KINETIC STUDIES OF THE THERMAL IODINE-CATALYZED ISOMERIZATION OF CIS- AND TRANS-DICHLORETHYLENE IN SEVERAL SOLVENTS

Thesis by

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Propositions

1. The vapor pressure and latent heat of evaporation of the volatile constituent from its solution may be derived from elimination curves of the type discussed by Embree in connection with the molecular still (<u>J. Ind. Eng. Chem.</u> <u>29</u>, 975 (1937)). The derivation has been carried out for a particular case.

2. The following mechanism agrees with experimental observations on the thermal isomerization of cis and trans dichlorethylene catalyzed by iodine:

$$I_2 \rightleftharpoons 2I$$
$$I - C \rightleftharpoons CI$$
$$I - T \rightleftharpoons TI$$
$$TI \rightleftharpoons CI$$

A guess as to the structure of the intermediates CI and TI might be that they are the erythro and threo dichloriodoethyl free radicals.

3. ΔH for the reaction cis-$C_2H_2Cl_2 \longrightarrow$ trans-$C_2H_2Cl_2$ is positive. From considerations of electrical interactions it can be argued that the resonance energy of cis $C_2H_2Cl_2$ ought to be larger than that of the trans isomer. That there is greater resonance in the cis isomer is in agreement with the inconclusive observation of Brockway, Beach, and Pauling that there is greater Cl=C double bond character in this isomer (<u>J.A.C.S.</u> <u>57</u> 2693 (1935)).

4. For the photochemical addition of chlorine and bromine, respectively, to the acetylene dichlorides similar reaction mechanisms may be proposed.

5. A measuring condenser of the construction shown in Fig. 1 was used for dielectric constant measurements, and an equation of the form $R = A - \frac{BC\varepsilon}{B - C\varepsilon}$ was assumed to relate the dielectric constant of the liquid to the total capacity, R, of the condenser. The constants A,B,C were determined by calibration with three standard fluids.

   The equation so obtained will hold for all values of ε if the inner and outer boundaries between fluid and glass are equipotential surfaces.

   If each element of the boundary may be considered an equipotential surface but if some elements differ in potential from others by a small fractional amount not greater than Δ, then within the calibration range the maximum fractional difference between the capacity which would be calculated by the above equation to correspond to a given dielectric constant of the filling fluid and the actual capacity of the condenser when filled with a fluid of that dielectric constant will be of the order of Δ^2.

