately equal to the true activation energy for exchange in these solvents.

EXCHANGE IN HEXANOL, DODECANOL AND ACETIC ACID

Exchange Mechanism; Effect of Hydrogen Iodide Concentration

The experimental rate constants for exchange in hexanol, dodecanol and acetic acid were found to increase with increasing hydrogen iodide concentration, contrary to the behavior predicted by equation (65). It is significant that the conductance of hydrogen iodide in these solvents indicated the presence of ion triplets as well as ion pairs:

$$H + I^- \rightleftharpoons HI$$
$$HI + H \rightleftharpoons H_2I^+$$
$$HI + I^- \rightleftharpoons HI_2^- \ .$$
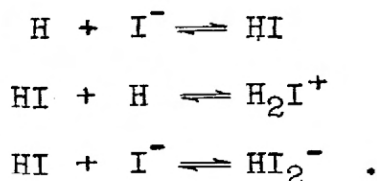
Hence, in addition to the iodide-ion butyl iodide mechanism, the possibility of mechanisms involving the triple ions must be considered.

Since it was shown by the attempt to exchange hydrogen

iodide with butyl iodide in toluene that the associated ion
pairs contribute little or nothing to the overall exchange
reaction, it is reasonable to assume that exchange between
the HIH^+ triple ions and butyl iodide will be negligibly
slow. However, exchange via the IHI^- triple ions may be
appreciable:

$$HI^* + HI_2^- \rightleftharpoons HI + HII^{*-} \quad ,$$
$$ c-x \quad\; j \qquad\quad a \quad\; z$$

$$BuI + HII^{*-} \xrightarrow[k_{-3}]{k_3} BuI^* + HI_2^- \quad .$$
$$b \quad\; z \qquad\qquad\quad x \qquad j$$
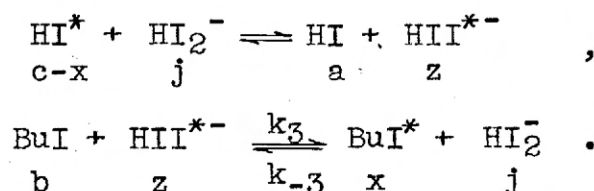
Since the concentrations of radioactive isotope used in these
experiments were of the order of 10^{-11} of the concentrations
of the stable isotope, it is extremely improbable that any
one triple ion contained more than one radioactive iodine
atom, and the active triple ions are accurately represented
by the formula HII^{*-}. Then if z and j are the concentra-
tions of active and inactive triple ion at time t, the ratio
of active iodine to inactive iodine in this inorganic species
will be equal to $z/2j$. Again it may be assumed that exchange
of iodine between inorganic species present is rapid and
therefore complete at all times, hence

$$\frac{c-x}{a_0} = \frac{z}{2j} \quad , \tag{71}$$

where a_0 is the total concentration of hydrogen iodide, and (c-x) is the total activity of the inorganic species at time t.

The rate of formation of active butyl iodide by the reaction of the triple ion with butyl iodide will be given by

$$\frac{dx}{dt} = k_3(zb) - k_{-3}(xj) \tag{72}$$

where b and x are the concentrations of inactive and active butyl iodide respectively. Although the exchange of active butyl iodide with inactive triple ion will always result in a transfer of radioiodine,

$$BuI^* + HI_2^- \xrightarrow{\ k_{-3}\ } \quad ,$$
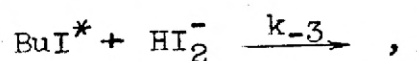
there is only a fifty percent probability that radioiodine will be transferred when an iodine atom is exchanged between an active triple ion and an inactive butyl iodide molecule:

$$HII^{*-} + BuI \xrightarrow{\ k_3\ } \quad .$$
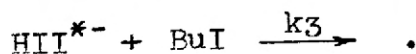
Hence the rate constants for the forward and reverse exchange of radioactive iodine are related by the equation

$$2k_3 = k_{-3} \quad , \tag{73}$$

and equation (72) becomes

$$\frac{dx}{dt} = k_3 \,(zb - 2xj) \quad . \tag{74}$$

Elimination of $\underline{z}$ using equation (71) leads to the relation

$$\frac{dx}{dt} = k_3 \left(\frac{2jb(c-x)}{a_o} - 2jx \right) \quad . \tag{75}$$

The overall exchange rate observed when both the simple ion and triple ion mechanisms are operative will be represented by the sum of equations (60) and (75):

$$\frac{dx}{dt} = ik_1 \left(\frac{b(c-x)}{a_o} - x \right) + 2jk_3 \left(\frac{b(c-x)}{a_o} - x \right) \quad . \tag{76}$$

This may be simplified and rearranged to give

$$\frac{dx}{b(c-x) - a_o x} = \frac{i}{a_o} k_1 dt + \frac{2j}{a_o} k_3 dt \quad . \tag{77}$$

By comparison of equation (77) with the differential equation obtained previously for the experimental rate constant k_e (equation 63),

$$\frac{dx}{b(c-x) - a_o x} = k_e dt \quad , \tag{63}$$

it is immediately evident that

$$k_e = \frac{i}{a_o} k_1 + \frac{2j}{a_o} k_3 \quad , \tag{78}$$

where $\underline{i}$ and $\underline{j}$ are the concentrations of simple and triple ions respectively, and a_o is the total hydrogen iodide con-

concentration.

The concentrations i and j may be replaced by the total concentration a_o and the dissociation constants, by the following argument. For the equilibria

1. $\quad HI \rightleftharpoons H^+ + I^-$
   $\quad\quad a \quad\quad h \quad\ i$,

2. $\quad H_2I \rightleftharpoons H^+ + HI$
   $\quad\quad\ l \quad\quad h \quad\ a$,

3. $\quad HI_2^- \rightleftharpoons HI + I^-$
   $\quad\quad\ j \quad\quad a \quad\ i$,
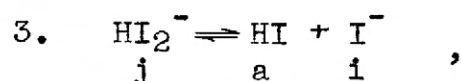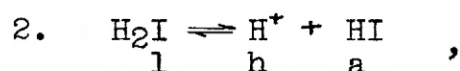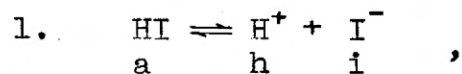
let a be the concentration of undissociated HI, h and i, the simple hydrogen and iodide ions; and j and l, the HI_2^- and H_2I triple ions. The constant K for the dissociation of hydrogen iodide is given by

$$K = hi/a \ ,$$

and the instability constants K_2 and K_3 of the triple ions are

$$K_2 = ha/l \ ,$$
$$K_3 = ia/j \ .$$

If a_o is the total hydrogen iodide concentration, iodine and hydrogen balances yield the equations

$$a_o = a + i + 2j + 1 \quad ,$$

and $\quad a_o = a + h + j + 21 \quad ,$

whence $\qquad i = h + 1 - j \qquad .$ (79)

The concentrations $\underline{h}$, $\underline{1}$ and $\underline{j}$ in equation (79) may be replaced by terms in $\underline{a}$ and $\underline{i}$ and the equilibrium constants:

$$i = \frac{Ka}{i} + \frac{a^2 K}{i\, K_2} - \frac{ai}{K_3} \quad .$$

This equation may be rearranged to give the iodide ion concentration in terms of $\underline{a}$ and the equilibrium constants,

$$i = \left(Ka \, \frac{(1 + a/K2)}{(1 + a/K3)} \right)^{\frac{1}{2}} \qquad . \tag{80}$$

Similarly, since $\qquad j = ai/K_3 \quad ,$

substitution for $\underline{i}$ according to equation (80) yields

$$j = \frac{a}{K_3} \left(Ka \, \frac{(1 + a/K2)}{(1 + a/K3)} \right)^{\frac{1}{2}} \qquad . \tag{81}$$

