

THE EFFECT OF PRESSURE ON FORWARD AND REVERSE

MENSCHUTKIN REACTIONS

A thesis presented for the
Degree of Doctor of Philosophy
of the
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by

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ABSTRACT

The effects of pressures up to 3000 atm. on the reaction rates of several forward and reverse Menschutkin reactions, and on the ionic dissociation of a quaternary ammonium salt are reported. The high pressure apparatus and experimental methods are described. A review of the controversy regarding the effect of pressure on Menschutkin reactions is presented. The results are discussed by examination of activation volumes.

The reverse reaction in nitrobenzene is shown to be first order in the concentration of quaternary salt ion-pairs. The change in the rate constant with concentration in ionizing and non-ionizing solvents is explained.

The apparent change of order with increasing pressure reported by Harris for the forward reaction of ethyl iodide with dimethylaniline in nitrobenzene is shown to be an autocatalytic effect associated with solvent freezing.

The activation volume for reverse Menschutkin reactions is much higher than has been supposed. For the decomposition of allyl-benzyl-methyl-phenyl ammonium bromide in chloroform it is + 13.6 cc/mole, not + 3.4 cc/mole as previously reported. For the decomposition of ethyl-dimethyl-phenyl ammonium iodide in nitrobenzene it is + 32.5 cc/mole. Previous measurements of the overall reaction volume are also partly in error, due to neglect

of the volume change accompanying ion-pair dissociation.

A complete volumetric description of the methyl iodide/ethylmethylaniline reaction system is developed. The transition state is closer to the reactants than to the products in regard to solvation and compressibility. About one-half of the activation volume for the forward reaction and almost all of the activation volume for the reverse reaction are due to solvation. Activation entropy changes are shown to be a poor criterion of the extent of solvation. The volumetric behaviour can be explained if the charges are half developed in the transition state. These conclusions are shown to be at variance with the theories of Gonikberg et al.

The effect of different solvents on the pressure effect is explained using Born's solvation theory.

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SECTION I. INTRODUCTION

I.A. SCOPE OF THESIS

1. Value of High Pressure Kinetic Studies

The effect of high pressure on reaction rate, as well as being intrinsically interesting, is often a powerful tool in differentiating between possible mechanisms and elucidating the course of reactions at atmospheric pressure. For this reason, and because of the increasing availability of reliable high pressure equipment, the pressure parameter has recently received increasing attention. The development of important commercial applications of high pressure chemistry has also focussed attention on this field.

Reactions in the liquid phase give the most useful information on the specific chemical effects of pressure. In gas reactions the chemical effects are difficult to separate from purely volumetric effects and variations in fugacity; in reacting solids, isothermal isobaric conditions are difficult to maintain.

Extreme pressures are not usually necessary to derive useful information on the chemical effects of pressure. In many cases pressures of less than 1000 atm. are quite sufficient, as the useful item of information is obtained by extrapolation of some parameter to atmospheric pressure. For instance, the activation volume of a reaction, useful in the study of reaction mechanism, is derived from the slope of the $\log \frac{k_p}{k_1}$ isotherm at 1 atm. pressure.

2. Menschutkin Reactions

Menschutkin reactions, reactions between a tertiary amine and an alkyl halide to form a quaternary ammonium salt, have been frequently studied under high pressures. These reactions proceed at a rate convenient for study, are relative free of side reactions and are considerably accelerated by pressure. As well, a great variety of reactants of widely differing structures (of both amine and halide) can be used and the reaction proceeds in many different solvents. Another advantage is that the reaction has been extensively studied at atmospheric pressure. Its known characteristics at atmospheric pressure can be of help in elucidating the pressure effect (as a corollary the measured effect of pressure helps in the interpretation of the reaction mechanism).

Menschutkin reactions proceed in the reverse direction as well, the quaternary ammonium salt decomposing into the tertiary amine and the alkyl halide. This decomposition could be classified as a Hofmann degradation. In this thesis it will be called, for convenience, a reverse Menschutkin reaction. In contrast to the considerable work done on forward Menschutkin reactions, only one measurement of the effect of pressure on reverse Menschutkin reactions has been reported⁽¹⁾, and this was of a single rate constant at only one pressure. In fact, the mechanism of reverse Menschutkin reactions at one atmosphere has not been properly elucidated.

A great deal of controversy has arisen as to the nature of the pressure effect on Menschutkin reactions, especially between those who consider that the acceleration of the reaction by pressure is due mainly to solvation of the transition state (notably Hamann et al.), and those who consider that the volume decrease of the reactants as they approach to form the transition state is responsible (notably Gonikberg et al.).

3. Main Purpose of this Research

It appeared that a comprehensive study of the effect of pressure on a Menschutkin reaction in both the forward and reverse directions would be useful in evaluating these theories. No such research had previously been reported, and, in fact, few reactions of any kind have been comprehensively studied in both directions under high pressures. The difference between the reported activation volumes for Menschutkin reactions and the total volume changes needed clarification. The activation volumes for the forward reaction are usually about half of the overall volume change (e.g. 25 cc/mole compared with 55 cc/mole) and the activation volume reported for the one reverse reaction studied (+ 3.4 cc/mole⁽¹⁾) is much too small to account for the discrepancy.

The following steps were required in making this comprehensive study :

- (i) selection of a reaction which proceeds at a convenient rate in both directions. (The reaction chosen was that of

N-ethyl-N-methylaniline with methyl iodide to form ethyl-dimethyl-phenyl ammonium iodide, in nitrobenzene solvent).

- (ii) Confirmation that the reverse reaction proceeds through the same transition state as the forward reaction. This involved determining the reaction products of the reverse reaction and the details of its mechanism. (The fact that neither first nor second order kinetics properly describe reverse Menschutkin reactions had not been previously explained).
- (iii) Measurement of the rates of the forward and reverse reactions under high pressures to determine the activation volumes of both.
- (iv) Measurement of the overall reaction volume change at one atmosphere pressure.
- (v) Measurement of the equilibrium constant for the dissociation of the quaternary salt into its constituent ions as a function of pressure and temperature. This was required for calculation of the part that dissociation plays in the overall reaction volume, as well as to elucidate the mechanism of the reverse reaction.

4. Other ^{or} Purposes

This comprehensive study of one reaction constitutes the main part of the research described in this thesis. However, three other associated pressure effects were investigated.

The only previous study of a reverse Menschutkin reaction under high pressure reported in the literature ⁽¹⁾ was of the

decomposition of allyl-benzyl-methyl-phenyl ammonium bromide in chloroform at 1 atm. and 2900 atm. The average activation volume calculated from this result (+ 3.4 cc/mole) has been widely quoted in support of various theories of the pressure effect. Since the true activation volume, measured from the slope of the $\log \frac{k_p}{k_1}$ isotherm at one atmosphere could be greatly different from this figure, it was decided to repeat the rate measurements over a range of pressures between 1 and 2900 atm.

The second effect was a report by Harris⁽²⁾ of a change in the order of reaction from second to first, with increasing pressure, in the reaction between N : N-dimethylaniline and ethyl iodide in nitrobenzene. An object of this research was to verify and explain this phenomenon. Data on the pressure effect on this reaction could also then be compared with that of Harris (loc.cit.) for the same reaction in methanol solvent.

Finally, it appeared to be of value to measure the effect of pressure (and hence the activation volume) on reverse Menschutkin reactions for which the effect of pressure in the forward direction had been reported. It was therefore decided to examine some of these systems to see if the reverse reaction occurred to an appreciable extent and at a rate convenient for study.

5. Contents of the Thesis

This thesis is divided into five sections. The first section includes introductory and theoretical considerations.

The theory of the mechanism of Menschutkin reactions is reviewed since the characteristics of the transition state are important in determining the pressure effect. The controversy over the nature of the pressure effect in Menschutkin reactions, which prompted this research, is also discussed.

The second section deals with apparatus and materials. The basic high pressure apparatus was available in the High Pressure Laboratory. This equipment, and the modifications required, are described.

The third section explains experimental procedures and calculations of primary data. The conductance method developed for the measurement of the rate of reverse Menschutkin reactions is more thoroughly discussed than the fairly straightforward volumetric methods used for the forward reactions. Calculation methods required to obtain the primary data (rate constants, dissociation constants) are described, and sample calculations given.

The results (Section IV) are listed only as the calculated rate constants and dissociation constants, since typical experimental measurements used in obtaining the data are given in Section III.

The results are discussed in Section V with particular reference to Hamann's and Gonikberg's theories of the pressure effect. The mechanism of reverse Menschutkin reactions is also discussed, and the apparent change of reaction order with pressure reported by Harris⁽²⁾ is explained.

IB. HISTORICAL REVIEW OF LIQUID PHASE REACTION
KINETICS AT HIGH PRESSURES

1. Introduction

A short account of past work on chemical kinetics in the liquid phase at high pressure is given below and the main contributions to the theory of the pressure effect are listed. (A full review of current theories will be given in Section IC).

Several thorough literature reviews on high pressure reaction kinetics are available, especially those of Strauss⁽³⁾⁽⁴⁾. (Others are those of Fawcett and Gibson⁽⁵⁾ and Bridgman⁽⁶⁾ for early work; and of Hamann⁽⁷⁾ for recent work). The literature from before 1928 was not directly consulted, data being obtained from these secondary references.

The specialized field of high pressure polymerization will not be included in this review. A good summary of this field is given in Hamann's book⁽⁷⁾.

2. Previous to 1940

Very little systematic work on the pressure effect on liquid phase reactions was done until the closing years of the last century, although some qualitative observations had earlier been made (e.g. Berthelot and Peon de Saint Giles⁽⁸⁾ found no change in the rate of esterification of acetic acid with ethanol at 100 atm.)

By 1890 techniques for achieving and maintaining pressures up to 3000 atm. had been developed and some of the physical effects

of pressure, such as liquid compression, had been investigated (much of this progress was due to Cailletet and Amagat; it is reviewed in Bridgman's book⁽⁶⁾). As well, by this time the groundwork of the theory of chemical kinetics had been laid.

The work of Roentgen⁽⁹⁾ in 1892 marked the beginning of systematic study of the pressure effect on reaction rate. Roentgen, and later Stern⁽¹⁰⁾ and Rothmund⁽¹¹⁾, studied the effects of pressures to 500 kg/cm² on the acid-catalyzed inversion of sucrose. Rothmund also observed the acceleration of acid-catalyzed ester hydrolysis by pressure, showing that this was a specific pressure effect, not due to changes in acid dissociation or concentration.

Rothmund fitted his results to an equation of the type :

$$\ln \frac{k_p}{k_l} = \frac{P\Delta V}{RT} \quad (I-1)$$

where k_p and k_l are the rate constants at P and 1 atm. respectively and P is the pressure. ΔV was considered a volume term, although its meaning was not understood. (Planck⁽¹²⁾ had derived the thermodynamic equation relating the equilibrium constant and the pressure in 1887).

It is interesting to note that the effect of pressure on ester hydrolysis and sucrose inversion, the subject of these pioneering studies, is still not completely understood⁽¹³⁾.

Cohen, Moesveld and co-workers (summarized in reference⁽¹⁴⁾) in the period 1909 to 1929 extended the study of ester hydrolyses

to 1500 kg/cm² and studied the effect of pressure on the bromate-bromide ion reaction.

During the 1930's, Fawcett, Gibson, Perrin and Williams (5), (15), (16), (1), (17), (18) measured the rates of a number of organic reactions to pressures of 12,000 atm. Among these were several forward and one reverse Menschutkin reactions. Perrin⁽¹⁸⁾ made an attempt to generalize the pressure effect, grouping the reactions into those greatly accelerated by pressure, those relatively unaffected by pressure and those retarded by pressure.

Newitt et al.⁽¹⁹⁾⁽²⁰⁾ at Imperial College in the late 1930's studied the effect of high pressures on a variety of reactions, including esterifications, ester hydrolyses and Knoevenagel condensations, all of which were accelerated by pressure.

During this period significant contributions to the theory of the pressure effect were made by Evans and Polanyi^{(21), (22), (23)} who derived the equation relating the effect of pressure on the rate constant to the volume change on formation of the transition state.

$$\frac{\partial \ln k}{\partial P} = - \frac{\Delta V^*}{RT} \quad (I-2)$$

They subdivided the activation volume, ΔV^* , into two terms, viz. ΔV_1^* , the change in volume of the reacting molecule when the transition state is formed, and ΔV_2^* , the corresponding change in volume of the surrounding solvent due to changes in solvation.

Stearn and Eyring⁽²⁴⁾ proposed a method for calculating the activation volume (and hence the effect of pressure on rate), but they assumed that all of the volume change was due to bond stretching or compression (ΔV_1^*).

3. Since 1940

Although the volume of research in the high pressure field has greatly expanded in the last twenty years, it has been confined to relatively few laboratories, because of the elaborate equipment required. Table I-1 lists some of the main laboratories engaged in research on simple organic reactions in the liquid phase (the specialized field of polymerization has not been included, although most of these laboratories have studied high pressure polymerization as well).

The most important recent contributions to the theory of the pressure effect have been made by Hamann and his co-workers. They criticized Stearn and Eyring's theories, pointing out that in reactions involving the appearance or disappearance of ionic changes, solvent effects are usually more important than intramolecular effects. They have supported this hypothesis with considerable experimental work.

As Hamann's theories were often a crystallization of current thought in the field of high pressure kinetics, they have been widely accepted. Gonikberg, however, has disputed Hamann's contention that solvation effects are the main cause of the

acceleration of forward Menschutkin reactions by pressure. Weale et al. and Brower et al. have also contributed to the study of these reactions, which will be more extensively discussed in Section IE.

Laidler's work has been mainly associated with aqueous ionic reactions at high pressures; he has proposed empirical formulas for calculating partial molar volumes of ions in aqueous solution as a start towards predicting the pressure effect.

Whalley has used high pressure kinetic studies to differentiate between possible reaction mechanisms. He has also proposed a theory of conformational effects⁽⁵²⁾.

Recently Berson and Benson⁽⁶⁹⁾ have discussed the theory of the pressure effect and have proposed a new approach involving the application of the Tait equation (for liquid compression) to the differential compression of the reactant and the activated complex.

Table I-1Some Recent Work on High Pressure Reactions

<u>Worker</u>	<u>References</u>	<u>Reactions</u>
<u>Hamann</u> et al.	(3) (4) (7)	Solvolysis of alkyl halides
C.S.I.R.O. H.P. Lab.	(25) to	Free-radical dissociations
University of Sydney	(35)	Halogenation of olefins
Australia.		Forward Menschutkin reactions
		Formation of urea
		Isomerizations
		Hydrogen exchanges
		Esterifications.
<u>Weale</u> et al.	(36) to (40)	Forward Menschutkin reactions
Imperial College,		Reverse Menschutkin reactions
London, England.		Isomerizations and re-arrangements
<u>Brower</u> et al.	(41) to (44)	Menschutkin reactions
New Mexico Inst. of		Racemization of biphenyls
Mining and Technology,		Decomposition of aromatic
U.S.A.		diazonium salts.
<u>Walling</u> et al.	(45) to (47)	Dimerization of isoprene
Columbia Univ. U.S.A.		Decomposition of peroxides
<u>Laidler</u> et al.	(48) to (51)	Various ionic reactions
University of Ottawa,		Hydrolyses of esters and amides
Canada.		Fading of organic dyes.
<u>Whalley</u> et al.	(13)(52) to	Hydrolyses of amides, esters,
National Research Council	(58)	epoxides, ethers, anhydrides,
Ottawa, Canada.		phosphates etc.
<u>Gonikberg</u> et al	(59) to (68)	Forward Menschutkin reactions
Zelinsky Inst. of		Halide exchange reactions
Organic Chemistry,		Friedel-Crafts substitutions.
Moscow, U.S.S.R.		

IC. THEORIES OF THE EFFECT OF PRESSURE ON REACTION RATE

1. Introduction

At first it was thought that the effect of pressure on reaction rate was due to changes in concentration and ionization caused by compression of the solution. Later it was seen that these factors alone could not account for the magnitude of the pressure effect often found.

It has been shown that changes in the rate of reaction with pressure in some cases correspond to changes in the viscosity of the solvent⁽⁷⁰⁾. However, aside from the fact that in some reactions the acceleration by pressure is roughly the same in solvents of widely differing viscosities⁽¹⁾, calculations by Evans and Polanyi⁽²²⁾ indicate that for a reaction with a normal activation energy the solution would have to approach the vitreous state before viscosity would appreciably affect the collision number. Hamann⁽³⁴⁾ has demonstrated this experimentally for some esterification reactions in different solvents at pressures up to 40,000 atm. He concludes that viscosities of 10^8 poise are required before viscosity begins appreciably to affect rate of reaction.

Michels⁽⁷¹⁾ suggested that high pressures might alter the electronic structure of the atoms or molecules and thus change the chemical activity. However, such changes in structure are not thought to occur below about 100,000 atm, except in the case of some metallic elements such as caesium⁽⁷⁾.

It has also been suggested that covalent bonds might be weakened or broken by very high pressures. Again, this effect would not be expected to occur at pressures normally used for kinetic studies. Hamann⁽¹⁷⁾ states that pressures in the order of 10^6 atm would be needed to break covalent bonds at room temperature. He has found no evidence of such effects in measurements of reaction rates to 45,000 atm⁽³⁰⁾.

None of the above effects appears to account for more than a very small part of the change of reaction rate with pressure. It is now recognized that the main principles governing the pressure effect are le Chatelier's principle and a rule which has been called "the principle of microscopic ordering".

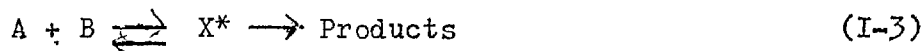
By le Chatelier's principle, which can be rigorously derived by thermodynamic reasoning, an increase in pressure operating on a process at equilibrium favours a change which tends to reduce the volume of the system. Volume changes on reaction in liquid solution are determined less by changes in the number of molecules (the main effect in gaseous reactions) than by the individual volumes of the molecules and their electrical properties, (through electrostriction of solvent). Le Chatelier's principle can be applied to rates of reaction if we consider not the overall volume change (which causes pressure to change the equilibrium position), but the volume change on formation of the activated complex. This is valid, since by the transition state theory the activated complex is considered to be

in equilibrium with the reactants. If the activated complex in the transition state occupies less volume than the initial reagents, the reaction will be accelerated by pressure (i.e. ΔV^* negative). This may be due to bond stretching or compression on formation of the activated complex, or changes in the electrical charges which cause electrostrictive changes in the solution volume. Conversely, if ΔV^* is positive, the reaction will be slowed by increasing the pressure.

The principle of microscopic ordering is an intuitive extension of le Chatelier's principle. It states that "an increase in pressure will in general increase the degree of order amongst the molecules of a substance⁽⁷⁾". Although this explains many physical transformations, it probably affects only certain specialized chemical reactions. Whalley⁽⁵²⁾ has recently discussed this effect (which he calls the "conformational effect") and has concluded that it has been proven to exist in only one chemical reaction (termination rate constant in the polymerization of styrene).

2. Transition State Theory and the Pressure Effect

The effect of pressure in reaction rate is best discussed by reference to the transition state theory. Reactions are assumed to proceed through a transition state in equilibrium with the reactants.



By application of statistical mechanics to the energetics of the reaction, equation I-4 can be developed⁽⁷²⁾⁽⁷³⁾⁽⁷⁴⁾.

$$k = \kappa \left(\frac{k_b T}{h} \right) K^* \quad (\text{I-4})$$

where K^* can be considered as the equilibrium constant for the equilibrium between the reactants and the activated complex, k is the rate constant, k_B is Boltzmann's constant, h is Planck's constant and κ is a constant called the transmission coefficient. The transmission coefficient represents the fraction of the activated complexes that are successful in leading to the final products; it is usually assumed to be unity⁽⁷⁴⁾.

From the usual thermodynamic identities, assuming the transmission coefficient to be unity, equation I-4 can be transformed to

$$k = \left(\frac{k_b T}{h} \right) e^{-\Delta F^*/RT} \quad (\text{I-5})$$

or

$$k = \left(\frac{k_b T}{h} \right) e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (\text{I-6})$$

or, since the activation energy may be assumed equal to the heat of activation⁽⁷³⁾,

$$k = e \left(\frac{k_b T}{h} \right) e^{\Delta S^*/R} e^{-E/RT} \quad (\text{I-7})$$

The quantities ΔF^* , ΔH^* and ΔS^* are the changes in these thermodynamic quantities on formation of the transition state. They are by definition the standard state values, the standard state being chosen to correspond with that used for the rate constants.

Taking logarithms of equation I-5 , differentiating with respect to pressure and using the identity $\frac{\partial F}{\partial P} = V$, the well-known equation linking the pressure and the rate constant with the volume of activation is obtained.

$$\frac{\partial \ln k}{\partial P} = -\frac{\Delta V^*}{RT} \quad (\text{I-8})$$

This equation has become the basis for the description of the effect of pressure on reaction rate. It should be noted that the true rate constant, based on activities (rather than concentrations) should be used. Otherwise, part of the measured pressure effect may be due to changes in the activity coefficients. This has been recognized by Benson and Berson⁽⁶⁹⁾ who have shown that considerable error in the activation volume may result if activity coefficient changes are neglected (especially for ionic reactions).

The assumption that the transmission coefficient is independent of pressure is also made in the development of equation I-8, although the dependence of κ on pressure is unknown⁽⁵²⁾.

Hamann⁽⁷⁾ has stated that the equilibrium constant K^* should be based on mole fraction or molal concentration scales, the use of the molar scale introducing small correction terms into equation I-8 , In fact, this depends on the standard states chosen in developing equation I-5 . Since these are usually in concentrations per unit volume⁽⁷³⁾, to be consistent the rate constant should be in concentration terms. The concentrations used to calculate the rate constants must

of course be corrected for solvent thermal expansion or compression.

3. Division of the Activation Volume into Two Terms

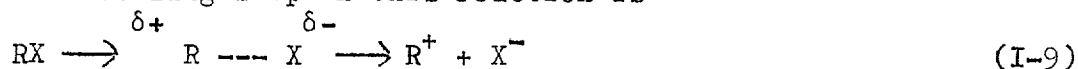
ΔV^* can be calculated from the integrated form of equation I-8 using rate constants measured at two different pressures. In practice, ΔV^* is found to change with pressure, sometimes quite rapidly, so it should be calculated from the slopes of tangents drawn to curves of $\ln k$ against P . The term "activation volume" is therefore not completely defined unless the pressure is stated but it usually refers to the volume change at 1 atm.

The activation volume can be conveniently divided into two terms following Evans and Polanyi⁽²¹⁾. ΔV_1^* represents the change in volume of the molecules themselves when they form the activated complex. ΔV_2^* is the corresponding volume change of the surrounding solvent, caused mainly by increased or decreased electrostriction of the solvent when charge changes occur in the reacting molecules on formation of the activated complex.

A complete knowledge of the structural and electrical properties of the reactants, transition state and solvent would allow ΔV^* to be exactly calculated. In the present state of knowledge it is possible to predict only the sign and order of magnitude of ΔV^* , although in simple cases its value can be approximately calculated.

It is usually difficult to separate ΔV_1^* from ΔV_2^* . In cases where a charge change occurs it has become widely accepted

that ΔV_2^* is the dominant term. This has been strikingly demonstrated for the S_N1 solvolyses of alkyl halides in hydroxylic solvents⁽²⁵⁾⁽²⁶⁾. The rate controlling step in this reaction is



Since bond stretching occurs, ΔV_1^* should be positive. However, the measured ΔV^* is negative and rather large (-17 cc/mole for t-butyl chloride in 80% ethanol), showing that ΔV_2^* must be several times larger than ΔV_1^* and of opposite sign.

Hamann⁽⁷⁾ has classified reactions on the basis of the charge change and the type of bond stretching or compression expected on formation of the transition state, and predicted qualitatively the pressure response expected for each type.

4. Factors Affecting ΔV_1^*

The term ΔV_1^* is a result of the reactant molecules in the transition state occupying more or less volume than they do in the initial state. Consider, for example, a unimolecular dissociation



There will obviously be an increase in volume on formation of the activated complex. If no opposing electrostriction effects occur (as in homolytic processes such as free radical dissociations), the reaction will be decelerated by pressure (the reverse of this reaction would of course be accelerated by pressure).

If the reaction mechanism, including the approximate geometry of the activated complex, is known, ΔV_1^* can be calculated.

This was first suggested by Stearn and Eyring⁽²⁴⁾. They calculated average molecular cross-sectional areas from the molar volumes of the reactants and the molecular length along the reaction co-ordinate, and estimated ΔV_1^* for bimolecular reactions by assuming a 1Å contraction on formation of the activated complex (for unimolecular reactions they assumed a 10% stretching of the breaking bond).

Although their theory completely ignored the effect of solvation changes, often the most important factor in determining the activation volume, it can predict the approximate effect that ΔV_1^* will have in determining the total activation volume. In cases where electrostriction is unimportant (i.e. $\Delta V_1^* \approx \Delta V^*$), this calculation should give a reasonable estimate of the activation volume. For example, Ewald⁽²⁹⁾ calculated the activation volume for the homolytic decomposition of pentaphenylethane to be + 10.5 cc/mole, assuming 10% bond stretching. The measured activation volume was + 13.1 cc/mole.

The calculation obviously becomes more indefinite with increasing complexity of the reaction. Uncertainties arise as to the average cross-sectional areas, the bond lengths in the transition state and other factors.

Gonikberg^{(59) to (68)} has suggested that ΔV_1^* for bimolecular reactions is mainly due to interpenetration of the non-bonded atoms of the two reactants on formation of the transition state. His work and theories have been mainly connected with forward Menschutkin

reactions, and will be discussed in detail in Section IE.

5. Factors Affecting ΔV_2^*

The volume of the solvent may change during the activation step due to rearrangement of the solvent molecules to accommodate themselves to the changing configuration of the reacting molecules, or because of electrostatic compression or decompression of the solvent due to charge changes in the reacting molecules. Hamann⁽⁷⁾ states that the first effect is probably unimportant. The second effect is due to the fact that development of a charge increases the attractive forces between the dipoles of the solvent (either permanent or induced by the charge) and the molecule. This effect can be approximately calculated from Born's theory (see Hamann⁽⁷⁾) for the free energy of solvation of a mole of ions in an infinite amount of solvent. If the ions are regarded as charged spheres in a continuum of dielectric constant ϵ , an equation relating the partial molar volume change to the properties of the solvent and ions can be developed. For a 1 : 1 electrolyte

$$\Delta \bar{V}_s = \frac{Ne^2}{r} \frac{\partial (1/\epsilon)}{\partial P} - Ne^2 \left(1 - \frac{1}{\epsilon}\right) \frac{\partial (1/r)}{\partial P} \quad (\text{I-11})$$

where $\Delta \bar{V}_s$ is the total value for the solvation of both ions in an infinite amount of solvent, r is the mean ionic radius of the two ions, e is the electronic charge, ϵ the solvent dielectric constant, and N Avogadro's number.

The difficulty in applying this theory to the calculation of ΔV_1^* is that the extent and precise location of the charge on

the activated complex and the effective radius are usually not known. Hamann has calculated that the development of a full electronic charge on a small spherical molecule would cause a decrease in volume of between 10 and 30 cc/mole in most solvents.

6. Effect of Pressure and Temperature on the Activation Volume

The activation volume changes with pressure, often quite rapidly. It can be defined as

$$\Delta V^* = \bar{V}^* - \sum \bar{V} \quad (\text{I-12})$$

where $\bar{V}^*$ and $\bar{V}$ are the partial molar volumes of the activated complex and the reactants. Differentiating with respect to pressure at constant temperature, equation I-13 is obtained.

$$\frac{\partial (\Delta V^*)}{\partial P} = \frac{\partial \bar{V}^*}{\partial P} - \sum \frac{\partial \bar{V}}{\partial P} \quad (\text{I-13})$$

If β is defined as the differential rate of change of the partial molar volume with pressure (i.e. the compressibility),

$$\frac{\partial (\Delta V^*)}{\partial P} = \beta^* \bar{V}^* - \sum \beta \cdot \bar{V} \quad (\text{I-14})$$

It can be seen that if the $\ln \frac{k_p}{k_1}$ versus P plot is a straight line so that ΔV^* does not change with pressure, the compressibilities of the activated complex and the reactants are roughly the same (since $\bar{V}^* \approx \sum \bar{V}$). Conversely, a sharply curved $\ln \frac{k_p}{k_1}$ versus P plot infers that the reactants and activated complex are different, at least so far as compressibility is concerned. This type of analysis is, of course, complicated when solvation occurs since the

dielectric constant of the solvent is changed by pressure as well. However, it gives some indication of the properties of the activated complex in the case of homolytic reactions.

The effect of temperature on the activation volume can be obtained using the thermodynamic relationship

$$\frac{\partial \Delta S^*}{\partial P} = - \frac{\partial \Delta V^*}{\partial T} \quad (\text{I-15})$$

If entropies of activation are measured over a range of pressures, the temperature coefficient of the overall volume change or of the volume of activation can be calculated, as has been outlined by Laidler⁽⁴⁹⁾.

7. Effect of Pressure on Electrolytic Dissociation

For the dissociation of the ion-pair A^+B^- into free ions



the equilibrium constant relationship is the van't Hoff equation

$$\frac{\partial \ln K_d}{\partial P} = - \frac{\Delta \bar{V}_d}{RT} \quad (\text{I-17})$$

$\Delta \bar{V}_d$ is the difference in partial molar volume between the ion-pair and the dissociated ions and K_d is the true equilibrium constant, calculated from the activities of the ions and ion-pairs.

Since no covalent bonds are made or broken in the dissociation process, the change in volume on dissociation is purely a solvation effect. The separate ions will be more tightly solvated than the ion-pair dipole and there will be a contraction in volume on dissociation. The dissociation will thus be favoured by pressure (increase in K_d).

Equation I-11 will apply to ion-pair dissociation equilibria. The volume change on dissociation will of course be the difference of two $\Delta \bar{V}_s$ terms, one for the solvation of the ion-pair and the other for the solvation of the individual ions.

Apparently no ion-pair dissociations have been measured at high pressures although an analogous phenomenon, the dissociation of weak bases and acids, has been the subject of considerable research (e.g. Hamann et al. (28), (75) to (79) and Ellis et al. (80), (82)).

ID. THE MECHANISM OF MENSCHUTKIN REACTIONS

1. Nucleophilic Aliphatic Substitution

Menschutkin reactions are an example of the general class called nucleophilic aliphatic substitutions, which can be represented by the general equation



The new bond is formed by co-ordination and the old one broken by heterolysis. The theory of the mechanism of these reactions has been described in many texts, notably by Ingold⁽⁸¹⁾.

In these reactions, Y becomes one electronic unit more positive, and X one unit more negative through electron transfer from the substituting agent Y to the centre of substitution in R, and from this centre to the expelled group X. Subject to this condition, the products can be any combination of electrically neutral, positive or negative species, depending on the state of electrification of the reactants.

Two reaction mechanisms are found in nucleophilic aliphatic substitutions, depending on the characteristics of the reactants and the solvent.

One of these, termed S_N2 (nucleophilic bimolecular substitution) by Ingold (loc.cit.) occurs in one stage, the two electron transfer steps occurring simultaneously. In this mechanism the transition state contains two partially formed bonds. Second order kinetics are usually found (except in cases where one reagent

is in constant excess, or buffering etc. occurs).

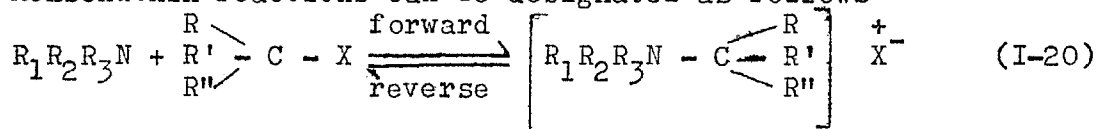
The second mechanism, S_N1 , involves two stages. The slow rate-determining stage is a primary cleavage of the compound substituted to form a carbonium ion, which then is quickly removed by reaction with the substituting agent.



In the limiting case, this mechanism leads to first order behaviour, but complex kinetics often occur (if, for example the reversal of the ionization is competitive in rate to the combination of the carbonium ion with the substituting agent).

2. Classification of Forward and Reverse Menschutkin Reactions

Menschutkin reactions can be designated as follows



Forward Menschutkin reactions have almost invariably been shown to proceed through the S_N2 mechanism. One case of S_N1 or partially S_N1 behaviour has been reported by Ingold⁽⁸³⁾⁽⁸⁴⁾ for reactions in liquid SO_2 . (Harris⁽²⁾ reported that a Menschutkin reaction appeared to change from S_N2 to S_N1 with pressure, but this will be refuted in this thesis).

The mechanism of reverse Menschutkin reactions has received little attention. The reaction has widely been assumed to be of the first order⁽¹⁾⁽⁸⁵⁾⁽⁸⁶⁾⁽⁸⁷⁾ but the mechanism involved has not

been definitely established. Elucidation of the mechanism has been hindered by the fact that usually no simple kinetic order has been observed in experimental studies of the reaction rate.

Williams, Perrin and Gibson⁽¹⁾ and Davies and Cox⁽⁸⁶⁾ found that the first order rate constant increased with dilution for decomposition in chloroform solution, the latter reporting a threefold increase in the rate constant on dilution from 0.05M to 0.003M. Davies and Cox (loc.cit.) found a slight increase in the first order rate for a reverse Menschutkin reaction in acetone, although the accuracy of this result is in doubt. Laidler⁽⁸⁸⁾ reported a marked increase in the equilibrium constant for some Menschutkin reactions in nitrobenzene when the initial reactant concentration was decreased. Since the forward reaction rate constant was known to be invariant with concentration, this would infer a large decrease in the reverse reaction rate constant with decreasing salt concentration, the opposite effect to that reported by Davies and Cox⁽⁸⁶⁾ and Perrin et al.⁽¹⁾.

Davies and Cox also reported (paradoxically) that although for two different runs of different initial concentrations the first order rate constant increased markedly on dilution, in any given run the rate constant remained reasonably steady, showing no great drift with conversion. They suggested that both the quaternary salt and one of the products (amine or halide) acted as catalysts of equal activity, the decreasing catalytic effect due to

the disappearance of the salt being balanced by the increasing catalytic effect of the amine (or halide).

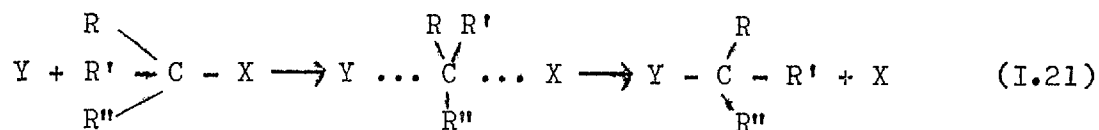
Hughes, Ingold and Patel⁽⁸⁹⁾ recognized that the decomposition of quaternary ammonium compounds could be either unimolecular or bimolecular depending on the electronic properties of the constituents, and Ingold⁽⁸¹⁾ has included them in the aliphatic nucleophilic substitution classification (S_N1 or S_N2). Later Hughes, Ingold and Pocker⁽⁹⁰⁾ have suggested that the halide ion must participate in sulphonium ion decompositions because of the principle of microscopic reversibility and the fact that it participates in the forward reaction (the formation of the sulphonium halide).

For the purposes of this discussion reverse Menschutkin reactions will be considered bimolecular (this does not of course stipulate the order of reaction). This position will be supported by experimental data in a later section.

3. Characteristics of the Transition State in S_N2 Reactions

Since the factors affecting rate of reaction are best understood in terms of the transition state theory, a short description of the transition state in S_N2 reaction will provide a convenient basis for further discussion.

The S_N2 mechanism involves an inversion of configuration due to the substituting agent combining with the carbon atom at the side opposite to that of the group being displaced.



In the transition state the three radicals R, R' and R'' are considered to lie in a plane, their bonds occupying positions 120° apart. The entering and leaving groups are attached to the carbon atom by semi bonds oriented at right angles to the R R' R'' C plane. This model minimizes repulsive energy in the transition state and has been "well established by kinetic investigations relating to the Walden inversion (Ingold⁽⁹¹⁾)".

In symmetrical substitutions, for example some halide exchanges, exact 120° and 90° angles are intuitively apparent. In more general cases deviation from these angles can be expected due to steric interactions between entering and leaving groups and the substituent groups on the carbon atom.

The bonds between the entering and leaving groups and the carbon atom will obviously be stretched, in comparison with normal bonds. Glasstone, Laidler and Eyring⁽⁷²⁾ assume an extension in the transition state of about 10% over the equilibrium interatomic distances. Dostrovsky, Hughes and Ingold⁽⁹¹⁾ have assumed a bond length equal to the covalent radius of the carbon atom plus the mean of the covalent and ionic radii of the entering or leaving group. This involves stretching of about 25% for a carbon-halogen bond.

The exact configuration, including bond stretching and deflection by steric interaction, could theoretically be calculated by minimizing the non-bonding and bonding energies between atoms in the transition state. This would be an incredibly complex calculation for any but the most simple case, even if sufficient data were available. Hughes, Ingold et al.⁽⁹²⁾ have, through a number of simplifying assumptions, calculated approximate transition state configurations for a number of bimolecular halide exchange reactions.

Depending on the electrical condition of the reactants, the transition state in S_N2 reactions can have either a full negative or full positive electric charge (separated between the incoming and leaving group), or a dipole, consisting of a partial positive charge on one group and a partial negative charge on the other. In Menshutkin reactions there are partial positive charges on the nitrogen atoms and partial negative charges on the halide atoms, the reactants being electrically neutral. The extent to which this charge is developed is the subject of much controversy. This controversy bears directly on the pressure effect and will be discussed in Section IE.

4. Constitutional Effects on the Rate of Menshutkin Reactions

General

The rate of Menshutkin reactions is affected by internal polarity effects of the reacting species, as well as by steric interference and solvent effects. In most cases the three factors

are operating simultaneously and identifying the quantitative contribution of each is difficult. Newman⁽⁹³⁾, referring to the differentiation of steric and polar effects, says : "There appears to be no way of settling this point experimentally since steric factors cannot be removed without changing the nature of the alkyl group which, in turn, may effect the polar factors in an unpredictable way".

Since forward and reverse Menschutkin reactions both occur through the same S_N2 mechanism the principles governing polar and steric effects will be the same in each. For clarity, the following discussions will be based on forward Menschutkin reactions with a note made of any significant differences arising when these principles are applied to reverse Menschutkin reactions.

Effect of the Nature of the Alkyl Group

Steric retardation in forward Menschutkin reactions results from interference of the groups attached to the α carbon with the approaching substituting agent, and also from steric interactions between the groups attached to the α carbon and the leaving halogen atom (when these groups are rotated from their normal tetrahedral positions in the alkyl halide to positions perpendicular to the α C - X bond). For a given substituting agent (amine, in the case of forward Menschutkin reactions), steric hindrance would decrease the reaction rate as follows :

me. > et. > i - pr. > t - bu. (I-22)

et. > iso-bu. > neo-pent. (I-23)

n-Pr and higher n-alkyl groups would be expected to behave similarly to et since steric interference can be minimized by rotation of the chain into a position of little interference.

Hughes, Ingold et al.⁽⁹¹⁾⁽⁹²⁾ and others (Laidler and Hinshelwood⁽⁸⁸⁾⁽⁹⁴⁾ for example) have held that important constitutional polarity effects as well as steric effects alter the rate of S_N2 reactions. The main constitutional polarity effect (disregarding solvent polarity effects for the present) is the inductive effect. Alkyl groups are more polarisable than hydrogen and thus in alkyl halides a methyl group is weakly electron-repelling when compared to a hydrogen atom. The carbon atom in a methyl halide will carry an induced positive charge in comparison to the carbon in an ethyl halide and will thus react more quickly with a basic or negatively charged substituting agent.

This effect will increase as more methyl groups are added to the α carbon in the halide, giving a rate series of $\text{me} > \text{et} > \text{i-pr} > \text{t-bu}$. Since this inductive effect is only feebly transmitted through the carbon chain, β -substituted alkyl halides such as n-pr, n-bu etc. and i-bu and neo-pent should behave similarly to the ethyl halide.

Hughes and Ingold⁽⁹²⁾ have calculated incremental activation energies due to steric hindrance for a number of halide exchanges and conclude that in the α -substituted series (me, et, i-pr, t-bu) about one half the incremental energy (i.e. between methyl and the

others) is due to steric interaction, and the remainder to inductive polar effects.

Evans et al.⁽⁹⁵⁾ to (98) have criticized these conclusions, pointing out the many assumptions required to calculate steric effects. Evans comments⁽⁹⁵⁾ that "the type of calculation involved here (referring to Ingold's calculation of steric effects) is not sufficiently exact to warrant such a quantitative conclusion ... for primary to tertiary halide series there is no evidence that the decrease in the bimolecular reaction rate is due to anything other than the increase in steric repulsion energy".

Brown et al.⁽⁹⁹⁾ also consider that inductive polar effects are unimportant compared to steric factors in determining the change of rate with alkyl halide structure. Some of their data is given in table I-2. The solvent is nitrobenzene and the nucleophilic reagent pyridine.

Table I-2
Constitutional Effects on Rate

	<u>MeI</u>	<u>EtI</u>	<u>i-PrI</u>
$k \times 10^6$, litres/mole/sec.	343.	18.3	0.941
$E_{act.}$, k.cals/mole	13.9	16.0	17.7
log A	6.72	6.98	6.93
ΔS^* , e.u.	- 29.8	-28.8	-29.5

As can be seen the decrease in reaction rate is largely an activation energy rather than entropy effect. This is generally found, though the somewhat decreased reactivity of the n-propyl

halide compared to the ethyl halide is probably an entropy effect⁽¹⁰⁰⁾ due to the specific orientation required of the end carbon in the n-propyl group to minimize steric repulsion in the transition state. The similarity in rate between n-propyl and higher n-alkyl groups is illustrated by some of Menschutkin's data (from Ingold⁽⁸¹⁾). The relative rate of reaction of triethylamine with a series of alkyl halides in acetone at 100°C was :

me 100, et. 8.8, n-pr 1.7, n-bu 1.2, n-hep. 0.9

n-oct 0.9, but iso-pr 0.18.