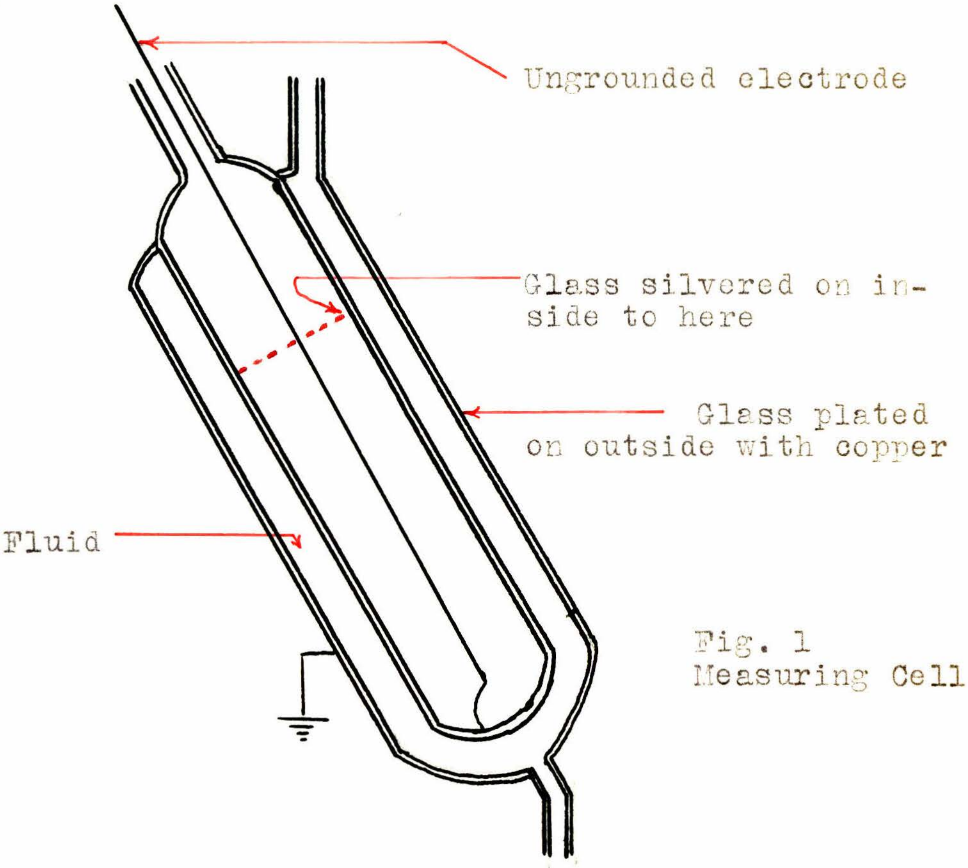


Fig. 1
Measuring Cell

6. Light from a quartz mercury arc does not affect the rate of reduction of copper oxide by hydrogen at temperatures around 200° C.

7. The evidence given by Price and Thorpe in support of the mechanism they propose for the thermal isomerization of ethyl maleate in the presence of bromine and anthracene is too meagre to exclude a simpler explanation (<u>J.A.C.S. 60</u>, 2839 (1938)).

8. There is a method of producing from an electric current containing components of various frequencies an amplitudes two corresponding currents similar to each other and to the original current in their component frequencies and amplitudes, but differing from each other in that each component in the one differs by a 90° phase angle from the corresponding component in the other.

The method is in some respects analogous to a standard method of resolving enantiamorphous isomers.

It might find application in single-sideband radio transmission.

9. There is merit in requiring the formulation of propositions by candidates for the Ph.D. degree in chemistry. It is possible that it would be worth while to permit students to register specifically for units for work on their propositions--perhaps to encourage them to do so.

10. Iodine shows an anomalous dipole moment in benzene and a conductance in cis-dichlorethylene. In connection with these phenomena and their possible explanation in terms of the formation of complexes the following measurements would be of interest to make:
a. Conductance of I_2 in $C_2H_4Cl_2$ alone and with C_6H_6 added. b. Conductance of I_2 in $C_2H_4Cl_2$ with trans $C_2H_2Cl_2$ added. c. Dipole moment of I_2 in trans-dichloroethylene. d. Dipole moment of I_2 in cyclohexane with benzene added. e. Comparative behavior of bromine.

11. The reported values of the dielectric constants of liquids are generally in very poor agreement. The preparation of a set of trustworthy values would be useful.

Acknowledgement

It has been a pleasure to conduct this research under the supervision of Professor Roscoe G. Dickinson. I wish to express my thanks to him for his assistance and interest in the work.

The research and the preparation of this dissertation have been facilitated, also, by the cooperation and assistance of a number of others. For this I acknowledge my indebtedness and gratitude to them; in particular, for the typing of this thesis, to my sister, Mary Hope Wood.

Abstract

An investigation of the thermal iodine-catalyzed isomerization of cis- and trans-dichlorethylene was carried out. The reaction cis$C_2H_2Cl_2 \longrightarrow$ trans$C_2H_2Cl_2$ and its reverse were studied in solutions in dichlorethylene, benzene, and cyclohexane, at different temperatures, and with different concentrations of iodine and dichlorethylene.

The following differential rate expression is in accord with the kinetic data for all the solutions studied:

$$\frac{d(C)}{dt} = \left[k\ K(T) + (C)\right]$$

in which equation k is a rate constant depending on iodine concentration

K is the equilibrium constant $\frac{(\text{cis}C_2H_2Cl_2)}{(\text{trans}C_2H_2Cl_2)}$

C and T are respectively cis- and trans-dichlorethylene

the concentrations are expressed in mol fractions

In 10 mol percent solutions of $C_2H_2Cl_2$ in benzene, over the temperature range studied (140° to 160° for k, 150° and 185° for K)

$$\frac{k}{\sqrt{(I_2)}} = 1.30 \times 10^{15}\ e^{-15650/T} \qquad K = .617\ e^{580/T}$$

when the time is expressed in hours.

In the other solvents the values of the numerical constants in these expressions were only slightly changed.

The mechanism following is proposed as probable for the reaction:

$$I_2 \rightleftharpoons 2I \qquad I + C \rightleftharpoons CI$$

$$CI \rightleftharpoons TI \qquad TI \rightleftharpoons T + I$$

For the estimation of the composition of the solutions containing the two dichlorethylene isomers a dielectric-constant measuring apparatus was built. With this apparatus curves relating dielectric constant to composition were obtained for several liquid systems.