If it is assumed that the dissociation of hydrogen iodide is small, the concentration $\underline{a}$ of the undissociated HI may be replaced by $\underline{a}_o$, the total hydrogen iodide concentration. Replacing $\underline{a}$ by $\underline{a}_o$, and substituting equations (80) and (81) into equation (78),

$$k_e = \left[\left(\frac{K}{a_o} \right)^{\frac{1}{2}} k_1 + \frac{2(a_o K)^{\frac{1}{2}}}{K_3} k_3 \right] \left(\frac{1 + a_o/K_2}{1 + a_o/K_3} \right)^{\frac{1}{2}} \quad . \tag{82}$$

Finally, if the triple ions are formed to the same extent, i.e.

if K_2 is equal to K_3, the last term vanishes and equation (82) reduces to one of the form

$$k_e = A/a_0^{\frac{1}{2}} + Ba_0^{\frac{1}{2}} \qquad , \qquad (83)$$

where

$$A = K^{\frac{1}{2}}k_1 \qquad , \qquad (84)$$

and

$$B = 2K^{\frac{1}{2}} k_3/K_3 \qquad . \qquad (85)$$

According to equation (83), if an exchange reaction proceeds by both a simple and a triple ion mechanism, at high dilution the observed rate constant should decrease with increasing hydrogen iodide concentration. However, at some concentration, the second term in this equation will become equal in magnitude to the first term, k_e will pass through a minimum, and the observed rate constant will then increase with increasing hydrogen iodide concentration.

The experimental rate constants for exchange in hexanol, dodecanol and acetic acid were found to increase somewhat with increasing hydrogen iodide concentration. The values of k_e in these solvents at $25^{\circ}C$. are given in Table XIX.

By rearranging equation (83),

$$a_0^{\frac{1}{2}} k_e = A + Ba_0 \qquad , \qquad (86)$$

it is evident that if the triple ion mechanism contributed to exchange in these solvents, and if the assumptions made

TABLE XIX

The Experimental Rate Constant, k_e, at
Various Hydrogen Iodide Concentrations, a_o, in
Hexanol, Dodecanol and Acetic Acid at $25^\circ C.$

n-Hexanol		n-Dodecanol		Acetic Acid	
a_o	k_e	a_o	k_e	a_o	k_e
0.0247	0.364	0.0119	0.174	0.0148	0.0352
0.0617	0.465	0.0228	0.197	0.0520	0.0521
0.0993	0.484	0.0603	0.248	0.0615	0.0611
0.123	0.486	0.125	0.319	0.104	0.0765
0.339	0.540	0.159	0.330	0.208	0.101
0.678	0.550	0.159	0.342	0.312	0.0980
		0.251	0.349		
		0.318	0.385		

in the derivation of equation (83) are valid, a plot of $a_o^{\frac{1}{2}} k_e$

versus a_o should result in a straight line with slope equal

to B and intercept equal to A. The curves corresponding to

equation (86) for exchange in these solvents are illustrated

in Fig. 9 and Fig. 10.

A linear relation was obtained for exchange in dodecanol

and acetic acid at low hydrogen iodide concentrations, but at

higher concentrations a decrease in the slope B was observed.

The omission of the term in K_2 and K_3,

$$\left(\frac{1 + a_o/K_2}{1 + a_o/K_3}\right)^{\frac{1}{2}} \quad ,$$

in the derivation of equation (83), may be responsible for this

departure from linearity. If K_2 is not equal to K_3, but is slightly greater than K_3, i.e. if the HI_2^- ions have a greater tendency to form than the H_2I^+ ions, this term will be less than unity at finite concentrations. Then at some concentration, governed by the absolute values of K_2 and K_3, this term will become appreciable and equation (83) will no longer be valid. The omission of this term will result in a decrease in slope with increasing concentration when $a_0^{\frac{1}{2}} k_e$ is plotted against a_0.

The other major assumption made in the derivation of equation (83), i.e. that the concentration of associated ion pairs is equal to the total hydrogen iodide concentration, will become less valid as the concentration decreases. Moreover, the larger the dissociation constant K, the greater will be this error. The failure of the experimental points for exchange in hexanol (Fig. 9) to obey the linear relation at low concentrations may be attributed to the error introduced by this assumption.

The constant terms in equation (83) obtained from the slope and intercepts of Fig. 9 and Fig. 10 are given in Table XX. An equation in A and B giving the concentration at which k_e should pass through a minimum may be obtained by differentiating equation (83) with respect to a_0 and setting

Fig. 9.

Application of Equation (86) to
Exchange in Hexanol and Dodecanol
at 25°C.
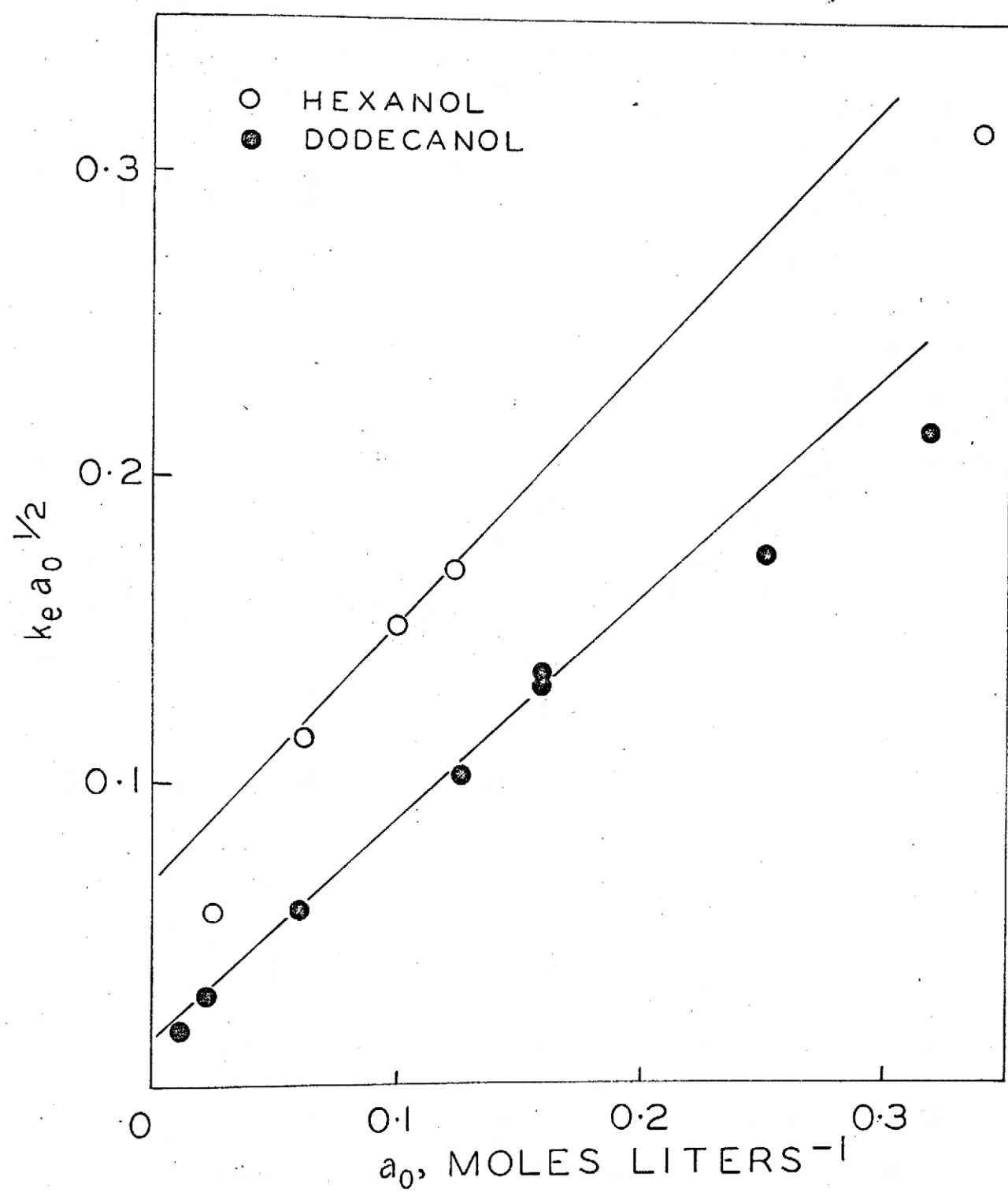
Fig. 10.