Effect of the Nature of the Amine

Both steric and polar constitutional factors due to the nature of the amine can affect the rate of forward Menschutkin reactions. It is known that the reactivity is a direct function of the basicity, unless there are large changes in steric interaction⁽⁹⁴⁾⁽¹⁰¹⁾. For example the rate of reaction of methyl iodide with the strong base triethylamine is about 80 times greater than its reaction with the weak base pyridine⁽⁹⁴⁾ despite the greater possibilities of steric hindrance in the former. The large effect that steric hindrance can have on the reaction rate is strikingly illustrated by the data of Brown and Cahn⁽¹⁰²⁾ for the reactions of mono-alkyl pyridines with methyl iodide in benzene and nitrobenzene. Bulky substituents in the 2 position on the pyridine ring greatly decrease the rate of reaction, due mainly to increases in activation energy.

Effect of the Species of Halogen Atom

In most substitutions the order of reactivity of different halides is $I > Br > Cl > F$, since the C - F bond is the strongest and the C - I bond the weakest⁽¹⁰³⁾. This was demonstrated by Winkler and Hinshelwood⁽¹⁰¹⁾ who found that ethyl iodide reacted approximately six times as quickly as ethyl bromide with pyridine in benzene, the effect being mainly due to decreased activation energy.

Constitutional Effects in Reverse Menschutkin Reactions

Steric effects in reverse Menschutkin reactions will operate similarly to those found in forward Menschutkin reactions. The approaching halide ion will be sterically repulsed by the alkyl groups in the α carbon and these groups, when rotated into the transition state configuration, will interfere with the leaving amine group. It should be recognized that steric effects in the forward and reverse reaction do not operate in opposite directions; the rate is slowed in both directions (this is intuitively obvious for the S_N2 symmetrical halide exchange reaction, for example). No data on steric effects in reverse Menschutkin reactions has been published.

Polar constitutional effects due to the nature of the alkyl group will occur in the reverse reaction, substituents on the α carbon which tend to make it more positive increasing the rate of reaction. This is a similar effect to that occurring in forward Menschutkin reactions.

However, polar constitutional effects due to the nature of the amine will be in the opposite direction in the reverse reaction to that in the forward reaction, as has been recognized by Laidler⁽⁸⁸⁾. More basic or nucleophilic amine groups will be more difficult to displace.

The effect of changing the halide ion will also be reversed, i.e. the quaternary chloride will be more reactive than the bromide. von Halban's data⁽¹⁰⁴⁾ on the decomposition of benzyl-methyl-phenyl-propyl ammonium halides in chloroform illustrates the expected trend in rate (bromide decomposes at twice the rate of the iodide), although steric effects (due to the larger iodide ion) may contribute to the rate increase.

5. Effect of Solvent on the Rate of Menschutkin Reactions

The effect of solvent on the rate of S_N2 reactions is largely determined by the charge type of the reaction. An increase in ion-solvating power of the medium will accelerate the creation and concentration of charges and inhibit their destruction and diffusion. In forward Menschutkin reactions a partially charged transition state is formed from neutral reactants; changing to a more polar solvent will generally increase the rate. By the same criterion, reverse Menschutkin reactions will be retarded by an increase in solvent polarity.

The solvating power of a solvent depends in a general way on its molecular dipole moment. Increased shielding of the dipole

charges will decrease the polarity. Thus the thinly shielded proton of the hydroxyl group has an important effect on the solvent polarity.

The general effect of solvent polarity on a forward Menschutkin reaction is given in table I-3. This data illustrates general trends only, as many discrepancies in the dipole moment/reaction rate series occur which must be explained by reference to other properties of the solvent and reactants (e.g. alcohols, as a special case, will be discussed later).

Table I-3

Relative Rate of Reaction, Pyridine + Ethyl Iodide ⁽¹⁰⁵⁾

Solvent	Dipole Moment Debye units ⁽¹⁰⁸⁾	Relative Rate
Benzene	0	1.00
Methanol	1.66	2.50
Ethanol	1.68	1.40
n-propanol	1.66	1.11
1-butanol	1.66	0.93
Acetone	2.72	12.80
Nitrobenzene	3.99	25.0

Discussion of solvent effects on reverse Menschutkin reactions is hampered by the scarcity of data and the doubtful reliability of the few reported data (due to change in rate constant with concentration changes). Data presented by

Syrkin and Gubareva⁽⁸⁷⁾, shown in table I-4, illustrates the expected trends, at least for the change from the polar solvent 10% aqueous acetone to chlorinated hydrocarbon solvents.

Table I-4

Decomposition of Allyl-dimethyl-p-bromophenyl

Ammonium Bromide

Solvent	Relative Rate	E calcs/mole	A sec. ⁻¹
10% aqueous acetone	1	31,300	2.9×10^{15}
Tetrachloroethane	460	28,000	5.0×10^{15}
Chloroform	260	30,400	1.6×10^{17}

Note : relative rates calculated from reference⁽⁸⁷⁾
at 25°C.

According to Ingold⁽⁸¹⁾, the effect of solvent polarity on the reaction rate in S_N2 reaction is mainly an activation energy effect, due to the higher heat of solution of the activated complex in a more polar solvent, although he recognizes that entropy effects will also occur since solvation increases the organization of solvent molecules, thereby decreasing the probability of the solvated state.

This has not been found generally true in forward Menschutkin reactions (there is not much data for the reverse reaction).

Pickles and Hinshelwood⁽¹⁰⁶⁾ measured the reaction rate of pyridine with methyl iodide in 13 solvents, mainly benzene derivatives, having dipole moments from 0 (CCl_4 , mesitylene, benzene) to 4.0 (benzonitrile, nitrobenzene) Debye units. They found that rate changes with increasing solvent polarity were mainly due to increases in the pre-exponential factor (i.e. the entropy of activation was less negative in more polar solvents).

Vorob'ev and Titova⁽¹⁰⁷⁾ have noted that for a given Menshutkin reaction the activation energy is invariably higher in alcohols than in other solvents; and that, except for alcohol solvents, the change from a non-polar to a polar solvent causes a relatively major increase in the activation energy and an increase in the pre-exponential factor (in the Arrhenius equation); and that the increase in reaction rate in polar as against non-polar solvents is therefore exclusively due to an increase in the pre-exponential factor. They explain the special effect of alcohols as being due to the formation of strong hydrogen bonds between the reactant amine and the alcohol, which must be broken to form the activated complex. The increased activation energy found in alcohols is due to the additional energy necessary to break these hydrogen bonds, and the decreased entropy of activation is due to the positive entropy of desolvating the reagents. Other polar solvents have the same effect as alcohols, except that the reactants are not as tightly solvated and the activation energy is consequently lower.

IE. CONTROVERSY OVER THE EFFECT OF PRESSURE

ON THE RATE OF MENSCHUTKIN REACTIONS

1. Perrin's Work

The first systematic work on Menschutkin reactions under pressure was done by Perrin and his co-workers during the 1930's. Their data has been summarized by Perrin⁽¹⁸⁾. Perrin's view was that the activated complex was probably closer to the products than to the reactants in character, and he considered that this was supported by the relatively small effect of pressure on the reverse Menschutkin reaction (the one reverse reaction studied was decelerated by a factor of 1.5 at 3000 kg/cm² pressure). The increasing acceleration of the forward reaction with increasing complexity of the reactants was also noted by Perrin. Some of Perrin's data is given in table I-5.

2. Theories of Stearn and Eyring

In their analysis of the pressure effect Stearn and Eyring⁽²⁴⁾ implied (by the nature of their calculation) that the transition state in Menschutkin reactions was similar in character to the reactants, an opposite view to that taken by Perrin. They calculated activation volumes for forward Menschutkin reactions by simply assuming a 1Å contraction in length along the reaction co-ordinate when the activated complex was formed from the reactants. They calculated a cross-sectional area from the molar volumes of the reactants divided by the length of the molecule along the reaction

Table I-5

Some Menschutkin Reactions Studied by Perrin⁽¹⁸⁾

Reaction	Solvent	Temp. °C	k_{3000}/k_1
Pyridine + methyl iodide	Acetone	60	6.78
Pyridine + ethyl iodide	Acetone	40	6.85
Pyridine + n-butyl iodide	Acetone	60	6.16
Pyridine + i-propyl iodide	Acetone	60	8.14
Triethylamine + i-propyl iodide	Acetone	60	16.0
Trimethylamine + i-propyl iodide	Acetone	60	16.4
N : N-dimethylaniline + i-propyl iodide	Acetone	60	25.5
Decomposition of allyl- benzyl-methyl-phenyl ammonium bromide	Chloroform	25	0.67

co-ordinate. This calculation assumed "that electrostriction changes on activation are not important". The agreement between their calculated activation volumes and those measured by Perrin was extremely good. For example, they calculated that the activation volume for the reaction of pyridine and methyl iodide should be -15.8 cc/mole and from Perrin's data $\Delta V^* = -16.3$.

Stearn and Eyring proposed that activation volumes could be calculated for unimolecular decompositions, again neglecting electrostriction effects and assuming 10% stretching of the breaking bond on formation of the transition state. Applying this calculation to the reverse Menschutkin reaction studied by Perrin, they obtained a ΔV^* of $+3.5$ cc/mole, which compares very closely with the value of $+3.4$ calculated from Perrin's results.

3. Hamann's Theories

Hamann and his co-workers⁽⁷⁾⁽²⁵⁾ proved that Stearn and Eyring's theories on the pressure effect were invalid for most reactions, the most important error being the neglect of solvent effects. Hamann⁽⁷⁾ attributed the effect of pressure on forward Menschutkin reactions mainly to increased electrostriction of the partially ionic transition state. He supported this by the following evidence :

- (i) The reactions will not occur in the gas phase but need a solvent or active surface to stabilize the transition state (confirmed by Moelwyn-Hughes and Hinshelwood⁽¹⁰⁹⁾).

- (ii) The reaction rate increases rapidly with increasing solvent dielectric constant (see, for example, ref. 106).
- (iii) There is a large negative activation entropy, probably due to solvent molecules becoming 'frozen' around partially ionic transition states (e.g. Harris and Weale⁽³⁹⁾ list activation entropies of - 18.9 to - 41.9 for a number of forward Menschutkin reactions in methanol, nitrobenzene and acetone).
- (iv) The acceleration by pressure is reduced if the alkyl halide is replaced by one with a larger halogen atom, which is consistent with the fact that solvent electrostriction varies inversely as the size of the charged group (e.g. at 25°C, k_{3000}/k_1 is 13.7 for the reaction of dimethylaniline with ethyl bromide in methanol, 11.9 for the same reaction with ethyl iodide⁽³⁰⁾).

Hamann attributed the good agreement of Stearn and Eyring's calculations with Perrin's results to the fact that the activation volumes were average figures, calculated from rates at 1 and 3000 atm., rather than the true activation volumes, calculated from the limiting slopes of the log k versus P isotherms.

Hamann recognized, however, that some of the activation volume in forward Menschutkin reactions would be due to intramolecular

volume changes, citing the difference in acceleration in the reactions of methyl and ethyl iodide with dimethylaniline⁽³⁰⁾ as an indication of this (for methyl iodide in methanol at 25°C, $k_{3000}/k_1 = 9.8$; for ethyl iodide, 11.9).

4. Gonikberg's Theories

Gonikberg and his co-workers have done a considerable amount of work on the effect of pressure on forward Menschutkin reactions.

In their first paper on this subject⁽⁵⁹⁾ they criticize Stearn and Eyring's "arbitrary" assumption severely. They say that the transition state in Menschutkin reactions closely resembles the unsolvated products of the reaction and support this by showing that the molar volume of the transition state for the ethyl iodide - pyridine reaction (calculated from Perrin's work⁽¹⁸⁴⁾) is almost identical to the molar volume of the pure quaternary salt in the molten liquid form. From Perrin's results ΔV^* was - 20 cc/mole; ΔV^* calculated from the difference in molar volumes between the reactants and the molten salt was - 20.5 cc/mole (-22.5 at 50°C).

As additional evidence they cite the insignificant effect of pressure on the reverse Menschutkin reaction studied by Perrin, and the fact that Perrin found little difference in acceleration when the solvent was changed from hexane to acetone⁽¹⁶⁾. Gonikberg attributed the difference between the activation volume of the forward reaction and the overall volume change (- 20 vs. - 43 to - 54 cc/mole) entirely to solvation of the product, (i.e. assumed no ΔV^* for reverse reaction).

In a later paper⁽⁶⁰⁾ they enlarged on the thesis that the transition state is unsolvated (although apparently they assume that the electronic charges are fully developed as in the quaternary salt). They also state that the magnitude of ΔV^* in different solvents indicates whether the activated complex is solvated or not. In criticism of Hamann's hypothesis⁽²⁵⁾ that high negative activation entropies in Menschutkin reactions indicate a loss of entropy due to solvent molecules being frozen around partially ionized transition states, they cite as proof the high negative entropies found in the absence of solvent in the dimerization of cyclopentadiene.

Hamann⁽³¹⁾ criticized Gonikberg's conclusions on Menschutkin reactions, mainly on the basis that Perrin's data at 1 and 3000 atm. did not provide an adequate basis for calculating ΔV^* at 1 atm. He agreed with Gonikberg that the molar volume of the transition state for Menschutkin reactions is close to that of the final products, citing the low ΔV^* (of + 3.5 cc/mole) obtained by Perrin for the one reverse Menschutkin reaction studied under pressure.

In answer to this criticism Gonikberg⁽⁶²⁾⁽⁶³⁾ repeated Perrin's work on the reaction of pyridine with ethyl iodide in acetone over a range of pressure between 1 and 3000 atm. ΔV^* was found to be - 30 cc/mole (later⁽⁶⁵⁾ amended to - 34). They also measured the overall volume change for the reaction in acetone, and found it to be - 54 to - 57 cc/mole. On the basis of these results Gonikberg admitted that some solvation effects occur in

forward Menschutkin reactions, but contended that they are small compared to the intramolecular volume change ΔV_2^* .

In another paper⁽⁶⁴⁾ Gonikberg et al. proposed another method of calculating ΔV_1^* . They assumed a transition state for Menschutkin reactions similar to that described in Section ID, with the exception that the length of the N - C bond in the activated complex was taken to be the same as in a normal molecule. On formation of this transition state some non-bonded atoms approached to a distance less than the sum of their van der Waal's radii. Gonikberg assumed that ΔV_1^* was the sum of the volume decreases due to interpenetration of these non-bonded atoms. He pointed out that the acceleration of Menschutkin reactions by pressure paralleled his calculated ΔV_1^* s, as shown in table I-6.

Table I-6

Gonikberg's Calculated ΔV_1^* ⁽⁶⁴⁾

Reaction	ΔV_1^* cc/mole	k_{3000}/k_1 in acetone
Pyridine + methyl iodide	- 9	6.8
Pyridine + ethyl iodide	- 14	7.9
Pyridine + i-propyl iodide	- 19	9.6
Dimethylaniline + i-propyl iodide	- 44	25.5

Later⁽⁶⁵⁾ they added the interpenetration of the alkyl groups on the halide with the halogen atom, giving a value of $\Delta V_1^* = -18\text{cc/mol}$

for ethyl iodide + pyridine (no account was taken of volume changes due to the leaving iodide atom). In this and later papers⁽⁶⁶⁾⁽¹¹⁰⁾ they presented data for the effect of pressure on this reaction in ethanol, nitrobenzene and cyclohexanone, calculating ΔV^* , the overall volume change ΔV_r , and an approximation of the extent of dissociation of the product salt. A summary of this data is given in table I-7. ΔV_r is the overall volume change and α the fraction dissociated.

Table I-7

Gonikberg's Measured ΔV^* , Ethyl Iodide + Pyridine
in Various Solvents

Solvent	Temperature °C	ΔV^* cc/mole	ΔV_r cc/mole	α
Acetone	40	- 34.0	- 63	0.20 to 0.22
Ethanol	50	- 27.8	-39 to -40	0.18 to 0.19
Nitrobenzene	50	- 23.8	-39 to -41	0.37 to 0.56
Cyclohexanone	50	- 26.8	- 40	0.15 to 0.19

Gonikberg and his co-workers attempted to calculate the number of molecules of solvent solvating the activated complex from the equation

$$\Delta V^* = \bar{V}^* - \bar{V} - n \bar{V}_0 \quad (\text{I-24})$$

where $\bar{V}^*$, $\bar{V}$ and $\bar{V}_0$ are partial molar volumes of the transition state, the reactants and the solvent and n is the number of solvating solvent molecules. I-24 can be differentiated with respect to V_0

if n is assumed independent of pressure to obtain

$$\frac{\partial \Delta V^*}{\partial V_0} = \frac{\partial}{\partial P} \left[\bar{V}^* - \frac{1}{2} \bar{V} \right] \frac{\partial P}{\partial V_0} - n \quad (\text{I-25})$$

Since the term in square brackets is known to be positive and $\frac{\partial P}{\partial V_0}$ is negative, I-24 can be reduced to

$$\frac{\partial \Delta V^*}{\partial V_0} = - (n + \beta) \quad (\text{I-26})$$

From plots of ΔV^* versus $\bar{V}_0$ they calculated the value of $\frac{\partial \Delta V^*}{\partial V_0}$ and hence a maximum value of n (if $\beta = 0$). n was estimated to be 1.5 in cyclohexanone, 1.9 in nitrobenzene, 1.7 in ethyl alcohol and 2.0 in acetone.

Another technique they used was to assume that the ratios of the volume effects due to solvation of the activated complex (ΔV_2^*), the undissociated product (ΔV_m) and the dissociated product ions (ΔV_i), was independent of the solvent. This enabled equations I-27 to I-30 to be written.

$$\frac{\Delta V_m}{\Delta V_i} = \beta \quad (\text{I-27})$$

$$\frac{\Delta V_2^*}{\Delta V_i} = \gamma \quad (\text{I-28})$$

$$\Delta V_s = \Delta V_i \alpha + \Delta V_m (1 - \alpha) \quad (\text{I-29})$$

$$\Delta V^* = \Delta V_1^* + \Delta V_2^* \quad (\text{I-30})$$

where γ and β are constants and α is the fraction of the product salt dissociated into ions. Combining these equations the following

relationship was obtained

$$\Delta V^* = \Delta V_1^* + \gamma \frac{\Delta V_s}{\alpha + \beta(1-\alpha)} \quad (\text{I-31})$$

ΔV_s for the pyridine/ethyl iodide reaction in the four solvents was obtained by subtracting from the measured overall reaction volume change the difference between the partial molar volumes of the pure reactants and the partial molar volume of the pure molten quaternary salt. (-22.5 cc/mole at 50°C). They then plotted ΔV^* against $\frac{\Delta V_s}{\alpha + \beta(1-\alpha)}$ assuming a value for β to give the best straight line. Extrapolation of this line to

$\frac{\Delta V_s}{\alpha + \beta(1-\alpha)} = 0$ yielded $\Delta V_1^* = -20$ cc/mole for $\beta = 1/5$ and $\gamma = 1/8$.

ΔV_1^* and δ were found to be relatively unaffected by changes in β (when $\beta = 1/10$, $\Delta V_1^* = -21$, $\gamma = 1/11$).

Gonikberg and his co-workers thus had calculated three values for ΔV_1^* for the reaction of ethyl iodide with pyridine :

- (1) - 22.5 cc/mole based on molar volumes of the reactants and the molten product.
- (2) - 18 cc/mole based on calculations of interpenetration volumes.
- (3) - 20 cc/mole calculated as outlined above.

They concluded that the number of molecules of solvent solvating the activated complex is 8 to 11 times less than in the solvation shells of the ions, and that the activated complex is relatively unsolvated.

In some later work Gonikberg and his co-workers⁽⁶⁷⁾⁽⁶⁸⁾ have measured the activation volumes for the reactions of methyl-substituted

pyridine with methyl, ethyl and isopropyl iodides in nitrobenzene solution. ΔV_1^* was calculated for these reactions by their "overlapping volume of non-bonded atoms" method but in this case 10% stretching of the forming and breaking bonds was assumed (they had previously assumed no stretching). Reasonable agreement between calculated and experimental results was claimed.

5. Weale's Theories

Weale et al.⁽³⁶⁾⁽³⁷⁾⁽³⁹⁾⁽⁴⁰⁾ have studied the effects of pressure on the rate of a number of forward Menschutkin reactions. They have in general agreed with Hamann that solvation effects are the important factor in the acceleration of Menschutkin reactions by pressure. Weale has shown⁽³⁶⁾⁽³⁷⁾ that high pressures apparently do not relieve steric hindrances due to the ortho effect in forward Menschutkin reactions.

Harris and Weale⁽³⁹⁾ reported the effect of high pressures on the rates of a number of Menschutkin reactions of varying complexity in methanol, and of one in nitrobenzene (the experiments in nitrobenzene were carried out by the present author). They found, as did Perrin, that the acceleration by pressure increased with increasing complexity of the reactants, as shown in table I-8.

Table I-8
Some Results of Harris and Weale (39)

Reaction	Solvent	Temp. °C	-ΔV* cc/mole	-ΔS* e.u.
Dimethylaniline + methyl iodide	methanol	52.5	26	30.4
Dimethylaniline + ethyl iodide	methanol	52.5	34	29.0
Dimethylaniline + n-butyl iodide	methanol	52.5	34	28.5
Dimethylaniline + i-propyl iodide	methanol	52.5	47	20.4
Quinoline + ethyl iodide	methanol	52.5	20	19.7
Benzyl dimethylamine + ethyl iodide	methanol	52.5	27	22.9
Tri-n-propylamine + ethyl iodide	methanol	52.5	24	20.2
Dimethylaniline + ethyl iodide	nitro- benzene	52.5	20	41.9

The reached the following conclusions :

- (1) The fact that ΔV^* is less than ΔV_s is no reason to doubt that solvation is the important accelerating effect; the changes in the transition state are not fully developed nor are the ions separated enough for complete solvation.
- (2) Although Goukberg's "overlapping volumes" theory predicts the trends in ΔV^* with reactant complexity, it does not explain why ΔV^* for the reaction of ethyl iodide and

dimethylaniline should be so much smaller in nitrobenzene.

(3) Although repulsions between non-bonded atoms do occur they are unlikely to give rise to the additive volume changes envisaged by Gonikberg.

(4) They suggest that possibly the increasing volume of activation and decreasing entropy as the complexity of the reactants is increased could be due to weaker solvation of a larger number of solvent molecules as the complex branches increasingly shield the charge-carrying centres.

6. Brower's Theories

Brower et al.⁽⁴¹⁾⁽⁴²⁾ have measured the effect of pressure on the rate of reaction of piperidine with haloquinolines and halonaphthalenes. They found $\Delta V^\ddagger$ s as high as - 64 cc/mole. Their results are difficult to compare with previous Menschutkin reactions because of the complexity of the reactions and the possibility of metastable intermediates.

7. Summary of Menschutkin Reactions studied at High Pressures

A summary of Menschutkin reactions which have been studied at high pressures is given in table I-9. With the exception of the one reverse reaction rate measured by Perrin⁽¹⁸⁾ at 2900 atm. and the reverse reaction studied in this research (for which preliminary results were given in ref.⁽⁴⁰⁾) all references are for forward Menschutkin reactions.

Table I-9

Menschutkin Reactions studied at High Pressures

<u>Hamann et al.</u>		<u>Solvent</u>	<u>Pressures, atm.</u>	<u>Ref.</u>
N : N-dimethylaniline + methyl iodide		Methanol	1500, 3000, 6000 9000, 12000, 15000	(30)
"	+ ethyl iodide	Methanol	" " "	"
"	+ ethyl bromide	Methanol	" " "	"
<u>Brower et al.</u>				
1-Bromonaphthalene + piperidine		Excess piperidine	4 - 5 pressures between 1, 1500 atm.	(41)
2-Bromonaphthalene +	"	"	" "	"
6-Bromoquinoline +	"	"	" "	"
8-Bromoquinoline +	"	"	" "	"
2-Bromoquinoline +	"	"	" "	"
Above 5 reactions repeated in		(40% piperidine 60% water	" "	(42)
2-Chloroquinoline + piperidine		Excess piperidine	" "	"
"	"	40% piperidine	" "	"
"	"	60% water	" "	"
"	"	cyclohexane	" "	"
<u>Gonikberg et al.</u>				
Pyridine + ethyl iodide		Acetone	250, 500, 750, 1000, 3000.	(62)
"	"	Ethanol		(110)
"	"	cyclohexanone	500, 1000, 2000	(66)
"	"	nitrobenzene	"	"
4-methylpyridine + ethyl iodide		"		(67)
2,6-dimethylpyridine + ethyl iodide		"		"
"	+ i-propyl iodide	"		"

<u>Reaction</u>	<u>Solvent</u>	<u>Pressures</u> <u>atm</u>	<u>Ref.</u>
<u>Perrin et al.</u>			
Pyridine + methyl iodide	Acetone	2900	(18)
" + n-butyl iodide	"	"	"
" + n-butyl bromide	"	"	"
" + i-propyl iodide	"	"	"
" + ethyl iodide	"	2880, 4840, 8220	"
Trimethylamine + i-propyl iodide	"	2900	"
Triethylamine + " "	"	2900	"
N : N-dimethylaniline + " "	"	2900, 4840, 8220, 11600	"
Decomposition of allyl-benzyl-methyl-phenyl ammonium bromide	Chloroform	2900	(18)
<u>Weale et al.</u>			
N : N-dimethyl o-toluidine	Methanol	1000, 2000, 3000	(36)
+ methyl iodide		4000, 5000	
" " "	Acetone	3000	(37)
N : N-dimethyl aniline + methyl iodide	Methanol	1500, 2875	(39)
" " " + ethyl iodide	"	1500, 2875, 4925	"
" " " + n-butyl iodide	"	1500, 2875	"
" " " + i-propyl iodide	"	1500, 2875	"
Quinoline + ethyl iodide	"	1500, 2875	"
Dimethyl benzylamine + ethyl iodide	"	1500, 2875	"
Tri-n-propylamine + " "	"	1500, 2875	"
N : N-dimethylaniline + " "	Nitro-benzene	1500, 2300, 2600	"
N-ethyl-N-methylaniline + methyl iodide	"	500, 1000, 1500	(40)
Decomposition of ethyl-dimethyl-phenyl ammonium iodide	"	200, 500, 1000, 2000	"

SECTION II. APPARATUS AND MATERIALS

II.A. Apparatus

1. Pressure Vessel and Auxiliary Equipment

Experiments at high pressures were carried out in a thermostatted pressure vessel (system shown in fig.II-1). These experiments included kinetic runs on forward Menschutkin reactions (volumetric analysis techniques), kinetic runs on reverse Menschutkin reactions (volumetric analysis techniques and conductometric methods), measurement of quaternary salt dissociation constants (conductometric method) and measurement of solution freezing pressures.

The primary pressure generator was a two stage hand operated ram pump A, developing up to 1000 atm. pressure. Reservoir B supplied the pump with liquid paraffin B.P., which was used throughout the system as the pressure transmitting fluid. The pump was connected by $\frac{3}{8}$ " o.d. by $\frac{1}{8}$ " i.d. stainless steel tubing to the intensifier-vessel combination G-H. By virtue of the difference in area of the two connected pistons in the intensifier, the pressure was magnified by a factor of approximately 5, allowing a pressure of 5000 atm. to be developed in the vessel.

Pressures of up to 3500 atm. could be obtained without utilizing the full travel of the intensifier piston; for operations in this region the vessel was closed at the top by a rubber O-ring and steel plug at J. For pressures between 3500 and the maximum

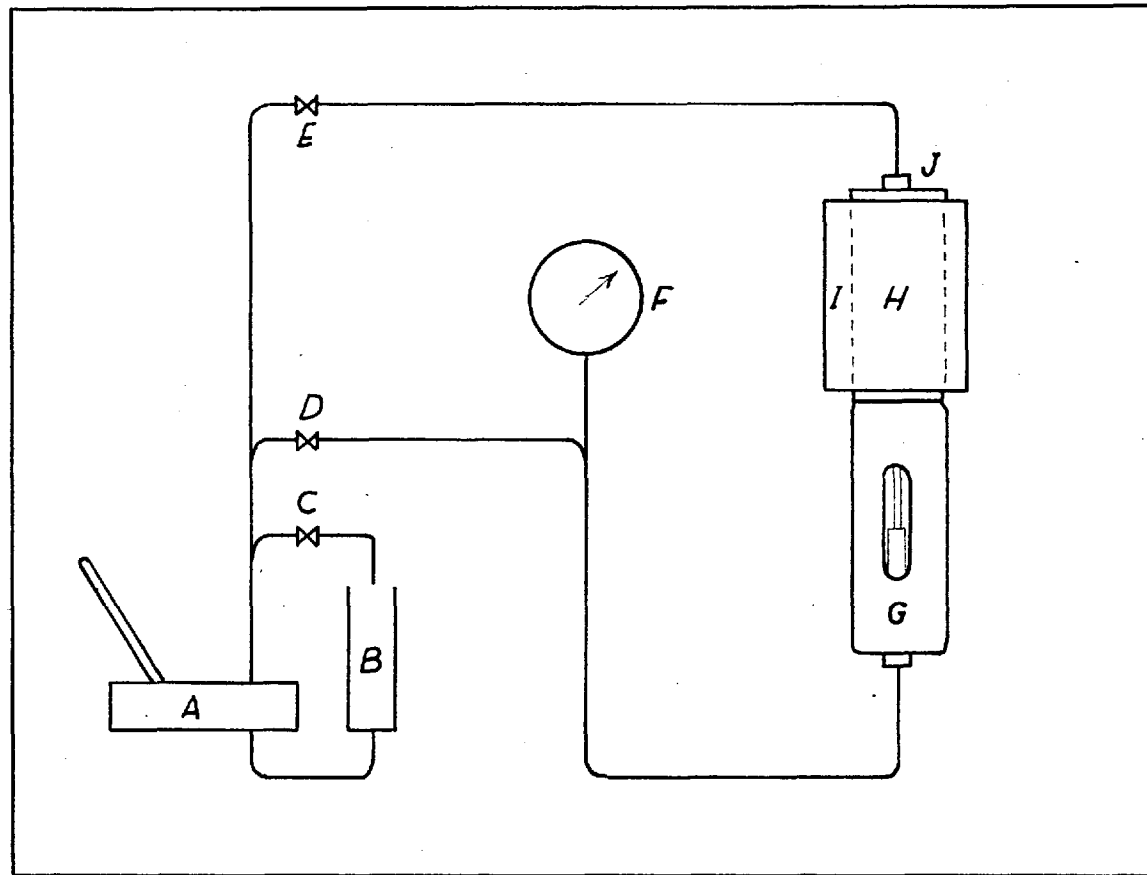


FIG. II-1 SCHEMATIC DIAGRAM OF HIGH PRESSURE SYSTEM

working pressure of 5000 atm. the vessel was primed to 1000 atm. before the intensifier was brought into use. For priming, an auxiliary line connected the pump directly to the vessel through valve E, with a connector instead of a plug at J.

The pressure vessel (fig.II-2) was made from two "Vibrac V-30" steel cylinders shrunk together, providing an inner reaction space $8\frac{1}{2}$ " long by $1\frac{1}{4}$ " diameter. The intensifier pistons and thrust blocks were made from oil-hardened, C.R.C. quality race steel bar. The high pressure piston was 0.6734" diameter and the low pressure piston 1.5000" diameter. Approximately 0.001" clearance between the pistons and cylinder provided a good sliding fit. Thrust on the low pressure piston was transmitted to the high pressure piston by a thrust block and thin copper washer which took up any difference in alignment.

The high pressure piston was sealed by a $\frac{3}{4}$ " long synthetic rubber Poulter packing, the low pressure piston by a Bridgman unsupported area packing. The seal between the top of the vessel and the plug or connector (for pressures below or above 3500 atm. respectively) was originally made by a steel lens ring. Recently, rubber O-rings have been used to make this seal without alteration of the original lens ring seats. These have proved both reliable and convenient.

The intensifier and vessel were enclosed for safety by $\frac{1}{4}$ " steel plate barricades.

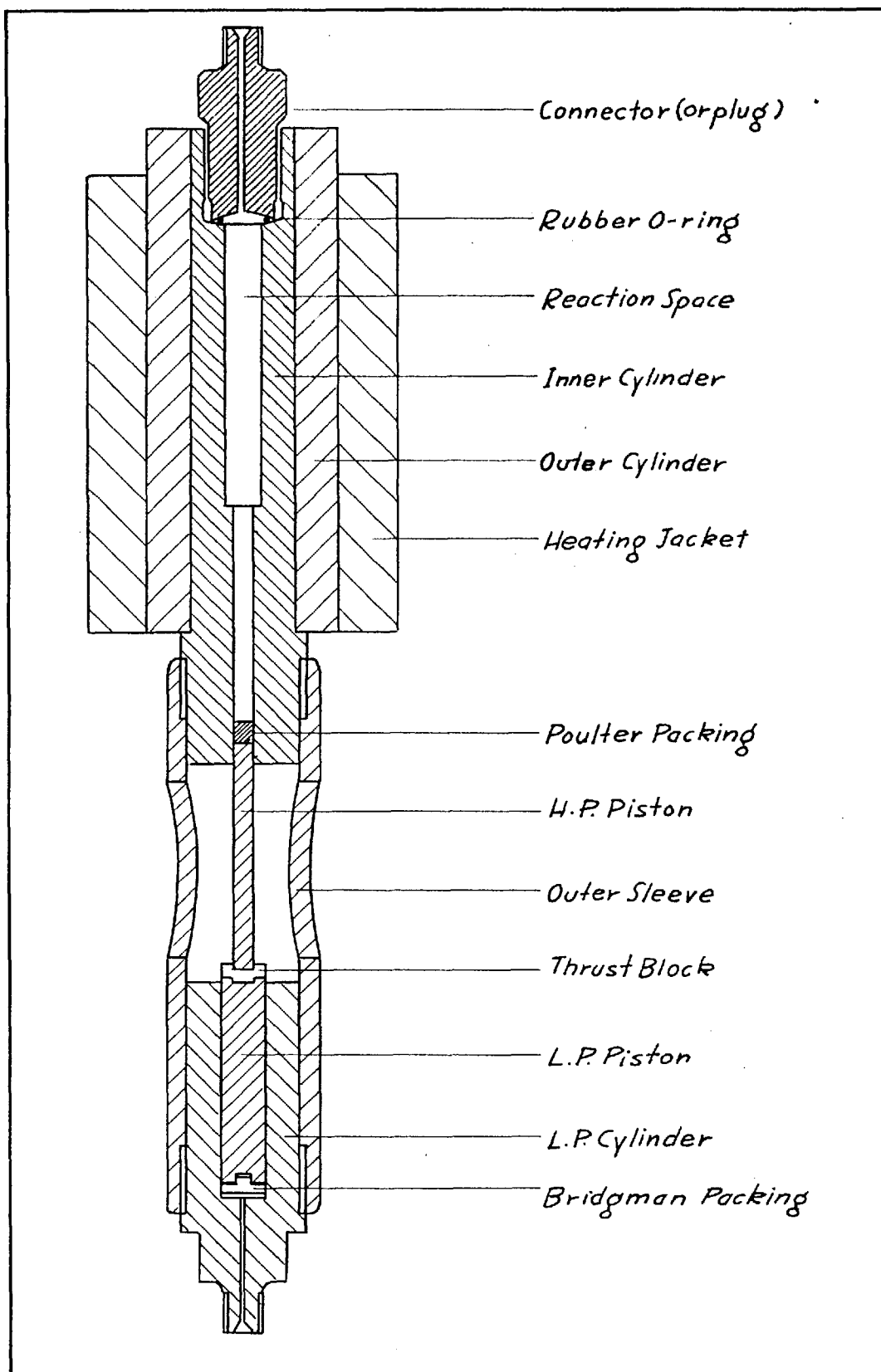


FIG. II-2 VESSEL-INTENSIFIER

2. Temperature Control of the Pressure Vessel

The pressure vessel was heated by an insulated 1000 watt electric heating jacket. A conventional Sunvic hotwire vacuum switch relay, operating through a mercury contact thermometer inserted between the vessel and the heater, provided on-off temperature control. The reaction temperature was measured before and after each run by immersing a thermometer in the oil contained in the vessel. Temperature constancy during a run depended on the "memory" of the control system, which in turn depended on maintenance of consistent contact between the control thermometer and the vessel wall. This contact was sometimes disturbed by shock or vibration during closing of the pressure vessel, resulting in a temperature drift. This behaviour seemed unavoidable, although it could be minimized by careful operation.

The temperature in the vessel showed a marked tendency to drift with changes in ambient temperature and rose about 0.1°C for every 1°C rise in ambient temperature. To prevent this drift the vessel was completely enclosed (using the existing steel plate walls and covering the top and bottom with fibre-board); the enclosure was then used as a secondary thermostat. It was equipped with a fan and heater and controlled by a mercury-toluene thermostat operating through a Sunvic relay. The temperature in the secondary thermostat would be maintained at about 5°C above room temperature to an accuracy of ± 0.3 , allowing temperature

control in the vessel to better than $\pm 0.05^{\circ}\text{C}$.

All thermometers used for measuring reaction temperature were marked in 0.1°C divisions and were calibrated against N.P.L. Standard thermometers at 10° intervals.

3. Measurement of Pressure

The pressure was measured on the low pressure side of the intensifier by a bourdon-tube gauge situated at F (see fig.II-1). This pressure was approximately one fifth of the actual vessel pressure, the piston area ratio being 4.962/1. Two pressure gauges were used, viz. a 0 - 500 atm. gauge marked off in 5 atm. divisions for pressures up to 1500 atm., and a 0 - 3000 atm. gauge marked off in 25 atm. divisions for pressures up to 5000 atm.

The recorded pressure on gauge F was calibrated against the vessel pressure by connecting a free-piston gauge to the top of the vessel. Calibration pressures were always approached from a lower pressure to avoid error from piston and packing friction, a procedure which was also followed in experimental runs. The maximum pressure measurable with the free piston gauge was 1000 atm. However, the calibration of the higher pressure gauge was extended to 3000 atm. using a new factory-calibrated bourdon-tube gauge. Linear extrapolation of the calibration lines was assumed for pressures above the highest calibration point (calibration graphs : figs. II-3, II-4). The accuracy of pressure measurement was estimated to be ± 5 atm. for pressures up to 1500 atm., and ± 25 atm. for pressures above 1500 atm. (gauge changed at 1500 atm.).