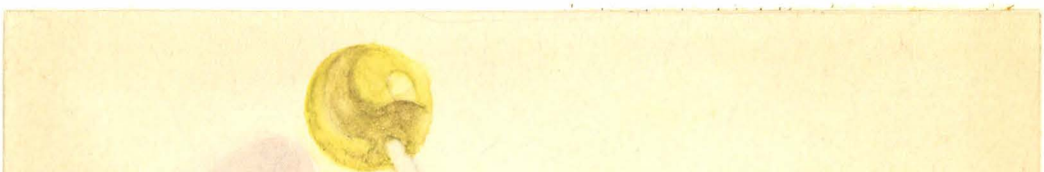
INTRODUCTION

Kinetic data of cis-trans isomerization reactions are not abundant. This research was undertaken in general to add to these data, and in particular to extend to another pair of isomers the investigation of the mechanism of iodine-catalyzed cis-trans isomerizations begun recently in these laboratories by Professor R. G. Dickinson and Mr. Harry Lotzkar.

The symmetrical dichlorethylenes were chosen for study because they are among the simplest of cis-trans isomeric pairs, because their dielectric properties offer a convenient means of analyzing their mixtures, and because they are readily available.

I

THEORETICAL



General Discussion

Cis-trans isomerism exhibited by substituted ethylenes having two different atoms or radicals attached to each carbon atom involved in the double bond is interpreted in terms of restricted rotation about a carbon-carbon double bond. The phenomenon of isomerization represents an alteration in configuration of the molecule which may be described as a 180° rotation relative to each other of the two double-bonded carbon atoms, with their substituents, about the double bond. In the case of an uncatalyzed thermal rearrangement of this kind, isomerization may occur when the thermal energy of the molecule is greater than the barrier restricting rotation. A substance which would reduce the rotation-restricting barrier without becoming permanently attached to the isomer would be expected to catalyze isomerization. Radiation absorbable by the isomers might also promote rearrangement by exciting the molecule to a state in which rotation could occur.

Many examples of isomerization reactions are known (1). One is that of the maleic-fumaric acid system. Isomerization in this system has been observed under each of the three conditions alluded to above, i.e. thermal (2), catalytic (3), and photochemical (4). Another example which might be mentioned because of its similarity to the reaction studied in this research is the conversion of cis-cinnamic acid to trans-cinnamic acid, which reaction is catalyzed by iodine (5).

It should be pointed out that isomerization may occur by other processes than one requiring a rotation about the double bond. Such a process is involved in Olson's theory(6) of the bromine-catalyzed isomerization of dibromethylene. The rearrangement may be pictured according to this theory as involving a Br^- ion which approaches the face of one of the double bonded carbon's tetrahedra opposite the bromine atom originally attached to this carbon atom. When the approaching bromine ion is close enough, the originally attached bromine atom goes off as a negative ion, the remaining positively-charged carbon atom inverts and forms a bond with the approaching bromine ion. This theory is analogous to that proposed for some Walden inversions occurring under similar conditions. As applied to Walden inversions the theory has received substantiation through experiments on inversions brought about by radioactive iodine (7). It is a theory which cannot be applied, however, to reactions catalyzed by ions other than those corresponding to the substituent groups in the isomerizing molecule, and is therefore not applicable to the reaction studied in this research.

Another theory of halogen-catalyzed isomerizations which is applicable to the present case has been suggested by Berthoud (8) in connection with a study of the iodine-sensitized photochemical isomerization of cinnamic acid. According to this theory the reaction catalyst is atomic iodine produced by photochemical dissociation of the iodine molecules. Presumably an iodine atom may react with the acid by breaking the double bond and attaching itself to one of the freed valences. This process supposedly leads to the formation of an unstable iodine-cinnamic acid complex with a single bond in place of the double bond. Because the strong rotation-restricting characteristics of the double bond are no longer present this complex may undergo a rotation before it decomposes, so that when this decomposition does take place either isomer may result depending on what configuration the complex happens to have at that time. This theory is much less restricted in scope than the ionic one discussed above, and is thought to offer an essentially correct explanation of the isomerization studied in this thesis.

The final product in a thermal isomerization, catalyzed or uncatalyzed, must obviously be an equilibrium mixture of the isomers. This is not true in the case of a photochemical isomerization. A case in point is that of maleic and fumaric acids. The free energy relations are such that at any temperatures suitable for experiments equilibrium corresponds to practically pure fumaric acid. Thus it is found that thermal catalyzed (3) and uncatalyzed (2) isomerizations are capable of converting maleic acid entirely into fumaric acid and are not capable of doing the reverse. It is possible, however, to convert fumaric acid to maleic acid by irradiation with ultraviolet light (4). The effectiveness of absorbed light in bringing about an isomerization, and the composition of the steady state mixture would be expected to depend on the absorption coefficients of the isomers for the radiation used, the type of excitation produced in the molecule by the radiation absorbed, and the behavior to be expected from a molecule thus excited. A theory of photochemical isomerization involving these considerations has been proposed by Olson(9).