Application of Equation (86) to Exchange
in Acetic Acid at 25°C.
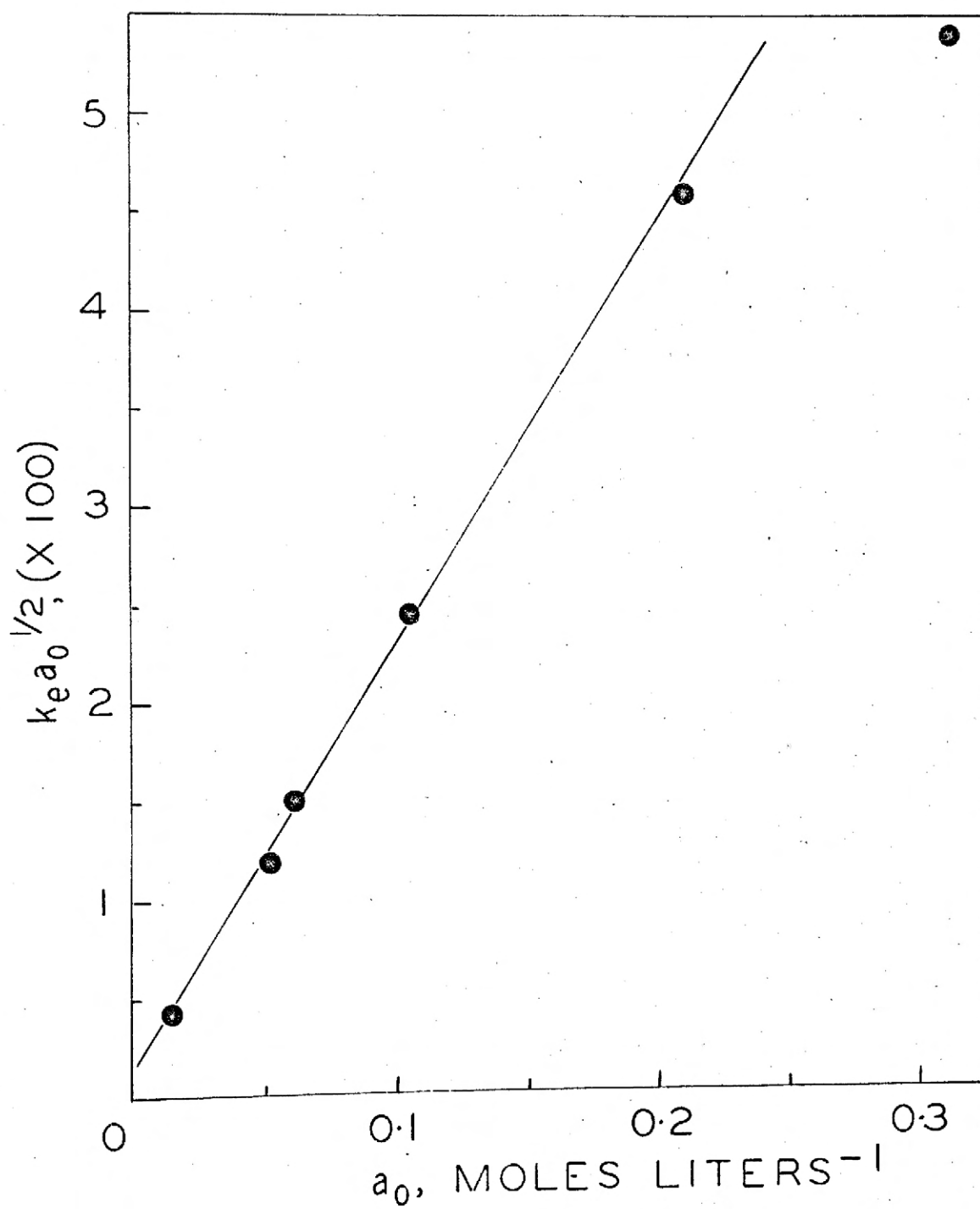
TABLE XX

The Constant Terms in Equation (83).
from Fig. 9 and Fig. 10

Solvent	A (Intercept)	B (Slope)
n-Hexanol	$0.067 \pm 50\%$	$0.85 \pm 25\%$
n-Dodecanol	$0.016 \pm 10\%$	$0.71 \pm 5\%$
Acetic Acid	$0.0014 \pm 10\%$	$0.22 \pm 5\%$

the result equal to zero.

$$\frac{dk_e}{da_o} = -\tfrac{1}{2} A a_m^{-3/2} + \tfrac{1}{2} B a_m^{-\frac{1}{2}} = 0 \quad ,$$

whence

$$a_m = A / B \quad . \tag{87}$$

Substitution of the experimental values of A and B in equation (87) indicated that a minimum in k_e should be observed at hydrogen iodide concentrations of 0.02 molar in dodecanol and 0.006 molar in acetic acid. Owing to the tendency of hydrogen iodide to react with trace impurities in the solvents, no exchange reactions were studied at concentrations less than 0.01 molar, hence the minimum concentration in acetic acid could not be verified. The failure of the minimum to appear in the rate constants for exchange in dodecanol at the lowest concentrations, 0.0228 and 0.0119 molar, is not significant since the difference in these

values of k_e is of the same order of magnitude as the counting error. Definite proof of a minimum with this solvent would also require rate constants at concentrations below 0.01 molar.

It is evident from the values of A and B in Table XX that for concentrations greater than 0.1 molar, the observed rate constant will be essentially equal to the second term in equation (83). For example, for exchange of butyl iodide with 0.1 molar hydrogen iodide in acetic acid,

$$k_e = A/a_0^{\frac{1}{2}} + Ba_0^{\frac{1}{2}} \quad , \tag{83}$$
$$0.074 = 0.004 + 0.070,$$

hence it appears that 95% of the exchange was due to the reaction of triple ions with butyl iodide.

Separation of the equilibrium and rate constants in equations (84) and (85) cannot be made from the rate data alone. However the approximate values of the equilibrium constants K and K_3, obtained from the conductance of hydrogen iodide in these solvents, were used to estimate the order of the rate constants k_1 and k_3. The results of these calculations are given in Table XXI.

TABLE XXI

Estimated Values of the Specific Rate Constants,
k_1 for the Simple Ion Mechanism and k_3
for the Triple Ion Mechanism

Solvent	K *	K_3 *	k_1 1/mole-hr.	k_3 1/mole-hr.
n-Hexanol	1×10^{-4}	2×10^{-2}	6.7	0.85
n-Dodecanol	4×10^{-6}	1×10^{-2}	8.0	1.8
Acetic Acid	7×10^{-7}	6×10^{-3}	1.7	0.8

* from Table VIII.