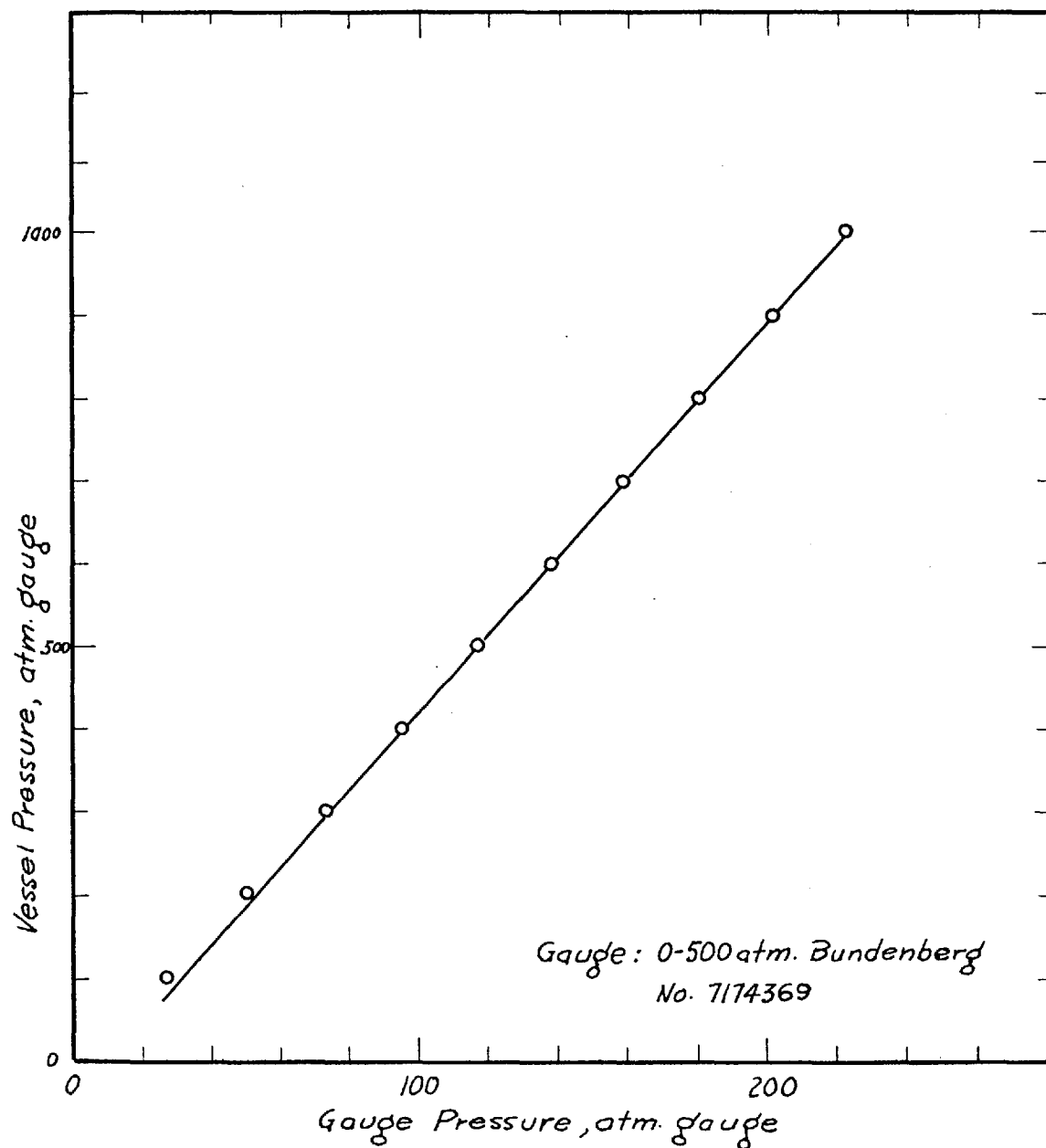


FIG II-3 CALIBRATION, 0-500 ATM. GAUGE

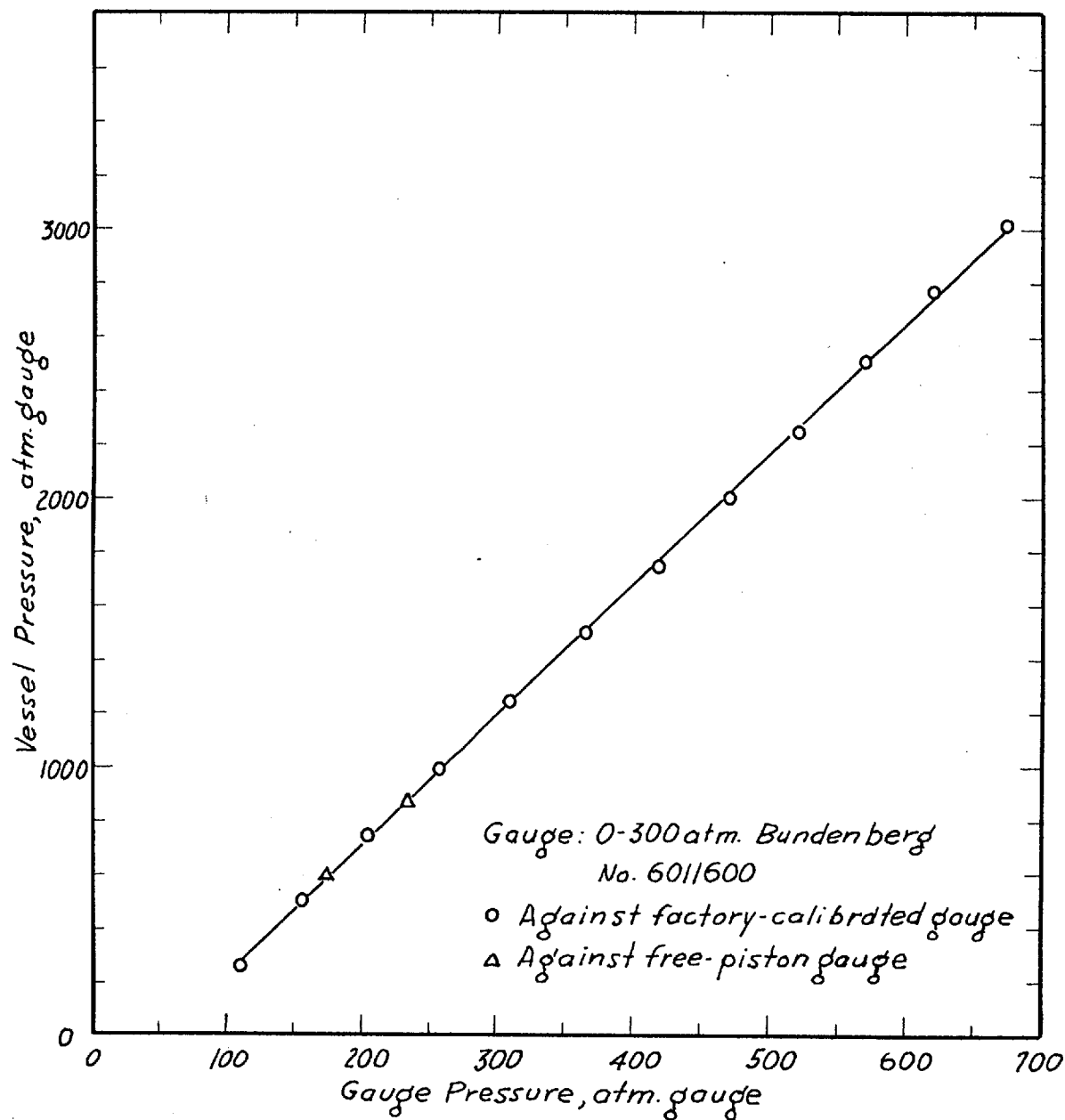


FIG. II-4 CALIBRATION, 0-3000 ATM. GAUGE.

4. Atmospheric Pressure Thermostats

Kinetic experiments at atmospheric pressure were carried out in a well stirred oil bath heated by a 150 watt electric bulb and controlled by a mercury-toluene thermoregulator operating in conjunction with a Sunvic relay. Temperature control was better than $\pm .02^{\circ}\text{C}$.

For the measurement of change of volume of reaction the dilatometer was enclosed in a glass case which was thermostatted to $\pm 0.05^{\circ}\text{C}$ using a mercury-toluene regulator and Sunvic relay.

5. Reaction Tubes

For pressure runs where conversion was determined by volumetric analysis, the reactants were contained in pyrex glass tubes about 15 cm. in length and 0.8 cm inside diameter. The tubes were fitted with ground-glass stoppers at the top and had 3 mm. diameter holes in the bottoms to allow pressure equalization. To avoid contamination of the reactants with the liquid paraffin which filled the vessel, the tube was floated on mercury in a steel bucket.

For atmospheric pressure kinetic runs the reagents were contained in sealed amber glass ampoules of 2, 5 or 10 cc. capacity.

6. Conductivity Equipment

Kinetic data for reverse Menshutkin reactions was obtained by observing conductance changes in the reacting solution. Quaternary salt dissociation constants were also obtained by the conductance method.

A vessel plug with two insulated electrodes, to which a high pressure conductivity cell could be connected was used in the measurement of conductances at high pressures. The plug was machined from "Vibrac V30" steel and the electrodes mounted on $\frac{1}{2}$ " centres as shown in fig.II-5. The electrodes were insulated from the plug by hollow ebonite cones machined to a thickness of about $\frac{1}{16}$ ", forced against the plug by silver steel cones cut at an angle of about 14° .

The plug was tested to 4000 atm. at room temperature and was subsequently used for several dozen runs at pressures to 3000 atm. and temperatures to 80°C with no leakage or electrical shorting.

The high pressure conductivity cell was suspended in a brass holder bolted to the bottom of the plug, electrical connection being made by wires from the electrodes dipping into mercury wells in the top of the cell.

Conductivity cells for high pressures were constructed from standard B-10 "Quickfit" cone and socket glass connectors, as shown in fig.II-6a. The electrodes were made from 0.006" thick platinum foil cut into rectangles approximately 0.6 cm x 0.6 cm and welded to 0.03" diameter platinum wire. The electrodes were fixed about 1 cm apart by fusing the wire through the top of the cell into short glass wells which held mercury to make contact with the wires from the plug. The cell capacity was approximately 8 mls. Spring connectors held the cell firmly together. Pressure equalization

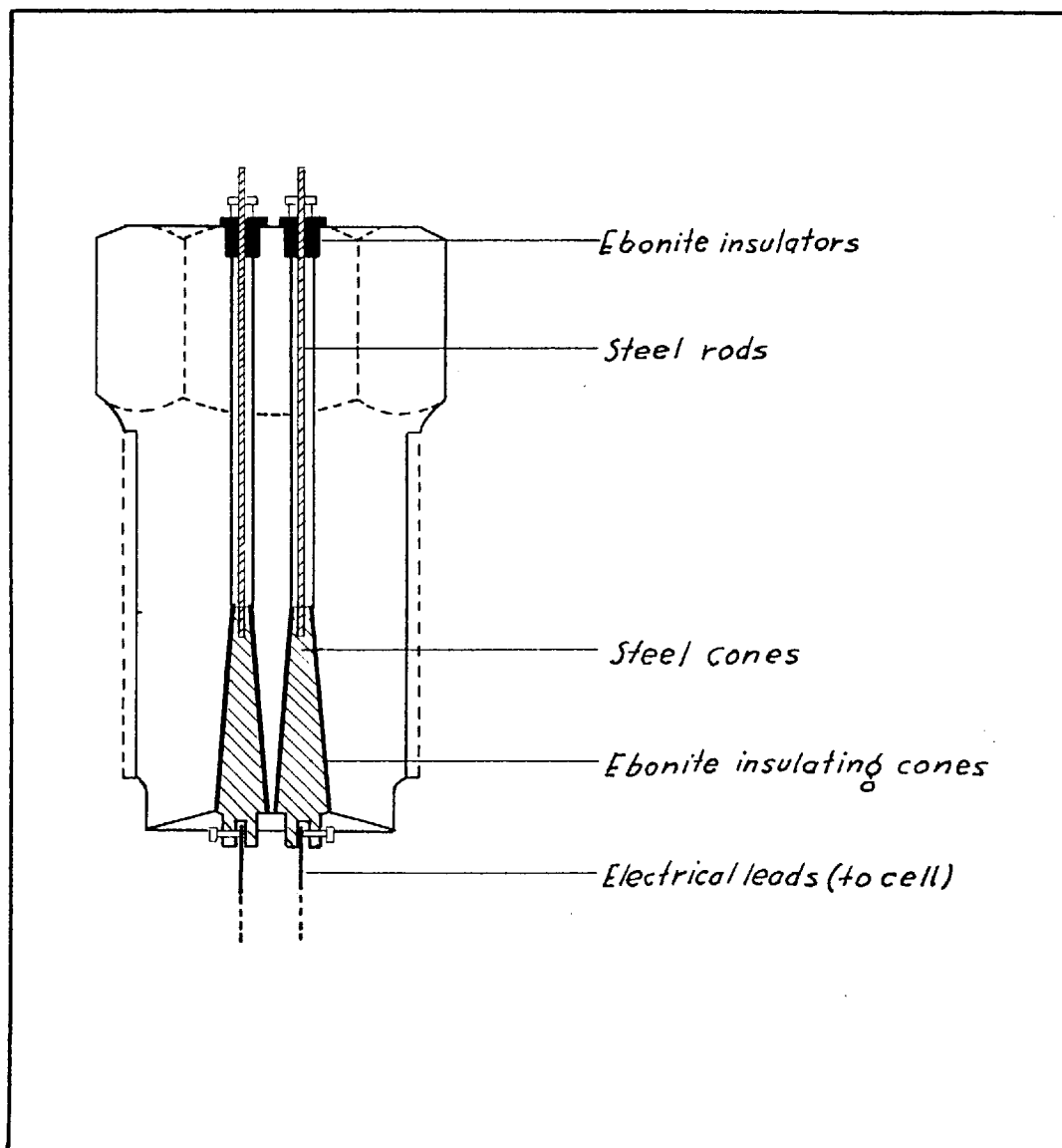


FIG. II-5 ELECTRICAL LEADS THROUGH PLUG

was effected through holes cut in the upper part of the glass bucket which held mercury to isolate the reactants from the liquid paraffin.

These cells were used up to 3000 atm., and proved satisfactory in this range. Cracking at the glass-metal electrode joint, which precludes use of a glass cell above 3000 atm.⁽⁷⁾, was not experienced.

Conductivity cells for use at atmospheric pressure were constructed using similar platinum stock and dimensions to those used for pressure cells. Capacity was approximately 11 mls. (see fig.II-6b).

All cells were lightly platinized with a solution of 2 gms chloroplatinic acid in 100 mls of 0.1 wt. % lead acetate solution (similar to platinizing solution recommended by Monk⁽¹¹¹⁾).

Conductances were measured with a Wayne-Kerr B221 Universal Bridge, a transformer ratio-arm bridge operating at 1592 c.p.s. (10,000 rads/sec.). The bridge measured conductances from 10^{-1} to 10^{-8} mhos to four significant figures with an accuracy of better than $\pm 0.2\%$. Balancing was effected by two "magic eyes" of different sensitivities. Capacitance decades could be adjusted to balance out any reactive term associated with the unknown conductance.

7. Dilatometer and Piezometer

For the measurement of overall volume changes during reaction a specially graduated double-ended dilatometer was used (fig.II-7a).

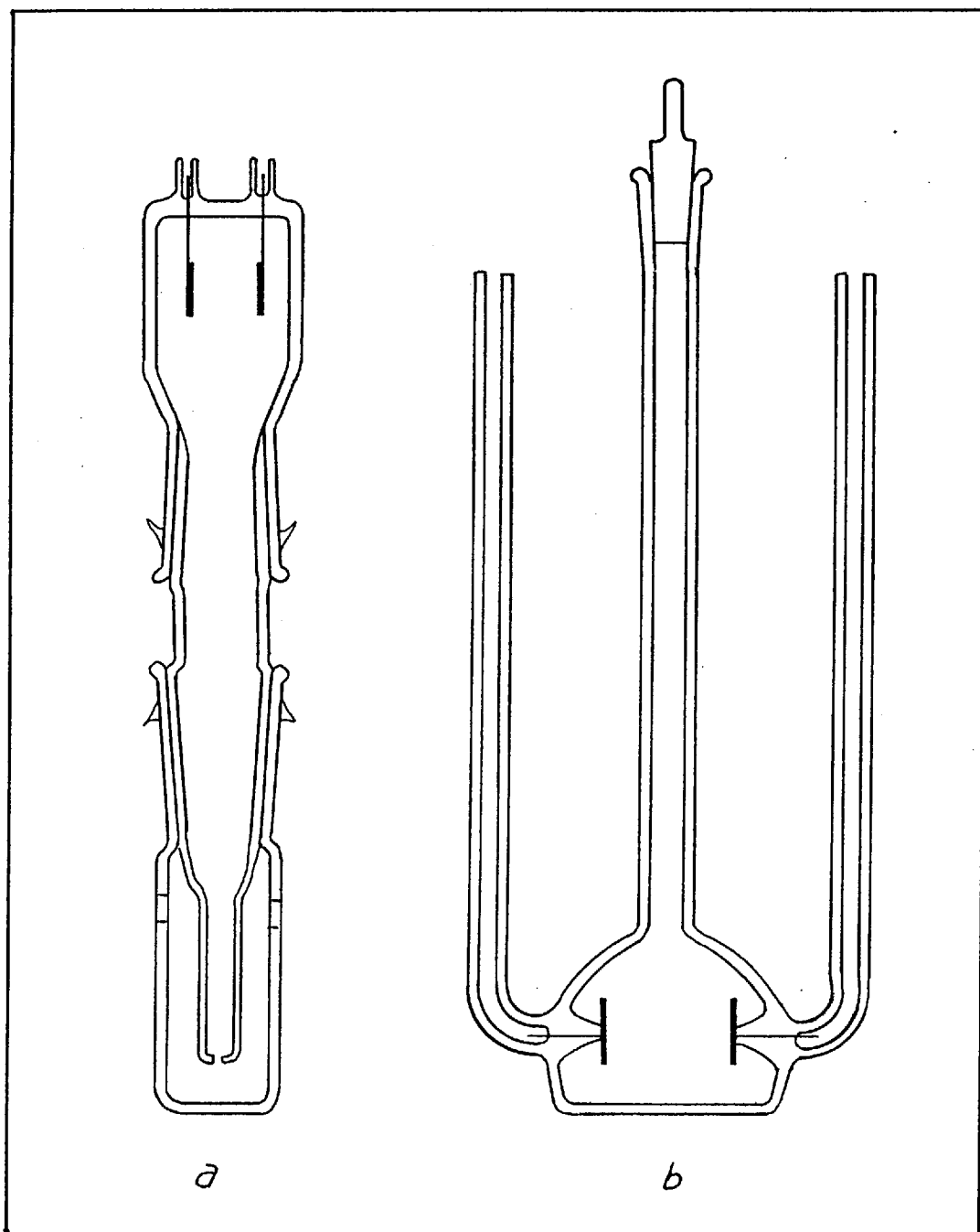


FIG. II-6 CONDUCTIVITY CELLS: *a*-PRESSURE; *b*-ATMOSPHERIC

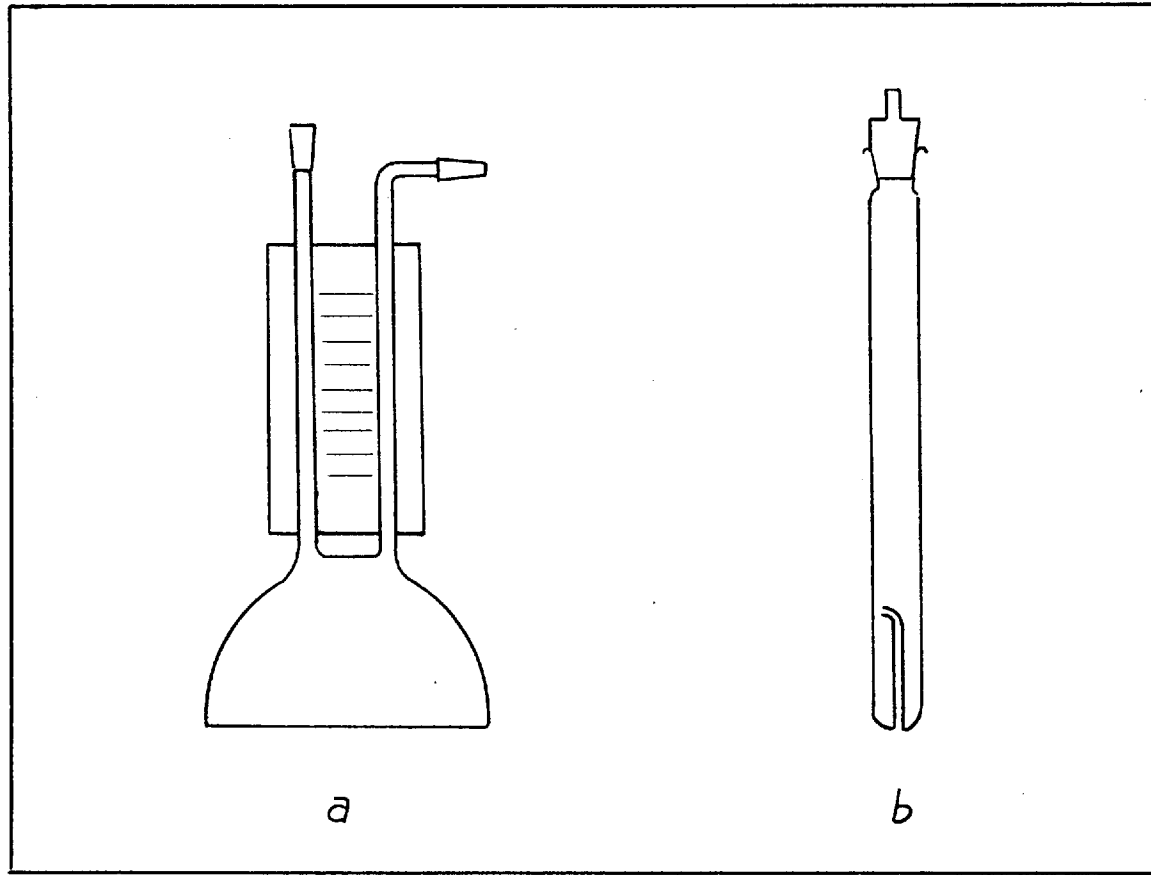
The bulb had a capacity of approximately 25 mls. and was made of well-annealed pyrex glass. The stems were 10 cm lengths of 1 mm i.d. precision-bore pyrex tubing smoothly joined to the bulb to prevent trapping of air bubbles. A uniformly ruled aluminium scale was rigidly attached to the glass stems with "Araldite". The stems were fitted with B-7 ground-glass cones and sockets to facilitate filling and emptying. The dilatometer was calibrated by weighing it filled with distilled water to a set scale level. Volumes at other levels were obtained by assuming a uniform tubing bore of 1 mm.

For a rough check of the freezing pressure of one reaction solution, isothermal compressions were measured using a re-entrant piezometer of the type used by Bett⁽¹²²⁾ (fig.II-7b). This had a capacity of about 4 mls.

II.B. Purification of Reagents and Solvents

1. Solvents

AnalaR nitrobenzene was dried over sodium sulphate and fractionated at 100 mm pressure under a dry nitrogen blanket. It was then stored over AnalaR activated alumina and filtered through a sintered glass funnel as required. The purified nitrobenzene melted at 5.7°C (recorded m.p. $5.76^{(108)}$). The measured specific conductance, $1 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$, while not as low as some values recorded in the literature (1×10^{-10} (112); $3 - 5 \times 10^{-9}$ (113); 0.9×10^{-8} (108)), was insignificant compared to the conductance of the lowest experimental solution.



FIGII-7 a- DILATOMETER ; b- PIEZOMETER

AnalaR chloroform was purified by the method used by Williams, Perrin and Gibson⁽¹⁾. The fraction boiling at 61.0 to 61.5°C was retained (recorded b.p. 61.15 - 61.27° (114)). No attempt was made to remove the small amount of ethanol added by the manufacturer to stabilize the solvent against breakdown to phosgene. The specific conductance was $6.7 \times 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ (recorded specific conductance $< 1 \times 10^{-10}$ (108)), which was again negligible compared to the conductance of the lowest experimental solution.

Methanol and acetone were purified for use as solvents in trial runs on reverse Menschutkin reactions. AnalaR methanol was purified by the procedure used by Harris⁽²⁾. AnalaR acetone was distilled, dried over calcium sulphate and fractionated under a blanket of dry nitrogen, a procedure which should reduce the water content to less than 10 p.p.m. (108). It was protected from contamination from atmospheric moisture in a flask equipped with drying tubes. Since only qualitative results were obtained for reactions in these solvents, accurate physical constants were not measured.

2. Alkyl Halides

AnalaR methyl and ethyl iodides were purified by the procedure used by Harris⁽²⁾. The iodides were washed with a 0.1 M sodium thiosulphate solution, with distilled water, with a 0.1 M sodium carbonate solution and finally again with distilled water. After drying overnight over calcium chloride, they were fractionated at

1 atm. away from direct sunlight. To prevent decomposition they were stored over mercury. The methyl iodide boiled at 42.5°C , the ethyl iodide at 72.5°C (recorded : 42.4 and 72.4°C respectively⁽¹¹⁵⁾). Both were water white and showed no discolouration even after several months.

Allyl bromide, obtained from British Drug Houses Limited was purified by the procedure used by Williams, Perrin and Gibson⁽¹⁾. After two fractionations the middle cut (representing about $\frac{1}{2}$ of the original material) was water white and boiled at 70.2 to 70.5°C (recorded : $70 - 71^{\circ}\text{C}$ ⁽¹¹⁶⁾). It showed no tendency to discolour when stored over mercury.

3. Amines

N : N-dimethylaniline and N-ethyl-N-methylaniline (both AnalaR grade) were purified by the method described by Evans, Watson and Williams⁽¹¹⁷⁾. The amine was refluxed with an equal amount of AnalaR acetic anhydride for several hours and then fractionated at 1 atms. The middle $\frac{2}{3}$ was retained. After drying overnight over AnalaR potassium hydroxide, the amine was fractionated under a dry nitrogen blanket at 10 - 15 mm pressure and stored under nitrogen in a desiccator. Both amines were a very light amber in colour which gradually deepened to a dark yellow on prolonged exposure to air. The dimethylaniline melted at 2.5°C (recorded m.p. : 2°C ⁽¹¹⁸⁾; 2.5°C ⁽¹¹⁹⁾). The melting point of ethyl-methyl aniline is not recorded in the literature. It boiled at

203 - 205°C, somewhat higher than the recorded boiling point (200 - 204⁽¹²⁰⁾) but chromatographic analysis failed to show any significant impurities.

N-benzyl-N-methyl aniline (Hopkin and Williams. Limited) was used as an intermediate in the preparation of allyl-benzyl-methyl-phenyl ammonium bromide. It was distilled twice under dry nitrogen at about 5 - 10 mm pressure, retaining about ½ of the original amount of amine, a similar procedure to that used by Williams, Perrin and Gibson⁽¹⁾. Its b.p. at 8 mm pressure was 161°C (recorded 161 - 2°C⁽¹¹⁶⁾). As the amine rapidly acquired a deep brown colour on contact with air, it was reacted immediately with allyl bromide to form the quaternary salt.

Pyridine, quinoline, tri-n-propylamine and N : N-dimethyl-o-toluidine were used to prepare quaternary salts for trial runs on reverse Menschutkin reactions. Pyridine was dried over KOH and distilled at one atmosphere. Dimethyl-o-toluidine was purified by the method used for dimethylaniline, previously described. Quinoline and tri-n-propylamine were not purified. Accurate physical properties of these amines were not measured.

4. Quaternary Salts

All salts were prepared by mixing equimolar quantities of the amine and halide and leaving them at a temperature of about 35 - 40°C until an appreciable amount of the salt had crystallized out (1 - 3 days). The salt was then collected on a sintered glass

funnel, washed several times with AnalaR petroleum ether (b.p. 40 - 60°C) and crystallized three times from methanol, by cooling and addition of diethyl ether. The salt was dried at ambient temperature in a vacuum desiccator and stored under vacuum in the dark.

Ethyl-dimethyl-phenyl ammonium iodide was prepared from purified methyl iodide and the appropriate amine. Its purity was checked by analysis for halide ion (found 45.7% I; theoretical 45.75%). Allyl-benzyl-methyl-phenyl ammonium bromide was prepared from purified allyl bromide and purified benzylmethyl aniline. The white crystalline salt melted sharply at 143.5°C (recorded : 144°C⁽¹⁾). The purity was also checked by analysis for percent halide (found 24.8% theoretical 25.11%).

Trimethyl-phenyl ammonium iodide, ethyl-pyridinium iodide, ethyl-quinolinium iodide and ethyl-tri-n-propyl ammonium iodide were made up from purified methyl or ethyl iodide and the appropriate amine (latter two amines unpurified). These were used for trial runs only and no purity checks were made.

All salts were crystalline white solids with the exception of ethyl-quinolinium iodide, which was a bright yellow.

SECTION III. EXPERIMENTAL PROCEDURES AND CALCULATION

METHODS

III.A Forward Menschutkin Reactions

1. Procedure for Kinetic Runs

Kinetic data for forward Menschutkin reactions was obtained from measurements of product quaternary salt concentrations as a function of time. Stock solutions of the amine and of the iodide in nitrobenzene were made up in 100 ml volumetric flasks, the solute being added by weight. These solutions were double strength so that mixing equal volumes of each would give a reacting solution of the desired molarity.

For high pressure runs the reactant solution, after thorough mixing, was poured into an inverted reaction tube containing a small amount of clean mercury. The tube was then carefully turned upright and placed in the steel bucket, which contained enough mercury to float the tube about $\frac{1}{2}$ " above the bottom. The bucket was placed in the pressure vessel, excess paraffin oil removed and the sealing O-ring and plug installed. The pressure was raised somewhat slowly to minimise the temperature effect of compression, pumping times of 1, $1\frac{3}{4}$ and $2\frac{1}{2}$ minutes being used for pressures of 500, 1500 and 3000 atm. respectively. On completion of the run the pressure was released, the reaction tube withdrawn and the reaction mixture poured into a flask to cool.

Zero reaction time was considered as half-way between the time pumping was started and the time full pressure was attained. The end of the run was taken as half-way between the time pressure release was begun and the time atmospheric pressure was reached (see table III-1).

Table III-1

Timing Data, Typical 1000 Atm. Run

Operation	Time, minutes
Reagents mixed	0
Into vessel	6
Start to pump	8
To 1000 atm.	9½
Start to release pressure	248½
To atmospheric pressure	249
Reaction solution out of vessel	250

$$\left. \begin{array}{l} 8 \\ 9\frac{1}{2} \end{array} \right\} 8\frac{3}{4}$$

$$\left. \begin{array}{l} 248\frac{1}{2} \\ 249 \end{array} \right\} 248\frac{1}{4}$$

Time used for
calculation -
240 min.

This procedure takes into account the increase in rate with pressure and the fact that the reaction is very slow at ambient temperatures. To diminish the effect of end errors, runs were usually 2 hours or longer. With these procedures satisfactory rate constants were obtained showing no consistent drift with time.

When the reacting solution had cooled to room temperatures it was analyzed for the quaternary salt by the following method :

- (i) 2 mls of the reactant solution were pipetted into a small separating funnel containing 25 mls of petroleum ether (b.p. 40 - 60°C) and 10 mls of distilled water.
- (ii) After thorough shaking, the water layer containing the quaternary salt was drained off. The mother liquor was then extracted with two more portions of water.
- (iii) A few mls of 6 N acetic acid and a few drops of Eosin indicator (0.1 wt % in 70% ethanol) were added to the total extract. It was then titrated with 0.01 M standard silver nitrate solution until the precipitate suddenly became intensely red.
- (iv) All reagents used were AnalaR grade. The solutions were made up from de-ionized distilled water. The sodium chloride solution for standardizing the silver nitrate was made up from AnalaR sodium chloride dried to a constant weight at 220°C.
- (v) Analysis was usually done in duplicate. The two titrations seldom differed by more than 1%.

For runs at one atmosphere the reacting solutions were sealed into 5 ml amber glass ampoules. Analysis procedure was the same as described for high pressure runs.

2. Calculation of Rate Constants

The initial concentrations of amine and iodide and the quaternary salt concentration were adjusted to reaction conditions

using the P-V-T data for nitrobenzene of Kuss⁽¹²¹⁾. Where the effect of the opposing reverse Menschutkin reaction could be neglected (high pressures and low temperatures shifted the equilibrium towards the quaternary salt), the rate constants were calculated from normal second order graphs of $1/(a - x)$ versus time, a being the original amine and iodide concentrations (equal) and x the measured salt concentration at the end of the run. Each rate constant was established from the results of four to eight runs. Typical data is shown in table III-2 and is plotted in figure III-1.

Table III-2

Typical Rate Data, No Equilibrium Effect

Reactants : methyl iodide + ethylmethylaniline			
Temperature : 50°C			
Pressure : 1000 atm.			
Initial concentration : 0.0508 M (0.05 M at 20°C, 1 atm)			
Time min.	$10^6 x$ moles/l	$10^6 (a - x),$ moles/l	$k \times 10^4$ l/mole sec.
100.0	6630	4417	4.92
151.5	9370	4143	4.90
200.0	1185	3895	4.99
252.0	1395	3685	4.92
Rate constant, from fig. III-1 : 4.92×10^{-4} l/mole sec.			

For conditions where neglecting the opposing reaction would have caused more than 0.5% error, the rate constants were calculated by the kinetic equation for a second order reaction opposed by one of the first order,

$$k = \frac{2.303x_e}{t(a^2 - x_e^2)} \log \frac{x_e(a^2 - xx_e)}{a^2(x_e - x)} \quad (\text{III-1})$$

In this equation x_e is the concentration of quaternary salt at equilibrium in moles/l and the other symbols are as previously defined. Since the reverse reaction rate constant increases with increasing salt concentration, x_e is not single valued. As an approximation, x_e was calculated using the reverse reaction rate constant at a salt concentration of $x/2$. Since conversions were kept below the point where a large correction to the rate constant was required, this uncertainty would not effect the results a great deal. A typical set of data is given in table III-3.

It should be mentioned that the reactions of dimethyl aniline are both opposed by the same reverse reaction. Since this reverse reaction forms methyl iodide and ethyl methyl aniline, a true equilibrium is not possible for the dimethyl aniline-ethyl iodide system. However, since this reaction was studied in the area where corrections due to equilibrium effects were small (usually less than 5%), the use of a pseudo-equilibrium constant would cause little error.

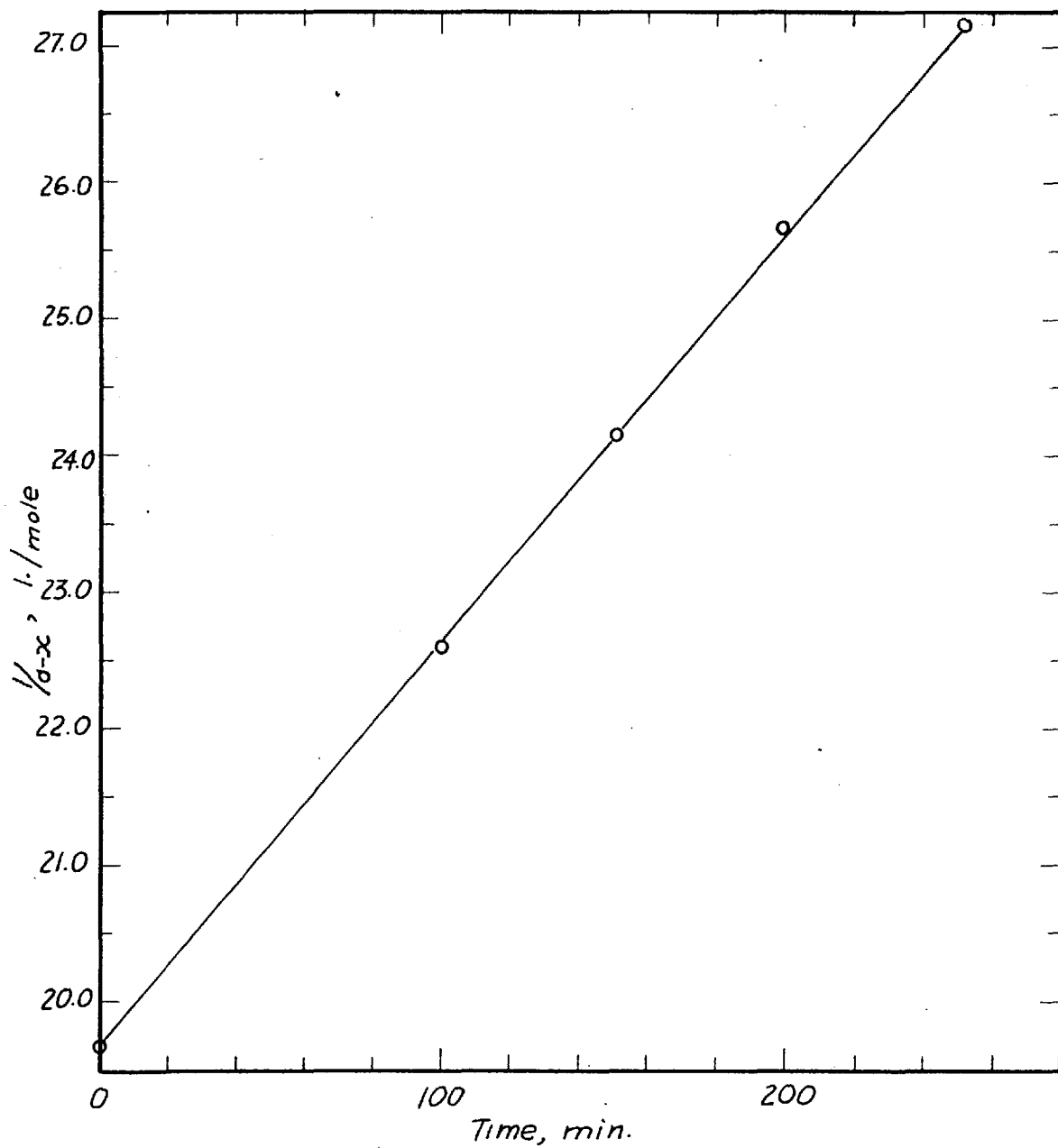


FIG. III-1 TYPICAL SECOND ORDER PLOT, METHYL IODIDE + DIMETHYLANILINE IN NITROBENZENE

Table III-3

Typical Data, Equilibrium Effect Considered

Reactants	: ethyl iodide + dimethyl aniline		
Temperature	: 52.5° C		
Pressure	: 1 atm.		
Initial concentration	: 0.09735 M. in both reagents : (0.1 M at 20° C and 1 atm.)		
Time mins.	x moles/l	k' x 10 ⁵ l/mole sec.	k x 10 ⁵ l/mole sec.
409	0.005021	2.28	2.29
426	0.005122	2.23	2.25
998	0.01109	2.20	2.28
1,137	0.01240	2.20	2.29
1,399	0.01460	2.16	2.29
1,626	0.01663	2.10	2.25
2,880	0.02569	-	-
6,034	0.03865	-	-
14,047	0.05311	-	-
20,490	0.05798	-	-
Rate constant, arithmetic average :			
2.28 x 10 ⁻⁵ l/mole sec.			

3. Methods for Autocatalysis Studies

Freezing Pressure of the Solution

A discontinuity in the rate constant-pressure curve was observed between 2360 and 2630 atm. in the reaction between ethyl iodide and dimethylaniline in nitrobenzene. To check for suspected solvent freezing in this area, solution compressions were measured at 2260 and 2730 atm. using a re-entrant piezometer (shown in fig.II-6b) and following the method of Bett⁽¹²²⁾.

The piezometer filled with reactant solution was placed in a steel bucket containing mercury as a seal and the whole placed in the pressure vessel. When the pressure was applied, mercury was forced up the re-entrant capillary tube and fell to the bottom of the piezometer. From the weight of mercury trapped in the piezometer the compression of the liquid was calculated at the known pressure and temperature. Compressions were calculated from the equation used by Bett⁽¹²²⁾,

$$(k_o)_p^T = \frac{(W_M)_o^T [1 - (k_M)_p^T] + (W_G)_o^T [1 - (k_G)_p^T]}{(W_Z)_o^T} + (k_G)_p^T \quad (\text{III-2})$$

where W_M is the weight of mercury trapped in piezometer in gms,

W_G is the weight of mercury needed to fill the capillary in gms,

W_Z is the weight of mercury needed to fill the total internal volume, including the capillary in gms; and

$(k_o)_p^T$, $(k_M)_p^T$ and $(k_G)_p^T$ are the compressions of the solution of mercury and of glass at $T^\circ\text{C}$ and P atm. in cm^3/cm^3 .

Bridgman's data⁽⁶⁾ for the compression of mercury at 20°C was used for $(k_M)_P^T$ and Bett's data for the compression of glass to 1000 bars⁽⁴²⁾ was extended linearly to estimate $(k_G)_P^T$. The inaccuracy due to these extrapolations would be slight, as the compressions of mercury and glass enter the calculations only as small corrections to the observed compression.

Kinetic Data above the Freezing Pressure

To obtain kinetic data above the freezing pressure of the reactant solution, no change from the normal experimental method was required, as the solvent had always melted by the time the pressure had been reduced to 1 atm and the reaction tube removed, and product crystallization was not observed.

Data above the freezing point was correlated better using a first than a second order relationship. (This will be explained in section VA).

Kinetic Data at High Initial Concentrations

In order to approximate concentration conditions obtaining with 0.1 M reagents above the solution freezing pressure, kinetic runs were done at 1 atm. with initial reagent concentrations of 0.5 M and 1 M in each reagent. Although the highly concentrated quaternary salt solutions produced in these runs appeared to remain in the supersaturated state under reaction conditions (and often would not crystallize at ambient temperatures if gently handled), crystallization during sampling precluded the use of normal volumetric sampling

methods. For these runs a weighed amount of reactant solution was used, the whole being washed out of the reaction tube and analyzed on completion of the run.

At high initial concentrations the decrease in volume of the solution on reaction (due to electrostriction of solvent around the charged product) must be considered in calculating kinetic data. Vorob'ev and Titova⁽¹²³⁾ found that for Menshutkin reactions

$$V_t = V_o (1 - bx) \quad (\text{III-3})$$

where V_o is the initial volume of solution,

V_t is the volume of solution at time t ,

x is the concentration of product salt, and

b is the molar volume of reaction.

From this relationship, using the measured molar volume change for the reaction of methyl iodide and ethyl methyl aniline (see Results Section IVC. Volume change for the two reactions in nitrobenzene should be almost identical, as the same product is formed), the corrected final concentration for each run was calculated. This was then used to calculate the rate constants.

III.B. Reverse Menshutkin Reactions

1. The Conductometric Method in Kinetics

Whenever a reaction occurs with a change in the number or kind of ions present so that the electrical conductivity changes, measurement of the conductance offers a convenient means of following the course of the reaction. The method has several advantages over

analysis by chemical methods. A continuous record of conversion can be obtained and since the conductance is sensitive to small relative changes in concentration, kinetic data can be obtained for small conversions. The main disadvantage of the technique is that usually no simple relationship exists between conductance and concentration, and calibration of the system is therefore required.

The conductometric method was thought to be particularly applicable to the study of reverse Menschutkin reactions in organic solvents. Since only the reactant (the quaternary salt) has any appreciable conductance, the decrease in conductance would give an indication of the extent of reaction. As well, it was desirable to study these decompositions over a small conversion, not only to eliminate equilibrium effects, but because the first order rate constant was known to change appreciably with concentration.

The determination of reaction rates by conductometric methods has been reported by a number of workers. Norris and Norton^{(124) - (127)} used conductometry to follow the solvolysis of organic halides in ethanol. It has also been used by Bateman, Hughes and Ingold⁽⁸⁴⁾ for study of Menschutkin reactions in liquid sulphur dioxide, by Jones and Worsfold⁽¹²⁸⁾ for halide exchange reactions in acetone and by Evans and Hamann⁽¹²⁹⁾ for the study of solvolysis of organic halide exchange reactions in various solvents. Fierens et al. have discussed the method⁽¹³⁰⁾ and have used it for

a large number of kinetic experiments. The conductometric method has been used for kinetic experiments at high pressures by Hamann and his co-workers. For example, Buchanan and Hamann⁽²⁵⁾ used changes in conductance to follow the course of unimolecular solvolyses.