It asserts that a light absorption effective in isomerization produces an electronically excited isomer molecule. A lower rotation-restricting barrier is attributed to the excited molecule than to the normal one. Accordingly, if the oscillational energy of the excited molecule is sufficient, it may actually rotate before returning to the normal state. Now if the potential energy of the configuration of the excited molecule corresponding to one of the isomers is different from that corresponding to the other, it is to be presumed that the velocity of rotation will be slower while the molecule is passing through the configuration with the higher energy. The time in this configuration will be longer than in the other. If the probability that an excited molecule will return to the normal state is independent of the configuration of the excited molecule and if the lifetime of a rotating molecule is long compared with its period of rotation its probability of returning as a cis molecule will be proportional to the fraction of the rotational period spent in the cis configuration (meaning by cis configuration any configuration which on deactivation produces a normal cis molecule). When the rotation is slow this fraction would be expected to be either very small or nearly 1 depending on whether the cis or trans configuration represents the lower potential energy, and it would be expected to approach ½ as the velocity of rotation becomes larger. With the mentioned assumptions the theory is seen to predict that the composition of mixtures of cis-trans isomeric pairs corresponding to the photochemical steady state would shift with increasing temperature toward one of half and half. It also explains the fact that it is often possible to obtain photochemically from the more stable isomer mixtures with a preponderance of the less stable one.

Olson and Maroney studied the photochemical isomerization of gaseous dichlorethylene (10). The values they obtained for the compositions of steady state mixtures at various temperatures did not differ very much from the values for the thermal equilibrium mixtures which they reported. This may be a fortuitous coincidence. On the other hand, subsequent to their experiments evidence has been brought forth indicating that chlorine atoms are produced in dichlorethylene by radiation of the proper wavelength (11). It is possible that under the conditions of Olson's and Maroney's experiments chlorine atoms were produced and that the isomerization was actually a chlorine-atom-catalysed isomerization. This would explain the similarity between the compositions at equilibrium and in the photochemical steady state.

A large variety of catalysts are effective in different isomerizations. Among them are halogens, hydrogen halides (12), oxides of nitrogen (13), colloidal sulphur (14), the alkali metals, palladium, platinum (15), selenium (16). An attempt has been made to correlate the effectiveness of these catalysts with the existence of unpaired electrons in them or in species in equilibrium with them (15). This attempt was somewhat discredited, however, by the finding (17) that the catalytic efficiency did not bear any simple relationship to the magnetic moment of the catalyst.

The question may be raised as to whether or not in the case of an isomerization involving rotation about the double bond an inversion is also required. If the rotation is pictured as occurring about one bond when by some means the other has been broken then, if the carbon atoms have retained their tetrahedral configuration, an inversion will certainly be necessary before the broken bond can be reformed with the molecule in the isomerized configuration. On the other hand, if the tetrahedral structure is lost during rotation the question as to whether or not an inversion accompanies the rotation is one of definition. The significant inquiry would seem to be as to whether an isomerization requires the occurrence of two distinct processes which may be called rotation and inversion, the rotation being able to occur without the necessary occurrence of the inversion, or whether it involves only one independent process. Experimental evidence on this point seems to be lacking.

Preliminary Discussion of Experimental Results

It would seem profitable at this point to anticipate the detailed presentation of the data obtained in this research and the discussion of individual series of experiments by a preliminary discussion of the conclusions to which these experimental data lead. This method of presentation should facilitate a criticism of the research in that it should be easier to bear in mind the comparatively few proposed generalizations while examining the experimental details than to remember all these details while examining the conclusions proposed to be drawn from them.

The reactions studied were the thermal iodine-catalyzed isomerizations

$$\mathrm{cis}C_2H_2Cl_2 \longrightarrow \mathrm{trans}C_2H_2Cl_2$$
$$\mathrm{trans}C_2H_2Cl_2 \longrightarrow \mathrm{cis}C_2H_2Cl_2$$

These reactions were carried out in the liquid state in systems containing only the two isomers and the catalyst, and also in solutions of these substances in benzene and in cyclohexane. The reaction temperatures varied from 140° to 160° in the rate experiment and were 150° and 185° in equilibrium experiments. Iodine concentrations varied from .014 to .0013 expressed in mol fractions, and experiments were also conducted in which no iodine was present. The dichlorethylene concentrations studied were 100, 20, 10, and 1 mol percent, the 20% and 1% solutions being represented each by only one experiment. The reason that more experiments at different concentrations were not made is that those that were made indicated no appreciable change in behavior with concentration, and that the analytical method employed was neither precise at low total $C_2H_2Cl_2$ concentrations nor at any total $C_2H_2Cl_2$ concentrations for which a separate calibration of dielectric constant of the solution against its composition in terms of cis- and trans-dichlorethylene had not been made. Variations in the reaction time of rate experiments were from about seven to about fifty hours.