Although the hydrogen iodide dissociation constants
(K) are subject to considerable uncertainty, owing mainly
to the use of Walden's rule in their estimation, they are
probably of the correct order of magnitude. Since K appears
to the one-half power in equation (84), even a ten-fold error
in the values assigned to it will not alter the value of the
rate constant k_1 more than three-fold. Therefore it is quite
reasonable to regard the values of k_1 listed in Table XXI
to be of the correct order of magnitude.

On the other hand, the values assigned to k_3 are
dependent on both K and the triple ion instability constant
K_3 (equation 85). In estimating the latter constant, it was
assumed that the conductance of the triple ions at infinite

dilution was equal to half the limiting conductance of the simple ions. If this assumption is correct, it appears that the rate of exchange of butyl iodide with the triple ion was less than half the rate of exchange of butyl iodide with the simple iodide ion.

The hypothesis that exchange of hydrogen iodide with butyl iodide in hexanol, dodecanol and acetic acid occurred by simultaneous simple ion - molecule and triple ion - molecule reactions appear to explain the experimental results. The treatment of the rate data according to this hypothesis indicates that the majority of the exchange for hydrogen iodide concentrations greater than 0.1 molar is due to the reaction of HI_2^- triple ions with neutral butyl iodide molecules. Moreover, the values of the individual rate constants, estimated on the assumption that the dissociation constants obtained from conductance data are of the correct order, indicate that the triple ion - molecule reaction is slower than the simple ion - molecule reaction. Consequently, it would appear that at concentrations greater than 0.1 molar, the majority of iodide ions formed by dissociation of hydrogen iodide in these solvents were associated with ion pairs to form HI_2^- triple ions.

Effect of Temperature

The experimental activation energies and the non-exponential parameters of the Arrhenius equation,

$$k_e = A \, e^{-Ee/RT} \quad , \tag{68}$$

for the exchange of 0.05 to 0.10 molar HI with butyl iodide in hexanol and acetic acid are given in Table XXII, and the corresponding activation energy curves are illustrated in Fig. 11. The temperature dependence of the exchange rate in dodecanol was not determined.

TABLE XXII

Arrhenius Line Parameters
for the Exchange of Hydrogen Iodide with n-Butyl Iodide
in Hexanol and Acetic Acid.

Solvent	log A	E_e Kcal./mole
n-Hexanol	13.2	18.4 ± 0.1
Acetic Acid	12.1	18.2 ± 0.1

Since k_e is a function of the hydrogen iodide concentration and the specific rate constants for simple and triple ion exchange, the experimental activation energy will be a function of a_o and the activation energies, E_1 and E_3, associated with the simple and triple ion mechanisms. From equations (68) and (83),

Fig. 11.

Temperature Dependence of Rate

of Exchange of Hydrogen Iodide

with Butyl Iodide in Hexanol

and Acetic Acid.
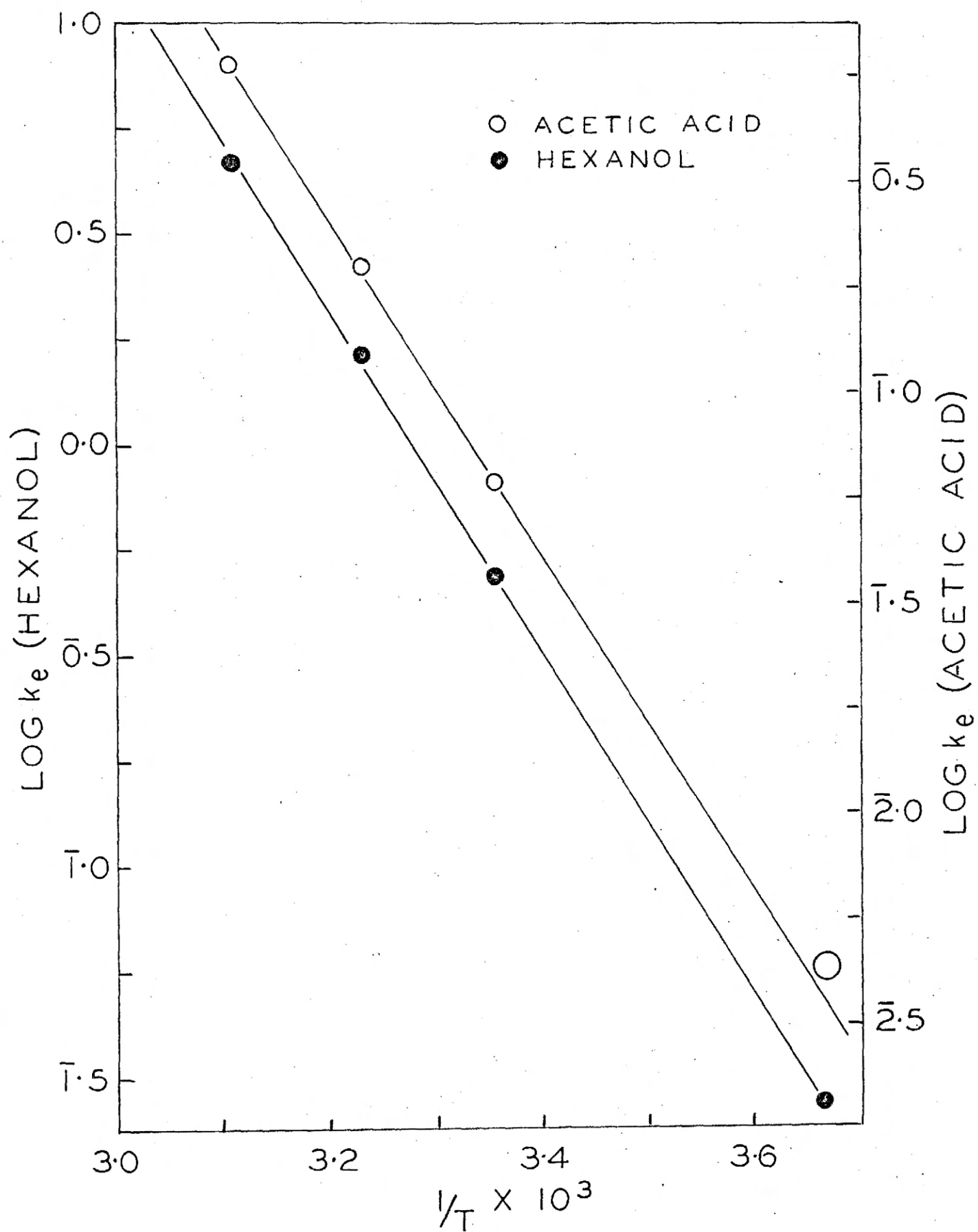
$$Ae^{-E_e/RT} = \left(\frac{K_1}{a_o}\right)^{\frac{1}{2}} A_1 e^{-E_1/RT} + \frac{2(K_1 a_o)^{\frac{1}{2}}}{K_3} A_3 e^{-E_3/RT} \quad . \quad (88)$$

Moreover, E_e will include the heat of dissociation of hydrogen iodide and the triple ion, hence it is not possible to obtain the pure activation energies E_1 and E_3 from the observed critical increment.

It was shown that most of the exchange in acetic acid for hydrogen iodide concentrations greater than 0.1 molar appears to occur by the triple ion mechanism, hence the first term on the right hand side of equation (88) is probably small at these concentrations. This would imply that the observed activation energy, 18.2 Kcal. per mole, is essentially the activation energy for reaction of the triple ion with butyl iodide. Therefore it appears that the activation energies for simple ion and triple ion exchange are of the same order of magnitude.