In all of the cases cited above, calibration of the solution conductance against the product concentration was carried out as a preliminary to kinetic runs. McGuire⁽¹³¹⁾ has used the conductometric method directly to obtain kinetic data for several reactions including forward Menschutkin reactions in methanol (data from McGuire's thesis was used to illustrate the conductometric method by Frost and Pearson⁽⁷⁴⁾). He assumed that the product salt concentration was directly proportional to the conductance. This is incorrect and McGuire's data must be considerably in error.

The conductance of ions at low concentrations in ionizing solvents obeys the Debye-Hückel-Onsager limiting equation⁽⁷³⁾, which predicts a term in $c_s^{3/2}$ as well as c_s . The D.-H.-O. equation is

$$\text{or } \Lambda = \Lambda_0 - (B_1 + B_2 \Lambda_0) \sqrt{c_s} \quad (\text{III-4})$$

$$C = \frac{\Lambda_0 c_s}{1000a} - \frac{(B_1 + B_2 \Lambda_0)}{1000a} (c_s)^{3/2} \quad (\text{III-5})$$

where c_s is the concentration of salt in moles/l.,

C is the conductance of solution at concentration c in mhos.,

Λ is the equivalent conductance at concentration c_s in mhos cm^2 ,

Λ_0 is the equivalent conductance at zero concentration in mhos cm^2 ,

a is the cell constant in cm^{-1} , and

B_1 and B_2 are constants depending on the temperature and the dielectric constant of the solvent.

At higher concentrations the conductance-concentration relationship is complicated by ion association and by failure of some of the assumptions inherent in the D.-H.-O. limiting law (notably the assumption that ions are point charges). In non-ionizing solvents a very complicated relationship occurs, since except at very low concentrations, not only non-conducting ion-pairs exist but also ion-triplets and higher associations, some of which contribute to the conductance.

2. Application to Reverse Menschutkin Reactions

In this work the kinetics of the decomposition of two quaternary salts were studied, one in nitrobenzene (an ionizing solvent) and the other in chloroform (a non-ionizing solvent). Typical conductance curves are shown in figures III-2 and III-3.

In calculating rate constants, the conductance-concentration curve was assumed to be a straight line over the concentration range covered in the run. Since most runs in nitrobenzene were done at 0.05 M, and in chloroform at 0.1 M, and conversions were usually kept less than 20%, this was a reasonably good assumption. The straight line was fixed for each kinetic experiment by determining two points on it. The conductance at the initial reactant concentration (as determined in the kinetic run) gave one point. The second point was obtained from a calibration run at a concentration corresponding to approximately 20% conversion of the quaternary salt. The equation linking the reactant concentration and the conductance

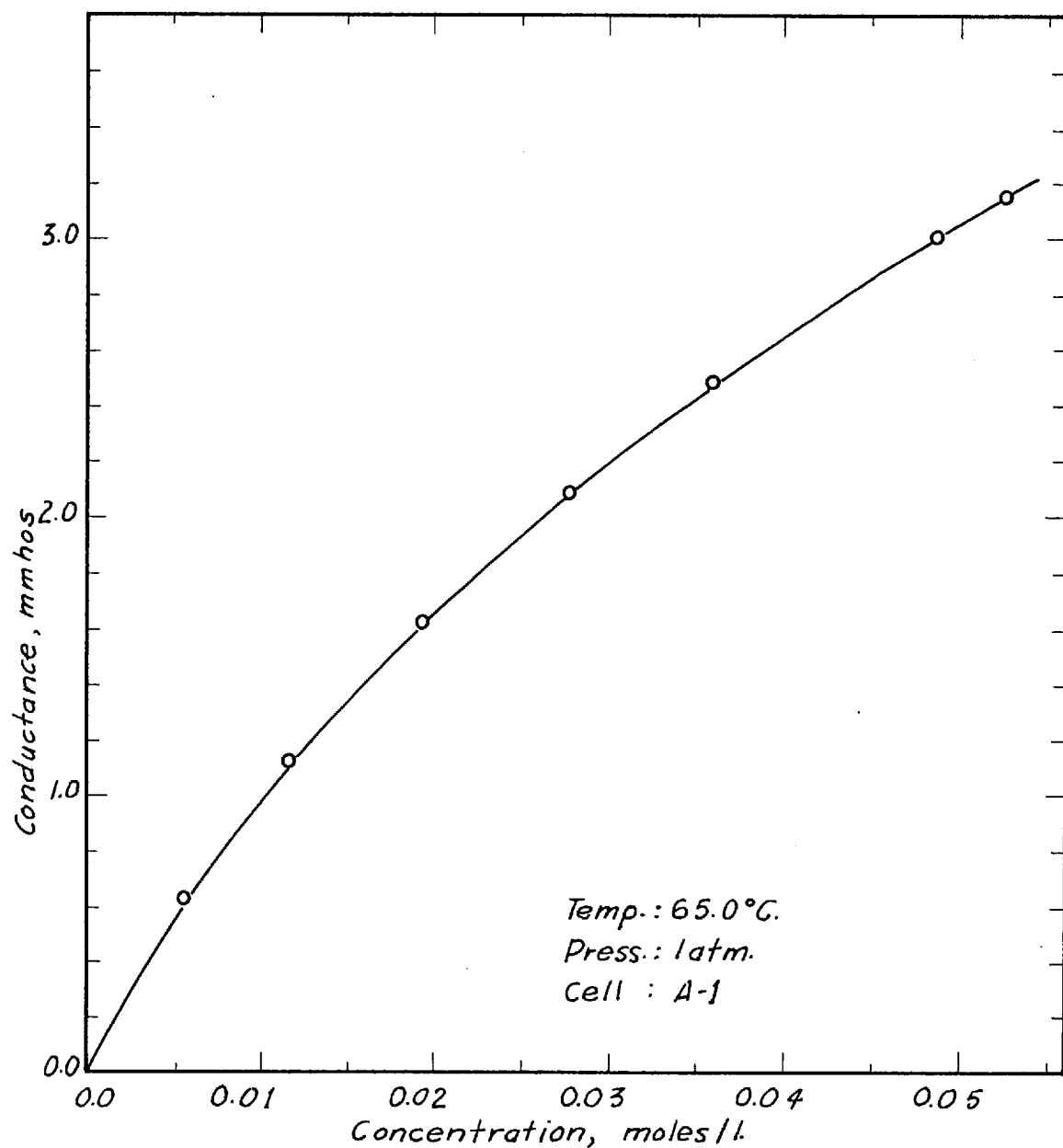


FIG. III-2 EXAMPLE OF CONDUCTANCE-CONCENTRATION RELATIONSHIP FOR ETHYL-DIMETHYL-PHENYL AMMONIUM IODIDE IN NITROBENZENE

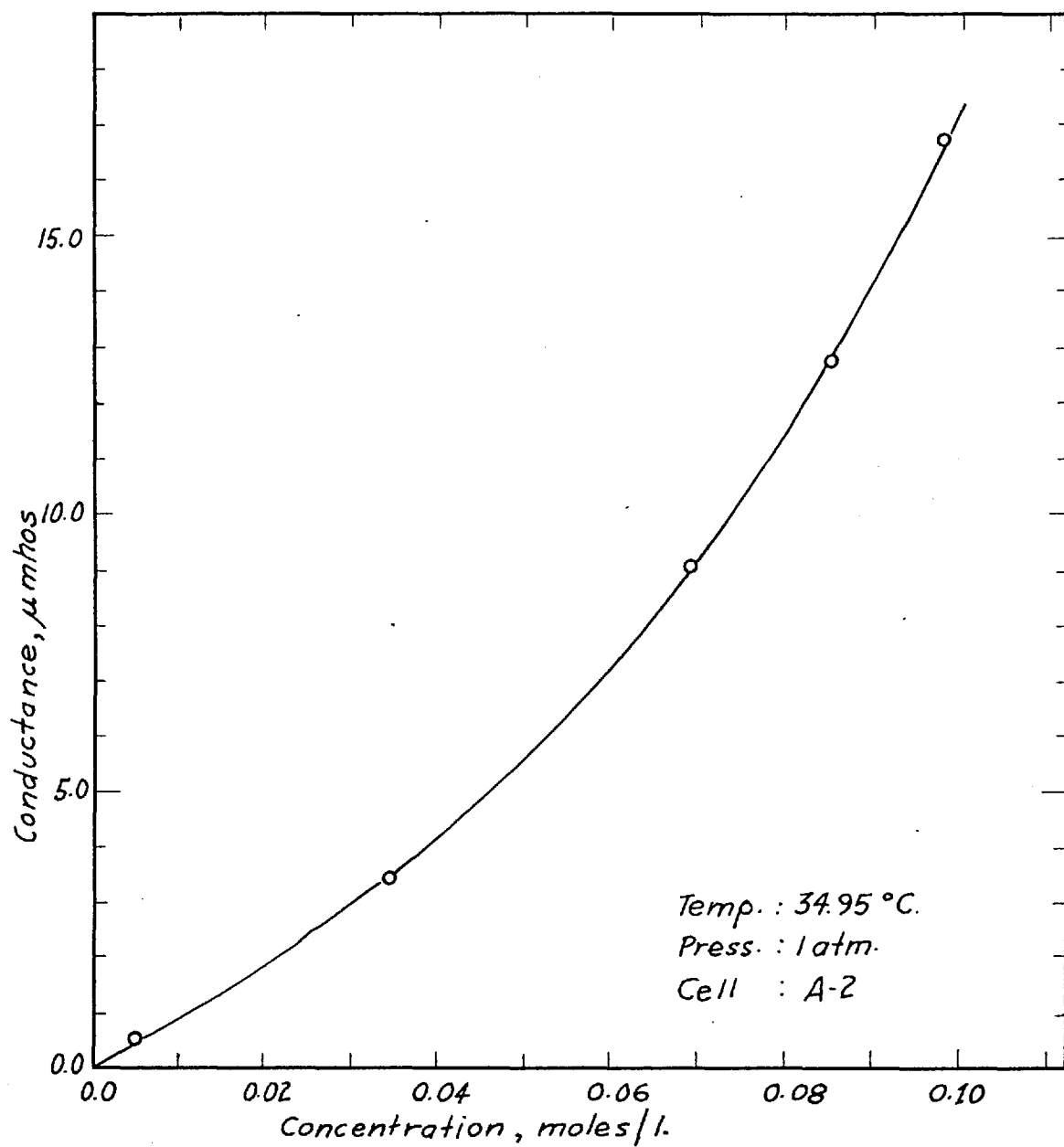


FIG. III-3 EXAMPLE OF CONDUCTANCE-CONCENTRATION RELATIONSHIP FOR ALLYL-BENZYL-METHYL-PHENYL AMMONIUM BROMIDE IN CHLOROFORM

at a fixed temperature and pressure is thus

$$C - C_o = \frac{C_c - C_o}{(c_s)_c - (c_s)_o} (c_s - (c_s)_o) \quad (\text{III-6})$$

where C refers to conductance in mhos, c_s to the quaternary salt concentration in moles/l and the subscripts o and c refer respectively to the initial and calibration conditions.

If the intercept on the C axis is termed C_∞

$$C_\infty = C_o - (c_s)_o \left[\frac{C_c - C_o}{(c_s)_c - (c_s)_o} \right] \quad (\text{III-7})$$

and equation III-6 can be re-arranged to

$$c_s = \frac{(c_s)_c - (c_s)_o}{C_c - C_o} (C - C_\infty) \quad (\text{III-8})$$

Combining III-8 with the usual first order kinetic equation

$$k = \frac{2.303}{t} \log \frac{(c_s)_o}{c_s} \quad (\text{III-9})$$

equation III-10 is obtained.

$$k = \frac{2.303}{t} \log \left[\frac{C_o - C_\infty}{C - C_\infty} \right] \quad (\text{III-10})$$

Similarly, since equation III-8 applies for the whole course of the kinetic run, the rate constant can be calculated over any time interval by equation III-11, where the subscript 1 refers to a specific time t_1 .

$$k = \frac{2.303}{t - t_1} \log \left[\frac{C_1 - C_\infty}{C - C_\infty} \right] \quad (\text{III-11})$$

C_{∞} was calculated from equation III-7 for each run. The point (t_1, C_1) was chosen from the data at a time when the run pressure and temperature had settled to a steady value, as indicated by the conductance - time charts (usually 30 - 50 min. at 1 atm. pressure and up to 70 min. at high pressures). Point (t_1, C_1) was used as a reference, rather than (t_0, C_0) , to eliminate as far as possible the effect of temperature and pressure fluctuations at the beginning of a run, and the uncertainty resulting from the derivation of C_0 by extrapolation.

Table III-4 presents data typical of that obtained at one atmosphere. This is plotted in fig.III-4.

Data at high pressure was less accurate than at atmospheric pressure due to less precise temperature control of the system and to pressure inaccuracies, both of these effects increasing with pressure. Calculations for a run at 1000 atm. and 65°C are given in table III-5 and fig.III-5. This is representative of the data obtained, although rate constants at lower pressures usually showed less spread. The accuracy of the rate constants at 1 atm. was estimated to be $\pm 3\%$, and at high pressures $\pm 5\%$.

Table III-4

Typical Rate Data, Reverse Menschutkin Reactionat Atmospheric Pressure

Reactant : ethyl-dimethyl-phenyl ammonium iodide in nitrobenzene Temperature : 58.75°C. Pressure : 1 atm. Initial concentration: 0.04843 M Conductivity cell : A - 1					
Time min.	$(t - t_1)$ min.	C, m mhos	$(C - C_\infty)$, m mhos	$\log \frac{(C - C_\infty)}{C - C_\infty} \times 10^3$	$k' \times 10^5$ sec. ⁻¹
0(t ₀)	-	(2.791)	-	-	-
35(t ₁)	0	2.766	1.939	0	0.576
65	30	2.746	1.919	4.50	0.576
99	64	2.724	1.897	9.51	0.570
130	95	2.704	1.877	14.14	0.570
169	124	2.686	1.858	18.70	0.580
234	199	2.637	1.810	29.90	0.576
254	229	2.619	1.792	34.24	0.575
310	275	2.594	1.767	40.34	0.563

Notes : (i) $C_\infty = 0.827$ m mhos, calculated from the following data :

initial concentration of kinetic run

- 0.04843; $C_0 = 2.791$ m mhos.

initial concentration of calibration run

- 0.03501; $C_0 = 2.247$ m mhos.

(ii) Derived rate constant, from fig.III-4: 0.570×10^{-5} sec.⁻¹

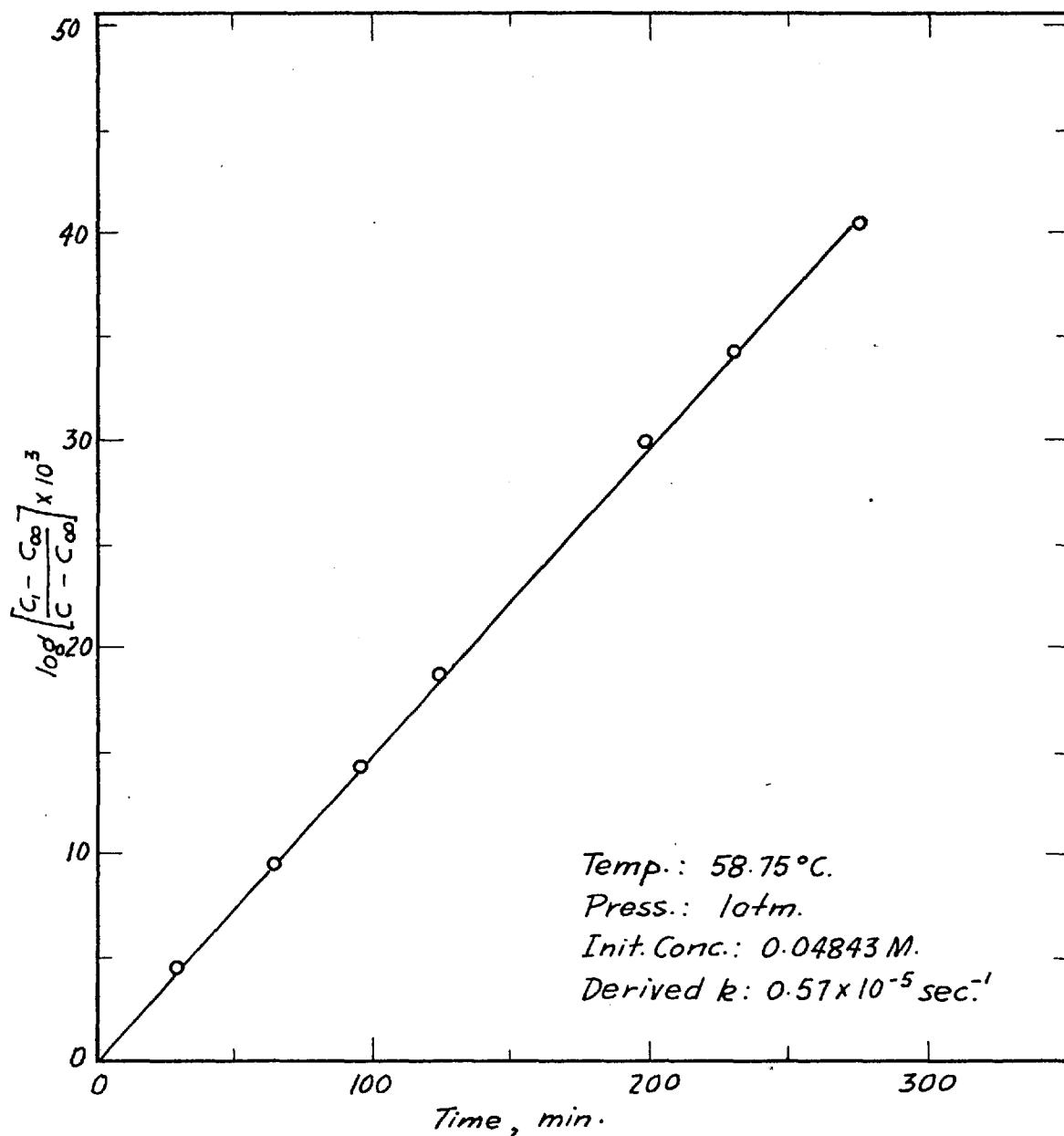


FIG. III-4 TYPICAL FIRST ORDER PLOT, DECOMPOSITION OF ETHYL-DIMETHYL-PHENYL AMMONIUM IODIDE IN NITROBENZENE

Table III-5

Typical Rate Data, Reverse Menschutkin Reaction
at High Pressure

Reactant : Allyl-benzyl-methyl-phenyl ammonium bromide in chloroform Temperature : 34.95°C Pressure : 2000 atm. Initial concentration : 0.09996 M. Conductivity cell : P - 1					
Time min.	$(t - t_1)$ min.	C, μ mhos	$(C - C_\infty)$ μ mhos	$\log\left(\frac{C_1 - C_\infty}{C - C_\infty}\right) \times 10^2$	$k' \times 10^3$ min. ⁻¹
0(t ₀)	-	(20.40)	-	-	-
41(t ₁)	0	19.17	30.01	0.0	-
71	30	18.23	29.07	1.382	1.06
101	60	17.42	28.26	2.610	1.02
133	92	16.48	27.32	4.079	1.03
162	121	15.75	26.59	5.255	1.00
181	140	15.30	26.14	5.996	0.99

Note : (i) $C_\infty = -10.84 \mu \text{ mhos}$, calculated from following data :

initial concentration, kinetic run - 0.09996 M;

$$C_0 = 20.40 \mu \text{ mhos}$$

initial concentration, calibration run - 0.08013 M;

$$C_0 = 14.20 \mu \text{ mhos}$$

(ii) Derived rate constant, from figure III-5: $1.02 \times 10^{-3} \text{ min}^{-1}$.

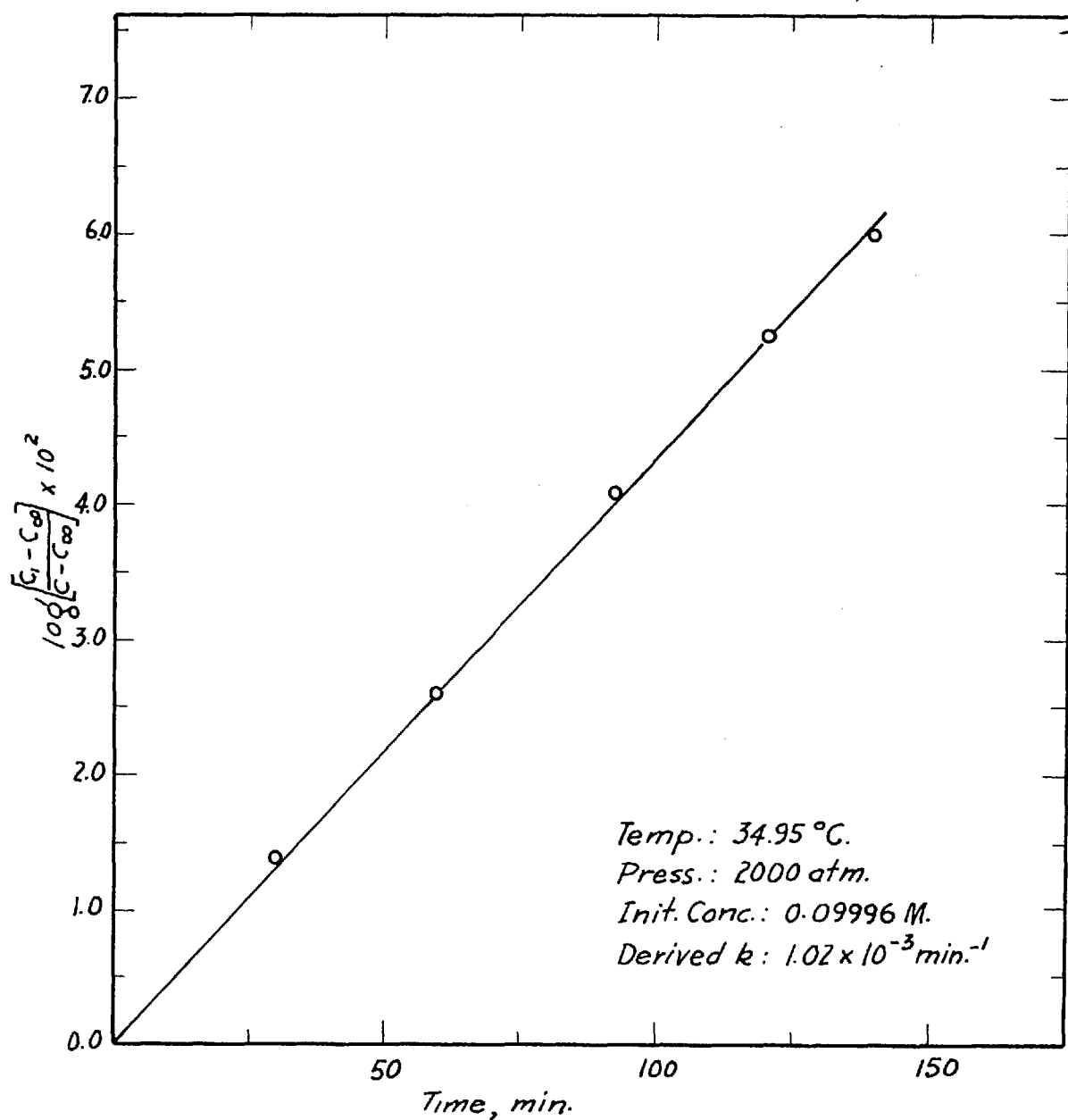


FIG. III-5 TYPICAL FIRST ORDER PLOT, DECOMPOSITION OF ALLYL-BENZYL-METHYL-PHENYL AMMONIUM BROMIDE IN CHLOROFORM

It has been noted that the apparent order of reverse Menschutkin reactions is not precisely first, but somewhere between first and second (Section ID). In the calculations just outlined it has been assumed to be first order. However, since conversions were kept low, the apparent first order constants can be considered as initial rates divided by average reactant concentrations and can thus be converted to the required order with little error. This can be illustrated by considering a hypothetical reaction where the initial reactant concentration is a and the concentration after t minutes is $0.8a$ (i.e. 20% conversion). The first order rate constant is $\frac{0.22318}{t}$; the second order rate constant is $\frac{0.25}{at}$. By dividing the first order constant by the average concentration $0.9a$, a second order constant of $\frac{0.24798}{at}$ is obtained. Compared to the true second order constant $\frac{0.22318}{at}$, there is less than 1% error.

3. Experimental Procedure, Conductometric Method

Reactant solutions were freshly made up for each run in 25 ml volumetric flasks. For the very dilute solutions used in some of the runs, more concentrated solutions were diluted by volume. Ethyl-dimethyl-phenyl ammonium iodide has limited solubility in nitrobenzene. Heating to $35 - 40^\circ$ was necessary to dissolve the salt at 0.05 M. Allyl-benzyl-methyl-phenyl ammonium bromide dissolved readily in chloroform.

The conductivity cells were always left filled with solvent to prevent electrode deterioration. They were thoroughly flushed with

the reactant solution before each run. Runs at atmospheric and high pressures were followed in cells of the types shown in figures II-6b and II-6a respectively.

For high pressure runs, the cell filled with reactant solution was inverted in the glass bucket containing the mercury seal, the whole being held together by springs. The cell was then suspended in a bracket from the pressure vessel plug, with electrical connection through insulated electrodes in the plug dipping into mercury wells at the top of the cell. The plug assembly was carefully tightened down to the vessel and the pressure slowly raised to the desired reaction temperature (1 - 2 min. taken for pumping). Conductance readings were begun after the cell had been in the bath a few minutes.

The conductance at the reaction temperature could not be directly measured, since decomposition with a resultant drop in conductance occurred before the cell had reached the bath temperature. To get the conductance at initial conditions, the conductance-time curve was extrapolated back to zero time (taken as the time the cell and its contents were put in the bath). Examples of these extrapolations are given in figure III-6. The curve at 1000 atm. and above was inverted due to heat of compression effects.

Some check runs were done using volumetric analysis of the quaternary salt to determine conversions. Analytical procedures were as outlined for forward Menshutkin reactions. For each run, two analyses were done, one on the initial reactant solution, the

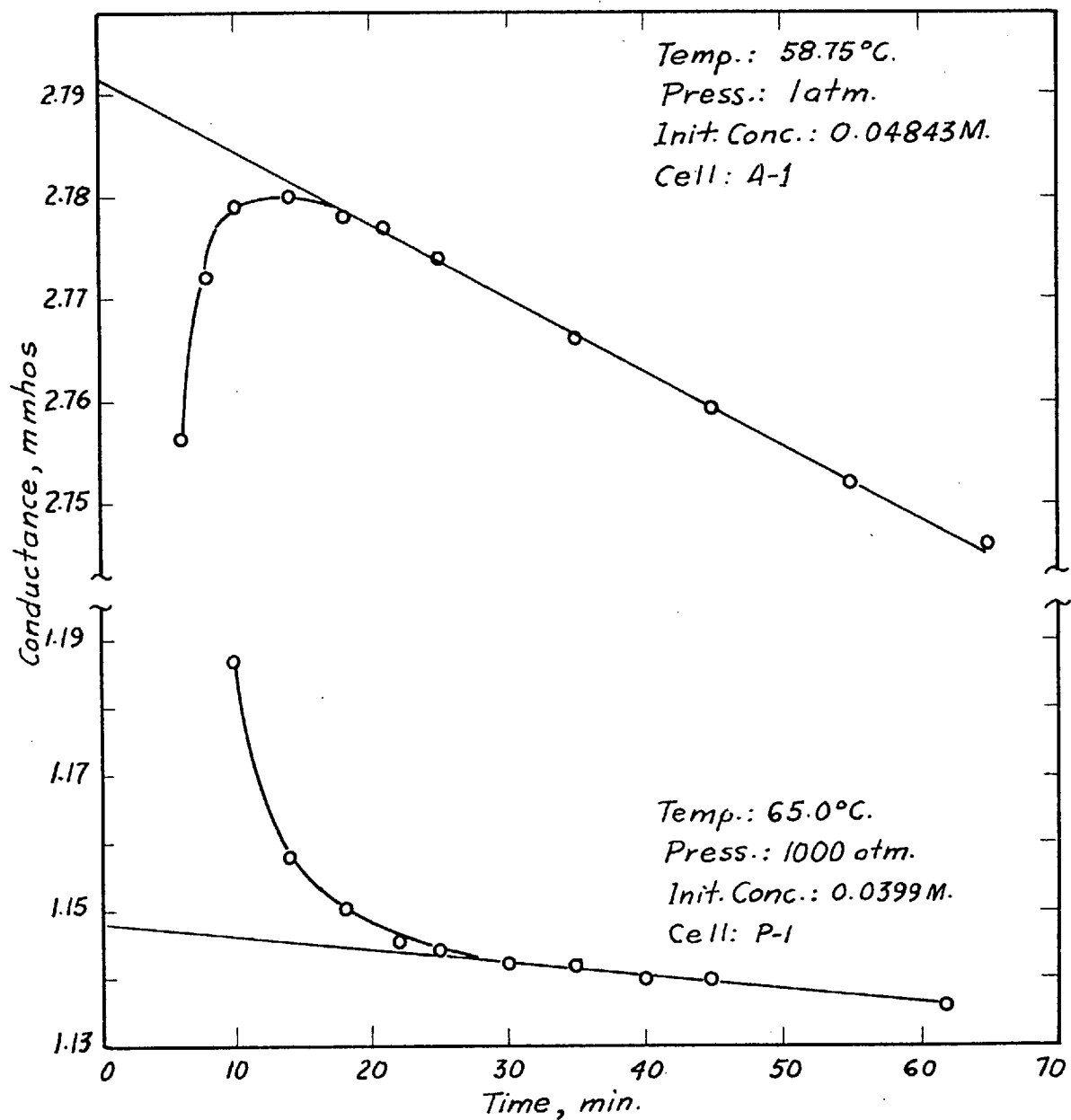


FIG. III-6 EXTRAPOLATION OF CONDUCTANCE DATA, ETHYL-DIMETHYL-PHENYL AMMONIUM IODIDE IN NITROBENZENE

other on the solution at the completion of the run. The rate constant was then calculated from the rates of the two titers.

4. Analysis of the Products of the Reverse Reactions

The products of decomposition of ethyl-dimethyl-phenyl ammonium iodide were determined by analysis. This salt could decompose to give three possible sets of products, depending on whether an ethyl, methyl or phenyl group split off to form the iodide. Since n-alkyl groups are ejected preferentially to phenyl groups, differentiation between only two sets of products was necessary. This was done by isolating the amine product from a decomposition and analyzing it chromatographically.

The salt was allowed to decompose for about 8 hours in nitrobenzene at 65°C and an initial concentration of about 0.2 M, conditions which approximated those used in kinetic experiments. The amine product was extracted from the solution with dilute HCl and precipitated with sodium carbonate solution. It was then put through an argon chromatograph (W.G. Pye and Company Limited) containing "Apiezon M" column packing.

By running the column at 100°C, excellent separation of the products was obtained. The identity of the peaks was confirmed by running an approximately equimolar synthetic mixture of the two purified anilines. This also confirmed that the detector was equally sensitive to each amine (i.e. molar ratio = ratio of peak areas). Traces of the solvent did not affect the analysis as nitrobenzene

comes off appreciably later than the amines (dimethyl aniline: 75 - 97 mins., ethylmethyl aniline 108 - 135 mins., nitrobenzene > 150 mins.). No other significant peaks appeared on the chromatograph. The molar ratio of the two amines was determined by measuring the relative areas under the peaks.

III C. Overall Volumes of Reaction

The overall volume of reaction (ΔV_r) for two Menschutkin reactions was measured. For the decomposition of ethyl-dimethyl phenyl ammonium iodide in nitrobenzene the overall volume of reaction at 25°C was determined by measuring the densities of a quaternary salt solution and the corresponding amine-iodide solution. A carefully calibrated double-ended glass dilatometer thermostatted in an air bath was used (see Apparatus). The solution levels were observed with a telescope mounted at a distance of about 3 ft. until they remained steady (the rate of reaction was negligible at this temperature).

Since the reaction products for the decomposition of allyl-benzyl-methyl-phenyl ammonium bromide in chloroform were not known (nor were the possible products commercially available for comparison) and the reaction proceeded at a significant rate even at 25°C, the above procedure could not be used. Instead, the quaternary salt was decomposed in the dilatometer at 34.95°C (where the rate of reaction had been previously measured) and the dilatometer levels observed at noted times during the decomposition.

The overall molar reaction volume was then calculated from the known reaction rate (corrected for equilibrium effects by the data of Williams, Perrin and Gibson⁽¹⁾). Since both methods involve the comparison of two densities rather than the absolute measurement of density (although the absolute density must be known approximately for the calculation) the result should be quite accurate.

III D. Electrolytic Dissociation of Quaternary Salts

1. Introduction

The dissociation constant of ethyl-dimethyl-phenyl ammonium iodide ion-pairs in nitrobenzene at various temperatures and pressures was required, both for determination of the volume of dissociation and to assist in elucidating the mechanism of the reverse reaction. A dissociation constant relationship was required which would accurately predict dissociation to 0.05 M (above the range of usual ion-pair dissociation constant calculations).

Conductance-concentration data for allyl-benzyl-methyl-phenyl ammonium bromide in chloroform was also obtained as an illustration of the ionic behaviour in that solvent. Dissociation constants were not calculated for this system, as dissociation is negligible. The following discussion therefore deals only with the dissociation of ethyl-dimethyl-phenyl ammonium iodide in nitrobenzene.

2. Experimental Method

Conductance-concentration data was obtained with the conductivity equipment used to study the kinetics of reverse Menschutkin reactions. Since decomposition of the quaternary salt, with

a corresponding drop in conductance occurred as soon as the cell was immersed in the bath, the conductance at the initial concentration had to be determined by extrapolation to zero time along the conductance-time curves (see figure III-6). 0.025 M solutions of ethyl-dimethyl-phenyl ammonium iodide in nitrobenzene (0.1 M for allyl-benzyl-methyl-phenyl ammonium bromide in chloroform) were accurately made up by weight. These were diluted by weight to obtain a range of concentrations.

Relative conductances were sufficient for the measurement of reaction rate, but for dissociation constants the absolute equivalent conductance was required. The conductivity cells were therefore standardized with a 0.1 M KCl solution, which has a known equivalent conductance of $128.96 \text{ ohms}^{-1} \text{ cm}^2$ at 25°C (73). The cell constants were all between 0.4 and 0.7 cm^{-1} .

Cell constants were assumed independent of pressure and temperature. Strauss⁽⁷⁷⁾ has calculated that the change in cell dimensions in a glass conductivity cell with pressure has an insignificant effect on the cell constant for pressures below 3000 atm. Robinson and Stokes⁽¹³²⁾ have given detailed calculations for the effect of temperature on the cell constants of cells of various geometric shapes. Using these calculations it was estimated that the maximum change in cell constant over the temperature range used in this research would be less than 0.1%.

3. Conductivity and Dissociation Relationships

The conductance of an electrolyte completely in the form of free ions is expressed at low concentrations by the Debye-Huckel-Onsager relationship (equation III-4). Allowing for ion association III-4 becomes⁽¹¹¹⁾

$$\Lambda_1 = \Lambda_0 - (B_1 \Lambda_0 + B_2) \sqrt{\alpha c_s} \quad (\text{III-12})$$

where Λ_1 is the equivalent conductance of a hypothetical fully dissociated solution at a concentration αc in mhos cm^2 ,

Λ_0 is the equivalent conductance at infinite dilution in mhos cm^2 ,

α is the fraction dissociated ($= \frac{\Lambda_1}{\Lambda_0}$),

c_s is the total salt concentration in moles/l., and

B_1 and B_2 are the constants of the limiting law, which for a given electrolyte charge type are functions of the temperature and of the solvent dielectric constant (Numerical values are listed by Monk⁽¹¹¹⁾).

This equation represents conductance data accurately to about 0.001 M, the limit depending somewhat on the solvent. Above this concentration the simplifying assumptions used to derive the D.-H.-O. equation (notably the assumption that ions behave as point charges) begin to cause significant deviations.

A number of equations which better describe the conductance-concentration relationship at higher concentrations have been proposed. A useful simplification of these very complicated equations has been

proposed by Robinson and Stokes⁽¹³²⁾ :

$$\gamma_i = \gamma_o - \frac{B_1 \gamma_o + B_2 \sqrt{\alpha c_s}}{1 + Ba \sqrt{\alpha c_s}} \quad (\text{III-13})$$

This is merely the limiting law with an added term in the denominator^{or} to allow for finite ion size, a being the ion size parameter and B a constant depending on the temperature and the solvent viscosity and dielectric constant.

The conductance is well represented by equation III-13 up to ionic concentrations of the order of 0.1 M, with proper choice of the ion-size parameter a . γ_i is not very sensitive to small changes in the value of a , at least at relatively low concentrations⁽¹³²⁾. The Bjerrum critical distance of approach, within which ions can be considered as ion-pairs, can be used to estimate the ion-size parameter (equations and tables for calculating Bjerrum distances are given by Monk⁽¹¹¹⁾).

In conjunction with equation III-13 the extended activity coefficient equation for 1 : 1 electrolytes must be used. It is

$$\log f_{\pm}^{\pm} = -A \frac{\sqrt{\alpha c_s}}{1 + Ba \sqrt{\alpha c_s}} \quad (\text{III-14})$$

where $f_{\pm}^{\pm}$ is the mean rational activity coefficient for anion and cation,

α , c_s , B and a are as previously defined, and

A is a constant depending on the temperature and the solvent dielectric constant.

The equation for the dissociation constant is

$$K_d = \frac{\alpha^2 c_s f_{\pm}^2}{(1 - \alpha)} \quad (\text{III-15})$$

Since the dissociation constant is in concentration terms, the activity coefficient, $f_{\pm}$, should strictly speaking be converted to $y_{\pm}$, but use of the rational (mole fraction based) activity coefficient introduces little error at ordinary concentrations (equations for calculating $y_{\pm}$ from $f_{\pm}$ are given by Robinson and Stokes⁽¹³²⁾).

4. Sample Calculation of Dissociation Constant

Dissociation constants were calculated from measurements of equivalent conductance as a function of concentration, using equations III-13, III-14 and III-15. The ion-size parameter a , calculated from the Bjerrum equations⁽¹¹¹⁾ for nitrobenzene at 1 atm. and 25°C, was 4.95Å. This figure was used at all temperatures and pressures; although a would change slightly with temperature and solvent dielectric constant, equation III-13 is relatively insensitive to small changes in a . The values of A , B , B_1 and B_2 were calculated from the appropriate values of the temperature and the solvent dielectric constant and viscosity (see next section for properties of nitrobenzene at high pressures), giving three equations in Λ_i , Λ_o , α , c_s , $f_{\pm}$ and K_d .

These equations were solved by the method suggested by Robinson and Stokes⁽¹³²⁾.

- (i) An approximate value of γ_o was obtained by extrapolating the experimental data on a γ versus $\sqrt{c_s}$ plot.
- (ii) For each experimental point, a value of α was assumed. This was used in equation III-13 to calculate γ_i . Since $\alpha = \gamma / \gamma_i$ the assumed value of α could be checked and the correct value approached by successive approximation.
- (iii) When α had been obtained, $f_{\pm}$ was calculated from equation III-14, and K_d from III-15. Thus a set of K_d values at the assumed value of γ_o were obtained.
- (iv) The procedure was repeated at different values of γ_o until the best set of values of K_d was obtained (set showing least scatter and drift).

This calculation will be illustrated using experimental data at 65°C and 1000 atm. Under these conditions, equations III-13, 14 and 15 become

$$\gamma_i = \gamma_o - \frac{(0.81135 \gamma_o + 49.503) \sqrt{c_s \alpha}}{1 + 2.4801 \sqrt{c_s \alpha}},$$

$$\log f_{\pm}^2 = \frac{-3.60902 \sqrt{c_s \alpha}}{1 + 2.4801 \sqrt{c_s \alpha}},$$

$$K_d = \frac{f_{\pm}^2 \alpha^2 c_s}{(1 - \alpha)}$$

conditions, and uncertainties as to the change in the dielectric constant of nitrobenzene with pressure (see below). At atmospheric pressure the dissociation constants showed considerably less drift.

5. Viscosity and Dielectric Constant of Nitrobenzene at High Pressures

The viscosity of nitrobenzene at 65°C and high pressures was obtained by interpolation in the data of Kuss⁽¹³⁴⁾, who reported viscosities of nitrobenzene to 2000 atm. at 25°C and 80°C.

The only data on the effect of pressure on the dielectric constant of nitrobenzene is that reported in the International Critical Tables, and it covers only the limited range of 1 to 56 atm. at 25°C. This data was extrapolated to 2000 atm. at 65°C, assuming the pressure coefficient to be independent of temperature (a reasonable assumption over a limited range of temperature, as shown by the data reported by Jacobs and Lawson⁽¹³⁷⁾ for other liquids). The equation which Rosen⁽¹³⁵⁾ found to correlate the data for 30 liquids to 12,000 atm. with an average deviation of less than 1%, was used for the extrapolation. This is

$$\frac{\epsilon_p + 2}{\epsilon_p - 1} = m V_o + b \quad (\text{III-16})$$

where ϵ_p is the dielectric constant, V_o the specific volume and m and b are constants for the particular liquid. The very accurate smoothed compressibilities of Gibson⁽¹³⁶⁾ were used to derive the constants m and b , the final equation being (for 65°C)

$$\frac{\epsilon_p + 2}{\epsilon_p - 1} = 0.13421 V_o + 0.99328$$

To solve this equation for high pressures, the compressibilities of Kuss⁽¹²¹⁾ were used, as they cover a greater range of pressures than those of Gibson (loc.cit.).