The important generalizations of the experimental observations that can be made are:

(1) That the expression for the rate of isomerization in solutions of 10 mol % $C_2H_2Cl_2$ in benzene may be represented by the equation

$$\frac{d(\mathrm{cis}C_2H_2Cl_2)}{dt} = k\,[K(\mathrm{trans}C_2H_2Cl_2) - (\mathrm{cis}C_2H_2Cl_2)]$$

where K is the equilibrium constant $\frac{(\mathrm{cis}C_2H_2Cl_2)}{(\mathrm{trans}C_2H_2Cl_2)}$

and $K = .617\ e^{+580/T}$

where k depends on the iodine concentration

and $k = 1.30 \times 10^{15}\ e^{-15550/T}\ \sqrt{(I_2)}$

where the concentrations are expressed in mol fractions. This equation represents the observed results over the complete range of conditions studied, within the experimental accuracy.

(2) That the rate expression is identical in form and its constants are nearly the same for reactions in the other solvents, i.e. in $\mathrm{cis}C_2H_2Cl_2$, $\mathrm{trans}C_2H_2Cl_2$, and C_6H_{12}.

Any proposed reaction mechanism must be compatible with these generalizations. As possibilities might be considered the two theories of halogen catalysis of cis-trans isomerization referred to in the general discussion. As mentioned there, the ion catalyzed mechanism in the form proposed by Olson (6) is not applicable; however, it would be possible to propose an ion catalyzed mechanism which would not be subject to the limitations of Olson's scheme. Moreover, such a mechanism would be expected to involve a half power dependence on iodine concentration as was observed. The alternative proposal of an atom-catalyzed reaction (8) would also lead to a square root dependence of rate on iodine concentration. This latter mechanism which has been accepted as preferable for reasons which will be discussed may be represented as involving the following elementary reactions.

$$I_2 \rightleftarrows 2I \quad (1) \text{ and } (1')$$

$$I + C \rightleftarrows CI \quad (2) \text{ and } (2')$$

$$CI \rightleftarrows TI \quad (3) \text{ and } (3')$$

$$TI \rightleftarrows T + I \quad (4) \text{ and } (4')$$

where C represents cis$C_2H_2Cl_2$

T represents trans$C_2H_2Cl_2$

CI represents a complex formed by the reaction between C and I

TI represents a complex formed by the reaction between T and I

The usual treatment of this reaction scheme assuming that the atoms and complexes remain at low concentrations yields the rate expression

$$-\frac{d(C)}{dt} = \sqrt{\frac{k_1}{k_{1'}}(I_2)}\;\frac{k_2k_3k_4(C) - k_{2'}k_{3'}k_{4'}(T)}{k_{2'}k_{3'} + k_{2'}k_4 + k_3k_4}$$

This mechanism and rate expression is identical in form with that suggested by Dickinson and Lotzkar (5) for the iodine catalyzed cis-cinnamic acid isomerization. The experimental results differ from theirs in that in their experiments the back reaction, trans $\longrightarrow$ cis, was negligible, whereas in the present case the velocities of both reactions are of the same order of magnitude and consequently none of the constants in the above rate expression is zero.

It may be seen that this derived rate expression is of the same form as the empirical one set forth in the first generalization and becomes equal to it upon equating.

$$\frac{k}{\sqrt{(I_2)}} = \sqrt{\frac{k_1}{k_1'}}\left[\frac{k_2k_3k_4}{k_2'k_3' + k_2'k_4 + k_3k_4}\right]$$

and

$$K = \frac{k_2'k_3'k_4'}{k_2k_3k_4}$$

There are two experimental observations which bear on the question of choosing between an ionic and an atomic mechanism for the catalysis. One is the second of the above generalizations particularly the part with reference to the near equality of the constants in the rate expression for the reaction in cis$C_2H_2Cl_2$ and in trans$C_2H_2Cl_2$ or benzene. If an ionic mechanism were involved a considerable effect on the rate might be expected by changes of solvent involving changes in dielectric constant of the solutions. The dielectric constant of cis$C_2H_2Cl_2$ is about 9.25 whereas that of benzene and of trans$C_2H_2Cl_2$ is about 2.25. The fact that the observed reaction rate starting with pure cis$C_2H_2Cl_2$

is almost the same as that starting with trans$C_2H_2Cl_2$ or that observed in benzene solutions indicates that this solvent effect was not present.