SOLVENT EFFECTS ON IODINE EXCHANGE

Effect of Solvent on Rate Constant

For the reaction of an ion with a neutral molecule, Laidler and Eyring have shown (33) that an increase in the dielectric constant of the medium should result in a decrease

in the specific rate constant according to the equation

$$\ln k_O = \ln k_g + \frac{(z\varepsilon)^2}{2 \mathcal{K} T} \left(\frac{1}{D} - 1\right)\left(\frac{1}{r_A} - \frac{1}{r^*}\right) , \quad (26)$$

where k_O is the specific rate constant at infinite dilution,

k_g is the rate constant for the reaction in an ideal gas,

$(z\varepsilon)$ is the total charge on the ion,

D is the dielectric constant of the medium, and

r_A and r^* are the radii of the ion and reaction complex, respectively.

Differentiation of equation (26) with respect to (1/D),

$$\frac{d (\ln k_O)}{d (1/D)} = \frac{(z\varepsilon)^2}{2 \mathcal{K} T} \left(\frac{1}{r_A} - \frac{1}{r^*}\right) , \quad (27)$$

indicated that a plot of $\ln k_O$ versus (1/D) should result in a straight line.

Since the exchange of iodine between hydrogen iodide and butyl iodide involved the reaction of an ion with a neutral molecule, the specific rate constants should decrease with increasing dielectric constant. Unfortunately, it was not possible to obtain rate constants at infinite dilution as required in equation (27); however the values of $k_e/\propto$ for exchange in methanol, ethanol and butanol may be used to test this relation. These values and the dielectric constants are given in Table XXIII, together with the rate constants

reported by Hodgson, Evans and Winkler for exchange of iodide
ion with butyl iodide in acetonitrile (17).

TABLE XVII

Change in Specific Rate Constant
with Dielectric Constant at 25°C.

Solvent	D	k_e 1/mole-hr.	k_e/α (k_1)	k_3 1/mole-hr.
Acetonitrile	36.7	10.9*		
Methanol	32.7	0.0563	0.23	
Ethanol	24.2	0.413 (0.36)**	1.17	
Butanol	17.3	0.561	6.0	
Hexanol	12.8	0.484	6.7	0.85
Dodecanol	6.15	0.319	8.0	1.8
Acetic Acid	6.27	0.0765	1.7	0.8

* Hodgson, Evans and Winkler (17); MI and BuI, where M
   is Na, Li and Cs,
** McKay (1); NaI and BuI, value at 25°C. estimated from
   Arrhenius line.

In view of the uncertainty in the values assigned to
the rate constants for exchange in hexanol, dodecanol and
acetic acid, quantitative comparison of these data is not
justified. Nevertheless, the predicted increase in rate con-
stant with decreasing dielectric constant is evident in the
alcohol series. The same trend is apparent in the rate con-
stants for triple ion exchange in hexanol and dodecanol.
However the rate of exchange in acetonitrile observed by
Hodgson et.al. is considerably greater than might be expected

in comparison with the rate in methanol and ethanol. Similarly, the rate in acetic acid appears to be slower than the rate in dodecanol, although these solvents have essentially the same dielectric strength.

The graph corresponding to equation (27) for acetonitrile, methanol, ethanol and butanol is given in Fig. 12. The points representing exchange in the alcohols give an essentially linear relation indicating that equation (26) is valid for this series of solvents. By substituting the slope of this line, the values of the constants and an assumed iodide ion radius of two angstroms in equation (27), the radius of the activated complex appears to be approximately 13 angstroms.

According to Fig. 12, exchange in acetonitrile is almost one hundred-fold faster than would be expected in an alcohol of the same dielectric constant. It is possible that this discrepancy may be due to a smaller activated complex in the nitrile than in the alcohols. If this is true, the radius of the activated complex in acetonitrile appears to be about 15% smaller than the radius in the alcohols. On the other hand, Laidler and Eyring are of the opinion that varying degrees of solvation of the ion are responsible for any failures in their rate constant-dielectric

Fig. 12.

Effect of Dielectric Constant on

the Rate of Exchange of Iodide

Ion with Butyl Iodide.
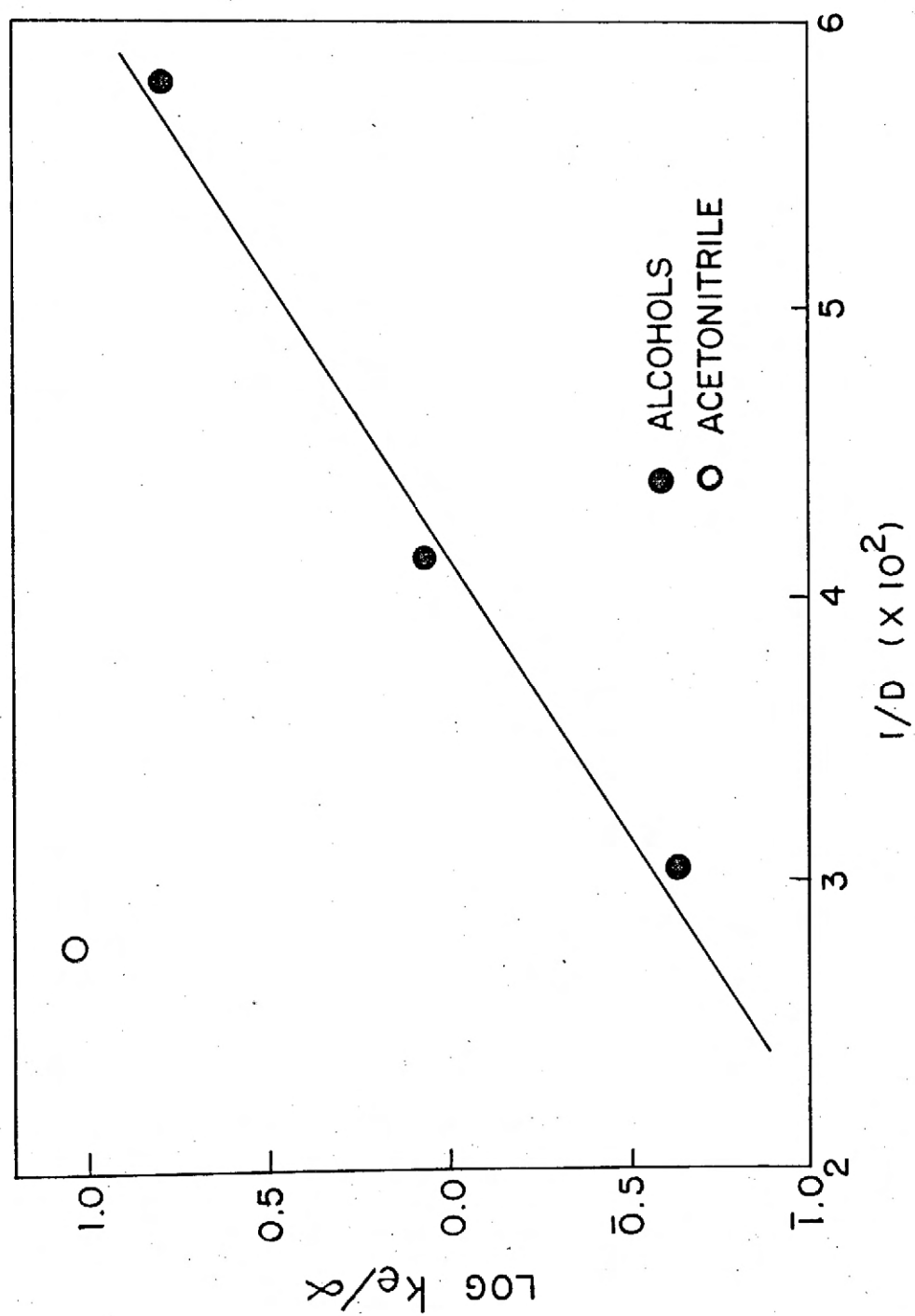
constant relation.