SECTION IV. RESULTSIV A. Forward Menschutkin Reactions1. Ethyl Iodide + Dimethylaniline in Nitrobenzene

Consolidated results for this reaction as a function of temperature and pressure at initial concentrations of 0.1 M (at 1 atm., 20°C) are given in table IV-1, and are represented graphically in figures IV-1 and IV-2. This data, originally presented in a paper by Harris and Weale⁽³⁹⁾, has been recalculated to take into account the precise effect of the reverse reaction. As well, revisions to the recorded pressures have been made, as a result of a subsequent accurate pressure calibration, and the rate has been measured at an additional pressure (800 atm.). All data has been corrected for the effects of solvent expansion or compression, and where necessary for equilibrium effects.

Table IV-1Effect of Temperature and Pressure onRate Constants

Initial Concentrations : all 0.1 M at 1 atm. and 20°C.

(amine and halide concentrations equal).

Pressure, atm.	Temperature, °C	$k \times 10^5$ l/mole sec.
1	47.5	1.61
1	52.5	2.28
1	57.5	3.20
800	52.5	4.21
1350	52.5	6.21
2080	52.5	9.58
2360	52.5	11.36

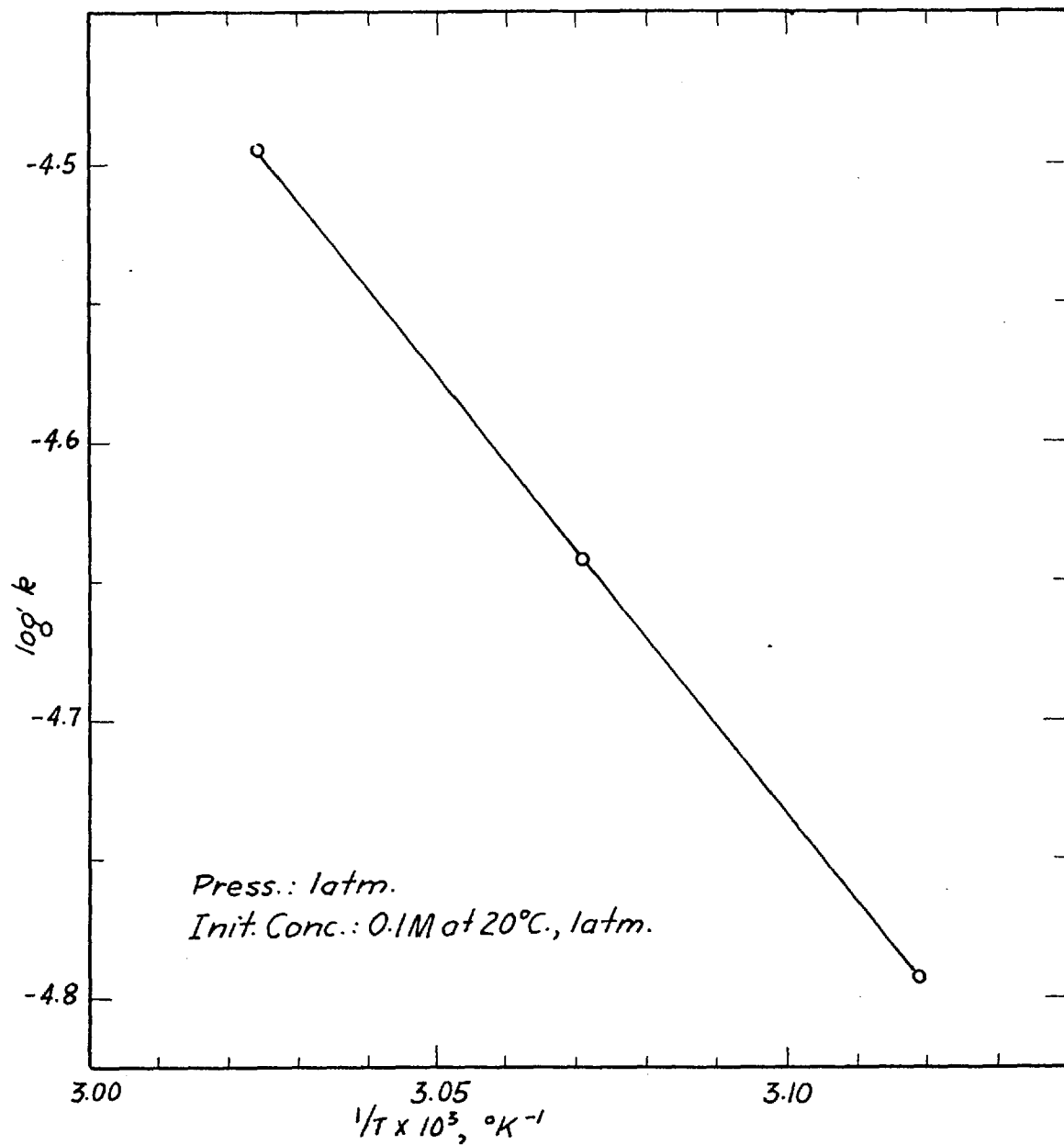


FIG. IV-1 ARRHENIUS PLOT, ETHYL IODIDE + DIMETHYLANILINE
IN NITROBENZENE

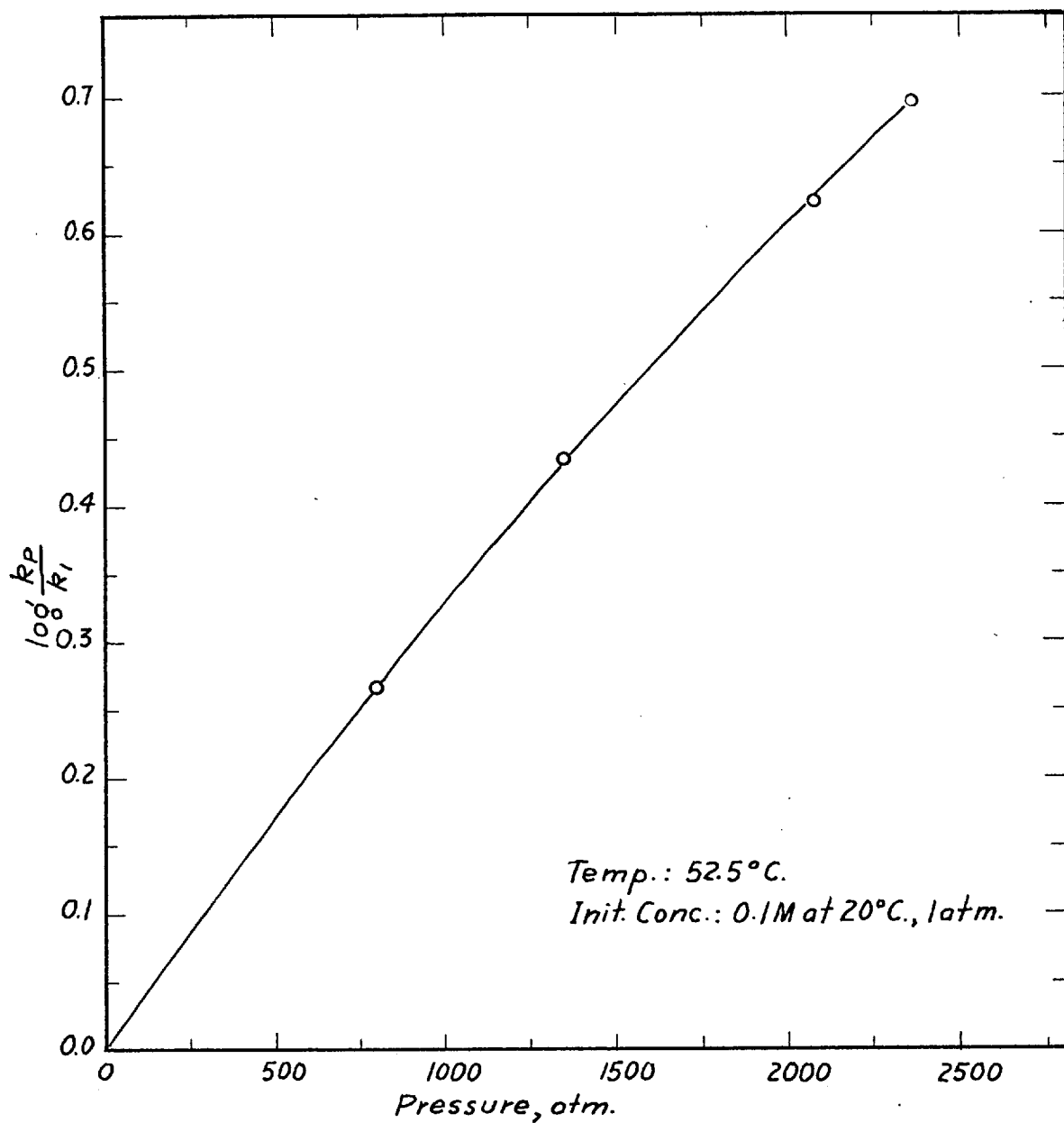


FIG. IV-2 EFFECT OF PRESSURE ON RATE CONSTANT, ETHYL IODIDE + DIMETHYLANILINE IN NITROBENZENE

2. Methyl Iodide + Ethylmethylaniline in Nitrobenzene

Rate constants for this reaction as a function of temperature and pressure at initial reactant concentrations of 0.05 M (at 1 atm. and 20°C) are given in Table IV-2 and plotted in figures IV-3 and IV-4. Rate constants at various initial reactant concentrations are given in table IV-3. All data has been corrected for the effects of solvent compression or expansion, and equilibrium effects have been taken into account where necessary.

Table IV-2Effect of Temperature and Pressure onRate Constants

Initial Concentrations : all 0.05 M at 1 atm. and 20°C

(amine and halide concentrations equal)

Pressure atm.	Temperature °C	$k \times 10^4$ l/mole sec.
1	30.0	0.612
1	40.0	1.26
1	50.0	2.43
1	60.0	4.48
500	30.0	0.935
500	40.0	1.85
500	50.0	3.48
500	60.0	6.36
1000	50.0	4.92
1500	50.0	6.50

Table IV-3Effect of Concentration on Rate Constants

Temperature : 40.0°C	
Pressure : 1 atm.	
Initial Concentration, amine and halide, moles/l	$k \times 10^4$ l/mole sec.
0.0246	1.27
0.0492	1.26
0.0984	1.31

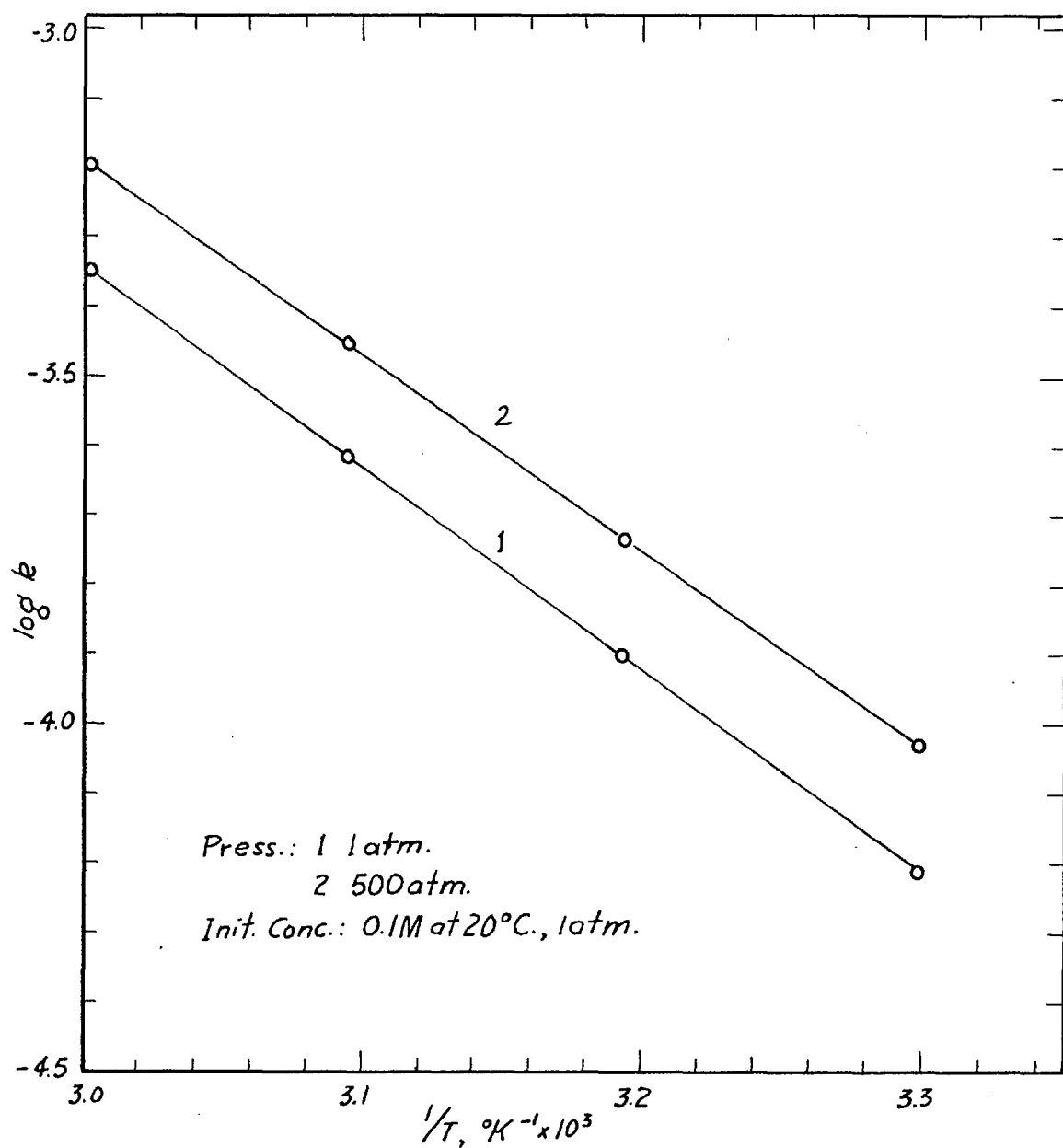


FIG. IV-3 ARRHENIUS PLOT, METHYL IODIDE + ETHYLMETHYL-ANILINE IN NITROBENZENE

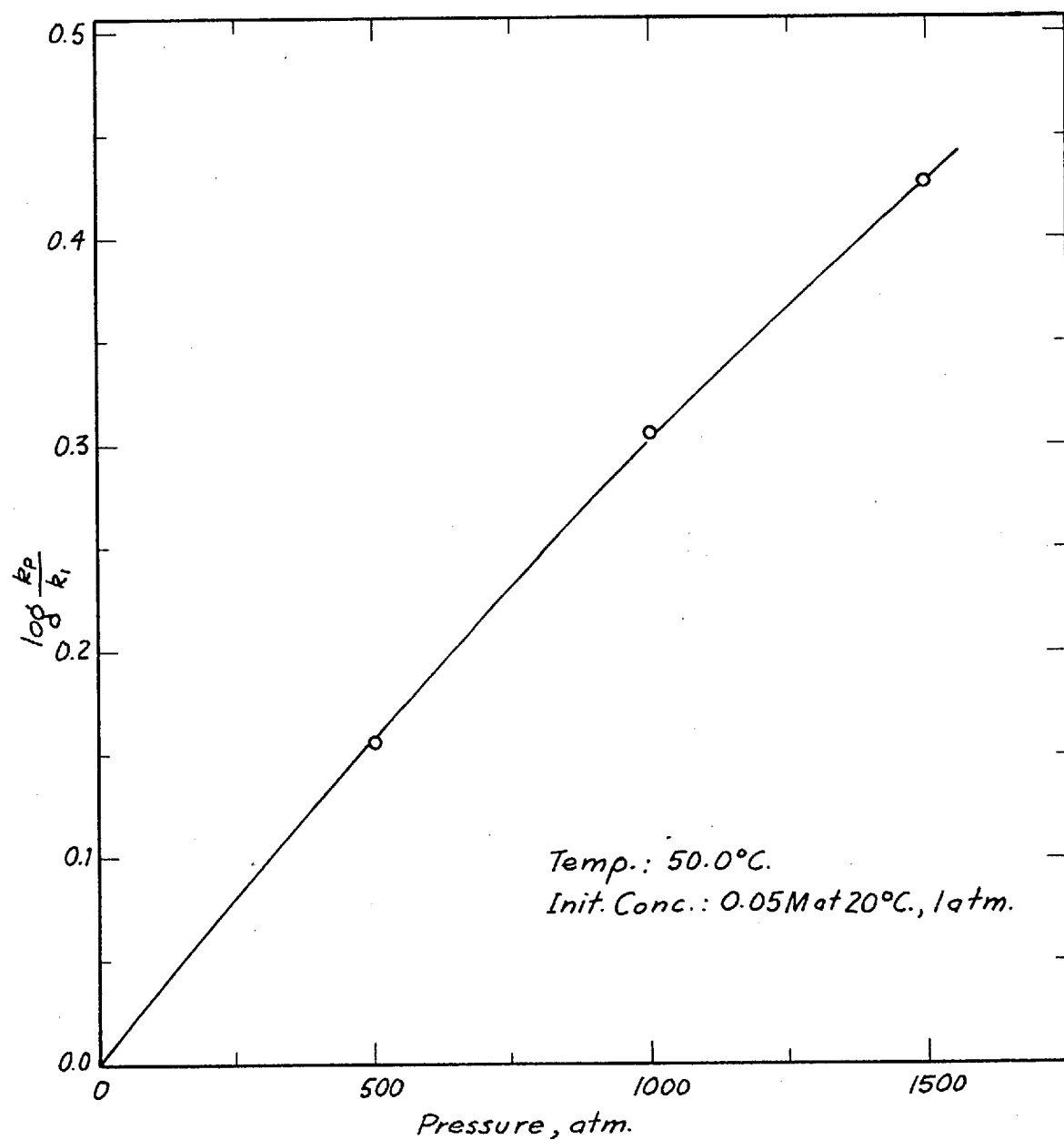


FIG. IV-4 EFFECT OF PRESSURE ON RATE CONSTANT, METHYL IODIDE + ETHYLMETHYLANILINE IN NITROBENZENE

3. Autocatalytic Effects, Forward Menschutkin Reactions

Harris⁽²⁾ has reported a change from first to second order kinetics in the reaction of ethyl iodide with dimethylaniline in nitrobenzene between 1500 and 2875 atm.

Kinetic experiments up to 3120 atm. showed that a discontinuity existed between 2360 and 2630 atm. Experiments with a piezometer proved the occurrence of solvent freezing in this region, as illustrated in table IV-4. Above the freezing point kinetic data superficially appeared to be first order (see table IV-5). This was found to be a concentration effect due to solvent freezing, superimposed on normal second order kinetics (see discussion), and could be duplicated at 1 atm. and 52.5°C by using a high initial concentration (see table IV-6).

The data above the freezing pressure has not been corrected for change in concentration due to compression and freezing, or to equilibrium effects, all of which are unknown. The data at atmospheric pressure and high initial concentrations has been corrected for solvent expansion and the volume change due to the reaction, but not for equilibrium effects.

Table IV-4.Check on Freezing Point of Reactant Solution

Temperature : 52.5°C		
Concentration : 0.1 M in each reactant at 20° 1 atm.		
	<u>2260 atm.</u>	<u>2730 atm.</u>
Measured solution compression ^{mls} /ml	0.0825	0.157
Calculated compression of nitrobenzene mls/ml (121)	0.0823	0.0966

Note : (i) The freezing pressure of pure nitrobenzene
at 52.5°C is 2120 atm⁽¹²¹⁾.

(ii) Calculated compression assumes that solvent
super-pressed above its freezing pressure.

Table IV-5Kinetic Data above the Solution Freezing Pressure

Temperature : 52.5°C				
Pressure : 2630 and 3120 atm.				
Concentration : 0.1 M in each reactant at 20°C, 1 atm.				
Pressure atm.	Time min.	x, moles/l	$k' \times 10^4$ sec. ⁻¹ (1st order)	$k' \times 10^3$ 1/mole sec. (2nd order)
2630	50.0	0.02857	1.12	1.34
"	76.5	0.03916	1.08	1.40
"	88.5	0.04525	1.13	1.56
"	102.5	0.05130	1.17	1.73
"	175.0	0.06950	1.13	2.17
3120	60	0.05011	1.93	2.79
"	91	0.07323	2.41	5.02
"	122	0.07610	1.96	4.35
"	135	0.08371	2.24	6.35
"	180	0.08700	1.89	6.20

Note : Second order rate constants were calculated using
 $a = 0.1 \text{ M}$, the actual concentration after freezing
being unknown.

Table IV-6

Autocatalysis at High Initial Concentrations

Temperature : 52.5°C					
Pressure : 1 atm.					
Time mins.	Initial concn, moles/l		x moles/l.	$k' \times 10^5$ sec. ⁻¹ (1st order)	$k' \times 10^5$ l/mole sec. (2nd order)
	halide	amine			
240	0.9740	0.9740	0.231	1.89	2.22
420	"	"	0.358	1.82	2.37
600	"	"	0.465	1.80	2.57
780	"	"	0.565	1.85	3.03
960	"	"	0.620	1.76	3.12
4000	"	"	0.885	-	-
120	0.487	0.487	0.0329	0.987	2.07
840	"	"	0.1680	0.839	2.15
1200	"	"	0.2232	0.850	2.42
1560	"	"	0.2558	-	-
2640	"	"	0.3330	-	-
240	0.974	0.487	0.119	(1.93 w.r.t. amine 0.90 w.r.t. halide)	2.08
240	0.487	0.974	0.176	(0.96 w.r.t. amine 2.07 w.r.t. halide)	2.22

IV B. Reverse Menschutkin Reactions1. Decomposition of Ethyl-dimethyl-phenyl Ammonium Iodide in Nitrobenzene

The effect of concentration on the first order rate constant is shown in table IV-7 and figure IV-5. Consolidated results for this reaction as a function of temperature and pressure are given in table IV-8 and figures IV-6 and IV-7. The decomposition product composition, as determined by vapour phase chromatography is given in table IV-9.

All data has been corrected for solvent compression or expansion using the P-V-T data of Kuss⁽¹²¹⁾. Conversions were kept below the point where a correction for the effect of the opposing reaction would have been necessary.

Table IV-7
Effect of Initial Concentration on Reaction Rate

Temperature		: 65.0		
Pressure		: 1 atm.		
a moles/l. $\times 10^3$	Conversion %	(c _s) avg. moles/l. $\times 10^3$	k' $\times 10^5$, sec ⁻¹	
			Conduct. method	Volumetric analysis
1.034	5	1.01	0.186	-
3.102	11	2.93	0.435	-
6.203	11.4	5.85	0.670	-
11.74	14.2	10.90	0.780	-
19.35	19.4	17.50	0.978	1.03
35.99	21.2	32.20	1.16	1.20
48.70	15.0	45.0	1.27	-
76.97	10.0	73.1	1.38	-

Note : (c_s)_{avg.} is the average concentration of the quaternary salt during the run.

Table IV-8

Effect of Temperature and Pressure on Rate Constants

Initial Concentrations : all approximately 0.05 M					
Press. atm.	Temp. °C	a moles/l.	Conversion %	(c _s) avg. moles/l.	k' x 10 ⁵ sec. ⁻¹
1	52.5	0.04893	10	.0465	0.255
1	58.75	0.04843	10	.0460	0.570
1	58.75				0.555
1	65.0	0.04870	16	.0450	1.27
1	71.25	0.04841	18	.0441	2.80
200	65.0	0.04911	12	.0462	0.960
500	52.5	0.05038	7	.0486	0.166
500	58.75	0.04952	7	.0478	0.357
500	65.0	0.04990	10	.0474	0.81
500	71.25	0.04958	12	.0466	1.83
1000	65.0	0.05150	8	.0494	0.667
2000	65.0	0.05225	7	.0504	0.592

Note : a is the initial concentration, (c_s)_{avg} the average concentration during the run.

Table IV-9Decomposition Products

Temperature	: 65.0°C
Pressure	: 1 atm.
Concentration	: 0.2 M
Product	Mole % in total product amine
N : N-dimethyl aniline	5.7
N-ethyl-N-Methyl aniline	<u>94.3</u>
	100.0

2. Decomposition of Allyl-benzyl-methyl-phenyl Ammonium Bromide
in Chloroform

The effect of pressure on this reaction is given in table IV-10 and figure IV-8. In figure IV-8, rate constants at pressures have been referred to the corresponding rate constants at 1 atm. (i.e. rate constants at pressure determined by volumetric analysis are referred to the rate constant found by the same method at 1 atm.)

All data has been corrected for solvent compression or expansion, using the P-V-T data for chloroform of Bridgman⁽¹³³⁾. No correction to the rate constants for equilibrium effects was necessary, as conversions were kept below the level at which the opposing reaction became significant (using the equilibrium constants of Williams, Perrin and Gibson⁽¹⁾ as a guide).

Table IV-10

Effect of Pressure in the Rate Constants for the Decomposition
of the Quaternary Salt in Chloroform

Temperature : 34.95°C Initial concentration : 0.1 M at reaction conditions			
Pressure atm.	k x 10 ³ min. ⁻¹		Ref. (1)
	Conduct. Method	Volumetric analysis	
1	1.46 } 1.43 } 1.44	1.41	1.58
500	1.21	1.16	-
1000	1.13	1.10	-
2000	1.02	-	-
2884	0.95	-	1.07

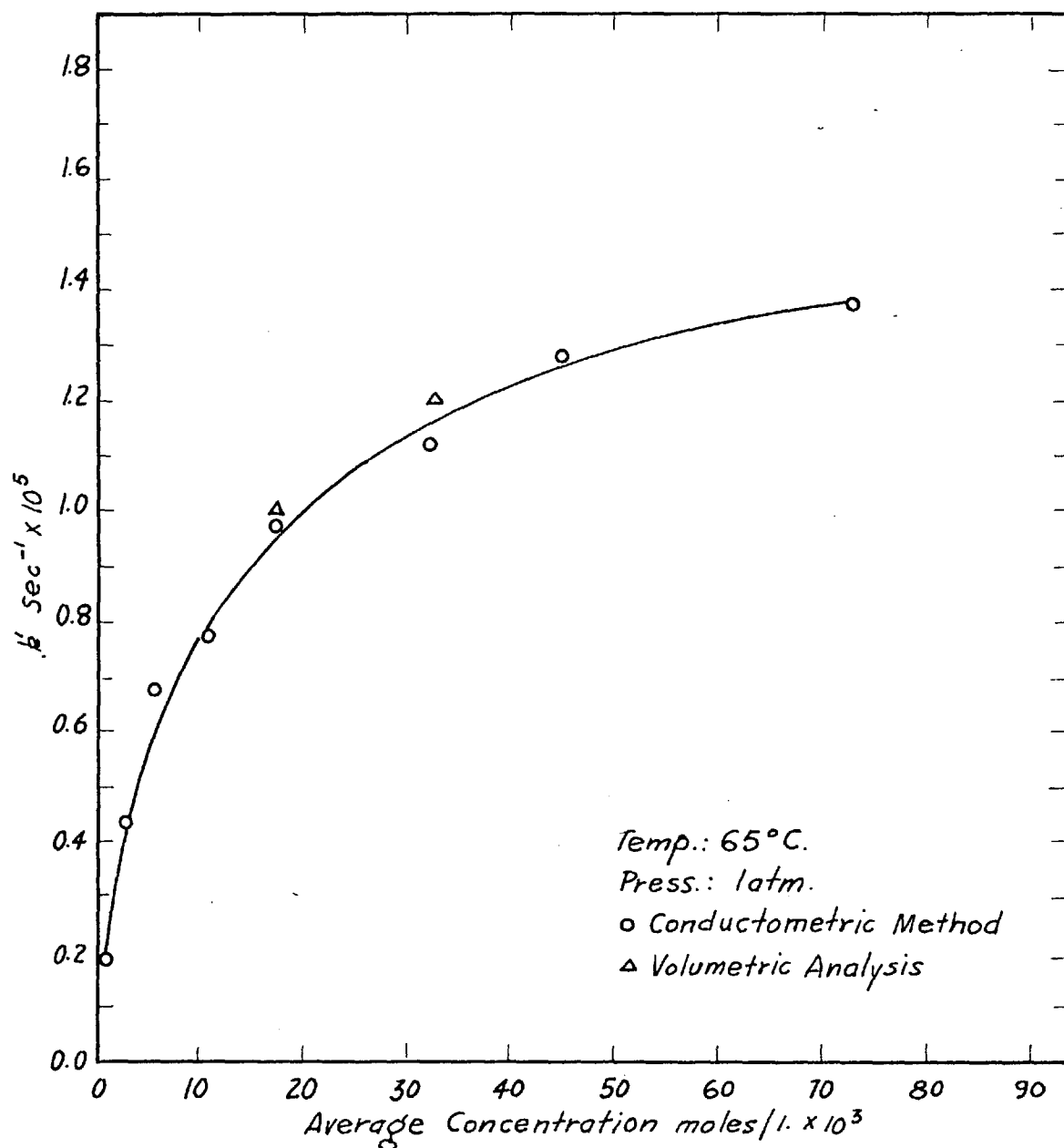


FIG. IV-5 EFFECT OF CONCENTRATION ON RATE OF DECOMPOSITION, ETHYL-DIMETHYL-PHENYL AMMONIUM IODIDE IN NITROBENZENE

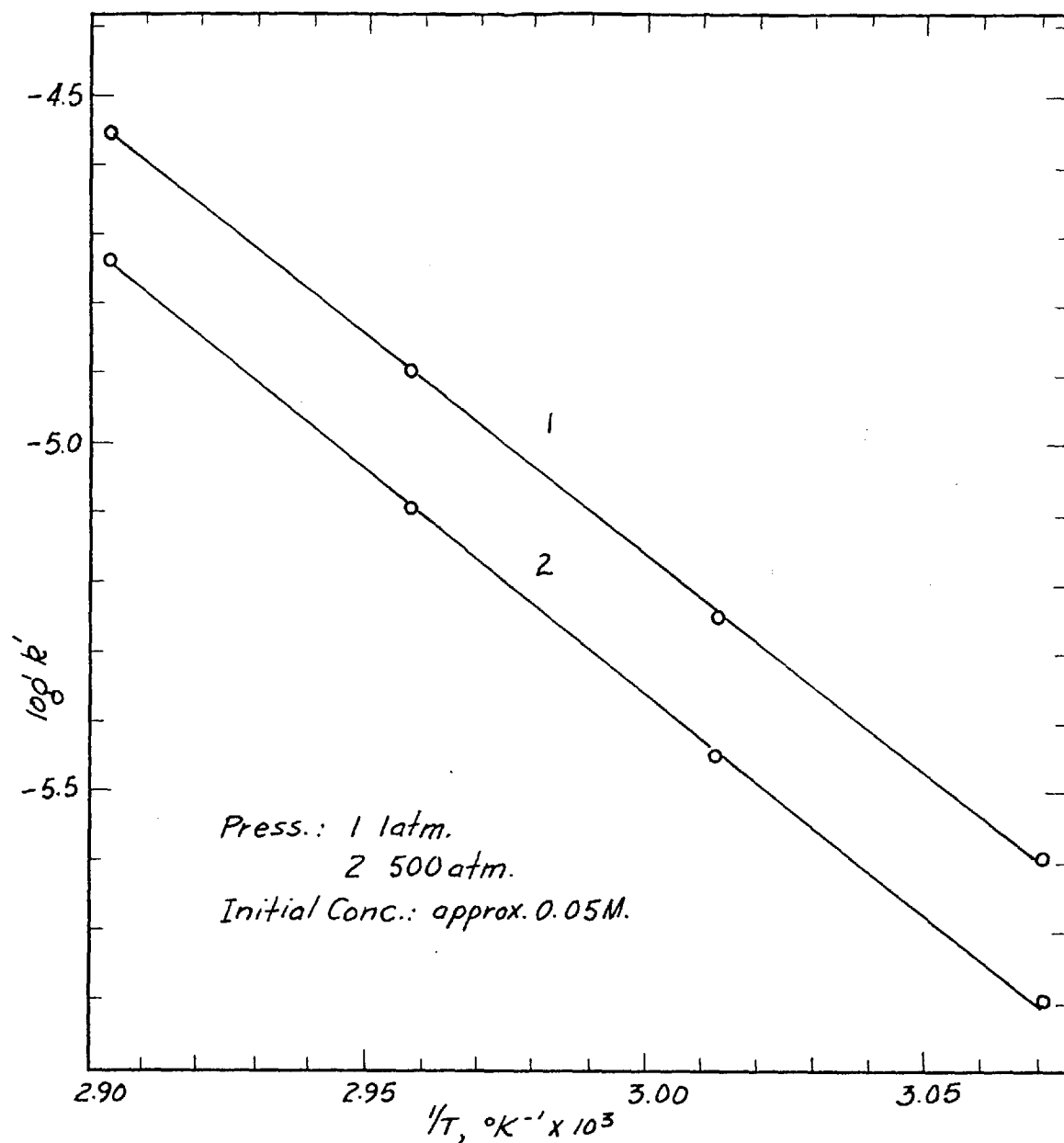


FIG. IV-6 ARRHENIUS PLOT, DECOMPOSITION OF ETHYL-DIMETHYL-PHENYL AMMONIUM IODIDE IN NITROBENZENE

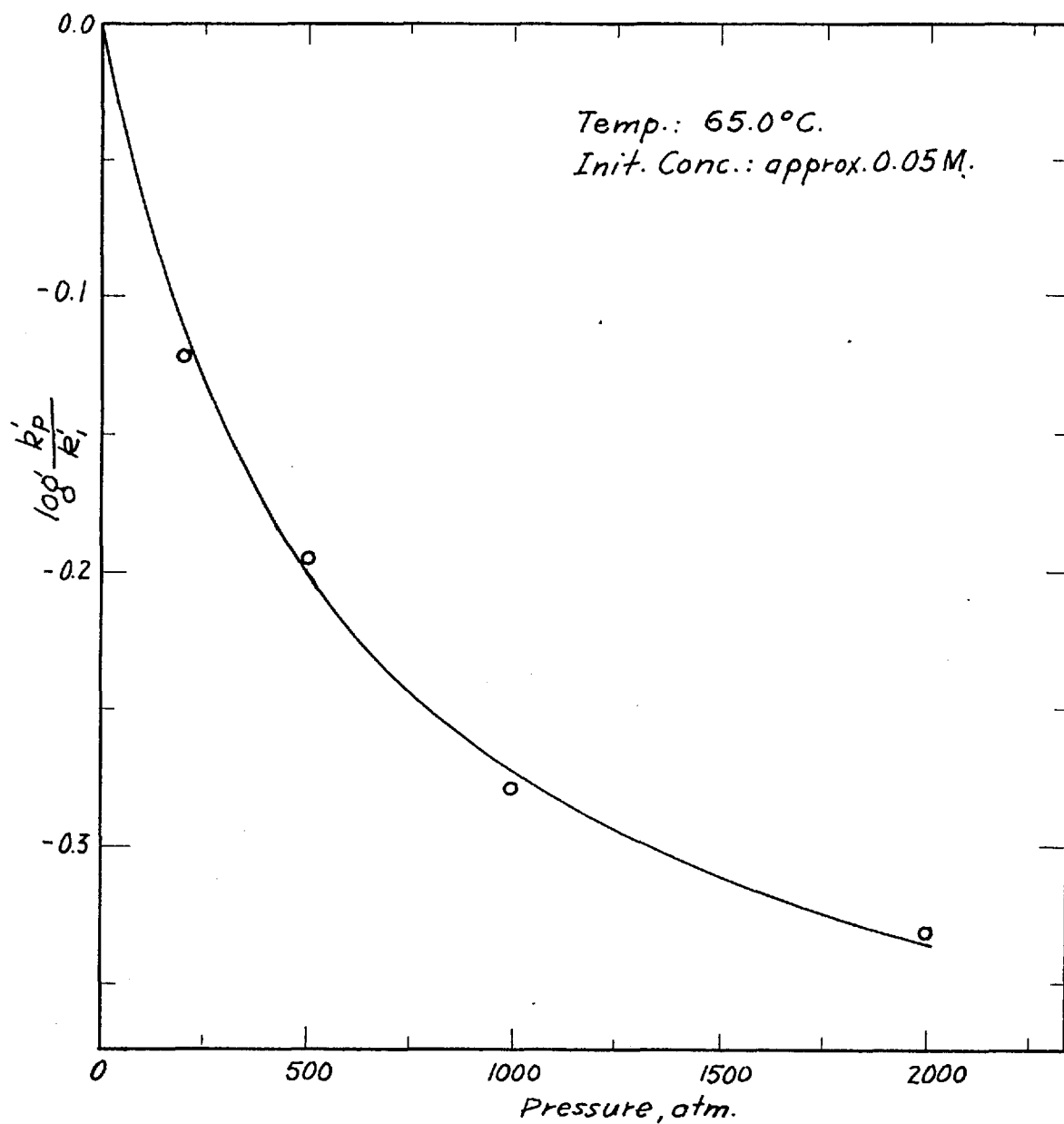


FIG. IV-7 EFFECT OF PRESSURE ON RATE CONSTANT,
DECOMPOSITION OF ETHYL-DIMETHYL-PHENYL
AMMONIUM IODIDE IN NITROBENZENE

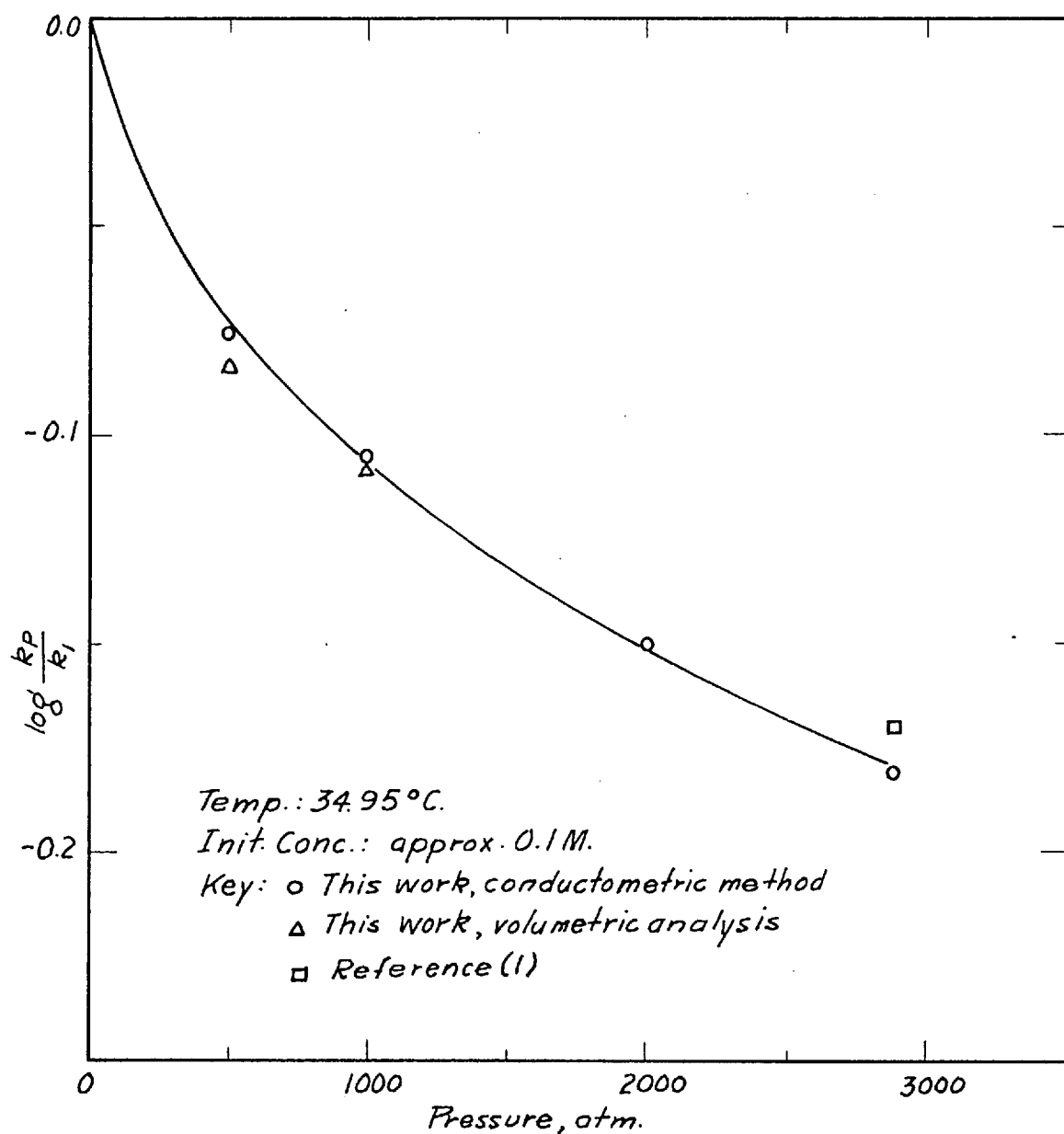
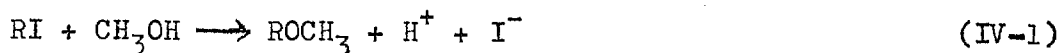


FIG. IV-8 EFFECT OF PRESSURE ON RATE CONSTANT,
 DECOMPOSITION OF ALLYL-BENZYL-METHYL-PHENYL
 AMMONIUM BROMIDE IN CHLOROFORM

3. Other Reverse Menschutkin Reactions

As well as the two studied in detail, several other reverse reactions were examined and abandoned as unsuitable for study. These were all reactions for which the corresponding forward reaction had been studied in detail by other workers.