The second observation which reinforces this argument against an ionic mechanism was made rather accidentally. It was originally proposed to determine the extent of the reaction in a given experiment by measuring the change in dielectric constant of the solution containing the iodine catalyst. In attempting to do this with some of the solutions in cis$C_2H_2Cl_2$ the electric oscillations in the dielectric constant apparatus were feeble and with the more concentrated iodine solutions it was impossible to set the circuit into oscillation. It was guessed that this quenching of oscillation was caused by dielectric losses in the solution due to conductance. To test this theory qualitative conductance measurements were made, and it was found that iodine solutions in cis$C_2H_2Cl_2$ did indeed conduct. The approximate data are as follows for conductance measurements made in a cell with reported cell constant k = 0.21 (specific conductance of cell filling liquid = k x measured conductance of cell).

Conc. of I_2 (gms/cc)	Solvent	Measured resistance of conductance cell (ohms)
.005	cis$C_2H_2Cl_2$	92,000
.02	cis$C_2H_2Cl_2$	63,000
saturated	CCl_4	$>10^7$
.05	C_6H_6	$>10^7$
0	cis$C_2H_2Cl_2$	6×10^6

These data imply that in the cis$C_2H_2Cl_2$ - I_2 solutions there is a considerable ionic concentration and that this is greater by a factor of at least 1000 than the ionic concentration in corresponding C_6H_6 - I_2 solutions. This experiment in connection with the observed solvent independence of the rate of isomerization speaks rather strongly against an ionic mechanism for the reaction.

Concerning the structural chemistry of the isomerization, in particular concerning the structure of the two postulated intermediate iodine-dichlorethylene complexes, and the question as to whether these two complexes should be considered as remaining for any considerable length of time as distinguishable from each other the results of the present research would seem to yield no information. Nor does it seem possible on the basis of any existing evidence to decide these questions.

Data possibly bearing by analogy on this question are these concerning the photochlorination and photobromination of the cis and trans dichlorethylenes. The reported facts are that:

(a) The rate of the photochlorination may be expressed by an equation of the form (22)(23)

$$\frac{-d\ C_2H_2Cl_2}{dt} = k(Cl_2)\sqrt{I\ abs}$$

(b) The initial rates of the photobrominations are given by expressions of the same form, although in this case the reverse reaction, i.e. the photo decomposition of $C_2H_2Cl_2Br_2$, will also occur (21)(23).

(c) The rates of the photochlorinations of the two isomers are identical (22)(23).

(d) The rates of the photobrominations of the two isomers are different by a factor of about two (19)(20).

(e) The quantum yields are high (21)(22)(23)(24).

The first and last of these facts have led Schumacher to propose the following chain reaction

$$Cl_2 \longrightarrow 2Cl \qquad 1$$

$$Cl + C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3 \qquad 2$$

$$C_2H_2Cl_3 + Cl_2 \longrightarrow C_2H_2Cl_4 + Cl \qquad 3$$

$$2\ C_2H_2Cl_3 \longrightarrow C_2H_2Cl_2 + C_2H_2Cl_4 \qquad 4$$

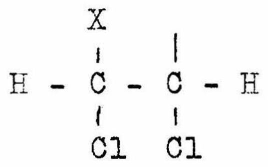
The rate expression to which such a mechanism leads is

$$-\frac{d(C_2H_2Cl_2)}{dt} = \frac{k_3}{\sqrt{k_4}}(Cl_2)\sqrt{I\ abs}$$

It is seen that the rate constant of reaction 2 is not involved.

This reaction mechanism seems to be a reasonable one. If it is to be accepted, then aside from the possibility of a coincidence, the equal chlorination rates of the cis and trans isomers imply that the $C_2H_2Cl_3$ produced in reaction 2 from trans-dichlorethylene must be the same as the $C_2H_2Cl_3$ produced from cis-dichlorethylene. Because of fact (b) quoted above, it would seem reasonable to assume the same type of mechanism for the brominations as for the chlorinations. If this is done, fact (d) requires that the intermediate, $C_2H_2Cl_2Br$, be different for different isomers.