Effect of Solvent on Activation Energy

The activation energies for iodide ion - butyl iodide exchange in methanol, ethanol and butanol have been listed in Table XXIII, along with the activation energy recorded by Hodgson et.al. for reaction in acetonitrile.

TABLE XXIII

Activation Energy for Exchange of Iodide Ion with Butyl Iodide in Various Solvents

Solvent	E_e, Kcal./mole
Acetonitrile	18.1 ± 0.1
Methanol	18.6 0.1
Ethanol	19.5 0.1
Butanol	19.4 0.1

Ogg and Polanyi have considered the activation energy of inorganic-organic halide interchange and exchange reactions to consist of four distinct energy terms. These are the energies required a) to overcome electrostatic interaction between ion and molecule, b) to distort the carbon - halide bond, c) to transform the tetrahedral organic configuration to that of the reaction complex, and d) to overcome the solvation barrier. Since only the solvent has been changed in the present study, the first three

energy terms will be constant and any difference in activation energies will presumably be due to solvation effects.

According to this hypothesis, it would appear that the affinity of the iodide ion for these solvents decreases in the order ethanol $>$ butanol $>$ methanol $>$ acetonitrile. Moreover, the difference in activation energies for exchange in ethanol and methanol indicates that the energy required to solvate the iodide ion in ethanol is about one kilocalorie per mole greater than the solvation energy in methanol.

Mishchenko has argued that the difference in lattice energy and integral heat of solution of a salt should be a measure of the heat of solvation of the ions of that salt (58). He estimated the heat of solvation of various ions by assuming ions of approximately the same size (eg. Cs^+ and I^-) to be solvated to the same extent. These calculations also indicate that solvation of the iodide ion in ethanol requires one kilocalorie per mole more than solvation in methanol. This seems to support the hypothesis that solvation effects are responsible for the variation in activation energy with the solvent medium.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

The contributions of this investigation to the knowledge of mechanisms of halide interchange between organic and inorganic halides, and the effect of the solvent medium on ion - neutral molecule reactions, may be summarized as follows:

1. Iodine is exchanged between sodium iodide and liquid hydrogen iodide at $-35°$ to $-45°C$. This exchange may be used to activate hydrogen iodide when the presence of a solvent is undesirable, with essentially complete recovery of the radioisotope.

2. The exchange iodine between sodium iodide and either hydrogen iodide or the halogen itself in n-hexanol was found to be too rapid at room temperature to be followed experimentally.

3. The exchange of hydrogen iodide with n-butyl iodide in toluene is negligibly slow at $50°C$. It would appear that under these conditions, butyl iodide and the associated ion pair, H^+I^-, do not exchange to any appreciable extent.

4. The exchange of hydrogen iodide with n-butyl iodide was found to be second order (i.e. dependent on the concentration of hydrogen and butyl iodides each to the first power) in methanol, ethanol, n-butanol, n-hexanol, n-dodecanol and

acetic acid, between 0° and 50^OC.

5. The rate data obtained for the exchange in methanol, ethanol and butanol may be interpreted on the basis of a rate controlling exchange between iodide ions and butyl iodide. The specific rate constants of 25^OC. for this step have been estimated by assuming reasonable values for the dissociation constants of hydrogen iodide in these solvents.

6. Exchange in hexanol, dodecanol and acetic acid appears to occur by reaction of butyl iodide with HI_2^- triple ions, as well as simple iodide ions. The kinetics indicate that the triple ion mechanism is predominant in dodecanol and acetic acid at hydrogen iodide concentrations greater than 0.1 molar.

Approximate values of the dissociation constants of hydrogen iodide and the associated ion triplets have been used to estimate the order of magnitude of the individual specific rate constants. These approximations indicate that the rate of exchange by the triple ion mechanism is less than half the rate of exchange by the simple ion mechanism. However, the activation energies for simple and triple ion exchange appear to be of the same order of magnitude.

7. In agreement with the solvent effect predicted by Laidler

and Eyring, the rate constant for iodide ion - butyl iodide
exchange appears to decrease with increasing dielectric
constant in the aliphatic alcohols. However, the exchange
in acetic acid appears to be slower than exchange in dodec-
anol, which has approximately the same dielectric constant.
Similarly, the rate observed by Hodgson et.al. for the ex-
change in acetonitrile is considerably greater than would
be expected in an alcohol of comparable dielectric strength.
Hence the rate constant - dielectric constant relation does
not appear to hold for solvents which are not homologous.
The reason for this failure is not clear, although it is
probably due, at least in part, to solvation effects.

6. The experimental activation energies, which include
small energy terms associated with the ionization constant
of hydrogen iodide, have been found to decrease in the order
ethanol $>$ butanol $>$ methanol $>$ acetonitrile. These small
differences are probably due to variation in the height
of the solvation barrier hindering the formation of the
reaction complex.

It must be emphasized that the values assigned to
the true rate constants are subject to the uncertainties
in the values accepted for the dissociation constants of
hydrogen iodide. However, pending more accurate knowledge

of the dissociation constants, the specific rate constants may be regarded as being of the correct order of magnitude.

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APPENDIX

The Exchange of Hydrogen Iodide with

n-Butyl Iodide in Methanol, Ethanol,

n-Butanol, n-Hexanol, n-Dodecanol

and Glacial Acetic Acid

Details of the Exchange Experiments.

TABLE A

The Exchange of Hydrogen Iodide with n-Butyl Iodide in Methyl Alcohol

Temp. °C.	Conc.HI M	Conc. BuI M	Time hr.	A	σ%	k_e 1/mole-hr.
0.0	0.0751	0.500	Zero	247		
			12	237	6.5	0.0093
			24	220	12.5	0.00932
			36	210	17.0	0.00881
			60	192	25.6	0.00837
			66	182	29.8	0.00909
			∞	30		
						$\overline{0.00874} \pm 3\%$
25.0	0.0563	0.625	Zero	248		
			2.0	205	18.9	0.157
			4.0	167	35.7	0.163
			5.5	146	44.9	0.160
			7.0	125	54.2	0.164
			8.0	115	58.6	0.162
			∞	21		
						$\overline{0.162} \pm 1\%$
36.2	0.0409	0.455	Zero	255		
			1.0	202	22.6	0.528
			2.0	160	40.6	0.536
			3.0	130	53.5	0.525
			3.5	116	59.5	0.531
			4.5	95	68.4	0.517
			5.5	80	74.9	0.507
			∞	21		
						$\overline{0.525} \pm 2\%$
36.2	0.107	0.286	Zero	247		
			1.0	215	17.8	0.507
			2.0	192	30.6	0.477
			3.0	168	43.9	0.500
			4.0	155	51.1	0.465
			5.0	140	59.5	0.469
			6.0	124	68.4	0.496
			∞	67		
						$\overline{0.480} \pm 3\%$

TABLE   A   (Cont'd)

Temp. °C.	Conc.HI M	Conc. BuI M	Time hr.	A	σ %	k_e 1/mole hr.
48.6	0.0751	0.200	Zero	247		
			1.0	183	35.8	1.66
			2.0	146	56.5	1.57
			3.0	124	68.8	1.46
			3.5	116	73.2	1.42
			4.5	97	83.9	1.53
			∞	68		
						$\overline{1.49 \pm 3\%}$

TABLE   B

The Exchange of Hydrogen Iodide with n-Butyl Iodide
in Ethyl Alcohol

Temp. °C.	Conc.HI M	Conc.BuI M	Time	A	σ %	k_e 1/mole hr.
0.0	0.0539	0.500	Zero	319		
			14	274	15.6	0.0215
			Zero	364		
			24	285	24.2	0.0208
			39	244	36.7	0.0212
			43	222	43.4	0.0238
						$\overline{0.0216 \pm 3\%}$
25.0	0.0866	0.200	Zero	572		
			3	474	24.6	0.315
			4	432	35.1	0.378
			5	404	42.1	0.381
			6	376	49.1	0.394
			∞	173		
						$\overline{0.382 \pm 2\%}$
25.0	0.0290	0.334	Zero	528		
			2	388	28.8	0.467
			3	331	40.5	0.477
			4	286	49.9	0.472
			5	246	58.0	0.478
			∞	42		
						$\overline{0.473 \pm 1\%}$