The decompositions of phenyl-trimethyl ammonium iodide, ethyl-tri-n-propyl ammonium iodide and N-ethyl quinolinium iodide were examined in methanol as solvent at 50 - 60°C and atmospheric pressure. (Harris⁽²⁾ has measured the corresponding forward reaction rate as a function of pressure for these reactions). In all of these reactions the conductivity increased rather than decreased with time, almost certainly because of solvolysis of the product halide by the methanol solvent⁽²⁶⁾, i.e.



N-ethyl pyridinium iodide (forward reactions studied at high pressures by Gonikberg⁽⁶²⁾⁽⁶³⁾⁽⁶⁶⁾⁽¹¹⁰⁾ would not decompose in acetone (at 55°C) or nitrobenzene (at 100°C).

N, N, N-trimethyl o-toluidinium iodide (forward reaction studied at high pressures by Weale⁽³⁷⁾) was only very slightly soluble in acetone (less than 0.005 M) and was therefore not easily studied. Approximate rate constants for three concentrations are given in table IV-11.

Table IV-11

Decomposition of N : N : N - trimethyl o-Toluidinium
Iodide in Acetone

Temperature : 55.0°C	
Pressure : 1 atm.	
a moles/l. x 10 ⁴	k' x 10 ⁵ sec. ⁻¹
1.4	0.24
3.9	0.38
34.0	1.5

IV.C. Overall Volumes of Reaction

The overall volume of reaction for the reaction of methyl iodide with ethylmethyl aniline to give ethyl-dimethyl-phenyl ammonium iodide, determined as outlined in section III C., is given in table IV-12. ΔV_r for this reaction was reported to be -55.8 in a preliminary report on this research, but later an error was found in the calculation.

ΔV_r for the decomposition of allyl-benzyl-methyl-phenyl ammonium bromide in chloroform is given in table IV-13.

Table IV-12Overall Volume of Reaction, Methyl Iodide + Ethylmethyl-
aniline in Nitrobenzene

Temperature	: 25°C.
Pressure	: 1 atm.
Concentration	: 0.02843 M.
Volume of Reaction	: - 62.8 cc/mole.

Table IV-13Overall Volume of Reaction, Allyl-benzyl-methyl-phenyl
Ammonium Bromide in Chloroform

Temperature	: 34.95°C.
Pressure	: 1 atm.
Initial concentration	0.0992 M
Conversion	: $\approx$ 40%
Volume of Reaction	: - 36.1 cc/mole

IV.D. Electrolytic Dissociation of Quaternary Salts

The dissociation constants of ethyl-dimethyl-phenyl ammonium iodide in nitrobenzene as a function of temperature and pressure are given in table IV-14 and figure IV-9.

Dissociation constants for allyl-benzyl-methyl-phenyl ammonium bromide in chloroform were not measured. However, one set of conductance-concentration data, illustrating the dissociation behaviour was obtained. This data is listed in table IV-15.

Table IV-14

Dissociation Constants, Ethyl-dimethyl phenyl Ammonium
Iodide in Nitrobenzene

Concentration range : 0.0001 to 0.0250 M		
Temp. °C	Pressure atm,	$K_d \times 10^2$ moles/l
25	1	1.28
65	1	1.02
65	500	1.51
65	1000	1.91
65	2000	2.43

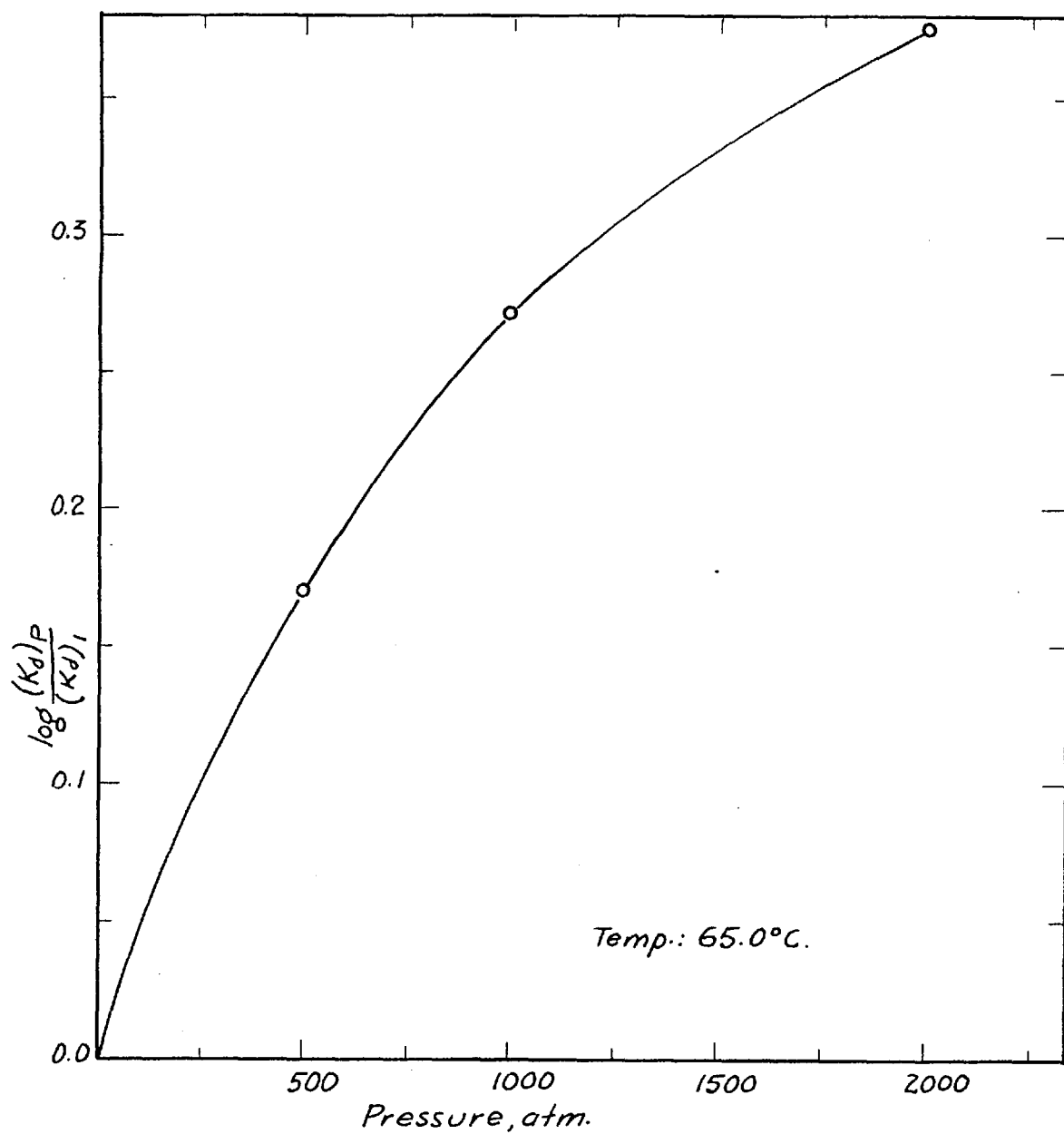


FIG. IV-9 EFFECT OF PRESSURE ON DISSOCIATION CONSTANT, ETHYL-DIMETHYL-PHENYL AMMONIUM IODIDE IN NITROBENZENE

Table IV-15

Conductance Data, Allyl-benzyl-methyl-phenyl
Ammonium Bromide in Chloroform

Temperature	: 34.95°C
Pressure	: 1 atm.
Cell	: A - 2
Concentration moles/l. x 10 ³	Specific Conductance mhos/cm x 10 ⁶
98.07	8.596
68.87	4.624
34.44	1.744
4.989	0.2622
2.495	0.1504
0.9978	0.07848

SECTION V. DISCUSSION OF RESULTS

V.A. Mechanism of Forward Menschutkin Reactions - Autocatalysis

Forward Menschutkin reactions usually proceed through the S_N2 mechanism and are kinetically of the second order. Harris⁽²⁾ however reported that in the reaction of ethyl iodide with dimethyl aniline in nitrobenzene at 52.5°C the order changed from first to second between 1500 and 2875 atm. He suggested that a change in mechanism occurred from S_N2 to S_N1 with the ionization of the iodide becoming the rate-controlling step at high pressures.

This reaction was repeated under conditions identical to those used by Harris, at pressures of 1, 800, 11350, 2080, 2360, 2630 and 3120 atm. A discontinuity in the rate occurred between 2360 and 3120 atm. as shown by fig.V-1. Harris's second order constants (at 1 and 1500 atm.) are too high by a factor of 10. If they are multiplied by 10^{-1} they are in satisfactory agreement with the present work, considering that Harris did not take solvent compression, thermal expansion or equilibrium effects into account. (Harris's value of k at 1 atm. and 52.5°C was 2.01×10^{-4} l./mole sec.; in this work k was found to be 2.28×10^{-5} l./mole sec.).

The discontinuity in the rate proved to be associated with freezing of the reactant solution. Measurements of the compression of the reactant solution showed that freezing occurred between 2260 and 2730 atm. (see table IV-4). This is somewhat above the freezing pressure of pure nitrobenzene (2120 atm. at 52.5°C ⁽¹²¹⁾).

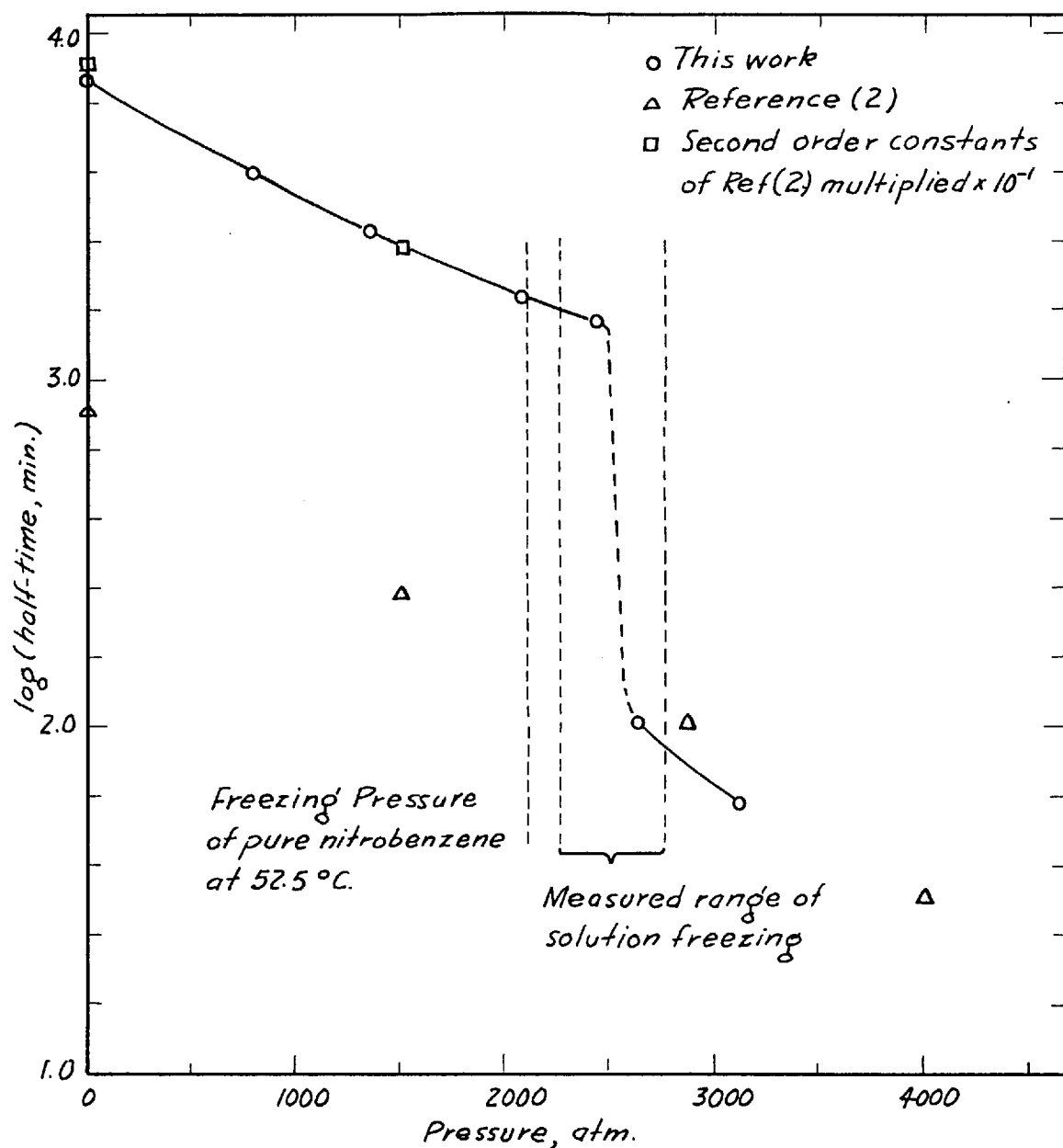


FIG. V-1 EFFECT OF PRESSURE ON RATE, ETHYL IODIDE + DIMETHYLANILINE IN NITROBENZENE AT 52.5°C.

due to superpressing and/or depression of the freezing point by the amine and halide solutes.

Above the solution freezing point the kinetic data for a given series of runs with equal initial amine and halide concentrations appeared ~~superficially~~ to be better fitted by a first than by a second order relationship. This can be seen from the data in table IV-5, although the results are understandably erratic.

It seemed evident that the behaviour of the reaction above the solution freezing point was a concentration effect, due to the large increases in the reactant concentration (and hence the product salt concentration). Kinetic experiments were then carried out at atmospheric pressure using high reactant concentrations (0.5 and 1.0 M - 10 times the earlier concentrations and therefore at 100 times the rate) to see if the behaviour observed above the freezing point could be duplicated. Identical behaviour was indeed observed as can be seen from the data in table IV-6. Some of this data is illustrated on first and on second order plots in fig.V-2 and fig.V-3. It can be seen that the first order relationship is the better fit. First order behaviour was however immediately lost when rate constants were measured at other initial concentrations, as can be seen from the data in table V-1.

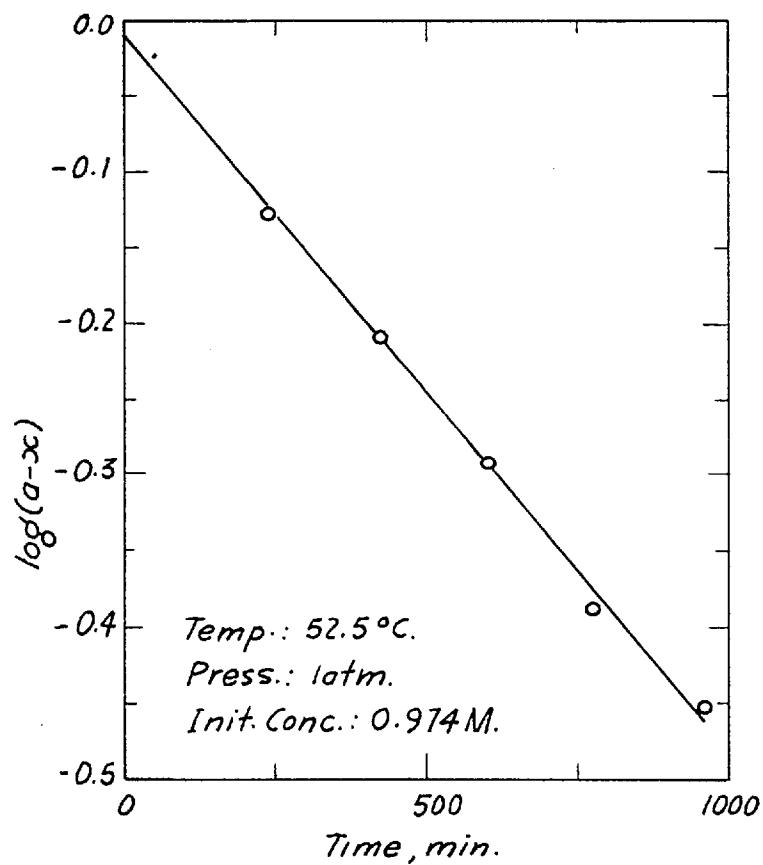


FIG. V-2 FIRST ORDER PLOT FOR
KINETIC DATA AT HIGH
INITIAL CONCENTRATIONS

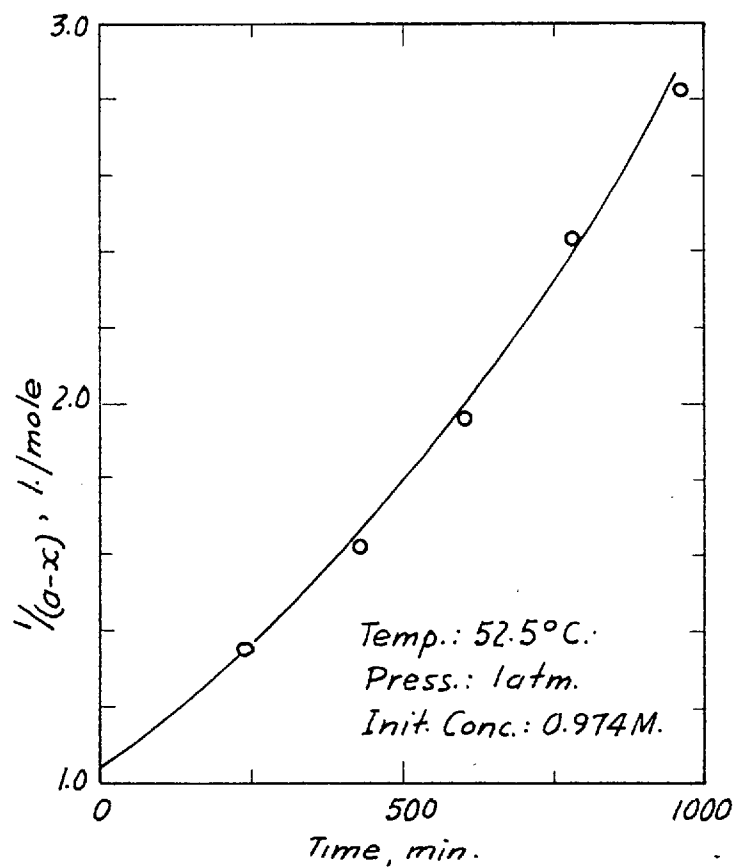


FIG. V-3 SECOND ORDER PLOT FOR
KINETIC DATA AT HIGH
INITIAL CONCENTRATIONS

Table V-1

Effect of Initial Concentration on Rate ConstantsDimethylaniline + Ethyl Iodide in Nitrobenzene

Temperature		: 52.5°C	
Pressure		: 1 atm.	
a moles/l.		$k' \times 10^5$ sec. ⁻¹	$k' \times 10^5$ l./mole sec.
amine	iodide	(first order)	(second order)
0.974	0.974	appr. 1.84 (fairly constant)	2.22 - 3.12 (increases)
0.487	0.487	appr. 0.87 (decreases)	2.07 - 2.43 (increases)
0.0974	0.0974	appr. 0.20 (decreases)	2.28 (constant)
0.487	0.974	(1.93 w.r.t. amine) (0.90 w.r.t. iodide)	2.08
0.974	0.487	(0.96 w.r.t. amine) (2.07 w.r.t. iodide)	2.22

It can be seen that the reaction is indeed second order, with some lesser superimposed concentration effects at high product salt concentration (high initial reactant concentrations and high conversions). The apparently good fit to first order behaviour in a set of runs at one concentration is mainly coincidental, and is assisted by the smoothing characteristics of the logarithmic first order equation.

The secondary concentration effects are no doubt due to autocatalysis by the product quaternary salt, a phenomenon which has been observed in forward Menschutkin reactions by several

workers⁽³⁹⁾⁽¹⁰⁵⁾⁽¹⁰⁷⁾⁽¹³⁸⁾. For equal initial amine and halide concentrations, autocatalysis can be represented by the kinetic equation

$$\frac{dx}{dt} = [k + f(x)] (a-x)^2 \quad (V-1)$$

where a and x have the normal meanings, k is the true second order rate constant, and $f(x)$ represents the increase in rate due to autocatalysis by the salt solution. If a linear relationship is assumed between k_{obs} and x ,

$$\frac{dx}{dt} = (k + px) (a-x)^2 \quad (V-2)$$

where p is a constant.

This can be integrated to

$$r \left[\frac{2.303}{(a+r)^2} \log \frac{a(r+x)}{r(a-x)} + \frac{x}{a(a+r)(a-x)} \right] = kt \quad (V-3)$$

where $r = k/p$.

The kinetic data for this reaction (with the exception of the data for unequal initial concentrations of amine and halide, which requires a different equation) recalculated using this equation is shown in table V-2 and figure V-4. The best fit was obtained at $r = 1.4$. The straight line in fig.V-4 is for $k = 2.28 \times 10^{-5}$ l./mole sec., the value found for experiments at low concentrations, where autocatalysis is negligible.

Table V-2

Rate Constants for Dimethylaniline + Ethyl Iodide in Nitrobenzene, calculated with allowance for autocatalysis

Temperature : 52.5°C Pressure : 1 atm.					
a moles/l.		t, min.	x, moles/l.	k' x 10 ⁵ l./mole sec.	k x 10 ⁵ l./mole sec.
amine	iodide				
0.974	0.974	240	0.2310	2.22	2.04
"	"	420	0.3580	2.37	2.07
"	"	600	0.4650	2.57	2.18
"	"	780	0.5650	3.03	2.43
"	"	960	0.6200	3.12	2.44
0.487	0.487	120	0.0329	2.07	2.04
"	"	840	0.1680	2.15	2.01
"	"	1200	0.2232	2.42	2.21
"	"	1560	0.2558	2.43	2.18
0.0974	0.0974	k independent of concentration at 2.28 x 10 ⁻⁵ l./mole sec.			

Note : (i) k' is the rate constant calculated from the usual second order equation. k is the rate constant calculated from equation V-3 with r = 1.4.

(ii) At a = 0.0974 M., x was always too low for any appreciable autocatalytic effect.

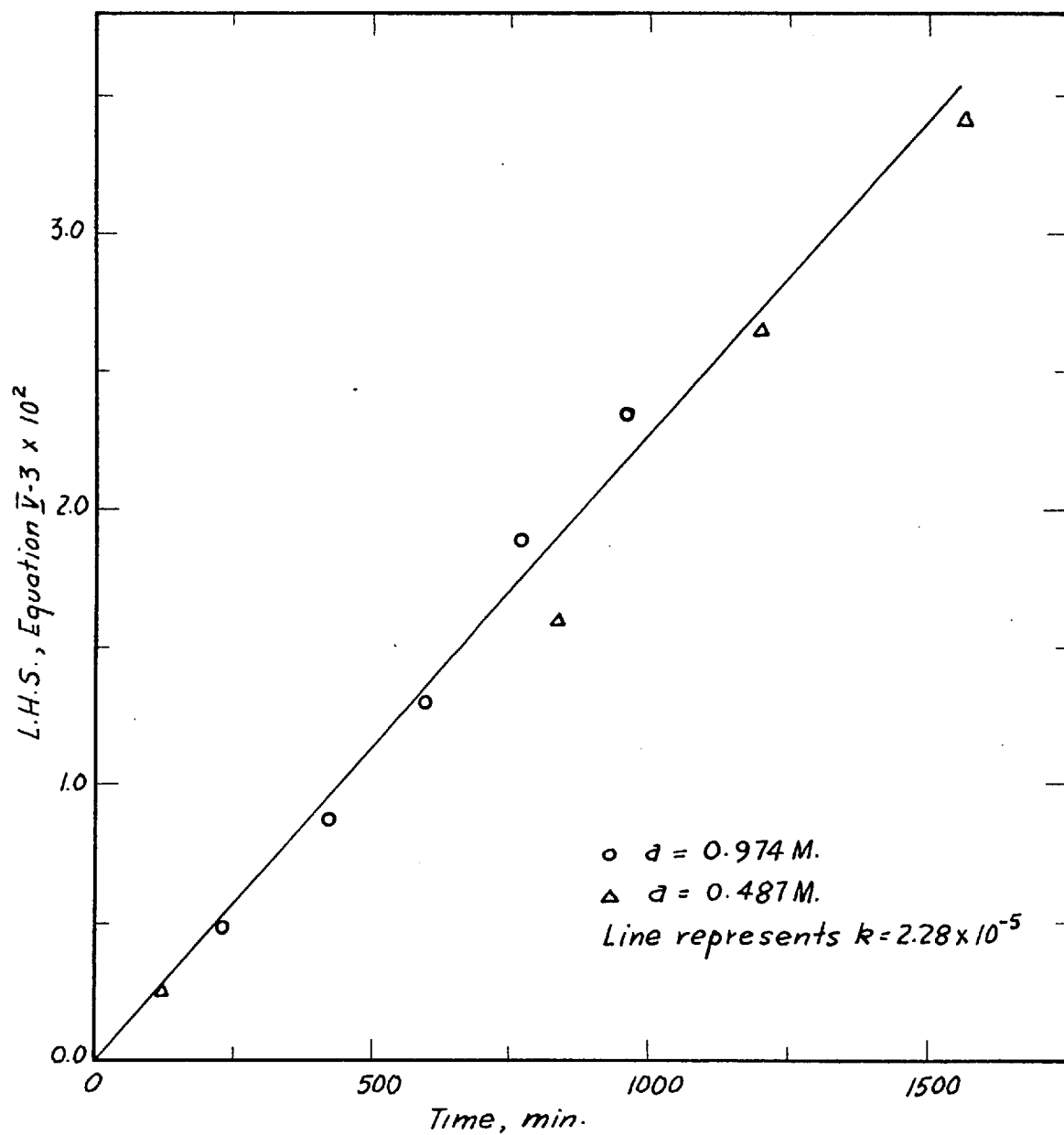


FIG. I-4 KINETIC DATA AT HIGH INITIAL CONCENTRATIONS
FITTED BY AUTOCATALYTIC EQUATION

The rate constants calculated by V-3 still increase with conversion, although the fit is much better than with the normal second order equation (the range of k is 2.01 to 2.44×10^{-5} and 2.07 to 3.12×10^{-5} respectively). This is understandable in view of the assumption of linearity between the apparent rate constant and x (equation V-2).

Frost and Pearson⁽⁷⁴⁾ have discussed this type of autocatalysis. They recognized that it is due to stabilization of the strongly dipolar transition state by the ionic atmosphere and calculated that the logarithm of the rate constant should be a linear function of the ionic strength. This would predict a relationship such as is shown in equation V-4.

$$\frac{dx}{dt} = (ke^{p\mu}) (a - x)^2 \quad (V-4)$$

where μ is the ionic strength and p a constant. Equation V-4 would be difficult to apply to this reaction, since because of ion-association the ionic strength is a complicated function of the salt concentration. However, equation V-4 would undoubtedly represent the data better than V-3, since there is an accelerating rate of increase of k' with x .

The following conclusions can be drawn from the study of this reaction :

- (i) No order change occurs with increasing pressure for this reaction in nitrobenzene. There is no evidence

that forward Menschutkin reactions in normal solvents occur through any mechanism other than S_N2 (except in liquid SO_2).

- (ii) The apparent order change observed by Harris⁽²⁾ is associated with freezing of the solution (between 2260 and 2730 atm. at $52.5^\circ C$) with a large increase in the concentration of the reactants and the product.
- (iii) The apparent first order behaviour within a given run is an autocatalytic effect. It is due to the ionic product stabilizing the dipolar transition state, resulting in an increase in the second order rate constant with conversion.

V.B. Mechanism of Reverse Menschutkin Reactions

1. General Discussion

As reported in section I.D, reverse Menschutkin reactions have long been assumed to be first order, although the mechanism has not been fully understood. Rate constants calculated as first order have been reported both to increase considerably with a decrease in initial salt concentration (in chloroform solution) and to decrease with decreasing salt concentration (in nitrobenzene).

Significant light can be shed on the problem of mechanism by consideration of the "principle of microscopic reversibility". This principle has been expressed as follows by Tolman⁽¹³⁹⁾ :

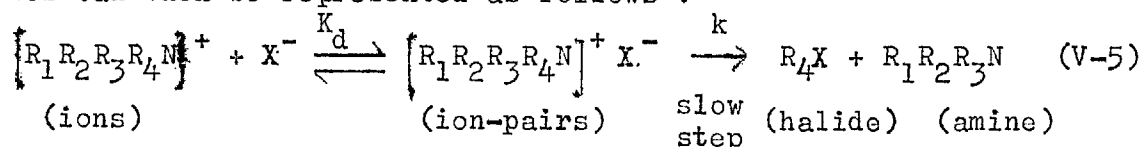
"under equilibrium conditions any molecular process and the reverse of that process will be taking place on the average at the same rate". Denbigh⁽¹⁴⁰⁾ in referring to this principle states : "This means that equilibrium is never maintained by a cyclic process at the molecular level". As a result of this principle the halide ion must be present in the transition state of the reverse reaction since it participates in the forward reaction (i.e. the reverse reaction must be S_N2 and must occur through the same transition state as the forward reaction). This has been qualitatively recognized by Hughes, Ingold and Pocker⁽¹⁹⁰⁾ for a similar reaction, the decomposition of trimethyl sulphonium salts in ethanol.

The fact that the reaction mechanism is bimolecular does not necessarily imply that second order kinetics should be found, and in fact reverse Menschutkin reactions usually approximate first order behaviour. This could be due to the reacting ions being already associated into ion-pairs, as has been suggested by Hamann⁽⁷⁾ in discussing the results of Perrin et al.⁽¹⁾ and by Ingold et al.⁽⁹⁰⁾ for the behaviour of trialkyl sulphonium salts in ethanol, but no quantitative evidence has yet been presented to prove these suggestions.

2. Ionizing Solvents

In ionizing solvents such as nitrobenzene the quaternary salt will exist partially as associated ion-pairs and partially as dissociated halide and ammonium ions. If the solvent ionizing power is great enough for complete dissociation, the reaction should

be kinetically of the second order. In solvents such as nitrobenzene a significant portion of the salt exists as associated ion-pairs which are in effect "permanently collided" kinetic entities. The kinetics can then be represented as follows :



The rate equation for this mechanism is :

$$\frac{d c_s}{dt} = - \frac{d c_{i.p.}}{dt} = k c_{i.p.} \quad (V-6)$$

where c_s is the total salt concentration, $c_{i.p.}$ is the concentration of associated ion-pairs and k is the time rate constant. Since

$$c_{i.p.} = (1 - \alpha) c_s \quad (V-7)$$

equation V-6 becomes

$$- \frac{d c_s}{dt} = k (1 - \alpha) c_s \quad (V-8)$$

$$\text{also } \log f_{\pm}^2 = - \frac{A \sqrt{\alpha c_s}}{1 + B a \sqrt{\alpha c_s}} \quad (III-14)$$

$$\text{and } K_d = \frac{\alpha^2 c_s f_{\pm}^2}{(1 - \alpha)} \quad (III-15)$$

Combining V-8, III-14 and III-15 by eliminating $f_{\pm}^2$ and α and integrating to give an equation linking the known quantities c_s , t and K_d to the unknown k would provide an elegant solution to the problem. However this would seem mathematically impractical.

It was explained in section III.B that the kinetic data for the decomposition of ethyl-dimethyl phenyl ammonium iodide in nitrobenzene were reported as apparent first order rate constants, or

$$k' = \left(\frac{-\frac{d c_s}{dt}}{(c_s)_{\text{avg}}} \right)_{\text{avg}}. \quad (\text{V-9})$$

$(c_s)_{\text{avg}}$ is used for consistency, since the average rate (over 5-20% conversion) was used to calculate k' . The conversion was kept low enough that little error would arise if the order was actually somewhat different from first order. Combining equations V-8 and V-9, equation V-10 is obtained

$$k = \frac{k'}{(1-\alpha)_{\text{avg}}}. \quad (\text{V-10})$$

True rate constants were calculated from the apparent rate constants using equation V-10, $(1-\alpha)_{\text{avg}}$ being calculated from the measured dissociation constant and the average salt concentration using equations III-14 and III-15 (for temperatures where K_d was not measured its value was obtained by interpolation in the data assuming a normal straight line plot of $\log K_d$ versus $1/T$). The results of these calculations for runs at 65°C and 1 atm. and a range of concentrations are given in table V-3 and are plotted in fig.V-5 and fig.V-6.

Table V-3

True Rate Constants, Decomposition of Ethyl dimethyl-
phenyl Ammonium Iodide in Nitrobenzene

Temperature : 65.0°C				
Pressure : 1 atm.				
$(c_s)_{\text{avg.}}$ moles/l. $\times 10^3$	$(1 - \alpha)_{\text{avg.}}$	$k'_1 \times 10^5$ sec. $^{-1}$ (1st Order)	k' l./mole sec. $\times 10^{-3}$ (2nd Order)	$k_1 \times 10^5$ sec. $^{-1}$ (1st Order)
1.01	0.0675	0.186	1.83	2.76
2.93	0.1427	0.435	1.46	3.05
5.85	0.2144	0.670	1.15	3.12
10.9	0.285	0.780	0.728	2.56
17.5	0.345	0.978	0.561	2.84
32.2	0.430	1.16	0.367	2.70
45.0	0.470	1.27	0.308	2.70
73.1	0.525	1.38	0.201	2.63

Note : Refer to table IV-7 for initial concentrations and conversions.

It can be seen that neither first nor second order relationships based on the overall salt concentration satisfactorily correlates the data; the former increases by a factor of 7 and the latter decreases by a factor of 11 with a 70 times concentration increase. However, rate constants calculated on the assumption that the rate

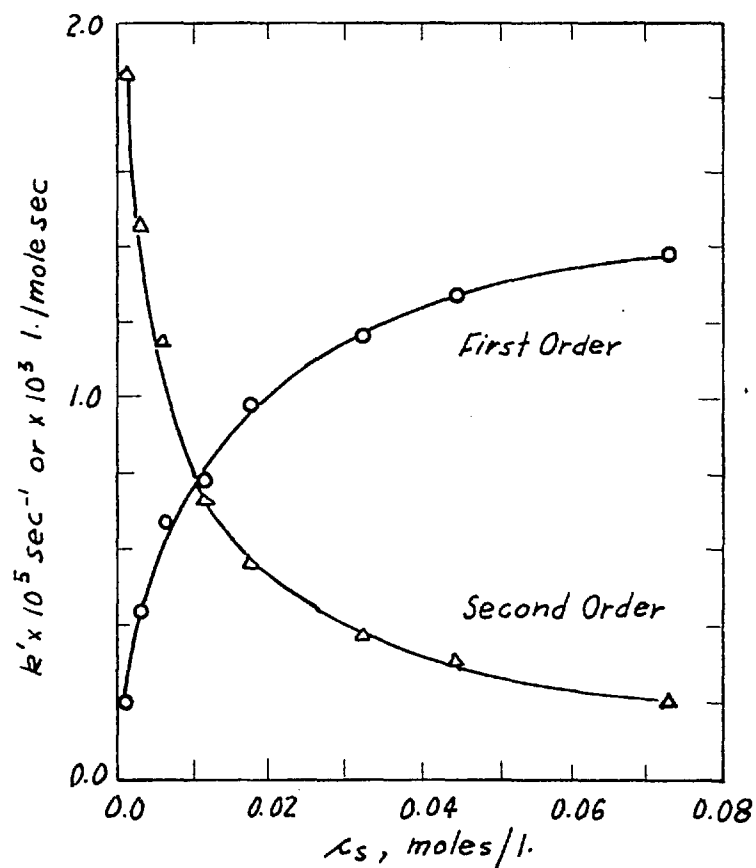


FIG. V-5 APPARENT RATE CONSTANTS
VERSUS AVERAGE SALT
CONCENTRATION

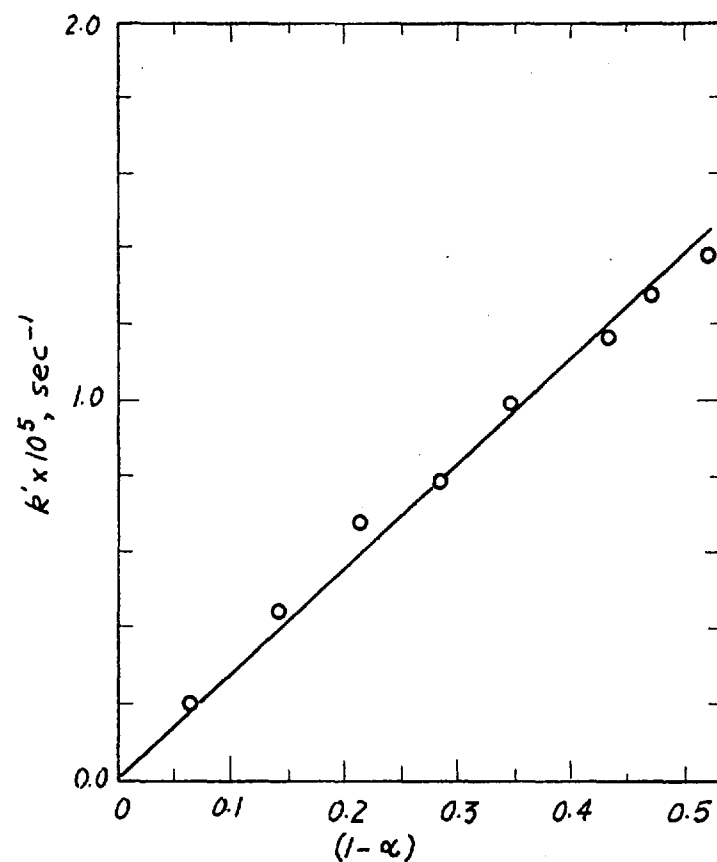


FIG. V-6 APPARENT FIRST ORDER
CONSTANTS VS. ION-PAIR
FRACTION

is first order with respect to the concentration of ion-pairs show no consistent drift over the same concentration range. The average deviation (5%) is reasonable, considering the approximations involved in the method and the fact that the constant is the product of two experimental measurements (K_d and k'). This is a powerful argument in favour of the proposed mechanism (equation V-5). The large positive activation volume of this reaction (+ 32.5 cc/mole, see section V.C). is also consistent with this mechanism; considerable desolvation with resulting expansion must occur when the fully developed charges on the ion-pairs are partially cancelled on formation of the transition state.

It was therefore assumed that the reaction is first order with respect to the concentration of ion-pairs, and all the rate constants were recalculated using equation V-10. These are given in table V-4. The effect of pressure on the apparent and true rate constants is shown in fig.V-7. (This will be discussed in a later section).

Table V-4

Recalculated Rate Constants, Decomposition of Ethyl-
dimethyl-phenyl Ammonium Iodide in Nitrobenzene

Initial Concentration : all approx. 0.05 M (actual corrected conc. given in Table IV-8					
Press., atm.	Temp. °C.	(c_s) avg. moles/l.	($1 - \alpha$) avg.	$k' \times 10^5$ sec. ⁻¹	$k = \frac{k'}{(1-\alpha)_{\text{avg}}} \times 10^5$
1	52.50	0.04648	0.4650	0.255	0.548
1	58.75	0.04601	0.4680	0.563	1.20
1	65.00	0.04500	0.4665	1.27	2.72
1	71.25	0.04405	0.4668	2.80	6.00
200	65.00	0.04616	0.4350	0.960	2.21
500	52.50	0.04862	0.4041	0.166	0.411
500	58.75	0.04779	0.4030	0.357	0.886
500	65.00	0.04741	0.4040	0.810	2.01
500	71.25	0.04661	0.4050	1.83	4.52
1000	65.00	0.04244	0.3705	0.667	1.80
2000	65.00	0.05042	0.3375	0.592	1.75

Note : (i) At pressures where K_d was not measured, it was obtained

assuming $\frac{(K_d)_p}{(K_d)_1}$ to be independent of temperature.