These two requirements exclude a number of otherwise possible structures for the intermediates. A probable structure which they do not exclude is the normal free radical structure.



$$\mathrm{H - \underset{Cl}{\overset{X}{C}} - \underset{Cl}{\overset{|}{C}} - H}$$

A structure of this kind will certainly fulfill the requirement of yielding identical radicals in the reaction between a chlorine atom and either cis- or trans-dichlorethylene. If this structure is correct for the intermediate in the photobromination, the interesting implication arises that the erythro and threo dichlorobromoethyl free radicals are distinct species and retain their distinct configuration until they react. This is because the rates of bromination of the two isomers are different, but according to the proposed mechanism do not depend on the rate of the elementary reaction involving these isomers, only on that of reactions involving the complexes.

The only relation between the foregoing argument concerning the probability that a free radical of this structure is the intermediate in the photobromination of dichlorethylene and the question of the structure of the intermediate in the iodine catalyzed isomerization of dichlorethylene is that both reactions are assumed to proceed by a halogen atom mechanism, and that bromine and iodine atoms are similar. No difficulty is introduced in having to assume retention of configuration of the bromo free radical until reaction with bromine while assuming an isomerization through the iodo free radical. In the bromination the free radicals are presumably used up very rapidly, whereas in the case of the isomerization they exist in equilibrium with the dichlorethylene and iodine.

By setting the exponent of e in the empirical expression for the temperature dependence of K equal to $\frac{\Delta H}{RT}$ for the reaction cis$C_2H_2Cl_2 \longrightarrow$ trans $C_2H_2Cl_2$ a value for **the** quantity, ΔH = 1150 cal/mol, may be obtained from the benzene solution data. The value obtained from the cyclohexane data is identical. The values of ΔF in cal/mol for the reaction at 150° calculated from the equilibrium constants are 750, 750, and 620 respectively, for the solvents dichlorethylene, benzene, and cyclohexane. From these values a value for ΔS for the reaction at 150° may be computed to be about 1 cal/mol degree.

II

THE EXPERIMENTAL RECORD

The Dielectric Constant Apparatus

The dielectric constant measuring apparatus was constructed in connection with this research. It employs the heterodyne method of comparing capacitances. The essential parts of the apparatus are (a) the power supply, (b) the detector-amplifier, (c) the crystal oscillator, (d) the oscillator containing the measuring cell or precision condenser in its resonant circuit, (e) the liquid containing capacitator or measuring cell, (f) the precision condenser.

(a) The Power Supply. A circuit diagram of the power supply is shown in Fig. 4a. It is in general of conventional design. The bank of neon bulbs was included in the circuit to improve the constancy of output voltage. They do not seem to be very effective for this purpose; however, as will be mentioned later, freedom from relatively slow voltage fluctuations is not essential. A 0-300 voltmeter measures the output voltage. By pressing the appropriate pushbutton a milliammeter measuring up to 50 milliamperes may be made to indicate either the total output current or the current through the neon bulbs.

The output (direct current and filament supply) is connected to each of three four-pronged female plugs from which it is taken by separate shielded cables to the two oscillators and to the detector.

(b) The Detector-Amplifier. There are no critical

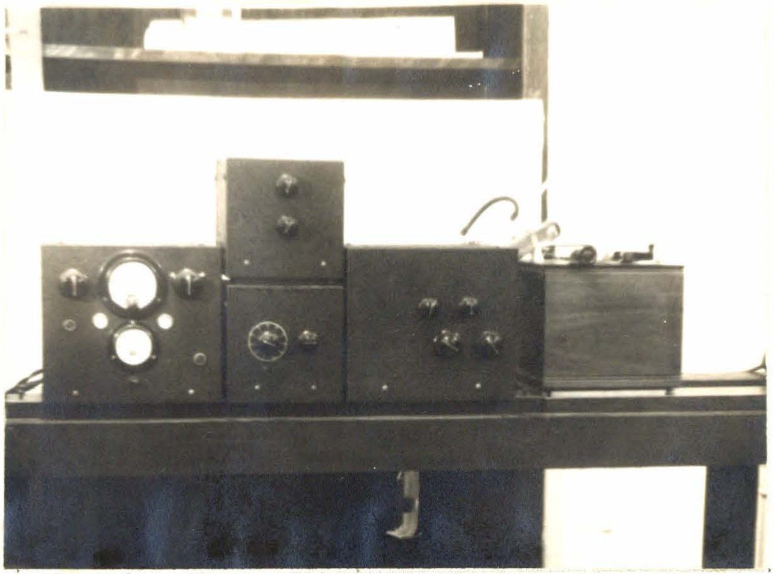


Fig. 2. Dielectric Constant Apparatus
(Front)