TABLE   B   (Cont'd)

Temp. $^{\circ}$C.	Conc.HI M	Conc.BuI M	Time hrs.	A	σ %	k_e 1/mole-hr.
25.0	0.00975	0.600	Zero	295		
			2.0	161	46.2	0.518
			2.5	138	54.2	0.512
			3.5	98	68.0	0.533
			4.5	75	76.0	0.520
			∞	5		
						$\overline{0.519} \pm 2\%$
25.0	0.0342	0.600	Zero	298		
			1.0	230	24.5	0.444
			2.0	177	42.9	0.444
			2.5	151	52.2	0.465
			3.5	114	65.3	0.478
			4.5	90	73.8	0.469
			∞	16		
						$\overline{0.469} \pm 3\%$
25.0	0.1025	0.600	Zero	295		
			1.0	232	25.0	0.409
			2.0	181	45.3	0.427
			2.5	166	51.2	0.409
			3.0	151	57.2	0.402
			3.5	133	63.9	0.414
			4.5	109	73.8	0.424
			∞	43		
						$\overline{0.413} \pm 2\%$
25.0	0.1675	0.600	Zero	272		
			1.0	218	25.2	0.378
			2.0	172	44.6	0.383
			3.0	144	59.9	0.397
			3.5	136	63.5	0.376
			4.5	117	72.5	0.375
			∞	58		
						$\overline{0.379} \pm 1\%$

TABLE B (Cont'd)

Temp. °C.	Conc.HI M	Conc.BuI M	Time hrs.	A	σ %	k_e 1/mole-hr.
25.0	0.244	0.600	Zero	272		
			1.0	223	25.4	0.347
			2.0	183	46.2	0.367
			2.5	168	53.9	0.368
			3.0	157	59.6	0.358
			3.5	147	64.8	0.352
			∞	79		
						$\overline{0.362 \pm 1\%}$
25.0	0.335	0.600	Zero	272		
			2.0	193	45.7	0.326
			2.5	176	55.2	0.334
			3.0	163	62.6	0.351
			3.5	156	66.7	0.337
			4.5	143	74.2	0.322
			∞	98		
						$\overline{0.333 \pm 2\%}$
34.7	0.0268	0.100	Zero	417		
			1.0	365	15.8	1.38
			2.0	320	30.1	1.43
			3.0	278	42.0	1.45
			4.0	247	51.4	1.43
			∞	86		
						$\overline{1.43 \pm 2\%}$
34.7	0.0356	0.267	Zero	368		
			1.0	270	30.5	1.20
			1.5	235	40.9	1.15
			2.0	193	53.9	1.27
			2.5	161	62.2	1.29
			3.0	144	69.0	1.27
			3.5	122	75.7	1.33
			∞	44		
						$\overline{1.27 \pm 2\%}$
48.6	0.0356	0.133	Zero	320		
			0.33	259	25.0	5.20
			0.67	206	45.3	5.34
			1.00	166	61.1	5.58
			1.33	139	71.8	5.76
			1.67	119	78.0	5.40
			∞	52		
						$\overline{5.56 \pm 3\%}$

TABLE C

The Exchange of Hydrogen Iodide with n-Butyl Iodide
in n-Butyl Alcohol

Temp. °C.	HI M	BuI M	Time hr.	A	σ %	k_e 1/mole hr.
0.0	0.102	0.625	Zero	241		
			22	169	34.6	0.0260
			30	148	44.9	0.0267
			42	128	54.4	0.0253
			49	112	62.0	0.0266
			66	95	70.3	0.0248
			∞	34		
						$\overline{0.0260} \pm 2\%$
25.0	0.102	0.625	Zero	312		
			1.0	222	33.6	0.566
			2.0	162	55.9	0.563
			3.0	122	71.0	0.565
			4.0	100	79.0	0.535
			5.0	83	85.5	0.530
			∞	44		
						$\overline{0.561} \pm 3\%$
36.2	0.170	0.375	Zero	272		
			0.25	234	20.6	1.72
			0.50	199	39.4	1.86
			0.75	174	53.0	1.89
			1.00	158	61.7	1.79
			1.25	140	71.4	1.89
			∞	87		
						$\overline{1.86} \pm 2\%$
36.2	0.0387	0.143	Zero	241		
			1.0	187	28.4	1.86
			2.0	148	49.0	1.88
			3.0	119	64.2	1.91
			4.0	103	72.6	1.80
			5.0	86	81.5	1.88
			∞	51		
						$\overline{1.87} \pm 1\%$

TABLE   C   (Cont'd)

Temp. °C.	HI M	BuI M	Time hr.	A	$\sigma\%$	k_e 1/mole-hr.
48.6	0.0387	0.143	Zero	241		
			0.33	183	30.5	6.15
			0.67	141	52.6	6.31
			1.00	112	67.9	6.38
			1.33	95	76.9	6.20
			1.67	84	82.7	5.90
			2.00	73	88.5	6.09
			∞	51		
						$\overline{6.15}\pm2\%$

TABLE   D

The Exchange of Hydrogen Iodide with n-Butyl Iodide
in n-Hexyl Alcohol

Temp. °C.	HI M	BuI M	Time hr.	A	$\sigma\%$	k_e 1/mole-hr.
0.0	0.0993	0.625	Zero	198		
			23	133	38.0	0.0282
			31	118	46.8	0.0276
			43	99	57.9	0.0273
			48	93	61.5	0.0269
			54	80	67.3	0.0280
			∞	27		
						$\overline{0.0276}\pm1\%$
25.0	0.0993	0.625	Zero	207		
			1.0	153	30.1	0.496
			1.5	135	40.2	0.473
			2.0	114	52.0	0.506
			3.0	88	66.5	0.490
			4.0	67	73.2	0.456
			∞	28		
						$\overline{0.484}\pm2\%$

TABLE   D   (Cont'd)

Temp. °C.	HI M	BuI M	Time hr.	A	σ %	k_e 1/mole-hr.
25.0	0.0247	0.800	Zero	266		
			0.5	230	13.9	0.368
			1.5	172	36.4	0.362
			2.0	150	45.0	0.362
			2.5	137	50.0	0.338
			∞	8		
						$\overline{0.364} \pm 2\%$
25.0	0.0617	0.800	Zero	266		
			0.5	222	17.8	0.454
			1.0	186	32.4	0.454
			1.5	153	45.7	0.472
			2.0	130	55.0	0.464
			2.5	117	60.4	0.464
			3.0	91	70.8	0.475
			∞	19		
						$\overline{0.465} \pm 1\%$
25.0	0.123	0.800	Zero	266		
			0.58	211	23.9	0.504
			1.0	183	36.2	0.488
			1.5	154	48.7	0.481
			2.0	130	59.2	0.484
			2.5	113	66.5	0.475
			3.0	97	73.5	0.491
			∞	36		
						$\overline{0.486} \pm 1\%$
25.0	0.339	0.800	Zero	442		
			0.5	348	27.6	0.556
			1.0	293	47.4	0.564
			1.5	254	60.3	0.542
			2.0	225	70.0	0.528
			2.5	200	77.8	0.528
			3.0	181	84.0	0.536
			∞	131		
						$\overline{0.540} \pm 2\%$

TABLE   D   (Cont'd)