$(K_d)_1$

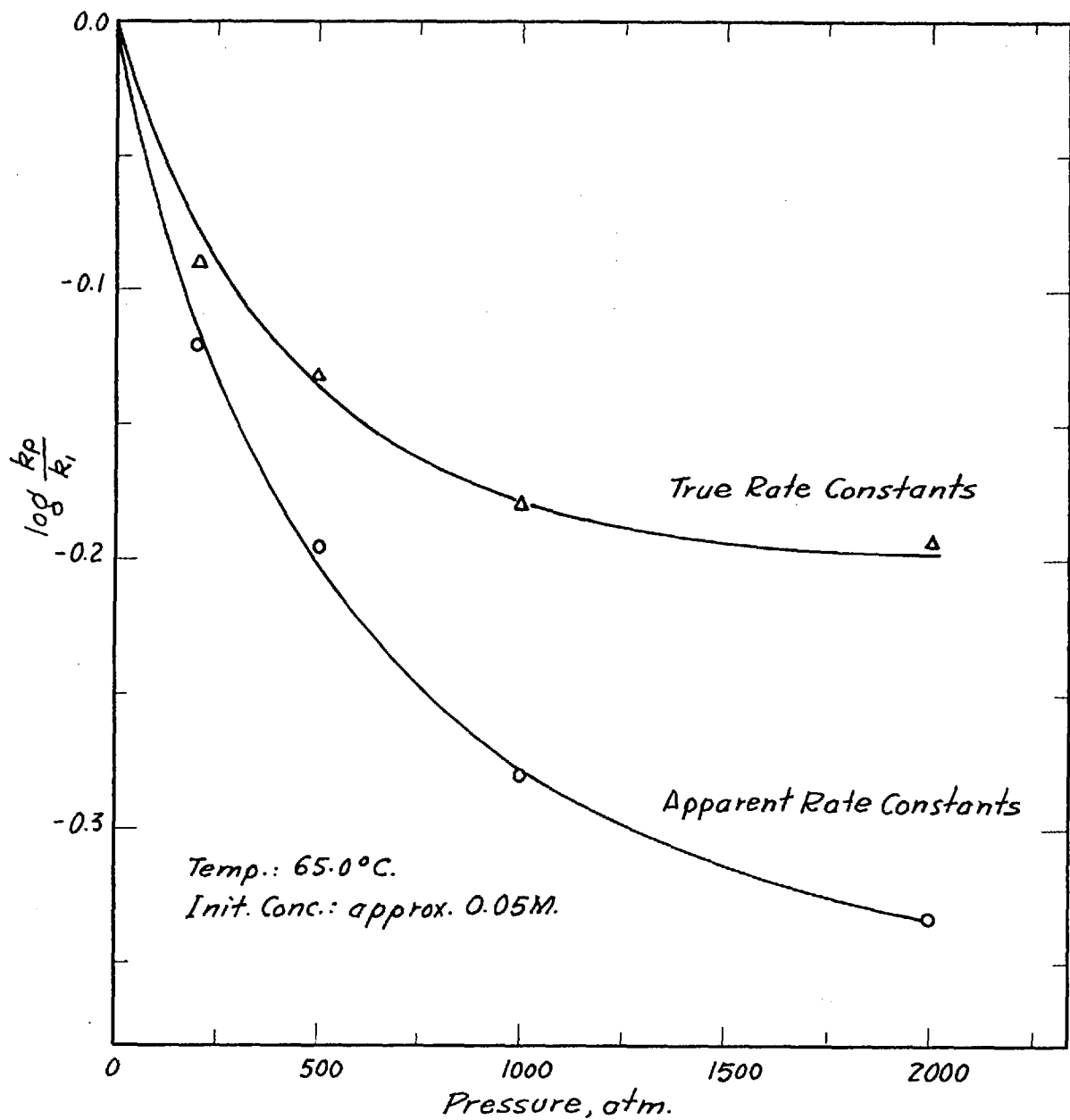


FIG. V-7 EFFECT OF PRESSURE ON RATE CONSTANTS, DECOMPOSITION OF ETHYL-DIMETHYL-PHENYL AMMONIUM IODIDE IN NITRO BENZENE

3. Non-ionizing Solvents

In non-ionizing solvents such as chloroform first order rate constants change in the opposite direction to that found in nitrobenzene, increasing with a decrease in concentration (see section I.D, part 2). Because of the low dielectric constant of chloroform ($\epsilon = 4.806$ at 20°C ⁽¹⁰⁸⁾) there is practically no dissociation. Most of the quaternary salt is present as ion-pairs, with a very small fraction as ions, and some as ion-triplets and higher ion-aggregates. This behaviour can be seen in fig. V-8, which is a log-log plot of the conductance data obtained for allyl-benzyl-methyl-phenyl ammonium bromide in chloroform (data from table IV-15). At low concentrations ions carry most of the current; if they carried it all the slope would be $-\frac{1}{2}$. As the concentration is increased simple ions are disappearing by adherence to the pairs, forming ion-triplets; if they carried all the current the slope would be $+\frac{1}{2}$. The minimum in the Λ versus C curve is therefore explained.

The concentrations of all species other than ion-pairs is very small, as can be seen from the low conductance (table IV-15). This can be illustrated by the data of Sadek and Fuoss⁽¹⁴¹⁾ for the dissociation of tetrabutyl ammonium bromide. In nitrobenzene at 25°C ($\epsilon = 34.69$) the ion-pair dissociation constant was 0.024; in an equimolar nitrobenzene/carbon tetrachloride solvent ($\epsilon = 15.69$) it was 0.00048. In chloroform the dissociation would be very much lower still.

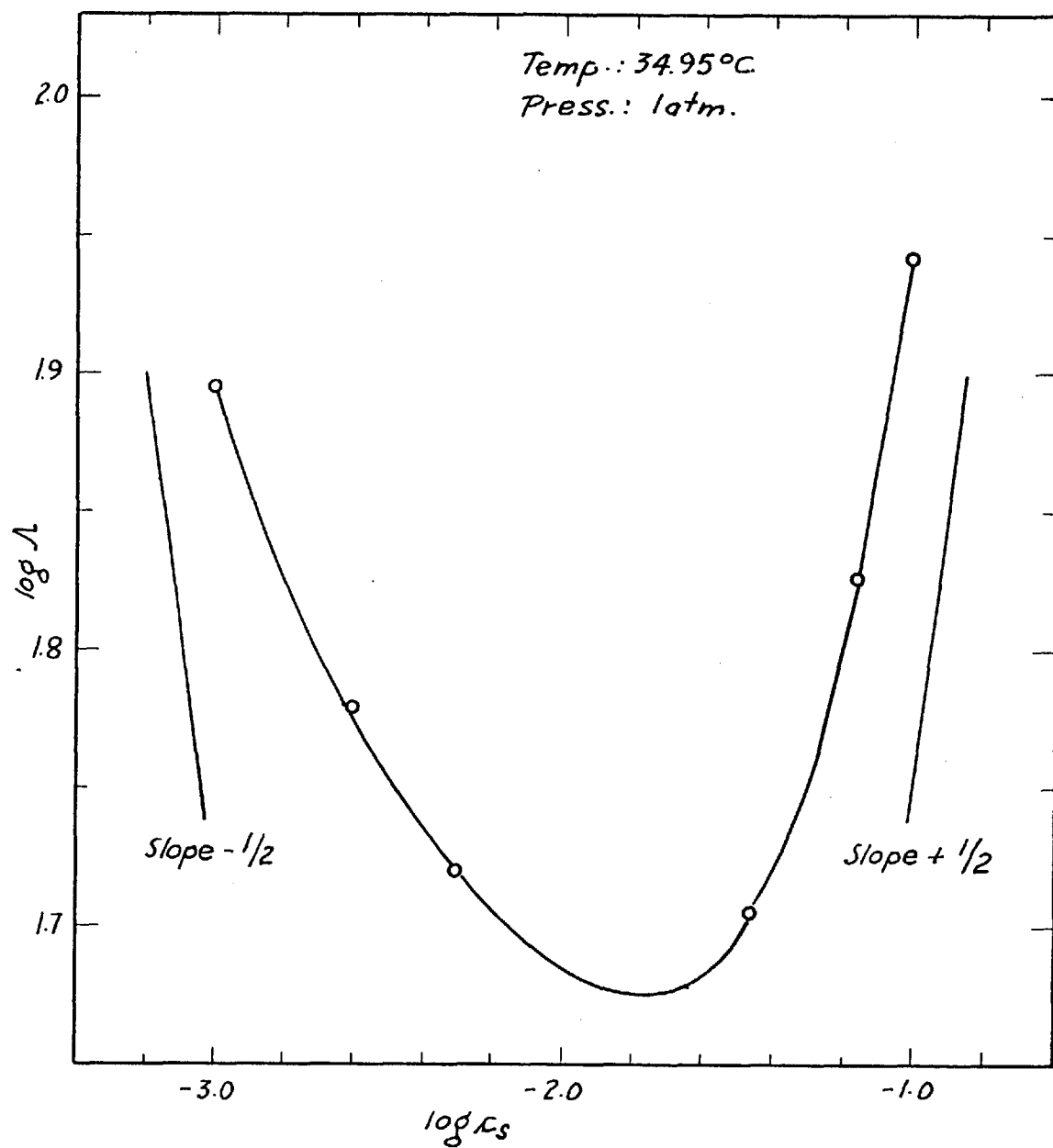


FIG. 7-8 EQUIVALENT CONDUCTANCE OF ALLYL-BENZYL-METHYL-PHENYL AMMONIUM BROMIDE IN CHLOROFORM

The increase in the rate constant for reverse Menschutkin reactions in chloroform when the concentration is decreased is almost certainly due to a type of electrostatic autocatalysis, operating in the opposite direction to that found for forward Menschutkin reactions. This effect is similar to the effect of changing the solvent polarity (a decrease in solvent polarity was seen in section I.D to increase the rate of reverse Menschutkin reactions). The ionic atmosphere tends to stabilize the strongly dipolar quaternary salt. This effect can operate in chloroform even though most of the salt is in the form of associated ion-pairs because of the low solvent dielectric constant and the resulting very great electrostatic force-range. The characteristics of polar reactions in such non-polar solvents has been discussed by Ingold⁽¹⁴²⁾. He notes as an example of the great force-range of electrostatic attraction in non-polar solvents that in benzene ($\epsilon = 2.25$) "even ion-pairs have a force-range ... which with polar reagents is of the order of magnitude of the spacings of solute neighbours at practical dilutions".

No corrections to the rate constants for dissociation were necessary for the decomposition of allyl-benzyl-methyl-phenyl ammonium bromide in chloroform, since the dissociation would be negligible at all temperatures and pressures.

V.C. The Effect of Pressure on Menschutkin Reactions

1. Introduction

The pressure effect is discussed mainly with reference to volumes of activation and overall reaction volume changes. The first part of the discussion illustrates the calculation of activation volumes and develops a complete volumetric description of the system ethyldimethylaniline + methyl iodide in nitrobenzene. In the second section the discrepancies and errors in previous measurement of activation volumes and overall volume changes for Menschutkin reactions are explained. This is followed by a criticism of the detailed theories which Gonikberg and his co-workers have postulated for the calculation of the activation volume for forward Menschutkin reactions. The methyl iodide/ethylmethylaniline system is then examined in detail in an attempt to explain the pressure effect, especially with reference to the calculation of the factors contributing to the activation volume. Finally, the effect of solvent on the pressure effect is discussed, with a comparison between the data obtained in this research for the reaction of ethyl iodide with dimethylaniline in nitrobenzene with the data of Harris for the same reaction in methanol.

2. Calculated Activation Volumes

Activation volumes for the four reactions studied in this research were calculated from the slopes of $\log \frac{k_p}{k_1}$ versus P graphs,

using equation I-8. The volume of dissociation of the ethyl-dimethyl-phenyl ammonium iodide ion-pairs was calculated from a similar plot of $\log \frac{(K_d)_p}{(K_d)_1}$ (equation I-17). In each case at least three duplicate graphs were drawn up and an average ΔV^* taken, to minimize the error involved in assessing the slope at a point on a curve (typical graphs are given in figs. IV-2, IV-4, IV-7, IV-8, IV-9 and V-7). Activation volumes for the decomposition of ethyl-dimethyl-phenyl ammonium iodide in nitrobenzene were calculated from the true rate constants (fig.V-7).

The calculated activation volumes and volumes of dissociation are given in table V-5 (note that reactions 1(a), 1(b) and 1(c) are for different parts of the same system).

From the activation volumes for the reaction of ethylmethyl-aniline with methyl iodide in nitrobenzene and the corresponding reverse reaction (reaction 1(a) and 1(b) in table V-5), the measured overall volume change for the reaction, and the volume of dissociation of the quaternary salt ion-pair (1(c) in table V-5), a complete volume description for this system can be developed. The reaction system can be written

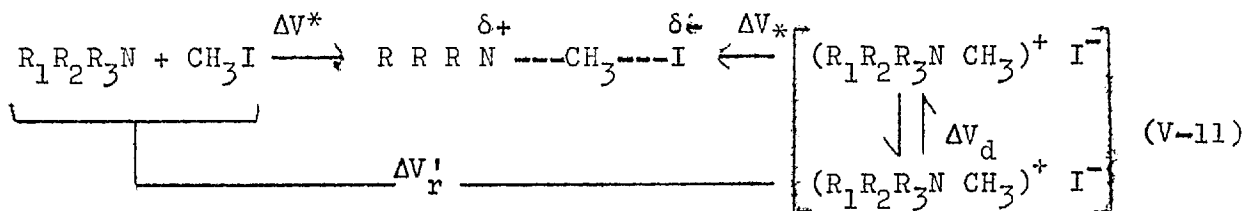


Table V-5

Activation Volumes and Volumes of Dissociation

(in cc./mole)

Reaction	Pressure, atm	1	500	1000	1500	2000
1(a) Ethylmethylaniline + methyl iodide in nitrobenzene at 50.0°C.			ΔV^*			-
			-20.4	-18.4	-16.5	-14.4
1(b) Decomposition of ethyl-dimethyl-phenyl ammonium iodide in nitrobenzene at 65°C.			ΔV^*			-
			+32.5	+ 8.5	+ 3.2	+ 1.0
1(c) Ion-pair dissociation of ethyl-dimethyl-phenyl ammonium iodide in nitrobenzene at 65°C			ΔV_d			-
			-28.1	-15.5	- 9.6	- 6.6
2. Dimethylaniline + ethyl iodide in nitrobenzene at 52.5°C			ΔV^*			
			-22.0	-20.3	-18.8	-17.2
3. Decomposition of allyl-benzyl-methyl-phenyl ammonium bromide in chloroform at 34.95°C			ΔV^*			
			+13.6	+ 5.1	+3.33	-
						+ 2.2

The measured overall volume change $\Delta V_r'$ is not a true overall volume since it includes a term due to the partial dissociation of the quaternary salt.

The first step in building up the volume picture is to convert all the activation volumes and overall volumes to the same temperature. This was done by calculating the activation entropies for the reactions and applying the identity I-15. Activation entropies were calculated from equation I-7

$$k = \frac{e k_b T}{h} e^{\frac{\Delta S^*}{R}} e^{\frac{-E}{RT}} \quad (\text{I-7})$$

by comparison with the Arrhenius equation

$$k = A e^{\frac{-E}{RT}} \quad (\text{V-12})$$

From these equations it is seen that

$$A = \frac{e k_b T}{h} e^{\frac{\Delta S^*}{R}} \quad (\text{V-13})$$

The pre-exponential factor A was calculated from normal Arrhenius plots using the method of least squares.

The values of A, E and ΔS^* are tabulated in table V-6 (corresponding values for the other reactions studied are included for completeness). It should be mentioned that the reverse reaction rate constants are not accurate enough for much reliance to be placed on the absolute value of the change of E and ΔS^* with pressure.

Table V-6

Arrhenius Parameters and Entropies of Activation

Reaction	P atm	A sec. ⁻¹ or l./mole sec.	E cals./ mole	ΔS* e.u.
1(a) Ethylmethylaniline + methyl iodide in nitro- benzene at 50.0°C	1 500	2.2x10 ⁴ 1.6x10 ⁴	13,160 12,690	-39.47 -40.03
1(b) Decomposition of ethyl- dimethyl-phenyl ammonium iodide in nitrobenzene at 65°C	1 500	7.2x10 ¹³ 5.8x10 ¹³	28,500 28,560	+ 4.03 + 3.61
2. Dimethylaniline + ethyl iodide in nitrobenzene at 52.5°C	1	1.2x10 ⁵	14,500	-36.04
3. Decomposition of allyl- benzyl-methyl-phenyl ammonium bromide in chloro- form at 34.95°C	1 2884	18.6x10 ¹⁷ 6.0x10 ¹⁷	29,660 29,200	+14.9 +12.6

For the forward reaction 1(a),

$$\frac{\partial \Delta S^*}{\partial P} = - \frac{\partial \Delta V^*}{\partial T} = - 0.0467 \text{ cc/mole } ^\circ\text{C}.$$

For the reverse reaction 1(b),

$$\frac{\partial \Delta S^*}{\partial P} = - \frac{\partial \Delta V^*}{\partial T} = - 0.0497 \text{ cc/mole } ^\circ\text{C}.$$

Since

$$\frac{\partial \Delta V_r}{\partial T} = \frac{\partial \Delta V^*}{\partial T} - \frac{\partial \Delta V^*}{\partial T} \quad \begin{array}{c} \text{forward} \\ \text{reverse} \end{array}$$

$$\frac{\partial \Delta V_r}{\partial T} = + 0.003 \text{ cc/mole } ^\circ\text{C}$$

These identities can be used to convert all the volume terms for the system to 65°C and to account for dissociation. The activation volume for the forward reaction at 65° is

$$-20.4 + (15 \times 0.0467) = -19.7 \text{ cc/mole}.$$

The measured overall volume change at 25°C and at a reactant and product concentration of 0.02843 M is -62.8 cc/mole (table IV-12).

The dissociation α at 0.02843 M, calculated from the results in table IV-14 using equations III-14 and III-15 is 0.6194. From these figures (assuming that the volume of dissociation at 25°C is the same as that measured at 65°C, i.e. -28.1 cc/mole) the part of the measured $\Delta V_r'$ which is due to dissociation is

$$0.6194 \times (-28.1) = -17.4 \text{ cc/mole}$$

and the reaction volume change at 25°C is -62.8 - (-17.4) = -45.4 cc/mole.

Since $\frac{\partial \Delta V_r}{\partial T}$ is negligible, ΔV_r at 65°C is also -45.4 cc/mole.

The complete volume terms for the system are shown in table V-7.

Table V-7

Volume Changes for the Reaction of Ethylmethylaniline
with Methyl Iodide in Nitrobenzene at 65°C and 1 atm.

Activation volume, forward reaction	- 19.7 cc/mole
Activation volume, reverse reaction	+ 32.5 cc/mole
Overall volume change ΔV_r , by difference	- 52.2 cc/mole
Overall volume change, from measured $\Delta V_r^{\ddagger}$ at 25°C , allowing for dissociation and converting to 65°C	- 45.4 cc/mole

Comparison between the overall volumes calculated by the two methods serves as a check on the accuracy of the measurements.

In view of the difficulty in determining the exact slope of a sharply curved plot (especially in the case of the reverse reaction - refer to figure V-7), and the inaccuracies involved in measuring and calculating the reverse reaction rate constant, the agreement is quite good.

3. Errors in Previous Measurements of the Effect of Pressure on Menschutkin Reactions

These new results explain the discrepancy previously reported between the overall reaction volume change and the activation volumes for forward and reverse Menschutkin reactions.

The activation volume for the reverse reaction is much larger than has previously been assumed. The activation volume for the decomposition of allyl-benzyl-methyl-phenyl ammonium bromide, calculated from Perrin's data⁽¹⁾ (+3.4 cc/mole), has been widely quoted as a typical value for reverse Menschutkin reactions, and it has been used in support of several theories of the pressure effect (e.g. by Perrin⁽¹⁾, Stearn and Eyring⁽²⁴⁾, Hamann⁽³¹⁾ and Gonikberg⁽⁵⁹⁾). The true value of the activation volume for this reaction at 1 atm. is about +13.6 cc/mole, i.e. exactly four times the value calculated from Perrin's results. In fact, ΔV^* for reverse Menschutkin reactions can be much higher even than +13.6 (e.g. +32.5 for the decomposition of ethyl-dimethyl-phenyl ammonium iodide in nitrobenzene).

The low value of ΔV^* calculated from Perrin's results is due to the sharp curvature in the $\log \frac{k_p}{k_1}$ versus P isotherm between 1 and 1000 atm. which could not be observed from Perrin's measurements at 1 and 2884 atm. (see fig. IV-8). $(\Delta V^*)_{\text{avg.}}$ calculated from the present results at 1 and 2884 atm. is +3.6 cc/mole. This emphasizes the importance of measuring the rate constant at low

pressures if the results are to be analyzed in terms of the activation volume, as has been recognized by Hamann⁽³¹⁾. Much of the work on the pressure effect on forward Menschutkin reactions can be criticized on the same grounds.

The effect of quaternary salt dissociation on the overall volume of reaction has not previously been measured. This effect can be large for reactions in ionizing solvents such as nitrobenzene or methanol and has contributed to the observed discrepancies in previous activation volume - overall volume comparisons. The measured overall volume for the reaction of ethylmethylaniline with methyl iodide is -62.8 cc/mole and the volume change due to the quaternary salt dissociation accounts for -17.4 cc of this amount.

It can be concluded from the comprehensive volume description given in table V-7 that the activated complex in Menschutkin reactions is less like the products and more like the amine and iodide reactants than has previously been thought, at least as far as volume considerations are concerned.

Similar conclusions can be drawn from a comparison of the activation and overall volumes for the reaction of allyl bromide with benzylmethylaniline to give allyl-benzyl-methyl-phenyl ammonium bromide. Here the activation volume for the reverse reaction at 34.95°C is +13.6 and the overall volume change is -36 cc/mole. The activation volume for the forward reaction by difference would be -22.4 cc/mole.

4. Criticism of Gonikberg's Theories

Analysis of the pressure effect is best attempted by considering the activation volume in two terms, ΔV_1^* and ΔV_2^* , as has been previously explained. If one of these terms could be calculated accurately the explanation and prediction of the pressure effect would be greatly facilitated. Since Gonikberg and his co-workers claim to be able to calculate ΔV_1^* for Menschutkin reactions, an analysis of their methods must precede discussion of the relative values of ΔV_1^* and ΔV_2^* . (A detailed description of Gonikberg's work with the appropriate references has been given in section I.E).

Gonikberg considers that the activated complex in Menschutkin reactions is relatively unsolvated compared to the product ions, although he also states that the molar volume of the activated complex is very similar to that of the pure (liquid) quaternary salt product (and thus infers that the charges are fully developed in the activated complex). He considers that the activation volume for forward Menschutkin reactions is mainly due to changes in the volume of the reactant themselves (i.e. $\Delta V_1^* \approx \Delta V^*$) with lesser contributions from changes in solvation (ΔV_2^*), and supports this by calculating ΔV_1^* in three different ways. These will be discussed in turn.

The first method used was to assume that ΔV_1^* is equal to the difference between the molar volumes of the pure liquid reactant molecules and of the quaternary salt in the pure liquid form.

From measurements of these molar volumes he calculated ΔV_1^* for the ethyl iodide/pyridine reaction to be -22.5 cc/mole at 50°C . This calculation assumes that there is no difference in the "free volume" between a normal organic liquid and a liquid ionic salt (free volume can be visualized as the difference between the volume of a liquid and the total volume of its constituent molecules based on van der Waal's radii). In fact, there should be less free volume in the molten salt due to compression of the ions together by electrostatic binding, especially if the constituent ions are relatively compressible, as would be expected for tetra-alkyl ammonium ions. All of the -22.5 cc/mole cited by Gonikberg could be due to "free volume" changes. In addition, the assumption that the activated complex in Menschutkin reactions resembles the molten salt has no justification.

Many of Gonikberg's later calculations are based on this rather doubtful estimate of ΔV_1^* . For example, he calculated ΔV_1^* for the same reaction to be -20 cc/mole, presumably using a different method of calculation (equation I-31) and thus corroborating the figure of -22.5 cc/mole. If equation I-31 is examined it is seen to include the basic assumption that $\Delta V_1^* = -22.5$ cc/mole (i.e. in the equation $\Delta V_s = \Delta V^* + 22.5$) so the agreement is hardly surprising.

Gonikberg has calculated ΔV_1^* by another independent method and obtained good agreement with the above two calculations. This method involved calculating the interpenetration volumes of bonded and non-bonded atoms as the reactants approach to form the transition

state, and assuming that ΔV_1^* is the sum of these overlapping volumes. This yielded a figure of $\Delta V_1^* = -18$ cc/mole for the pyridine/ethyl iodide system, most of which was due to the interpenetration of non-bonded atoms.

The non-validity of this calculation will be demonstrated by calculating the interpenetration volumes for the reaction of methyl iodide with ethylmethylaniline by Gonikberg's method and by variations of his method. The activated complex in this reaction is diagrammatically represented in fig.V-9. The hydrogen atoms on the halide have rotated from their normal tetrahedral position into a plane perpendicular to the C-I-N bond line. The CH_3 , C_2H_5 and C_6H_5 groups are disposed tetrahedrally on the nitrogen atom in a direction away from the forming N-C bond (this is the normal amine and quaternary salt configuration⁽¹⁴³⁾).

The C-I and N-C bonds will be stretched compared to normal bonds. Gonikberg has assumed either no stretching or 10% stretching (after Glasstone, Laidler and Eyring⁽⁷²⁾). A better estimate can be obtained by adding the covalent radius of carbon to the mean of the covalent and ionic radii of the N or I atom. Ingold⁽⁹¹⁾⁽⁹²⁾ has found that this method gives values in good agreement with those calculated from fundamental atomic interaction for the stretched bond distances in the similar transition states in $\text{S}_{\text{N}}2$ halide exchange reactions. An extension of about 25% is obtained by this method.

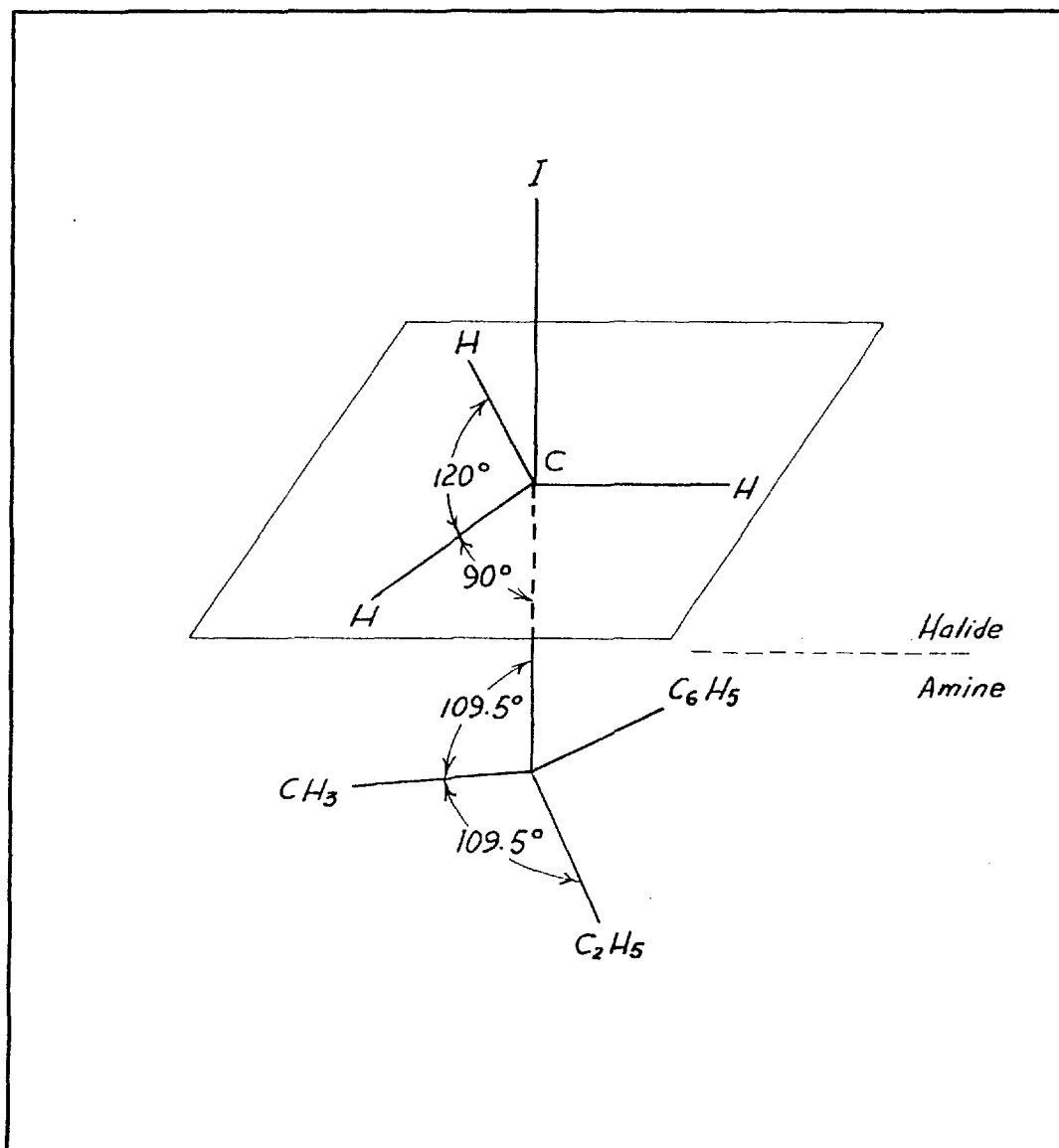


FIG. V-9 ACTIVATED COMPLEX IN THE REACTION OF METHYL IODIDE WITH ETHYLMETHYLANILINE

The amine configuration does not change on formation of the activated complex. The ethyl group on the amine can be considered equivalent to a methyl group for convenience in calculation, since examination of an ethylmethylaniline molecular model shows that the end CH_3 in the ethyl radical can rotate to the back of the molecule out of the way of the incoming alkyl halide. Gonikberg has assumed a planar configuration for amine molecules of this type (all carbons in the amine in the same plane as the N atom) but there seems little justification for this assumption.

In calculating the interpenetration volumes, the following interactions must be included (all of course as differentials between the initial and transition states) :

- (i) Interpenetration of H atoms on the halide into the methyl, ethyl and phenyl groups of the amine and into the N atom.
- (ii) Interpenetration of the carbon on the alkyl halide into the N atom and alkyl groups of the amine.
- (iii) Relief of interpenetration between the iodine atom and the carbon and hydrogen atoms of the alkyl halide due to the partial withdrawal of the iodine atom and the rotation of the hydrogen atoms into the planar configuration.

Gonikberg has omitted some of these terms in some of his calculations and included them in others.

There is much evidence that the van der Waal's radius of a covalently bound atom is considerably shortened in the region

close to the bonding direction. This must be assumed, according to Pauling⁽¹⁴⁴⁾, in order to account for the apparent lack of steric strain in molecules such as carbon tetrachloride. In the iodine atom the effective radius is reduced from 2.15Å (the v.d.W radius) at the side opposite to the carbon bond to 1.33Å (the covalent radius) at the carbon-iodine bond. In Ingold's calculations of steric repulsions in similar transition states (loc.cit.) he assumed the function

$$r_{\text{eff.}} = r_{\text{max.}} - 0.4 (1 + 2 \cos \theta) \quad (\text{V-14})$$

for the shortening of v.d.W. radii at interference angles less than 90°. Here $r_{\text{eff.}}$ is the effective v.d.W. radius, $r_{\text{max.}}$ the maximum (or normal) v.d.W. radius and θ the angle between the line of interference of the non-bonded atoms and the closest covalent bond of the atom under consideration. For partially ionic species, such as the iodine atom would be in the activated complex, he assumed a shallower function

$$r_{\text{eff.}} = r_{\text{max.}} - 0.2 (1 + 2 \cos \theta) \quad (\text{V-15})$$

The details of these functions have little real justification but they must give a better approximation than to neglect the v.d.W. radius shortening entirely, as Gonikberg has done. The functions predict that no steric strain will occur in a normal alkyl halide molecule, and thus simplify the calculations somewhat.

Gonikberg's calculations and some modifications made to them by the author will be illustrated for the reaction of ethylmethyl-aniline with methyl iodide. Table V-8 lists the pertinent atomic

properties required for the calculation. Table V-9 gives an outline of the assumptions made for each calculation along with the resulting ΔV_1^* .

Table V-8

Atomic Dimensions required for the Calculation of Steric Interaction Volumes

	<u>v.d.W. radii</u>	<u>covalent radii</u>
Carbon	1.6 (91)	0.77 (91)
Hydrogen	1.2 (64)	0.32 (91)
Nitrogen	1.6 (64)	0.7 (81)
Iodine	2.15 (91)	1.33 (91)
Methyl	2.0 (64)	-

Bond lengths

C - I	2.10 (91)
C - N	1.5 (64)
C - H	1.10 (64)
C - C	1.55 (64)
C - C (benzene)	1.39 (81)

Note : The values used by Ingold⁽⁹¹⁾ are in substantial agreement with these used by Gonikberg, except for the value of the v.d.W. radius of carbon which Ingold takes as 1.6 and Gonikberg as 1.8Å. Ingold's value seems the more reasonable (see ref.(91)).

Table V-9

Calculation of ΔV_1^* for Ethylmethylaniline + Methyl Iodide by
Gonikberg's Methods

(Measured $\Delta V^* = -20.4$ cc/mole)

ΔV_1^*
cc/mole
(calculated)

Method originally used by Gonikberg (64)

- (i) Normal bond lengths in C-I and C-N bonds.
- (ii) All carbons in amine in a plane perpendicular to the N-C-I line.
- (iii) No account taken of volumes of separation of iodine atom. - 17.8
- (iv) Some compressions omitted, i.e. between the alkyl halide carbon and the radicals on the amine.
- (v) No shortening of v.d.W. radii towards bonding direction.
- (vi) Methyl and ethyl groups on amine considered as spheres of v.d.W. radii 2.0Å.

Modified method used by Gonikberg (65)

As above except :

- (i) Compression of hydrogen atoms on the alkyl halide into the iodine atom as they take up the planar configuration is included. - 32.5
- (ii) The compressions previously omitted by Gonikberg are included.

Second modified method of Gonikberg⁽⁶⁸⁾

As above except :

 ΔV_1^*
 cc/mole
(calculated)

- (i) 10% stretching of the activated C-I and C-N bonds is assumed.

- 16.3

- (ii) The tetrahedral angle for the amine groups is used instead of the planar configuration.

Method as revised by author

As above except :

- (i) Ingold's calculation is used for stretching of the activated bonds: C-I = 2.52Å, C-N = 1.92Å
- (ii) Ingold's more reasonable value for the v.d.W. radius of carbon of 1.6Å (Gonikberg had used 1.8) is employed.

- 6.1

Method as further revised by author

As above except :

- (i) Ingold's functions are used to estimate shortening of v.d.W. radii. This eliminates steric strain in the initial halide structure, and most of the overlapping of non-bonded atoms.
- (ii) The atoms of the alkyl groups of the amine are considered separately (rather than taking each group as a spherical entity). The alkyl groups of the amine are allowed to rotate on their C-C axis to minimize interference with the H atoms on the alkyl halide.

- 0.4

It is seen that this type of calculation, even if justifiable, is very sensitive to the degree of bond stretching in the activated complex and to the extent of shortening of the van der Waal's radius. The last calculation in table V-9 includes the best information on these two phenomena which seems available. It predicts that $\Delta V_1^* \approx 0$. This obtains because in the activated complex the hydrogen atoms on the alkyl halide are just touching the alkyl groups on the amine, with negligible interpenetration. The overlapping between the N and C atoms is almost balanced by the decrease in the overlapping between the C and I atoms.

The last calculation predicts that $\Delta V_1^* \approx 0$, rather than $\Delta V_1^* \approx \Delta V^*$ (as Gonikberg had predicted from his calculations). The correlation that Gonikberg obtained between his calculated ΔV_1^* values and measured ΔV^* values as the reactant complexity is increased is easily explained. It has long been recognized that ΔV^* increases with reactant complexity and Gonikberg's interpenetration volumes are a function of the reactant complexity as well.

If ΔV_1^* were as high as Gonikberg considers it to be (i.e. - 18 to -22.5 cc/mole for the ethyl iodide/pyridine reaction) it would have to be assumed that no solvation effects occur in such solvents as nitrobenzene ($\Delta V^* = - 23.8$ cc/mole from table I-7). This does not fit in with other observations such as the effect of dielectric constant on the reaction, the absence of a reaction in the gas phase and so on. It must be concluded that Gonikberg's methods for calculating ΔV_1^* have little justification in theory or fact.

5. The Effect of Pressure on the Methyl Iodide/Ethylmethylaniline Reaction System.

The failure of Gonikberg's theory of calculating ΔV_1^* from interpenetration volumes would seem to be due to two reasons. Firstly, although the atoms forming the C-I and C-N bonds can be considered to interpenetrate or overlap as the bonds are formed or broken, the non-bonded atoms on the alkyl halide and the amine do not overlap to any extent. Steric repulsion between these non-bonded atoms causes the amine and alkyl halide to fit together in a manner which minimizes steric repulsions. Bond bending will contribute to minimizing these repulsions, as has been demonstrated by Ingold et al. (92).

Secondly, the solvent cannot be considered as a continuous medium, as Gonikberg has done. This can be seen by reference to figure V-10. If two perfectly spherical atoms of $2.0\text{\AA}$ v.d.W. radii are considered to penetrate together so that their centres are $2.14\text{\AA}$ apart (numerical values are from some of the calculations for table V-9) the volume of interpenetration, represented by the shaded area, is 5.53 cc/mole . For the purpose of discussing the pressure effect however, a better approximation would be to assume a cylinder of $4.0\text{\AA}$ diameter decreasing in length by $1.86\text{\AA}$ (i.e. $8 - (2 + 2 + 2.14)$) which is equivalent to 14.1 cc/mole . The solvent molecules, of corresponding size to the reacting molecules, cannot be considered to fill completely the spaces marked "a" on the diagram.

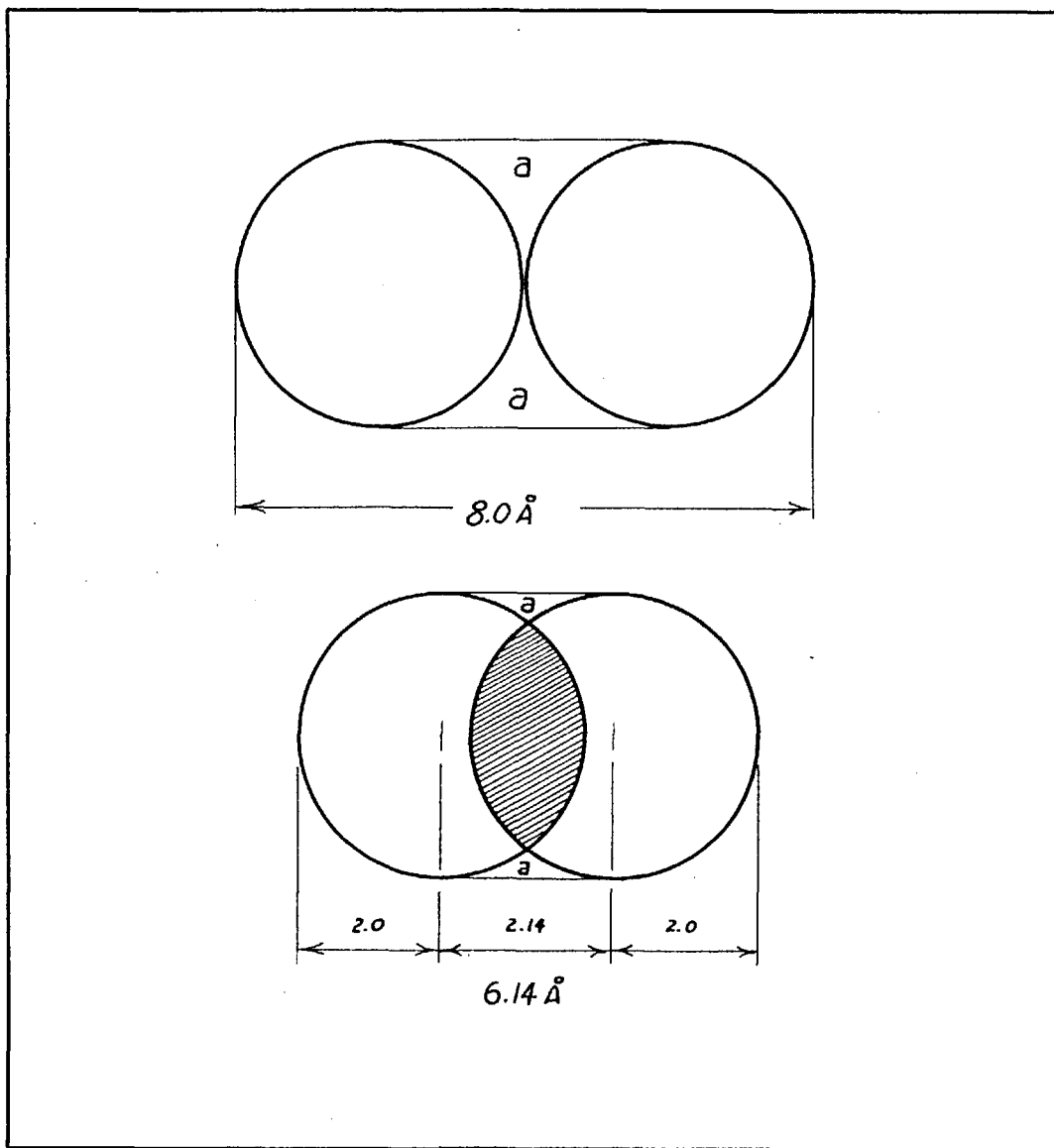


FIGURE V-10 INTERPENETRATION OF TWO SPHERES OF RADIUS $2 \text{ \AA}$

This brings us back to a calculation similar to that originally proposed by Stearn and Eyring⁽²⁴⁾ for the calculation of ΔV^* (see section I.C.), which may legitimately be used to estimate ΔV_1^* instead of the total activation volume. The reacting molecules are considered as a cylinder which decreases in length as the activated complex is formed from the reactants. This calculation cannot, of course, be considered exact because the cross-sectional area of complex molecules is not known, nor is the quantitative effect of the solvent molecule size predictable.

Considering the reaction of ethylmethylaniline with methyl iodide, the decrease in length along the reaction co-ordinate has been estimated to be between 0.86 and 1.26Å. If the ethylmethylaniline molecule is considered equivalent to the trimethylamine molecule (the cross-sectional area of the alkyl halide will determine the size of the cylinder) the reaction can be represented as shown in fig.V-11. The contraction along the reaction co-ordinate can be arrived at as follows :

In initial state

v.d.W. radius of nitrogen	1.60
v.d.W. radius of carbon	1.60
normal C-I bond length	<u>2.10</u>
	5.30

In transition state

partially formed N-C bond	1.92
partially formed C-I bond	<u>2.52</u>
	4.44
Contraction in length	0.86Å

If the effective v.d.W. radius of the methyl group ($2.0\text{\AA}$) is used for the initial state instead of that of the carbon, the contraction in length is $1.26\text{\AA}$. If an effective diameter of $4\text{\AA}$ is chosen (I-4.3, CH_3 -4.0, N-3.2) the volume contraction is between 6.5 and 9.5 cc/mole. Similarly there is a contraction of between 6.5 and 9.5 cc/mole when the transition state is formed from the final state (quaternary salt). It should be noted that these volume changes are mainly due to interpenetration of the bonding atoms (not of the non-bonding atoms), and some re-orientation of the molecules to a configuration more economical of space.

Similar calculations could be made for other alkyl halides, and the value of ΔV_1^* so obtained would obviously be a function of the complexity of the molecule. For example, for tertiary-butyl iodide the contraction in length would be greater, since the effective v.d.W. radius of the tertiary butyl group is greater than that of the methyl group, and the cross-sectional area is greater.

If it is assumed that ΔV_1^* for both the forward and the reverse reaction in the system ethylmethylaniline + methyl iodide is -8 cc/mole (mean of -6.5 and -9.5), the volumetric behaviour will be as shown in table V-10.

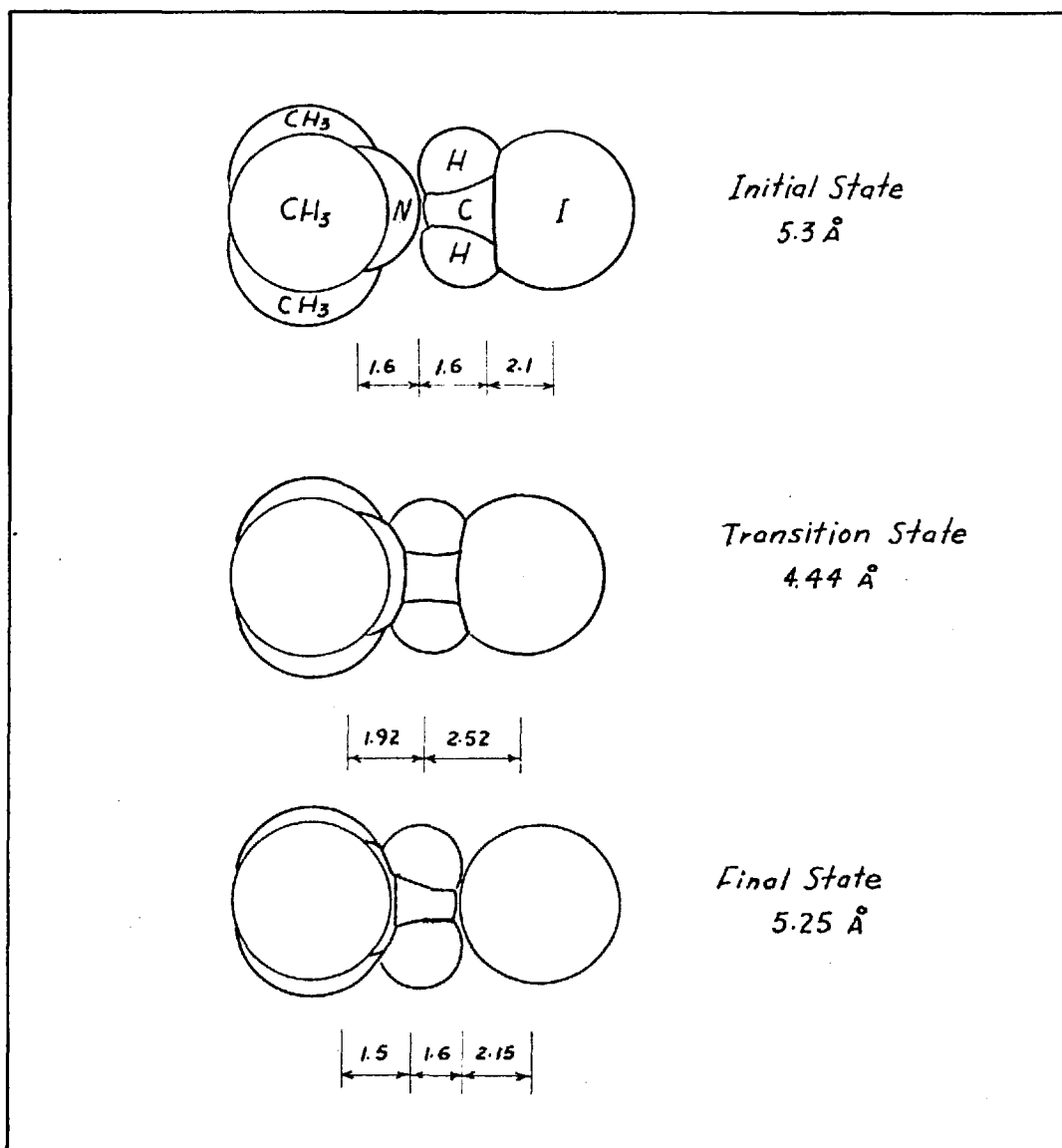


FIG. V-II MOLECULAR DIAGRAM FOR THE REACTION OF METHYL IODIDE WITH TRIMETHYLAMINE

Table V-10

Activation Volumes for the Reaction of Ethylmethylaniline
with Methyl Iodide in Nitrobenzene at 65°C and 1 atm.

	ΔV_1^*	ΔV_2^*	ΔV^*
Forward reaction	- 8	- 11.7	- 19.7
Reverse reaction	<u>- 8</u>	<u>+ 40.5</u>	<u>+ 32.5</u>
Overall reaction	0	- 52.2	- 52.2

There is a decrease in volume due to solvation of - 52.2 cc/mole for the whole reaction and no effective decrease due to ΔV_1^* (the ΔV_1^* terms are equal in magnitude but opposite in sign). It can be seen that the activated complex is much less solvated than the product ion-pair, and **very** much less solvated than the dissociated product ions would be. Solvation appears to account for somewhat more than half of the activation volume for the forward reaction. For the reverse reaction ΔV_1^* and ΔV_2^* are opposing; the deceleration of the reaction **by pressure** is therefore wholly a solvation effect.

These conclusions are to some extent in agreement with those of Gonikberg, although it has been shown that his theories for calculating the activation volume have little foundation and his conclusion that $\Delta V_1^* \gg \Delta V_2^*$ is not borne out. In addition it is seen that there is little difference between the molecular volume

of the reactants and that of the products except for solvation. Gonikberg considered there to be about a 20 cc/mole difference, based on his density measurements on the molten quaternary salt. The theories of Perrin et al. and of Hamann that the activation volume for the forward reaction is close to the overall volume change and that the activated complex is almost as fully solvated as the product quaternary salt are also not in agreement with these results.

Some idea of the approximate charge on the activated complex can be gained by examination of the ΔV_2^* terms. Born's theory (see section I and equation I-11) predicts that if the effective radius of the charge is kept constant the solvation volume will vary as the square of the charge. If it is assumed that there is no change in the effective radius of the charges between the initial, transition and final states, the charge on the activated complex can be approximately calculated, as shown in table V-11.

Table V-11

Fractional Ionic Charges in the Transition State Estimated
for Various Values of ΔV_2^*

	$-\Delta V_2^*$ cc/mole	Charge on N atom +	Charge on I atom -
Initial state	0	0	0
	0.52	0.1	0.1
	2.1	0.2	0.2
	4.7	0.3	0.3
	8.3	0.4	0.4
Transition state	<u>11.7</u>	<u>0.48</u>	<u>0.48</u>
	13.0	0.50	0.50
	18.8	0.60	0.60
	25.6	0.70	0.70
	33.4	0.80	0.80
	42.0	0.90	0.90
Final state	52.2	1.0	1.0

Although this calculation is far from precise (it neglects, for example, changes in the effective radii of the charges), it predicts that if the charges are about half developed in the transition state, there must be an appreciable ΔV_2^* for the forward reaction and a very much larger ΔV_2^* for the reverse reaction. The fact that the volume of solvation when $\frac{1}{2}$ charges are developed is only $\frac{1}{4}$ of the total solvation volume when full charges are developed (13/52.2) is due to the function involving the charge to the second power. Conversely, if it is assumed that the charges are half developed in the transition state (a reasonable assumption, and one that has been used before, e.g. by Ingold⁽⁹¹⁾⁽⁹²⁾), the approximate magnitude of ΔV_2^* for the forward reaction is seen to be -13.0 cc/mole. ΔV_1^* would then be $-19.7 + 13 = -6.7$ cc/mole, which is in agreement with the figure of -6.5 to -9.5 previously calculated.

Some additional information on the transition state can be derived from consideration of the change in the activation volume with pressure. As outlined in section I.C. the rate of change of ΔV^* with pressure (i.e. the extent of curvature of the $\log \frac{k_p}{k_1}$ versus P plot) is a measure of the relative compressibilities of the initial and transition states. From graphs of ΔV^* versus P for the forward and reverse reactions (figure V-12) it can be seen that ΔV^* changes much more rapidly with pressure for the reverse than for the forward reaction. The transition state compressibility is therefore

much closer to that of the amine and iodide reactants than to that of the quaternary salt. This would be expected, since the solvent molecules "frozen" around the charged product would be relatively incompressible. This type of analysis is only very approximate, because the change in ΔV^* with pressure is a function of the change in solvent dielectric constant as well as of the compressibilities when solvation is involved. It can however indicate the similarity between the initial and transition states.

It has often been noted⁽⁷⁾⁽²⁵⁾⁽⁷²⁾⁽⁸⁷⁾ that the entropy of activation for forward Menschutkin reactions is usually similar in magnitude to the overall entropy change (although most determinations of the overall entropy are in doubt because concentration factors affecting the reverse reaction rate have not been considered). This has been cited as evidence that the transition state in Menschutkin reactions is almost as fully solvated as the product ions, the large negative activation entropy being due to "freezing" of the solvent molecules around the ionic activated complex. This theory has a direct bearing on the pressure effect, since the extent of solvation of the transition state affects the activation volume.

A similar entropy effect has been obtained in the methyl iodide/methylethylaniline system, the activation entropies for the forward and reverse reactions being -39.47 and $+4.03$ e.u. respectively (see table V-6).

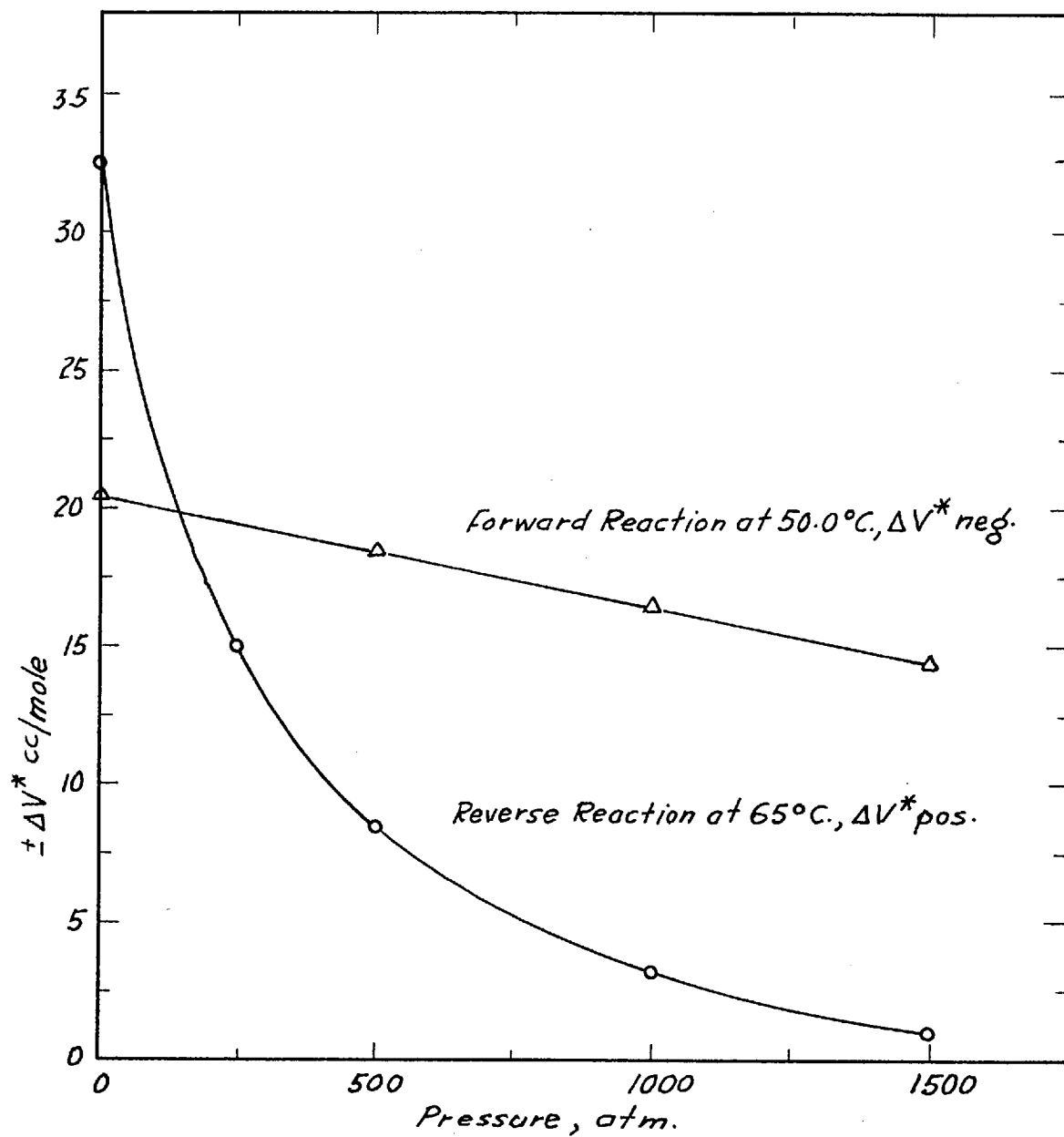
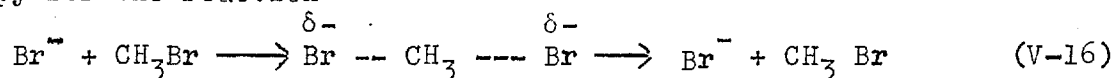


FIG. V-12 EFFECT OF PRESSURE ON ACTIVATION VOLUMES
METHYL IODIDE/DIMETHYLANILINE SYSTEM

Obviously the activated complex is close in character to the products if the entropy changes alone are considered. However, to extend this to the conclusion that the ionic charges and the solvation are almost as completely developed in the activated complex as in the product ions is to ignore the complexity of the entropy terms.

Hughes, Ingold et al.⁽⁹²⁾ calculated activation entropies for symmetrical halide exchange reactions, ignoring solvation effects. (These S_N2 reactions are essentially similar to Menschutkin reactions). They calculated that the activation entropy for the reaction



considering translational, rotational and vibrational contributions would be -14.03 e.u. (the same in each direction).

Let us assume that there is a similar "chemical" contribution of -14.03 to the entropy of both the forward and the reverse reactions in the methyl iodide/ethylmethylaniline system. The "solvation" entropy in the forward reaction would then be $-39.47 - (-14.03) = -25.44$ e.u.; in the reverse reaction the "solvation" entropy would be $+4.03 - (-14.03) = +18.06$ e.u. The "solvation" ΔS^* is seen to act in the same direction as the "chemical" ΔS^* in the forward reaction, while in the reverse reaction the two effects are in opposition, thus masking the solvation ΔS^* .

A comparison of the entropy of activation of the forward reaction with the overall entropy changes is therefore not a proper basis for deciding the relative solvations of the transition state and the final product. The "chemical" activation entropy for Menschutkin reactions could be greater in magnitude than 14.03 e.u., since the rotational entropy of the amine molecule is also involved (it is not for halide exchange reactions). If this were the case, the solvation entropy for the reverse reaction could be greater than for the forward reaction.

6. Effect of Solvent on the Pressure Effect - Ethyl Iodide + Dimethylaniline

The effect of solvent on the activation volume also gives some indication of the relative sizes of ΔV_1^* and ΔV_2^* . If for the forward reaction $\Delta V_1^* \gg \Delta V_2^*$ as Gonikberg considers it to be, there should be little difference in ΔV^* in different solvents (ΔV_1^* would not change). Harris and Weale⁽³⁹⁾ found the activation volume for the reaction of ethyl iodide with dimethylaniline in methanol at 52.5°C to be -34 cc/mole. In the present work for the same reaction in nitrobenzene the activation volume was found to be -22.0 cc/mole.

The activation volume for this reaction in acetone can be approximated by comparison with the data of Perrin⁽¹⁸⁾ and of Harris and Weale⁽³⁹⁾ for the reaction of dimethylaniline with iso-propyl iodide in acetone and methanol.

$$\frac{\frac{k_{2900}}{k_1} \text{ (in acetone)}^{(18)}}{\frac{k_{2900}}{k_1} \text{ (in methanol)}^{(39)}} = \frac{25.5}{14.4}$$

$$\therefore \frac{\Delta V^* \text{ (in acetone)}}{\Delta V^* \text{ (in methanol)}} = \frac{\log 25.5}{\log 14.4} = 1.26$$

$\therefore \Delta V^*$ for dimethylaniline + ethyl iodide in acetone
is $1.26 \times -34.0 = -43$ cc/mole.

This figure is of course only a very rough estimate, but is valuable for comparison purposes.

The change in the activation volume with solvent can be understood by comparison with the theoretical partial molar volumes of solvation of ions in the solvent. Strauss⁽⁷⁹⁾ has calculated these volumes for the ions $C_s^+ + F^-$ in a number of solvents from the Born equation (I-11). Some of these are listed in table V-12 along with the activation volumes for the dimethylaniline/ethyl iodide reaction. The solvation volume for nitrobenzene is smaller than for methanol although the dielectric constants are much the same, because $\frac{\partial \epsilon}{\partial p}$ is much lower for nitrobenzene than for methanol.

Table V-12

Theoretical Molar Volume Changes for the Solvation of the
Ion Pair $C_B^+ + F^-$ (with ΔV^* for comparison)

Solvent	Dielectric Const. at 25°C ⁽¹³²⁾	$\Delta \bar{V}_s$ cc/mole	ΔV^* cc/mole
Water	78.30	- 19.7	-
Nitrobenzene	34.82	- 27.0	- 22
Methanol	32.63	- 42.1	- 34
Ethanol	24.30	- 53.8	-
Acetone	20.70	- 74.8	- 43

Note : (i) $\Delta \bar{V}_s$ is at 30°C.

(ii) All $\Delta \bar{V}_s$ values are as calculated by Strauss⁽⁷⁹⁾ except that for nitrobenzene, which has been calculated from the dielectric constant data developed in section III.D.

The difference in activation volumes cannot be accounted for unless a considerable amount of ΔV^* is due to solvation. If a value for ΔV_1^* is assumed, ΔV_2^* can be calculated for nitrobenzene. From this figure the ΔV_2^* for the other solvents can be calculated by ratio from Strauss' $\Delta \bar{V}_s$ figures. For example if ΔV_1^* is -10 cc/mole, ΔV_2^* in nitrobenzene is -12 cc/mole. ΔV_2^* in acetone should be

$\frac{-74.8}{-27.0} \times -12 = -33.2$ cc/mole. ΔV^* for acetone should be
 $-33.2 + (-10) = -43.2$ cc/mole. The results of calculations of
 this type are given in table V-13.

Table V-13

Calculated ΔV^* for Dimethylaniline + Ethyl Iodide in Various Solvents

Assumed ΔV_1^* Solvent	- 20	- 15	- 10	Measured ΔV^*
Nitrobenzene	- 22	- 22	- 22	- 22
Methanol	- 23.2	- 25.8	- 30.7	- 34
Acetone	- 25.5	- 34.4	- 43.2	- 43

The change in ΔV^* with solvent is seen to be best explained with a ΔV_1^* of about -10 cc/mole. This is much smaller than Gonikberg's theories would predict. Using his latest method, outlined in table V-9, ΔV_1^* for this reaction was calculated to be -22.6 cc/mole (his earlier methods would predict ΔV_1^* values as high as -44.2 cc/mole). It is however of the order that would be obtained by a calculation similar to that used in the previous section to predict a ΔV_1^* of -6.5 to -9.5 cc/mole for the reaction of ethylmethyl aniline with methyl iodide.

The activation volume decreases with pressure, as shown in table V-14. The data for the reaction in nitrobenzene is from

this work and the data for methanol from Harris' research⁽²⁾.

Table V-14

Effect of Pressure on Activation Volume, Dimethylaniline +
Ethyl Iodide at 52.5°C

Pressure atm.	Nitrobenzene	Methanol
1	- 22.0	- 34.0
500	- 20.3	- 27.5
1000	- 18.8	- 21.7
1500	- 17.2	- 18.0
2000	- 15.9	- 15.6

This difference in the response of ΔV^* to pressure has previously been attributed to the differences in compressibility between the two solvents. A more logical explanation is derived from an examination of the two terms comprising the activation volume and their expected response to pressure. As mentioned in the previous section, the change in ΔV^* with pressure is a function of the relative compressibilities of the initial and transition states. If no solvation occurs (i.e. the total activation volume is ΔV_1^*) there would probably be no great difference in the compressibilities of these two states, and the $\Delta V^*/P$ plot would be relatively straight. In other words, ΔV_1^* would not be expected

to change radically with pressure. On the other hand, volume changes due to solvation often decrease quite rapidly with pressure, as Strauss⁽⁷⁹⁾ has pointed out. This occurs because of changes in the dielectric constant of the solvent with pressure (and also changes in the rate of change of dielectric constant). ΔV_2^* thus decreases rather quickly with pressure, relative to ΔV_1^* . In methanol ΔV_2^* would change more rapidly than in nitrobenzene, because of the greater response of the dielectric constant to pressure in the former solvent.

Two reasons for the differing response of ΔV^* to pressure in the two solvents can thus be seen. Firstly, ΔV_2^* is a much larger part of ΔV^* in methanol than in nitrobenzene; since ΔV_2^* changes more rapidly than ΔV_1^* with pressure, the total activation volume changes more rapidly with pressure in methanol. Secondly, ΔV_2^* changes more rapidly with pressure in methanol than in nitrobenzene, causing ΔV^* also to change more rapidly. This latter effect is probably a relatively minor one.

V.D. Conclusions

1. Mechanism of Forward Menschutkin Reactions

From the study of the reaction of dimethylaniline with ethyl iodide as a function of temperature, pressure and concentration, the following conclusions can be drawn :

- (i) There is no change in the reaction order or mechanism with increasing pressure.
- (ii) The apparent order change reported by Harris⁽²⁾ for this reaction is associated with solvent freezing between 2260 and 2730 atm. with a resulting large increase in the reactant and product concentration.
- (iii) The kinetic behaviour above the solvent freezing point is due to the autocatalytic effect of the high concentrations of the product quaternary salt superimposed on normal second order behaviour; it can be duplicated at atmospheric pressure with high reactant and product concentrations.
- (iv) The autocatalytic effect is most probably due to stabilization of the partially ionic activated complex by the ionic atmosphere of the quaternary salt. The kinetic results can be reasonably well described by an equation of the type

$$\frac{dx}{dt} = (k + px)(a - x)^2 \quad (V-2)$$

although the relationship is undoubtedly more complicated.

2. Mechanism of Reverse Menschutkin Reactions

From the detailed study of the decomposition of ethyl-dimethyl-phenyl ammonium iodide in nitrobenzene and the ion-pair dissociation of this salt, the following conclusions can be drawn :

- (i) The reaction is bimolecular (S_N2) and proceeds through the same transition state as the corresponding forward reaction.
- (ii) It is first order w.r.t. the concentration of ion-pairs, which explains the decrease in the reaction rate with decreasing concentration.
- (iii) This behaviour should be found for most reverse Menschutkin reactions in ionizing solvents, and therefore the rate constants reported in the literature cannot be considered as true constants.

The decomposition of allyl-benzyl-methyl-phenyl ammonium bromide in chloroform was not studied in detail, but the following conclusions can be drawn :

- (i) There is practically no electrolytic dissociation of the salt under ordinary conditions.
- (ii) The increase in the rate constant with decreasing salt concentration is almost certainly due to electrostatic autocatalysis. The ionic atmosphere stabilizes the quaternary salt. This effect is facilitated by the great electrostatic force-range in solvents of low dielectric constant.

3. Effect of Pressure on Menshutkin Reactions

The following general conclusions can be drawn about the measurement of the volume terms associated with the pressure effect :

- (i) The activation volume for reverse Menshutkin reactions is much higher than has previously been thought. (The figure of + 3.4 cc/mole calculated from Perrin's results⁽¹⁾, which has been widely quoted as typical of these reactions is incorrect and should be + 13.6 cc/mole. The error is due to the sharp curvature in the $\log \frac{k_p}{k_1}$ versus P plots which could not be foreseen from Perrin's results. ΔV^* can be even higher (+32.5 cc/mole for the other reverse reaction studied).
- (ii) The overall volumes of reaction previously reported for Menshutkin reactions in ionizing solvents have not been corrected for quaternary salt dissociation and must be therefore somewhat in error.

From a theoretical examination, Gonikberg's methods of calculating ΔV_1^* for Menshutkin reactions are shown to be not valid. A modification of the methods of Stearn and Eyring is shown to be more logical.

A complete volumetric description of the ethylmethylaniline/methyl iodide reaction system has been developed from measurements of the rates of the forward and reverse reactions, the dissociation of the product salt, and the overall volume change. The following

conclusions regarding the transition state and the pressure effect have been drawn from examination of this system:

- (i) The transition state is closer in character to the amine and iodide reactants and less like the quaternary salt than has previously been thought (ΔV^* forward = -20.4, ΔV^* reverse = +32.5 cc/mole).
- (ii) The activation volume for the forward reaction is comprised of a ΔV_1^* of about -8 cc/mole and a ΔV_2^* of about -12 cc/mole (i.e. more than half is due to solvation).
- (iii) The activation volume for the reverse reaction is almost entirely due to solvation.
- (iv) The activated complex is much less solvated than the product quaternary salt ion-pair.
- (v) The volume effects can be explained if the charges in the activated complex are about half developed.
- (vi) The transition state compressibility is much closer to that of the amine and iodide than to that of the less compressible quaternary salt. This explains the different responses of the activation volumes to pressure.
- (vii) The entropy of activation for the forward reaction is much larger in magnitude and opposite in sign to the entropy of activation for the reverse reaction (-39.47 and + 4.03 e.u.). This is not a criterion of the relative solvations, since

the "chemical" solvation effects are added to the "solvation" entropy effects in the forward reaction, but oppose them in the reverse.

(viii) These conclusions are not in accord with those of Perrin or of Hamann, who considered the transition state to be close in character to the quaternary salt; nor are they in agreement with the theories of Gonikberg et al.

From a comparison of the effects of pressure on the dimethyl-aniline/ethyl iodide reaction in nitrobenzene, methanol and acetone (latter two by other workers) the following conclusions can be drawn :

- (i) The difference in the activation volumes at one atmosphere can be readily explained from examination of the solvent physical properties, in the light of Born's solvation theory.
- (ii) Because of (i) there is a greater ΔV_2^* for the reaction in methanol and acetone than in nitrobenzene. This explains the less rapid decrease in ΔV^* with pressure in nitrobenzene (ΔV_2^* decreases more rapidly than ΔV_1^* with pressure).

REFERENCES

1. E.G. Williams, M.W. Perrin Proc. Roy. Soc. A154, 684 (1936).
and R.O. Gibson
2. A.P. Harris, . . Ph.D. Thesis, University of London (1959)
3. W. Strauss, University of Sheffield Fuel Society
Journal, Vol. 8 (1957).
4. W. Strauss, Brit. Chem. Eng. 4, 386 and 521 (1959).
5. E.W. Fawcett and R.O. Gibson, J. Chem. Soc., 1934, 386.
6. P.W. Bridgman, The Physics of High Pressure,
G. Bell and Sons (1949).
7. S.D. Hamann, Physico-Chemical Effects of Pressure,
Butterworths Scientific Publications (1957)
8. M. Berthelot and Annes. Chim. (Phys), 36, 231 (1862).
L. Pean de St. Giles,
9. W.C. Roentgen, Ann. Phys. Lpz., 45, 98 (1892).
10. D. Stern, ibid, 59, 659 (1896).
11. V. Rothmund, Z. phys. Chem., 20, 168 (1896).
12. M. Planck, Ann. Phys. Lpz., 32, 462 (1887).
13. E. Whalley, Trans. Faraday Soc., 55, 798 (1959).
14. A.L. Th. Moesveld and Z. phys. Chem. 138, 169 (1928).
W.A.T. de Meester,
15. E.W. Fawcett and R.O. Gibson, J. Chem. Soc., 1934, 396
16. E.W. Fawcett, R.O. Gibson Proc. Roy. Soc., A150, 223 (1935).
and M.W. Perrin,

17. M.W. Perrin and E.W. Williams, Proc. Roy. Soc., A159, 162 (1937).
18. M.W. Perrin, Trans. Faraday Soc., 34, 144 (1938).
19. D.M. Newitt, R.P. Linstead, J. Chem. Soc., 1937, 876.
R.H. Sapiro and R.J. Boorman,
20. S. P'Eng, R.H. Sapiro, ibid, 1938, 784.
R.P. Linstead and D.M. Newitt,
21. M.G. Evans and M. Polanyi, Trans. Faraday Soc., 31, 875 (1935).
22. M.G. Evans and M. Polanyi, ibid, 32, 1333 (1936).
23. " " ibid, 33, 448 (1937).
24. A.E. Stearn and H. Eyring, Chem. Revs., 29, 509 (1941).
25. J. Buchanan and S.D. Hamann, Trans. Faraday Soc., 49, 1425 (1953).
26. H.G. David and S.D. Hamann, ibid, 50, 1188 (1954).
27. H.G. David, S.D. Hamann Austral. J. Chem., 8, 285 (1955).
and S.J. Lake,
28. A.H. Ewald and S.D. Hamann ibid, 9, 54 (1956).
29. A.H. Ewald, Disc. Faraday Soc., 22, 138 (1956).
30. S.D. Hamann and D.P. Teplitzky, ibid, 22, 114 (1956).
31. S.D. Hamann, Austral. J. Chem., 9, 533 (1956).
32. W. Strauss, ibid, 10, 381 (1957).
33. A.H. Ewald, S.D. Hamann and J.E. Stuchbury, Trans. Faraday Soc., 53, 99 (1957).
34. S.D. Hamann, ibid, 54, 507 (1958).
35. A.H. Ewald, ibid, 55, 792 (1959).

36. K.E. Weale, J. Chem. Soc., 1954, 2959.
37. K.E. Weale, Disc. Faraday Soc., 22, 122 (1956).
38. R.T. Harris and K.E. Weale, J. Chem. Soc., 1956, 953.
39. A.P. Harris and K.E. Weale, *ibid*, 1961, 146.
40. J.M. Stewart and K.E. Weale, Proc. Chem. Soc., 1961, 389.
41. K.R. Brower, J. Amer. Chem. Soc., 80, 2105 (1958).
42. K.R. Brower, *ibid*, 81, 3504 (1959).
43. K.R. Brower, *ibid*, 82, 4535 (1960).
44. D.R. McKelvey and . . J. Phys. Chem., 64, 1958 (1960).
K.R. Brower,
45. C. Walling and J. Pellon, J. Amer. Chem. Soc., 79, 4786 (1957).
46. C. Walling and J. Peisach, *ibid*, 80, 5819 (1958).
47. C. Walling and G. Metzger, *ibid*, 81, 5365 (1959).
48. C.T. Burris and Trans. Faraday Soc., 51, 1497 (1955).
K.J. Laidler,
49. K.J. Laidler, Disc. Faraday Soc., 22, 88 (1956).
50. K.J. Laidler and D. Chen, Trans. Faraday Soc., 54, 1026 (1955).
51. D.T.Y. Chen and K.J. Laidler, Can. J. Chem., 37, 599 (1959).
52. E. Whalley, *ibid*, 36, 228 (1958).
53. J. Koskikallio and Trans. Faraday Soc., 55, 815 (1959).
E. Whalley,
54. J. Koskikallio and Can. J. Chem., 37, 783 (1959).
E. Whalley,
55. J. Koskikallio and *ibid*, 37, 788 (1959).
E. Whalley,

56. J. Koskikallio, D. Pouli and E. Whalley, Can. J. Chem., 37, 1360 (1959).
57. A.R. Osborn and E. Whalley ibid, 39, 597 (1961).
58. A.R. Osborn, T.C.W. Mak and E. Whalley, ibid, 39, 1101, (1961).
59. M.G. Gonikberg and G.S. Povkh Zhur. Fiz. Khim., 23(4), 383 (1949) D.S.I.R. translation).
60. M.G. Gonikberg, Doklady Akad. Nauk. S.S.S.R., 102, 117 (1955). (C.S.I.R.O. (Australia) translation).
61. M.G. Gonikberg, V.B. Miller, M.B. Neiman, F.S. D'yachkovsky, Zhur. Fiz. Khim., 30, 784 (1956).
G.I. Likhtenshtein and
A.A. Opekunov,
62. M.G. Gonikberg and V.M. Zulin, Austral. J. Chem., 11, 285 (1958).
63. M.G. Gonikberg, Zhur. Fiz. Khim., 32, 2216 (1958) (N.R.C. (Canada) translation).
64. M.G. Gonikberg and A.I. Kitaigorodskii, Doklady Akad. Nauk. S.S.S.R., 122, 231 (1958) (Consultants Bureau translation).
65. M.G. Gonikberg and B.S. El'yanov Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk., 4, 629 (1960) (Consultants Bureau translation).
66. M.G. Gonikberg and B.S. El'yanov Doklady Akad. Nauk. S.S.S.R., 130, 545 (1960) (Consultants Bureau translation).
67. M.G. Gonikberg and B.S. El'yanov, ibid, 138, 1103 (1961).

68. M.G. Gonikberg,
B.S. El'yanov and
V.M. Zhulin, paper to be presented at the Symposium
on the Physics and Chemistry of High
Pressures, 3rd Congress of the
European Federation of Chemical
Engineering, London, June 1962 (to be
published by the Society of Chemical
Industry) (preprint in English).
69. S.W. Benson and J.A. Berson, J. Amer. Chem. Soc., 84, 152 (1962).
70. E.A. Moelwyn-Hughes, Kinetics of Reactions in Solution,
Oxford University Press (1947).
71. A. Michels, Proc. Roy. Soc., A127, 258 (1930)
72. S. Glasstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes,
McGraw-Hill Book Co. (1941).
73. S. Glasstone, Textbook of Physical Chemistry,
D. van Nostrand Co., 2nd Edition (1946).
74. A.A. Frost and R.G. Pearson, Kinetics and Mechanism,
John Wiley and Sons (1953).
75. S.D. Hamann and W. Strauss, Trans. Faraday Soc., 51, 1684
76. S.D. Hamann and W. Strauss, Disc. Faraday Soc., 22, 70 (1956).
77. W. Strauss, M.Sc. Thesis, University of Melbourne,
(1956).
78. S.D. Hamann and S.C. Lim, Austral. J. Chem., 7, 329 (1954).
79. W. Strauss, ibid, 10, 359 (1957).
80. R.J.H. Clark and A.J. Ellis, J. Chem. Soc., 1960, 247.
81. C.K. Ingold, Structure and Mechanism in Organic
Chemistry,
G. Bell and Sons (1953).

82. A.J. Ellis, J. Chem. Soc., 1959, 3689.
83. M.L. Bird, E.D. Hughes and C.K. Ingold, ibid 1954, 634.
84. Bateman, E.D. Hughes and C.K. Ingold, ibid 1940, 1011.
85. H. Essex and O. Gelormini, J. Amer. Chem. Soc., 48, 882 (1926).
86. W.C. Davies and R.G. Cox, J. Chem. Soc., 1937, 614.
87. J.K. Syrkin and M.A. Gubareva, Acta Physicochimica U.R.S.S., 8, 236 (1938).
88. K.J. Laidler, J. Chem. Soc., 1938, 1786.
89. E.D. Hughes, C.K. Ingold and C.S. Patel, ibid, 1933, 526.
90. E.D. Hughes, C.K. Ingold and V. Pocker, Chem. and Ind. (London), 1959), 1282.
91. I. Dostrovsky, E.D. Hughes and C.K. Ingold, J. Chem. Soc., 1946, 173.
92. P.B.D. de la Mare, L. Fowden, E.D. Hughes, C.K. Ingold and J.D.H. Mackie, ibid, 1955 (3200).
93. M.S. Newman, Steric Effects in Organic Chemistry. J. Valey and Sons (1956).
94. C. Hinshelwood, K.J. Laidler and E.W. Timm, J. Chem. Soc., 1938, 848.
95. A.G. Evans, M.G. Evans and M. Polanyi, J. Chem. Soc., 1947, 558.
96. A.G. Evans, Nature, 157, 438 (1946).

97. A.G. Evans, Nature, 158, 586 (1946).
98. A.G. Evans, Trans. Faraday Soc., 42, 719 (1946).
99. H.C. Brown and A. Cahn, J. Amer. Chem. Soc., 77, 1715 (1955).
100. T.I. Crowell and L.P. Hammett ibid, 70, 3444 (1948).
101. C.A. Winkler and J. Chem. Soc., 1935, 1147.
C.N. Hinshelwood,
102. H.C. Brown and X.R. Mihm, J. Amer. Chem. Soc., 77, 1723 (1955).
103. H.L. Heys, An Introduction to Electronic Theory
of Organic Compounds.
G. Harrap and Co. (1960).
104. H. von Halban, Z. phys. Chem., 77, 719 (1911).
105. J.F. Norris and S.W. Prentiss, J. Amer. Chem. Soc., 50, 3042 (1928).
106. N.J.T. Pickles and J. Chem. Soc., 1936, 1353.
C.N. Hinshelwood,
107. N.K. Vorob'ev and Izvest. Vysshikh. Ucheb. Zavedenii,
G.F. Titova Khim-i Khim. Tekhnol. 1958(2), 17.
(D.S.I.R. translation).
108. A. Weissberger, Organic Solvents (Vol.VII of Technique
E.S. Proskauer, of Organic Chemistry), 2nd Edition,
J.A. Riddick and E.E. Toops, Interscience Publishers (1955).
109. E.A. Moelwyn-Hughes and J. Chem. Soc., 1932, 230.
C.N. Hinshelwood,
110. M.G. Gonikberg and Izvest. Akad. Nauk.S.S.S.R., Otdel,
B.S. El'yanov Khim. Nauk., 413 (1959).
111. C.B. Monk, Electrolytic Dissociation,
Academic Press (1961).

112. C.R. Witschonke and J.Amer. Chem. Soc., 69, 2472 (1947).
C.A. Kraus,
113. H. Sadek and R.M. Fuoss *ibid*, 72, 301 (1950).
114. J. Timmermans Physico-Chemical Constants of Pure
Organic Compounds,
Elsevier Publishing Co. (1950).
115. T.E. Jordan, Vapour Pressures of Organic Compounds.
Interscience Publishers (1954).
116. I.M. Heilbron and Dictionary of Organic Compounds,
H.M. Bunbury, Eyre and Spottiswoode (1934).
117. D.P. Evans, H.B. Watson J. Chem. Soc., 1939, 1345.
and R. Williams,
118. L.F. Fieser and M. Fieser, Organic Chemistry, 3rd Edition.
Reinhold Publishing Co. (1956).
119. N.I. Sax, Dangerous Properties of Industrial
Materials,
Reinhold Publishing Co. (1957).
120. Ya Ya Makarov-Zemlyanskii, J. Appl. Chem. (U.S.S.R.) 10,
S.F. Filatov and 660 - 70 (1937).
V.S. Velichkin,
121. E. Kuss, Z. angew. Physik, 4, 201 (1952).
122. K.E. Bett, Ph.D. Thesis, University of London, (1959)
123. N.K. Vorob'ev and Izvest. Vysshikh Uchels. Zavedenii,
G.F. Titova, Khim. i Khim. Tekhnol., 1959(5), 685.
(D.S.I.R. translation).
124. J.F. Norris and A.A. Morton, J.Amer. Chem. Soc., 50, 1795, (1928).
125. J.F. Norris and C. Banta, *ibid*, 50, 1804 (1928).

126. J.F. Norris and J.T. Blake, *ibid*, 50, 1808 (1928).
127. J.F. Norris and *ibid*, 50, 1813 (1928).
D.V. Gregory,
128. B. Jones and D.J. Worsfold, *Nature*, 167, 1072 (1951).
129. A.G. Evans and S.D. Hamann, *Trans. Faraday Soc.*, 47, 25 (1951).
130. P.J.C. Fierens, A. Halleux, *Bull. Soc. Chim (Belg.)* 64, 191, (1955).
and H. Hannaert,
131. W.J. McGuire, M.S. Thesis, Northwestern University,
Evanston, Ill. (1949).
132. R.A. Robinson and R.H. Stokes, *Electrolyte Solutions*, 2nd Edition,
Butterworths Scientific Publications (1955).
133. P.W. Bridgman, *Proc. Amer. Acad. Arts and Sci.* 77,
129 (1948).
134. E. Kuss, *Erdol u Kohle*, 6, 266 (1953).
135. J.S. Rosen, *J. Chem. Phys.*, 17, 1192 (1949).
136. R.E. Gibson and *J. Amer. Chem. Soc.*, 61, 2877, (1939).
O.H. Loeffler,
137. I.S. Jacobs and A.W. Lawson, *J. Chem. Phys.*, 20, 1161 (1952).
138. K.J. Laidler and *J. Chem. Soc.*, 1938, 858.
C. Hinshelwood,
139. R.C. Tolman, *The Principles of Statistical
Mechanics*,
Clarendon Press (1938).
140. K.G. Denbigh, *The Thermodynamics of the Steady
State*,
Methuen and Co. Ltd. (1951).

141. H. Sadek and R.M. Fuoss, J. Amer. Chem. Soc., 76, 5905 (1954).
142. C.K. Ingold, Proc. Chem. Soc., 1957, 279.
143. I.L. Finar, Organic Chemistry, Vol.II,
Longmans, Green & Co. (1956).
144. L. Pauling, The Nature of the Chemical Bond,
3rd Edition,
Cornell University Press (1960).