Temp. °C.	HI M	BuI M	Time hr.	A	σ %	k_e 1/mole-hr.
25.0	0.678	0.800	Zero	441		
			0.5	357	34.5	0.569
			1.0	309	55.5	0.550
			1.5	278	68.5	0.522
			2.0	251	79.8	0.544
			2.5	233	87.4	0.561
			3.0	223	91.3	0.550
			∞	203		
						$\overline{0.550} \pm 2\%$
36.2	0.118	0.556	Zero	198		
			0.25	158	24.5	1.68
			0.50	129	42.3	1.64
			0.75	104	57.7	1.72
			1.00	91	66.4	1.62
			1.25	78	73.6	1.58
			∞	35		
						$\overline{1.65} \pm 2\%$
36.2	0.0442	0.250	Zero	198		
			0.5	165	19.7	1.50
			1.0	134	38.1	1.63
			1.5	114	50.0	1.58
			2.0	98	59.5	1.55
			2.5	86	66.7	1.51
			3.0	75	73.3	1.51
			∞	30		
						$\overline{1.55} \pm 2\%$
48.6	0.0756	0.214	Zero	180		
			15	145	26.3	4.25
			25	122	43.6	4.81
			35	112	51.1	4.28
Time in minutes			45	98	61.6	4.46
			55	86	70.7	4.67
			65	75	78.9	5.02
			∞	47		
						$\overline{4.63} \pm 3\%$

TABLE E

The Exchange of Hydrogen Iodide with n-Butyl Iodide
in n-Dodecyl Alcohol at $25.0^{\circ}C$.

HI M	BuI M	Time hr.	A	$\sigma \%$	k_e 1/mole-hr.
0.0119	1.00	Zero	333		
		1.5	255	23.6	0.176
		2.5	214	36.1	0.176
		3.5	182	45.7	0.172
		5.0	141	58.1	0.171
		6.5	113	66.7	0.166
		∞	3		
					$\overline{0.174} \pm 2\%$
0.0228	1.00	Zero	349		
		1.5	260	26.1	0.198
		2.5	210	40.6	0.202
		3.5	179	49.9	0.193
		5.0	133	63.4	0.197
		5.5	123	66.3	0.193
		6.5	100	73.0	0.197
		∞	8		
					$\overline{0.197} \pm 2\%$
0.0603	1.00	Zero	387		
		1	298	24.4	0.262
		2	235	41.6	0.254
		3	189	54.2	0.246
		4	147	65.8	0.253
		5	123	72.1	0.242
		6	101	78.6	0.244
		∞	22		
					$\overline{0.248} \pm 2\%$
0.125	1.00	Zero	419		
		1	306	30.4	0.323
		2	223	52.7	0.333
		3	176	65.4	0.319
		5	112	82.5	0.309
		∞	47		
					$\overline{0.319} \pm 3\%$

TABLE E (Cont'd)

HI M	BuI M	Time hr.	A	σ %	k_e 1/mole-hr.
0.159	0.333	Zero	439		
		1.0	394	15.1	0.331
		2.0	355	28.3	0.339
		3.0	323	39.1	0.337
		3.5	312	42.8	0.326
		4.0	297	47.8	0.329
		5.0	272	56.2	0.335
		∞	142		
					$\overline{0.330}\pm 2\%$
0.159	1.00	Zero	475		
		1.0	342	32.5	0.340
		1.5	290	45.1	0.346
		2.0	249	55.1	0.345
		2.5	215	63.4	0.343
		3.0	192	68.0	0.334
		3.5	177	72.7	0.320
		∞	65		
					$\overline{0.342}\pm 2\%$
0.251	1.00	Zero	387		
		0.384	339	15.5	0.350
		1.0	274	36.6	0.366
		2.0	208	57.9	0.345
		2.5	177	68.0	0.346
		3.0	158	74.2	0.356
		3.5	147	77.7	0.342
		∞	78		
					$\overline{0.349}\pm 2\%$
0.318	1.00	Zero	512		
		0.5	421	22.9	0.393
		1.0	358	39.8	0.385
		1.5	302	54.0	0.392
		2.0	268	62.7	0.374
		2.5	230	72.2	0.389
		3.0	207	78.4	0.379
		∞	123		
					$\overline{0.385}\pm 2\%$

TABLE F

The Exchange of Hydrogen Iodide with n-Butyl Iodide
in Glacial Acetic Acid

Temp. °C.	HI M	BuI M	Time hr.	A	σ %	k_e 1/mole-hr.
0.0	0.0819	1.00	Zero	237		
			24	212	11.3	0.00458
			43	198	17.6	0.00405
			∞	16		
						$\overline{0.0043} \pm 10\%$
25.0	0.0148	1.00	Zero	276		
			6	225	18.8	0.0344
			8	208	25.0	0.0345
			10	195	29.9	0.0350
			12	178	34.8	0.0351
			14	160	42.7	0.0392
			∞	4		
						$\overline{0.0353} \pm 2\%$
25.0	0.0520	1.00	Zero	264		
			4	217	18.7	0.0492
			6	196	27.7	0.0514
			8	174	36.9	0.0525
			10	157	42.7	0.0530
			12	143	48.1	0.0519
			14	134	51.8	0.0497
			∞	13		
						$\overline{0.0521} \pm 3\%$
25.0	0.0615	0.625	Zero	258		
			5	214	18.7	0.0609
			8	190	29.0	0.0623
			12	167	38.7	0.0595
			15	146	47.7	0.0629
			18	133	52.4	0.0600
			∞	23		
						$\overline{0.0611} \pm 2\%$

TABLE F (Cont'd)

Temp. °C.	HI M	BuI M	Time hr.	A	σ %	k_e 1/mole-hr.
25.0	0.104	1.00	Zero	266		
			4	200	27.4	0.0724
			6	170	39.9	0.0766
			8	147	49.7	0.0776
			10	127	57.6	0.0761
			12	112	63.9	0.0768
			14	102	68.0	0.0735
			∞	25		
						$\overline{0.0765} \pm 3\%$
25.0	0.208	1.00	Zero	230		
			1	208	11.6	0.102
			2	189	21.6	0.101
			3	170	31.6	0.105
			4	155	39.5	0.104
			5	145	44.1	0.0961
			6	138	48.4	0.0920
			∞	40		
						$\overline{0.101} \pm 3\%$
25.0	0.312	1.00	Zero	226		
			1	205	12.1	0.103
			2	185	23.7	0.103
			3	170	32.4	0.0991
			4	157	39.9	0.0969
			5	145	46.7	0.0956
			6	136	52.6	0.0950
			∞	54		
						$\overline{0.0980} \pm 3\%$
36.2	0.0819	1.00	Zero	237		
			1.0	193	20.1	0.209
			3.0	131	48.4	0.205
			3.5	122	52.5	0.199
			4.5	103	61.5	0.198
			5.5	87	68.5	0.196
			∞	18		
						$\overline{0.200} \pm 2\%$

TABLE F (Cont'd)

Temp. °C.	HI M	BuI M	Time hr.	A	σ %	k_e 1/mole-hr.
48.6	0.0467	0.715	Zero	263		
			0.5	210	21.4	0.638
			1.0	168	38.4	0.645
			1.5	143	48.6	0.594
			2.0	123	56.7	0.559
			2.5	102	65.2	0.565
			3.0	88	71.2	0.555
			∞	16		
						$\overline{0.594} \pm 3\%$
48.6	0.117	0.286	Zero	256		
			1	209	25.8	0.747
			2	174	45.1	0.757
			3	153	56.6	0.700
			4	133	67.5	0.708
			5	118	75.9	0.716
			∞	74		
						$\overline{0.726} \pm 2\%$