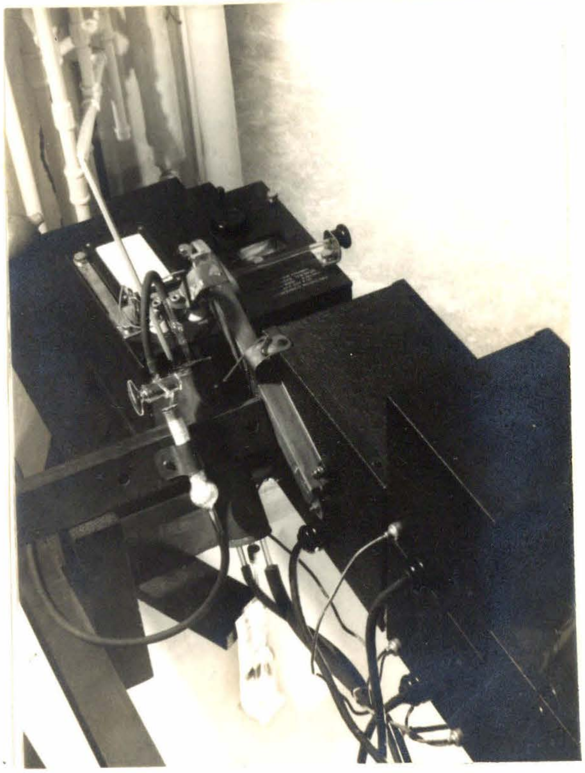


Fig. 3. Dielectric Constant Apparatus
(Back)

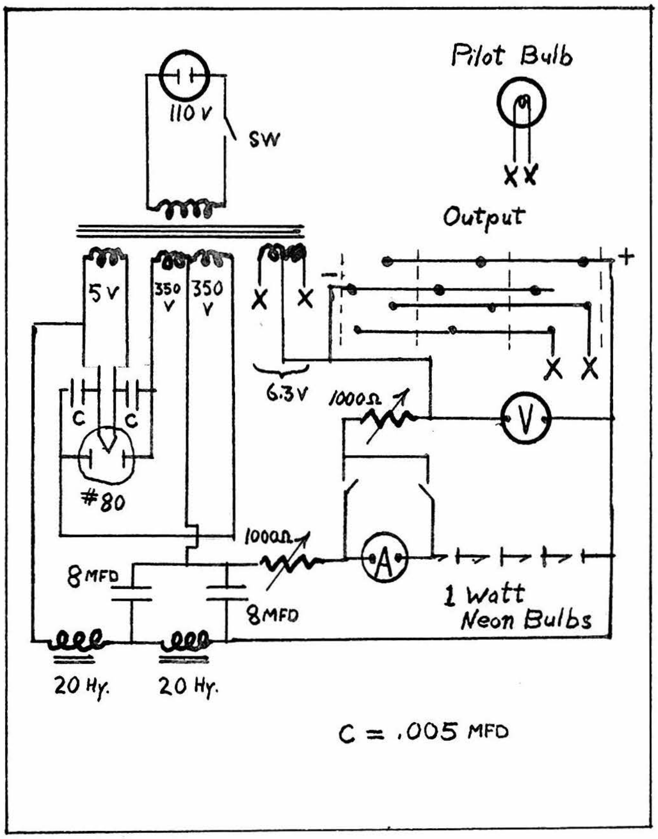


Fig. 4a. Power Supply

requirements for this part of the apparatus. The circuit used was described in the Radio Amateur's Handbook, 14th edition on page 119, as a "A Shielded Two-Tube Receiver" A 6K7G and a 6C5 were used in place of the tubes suggested in the description. The power is brought in by a cable at the back. There are also two small plugs for coupling the oscillator outputs to the detector tuning coil by a link, and a plug for an earphone or speaker.

(c) The Crystal Oscillator is controlled by a quartz plate resonating at 1.75 megacycles. This crystal is mounted in a thermostating unit to increase frequency stability. As a matter of fact great stability of this frequency against slow drifts is not required, but it was originally thought that the circuit might be arranged in a way that would make this desirable. In the power supply leads from each of the oscillators is included a r.f. choke coil to prevent undesired coupling between the oscillators. It was found that this addition to the circuit made possible obtaining beat notes of a few cycles per second, whereas before the chokes were inserted, audio frequencies of less than several hundred cycles could not be obtained because of the locking of the oscillators. There are two controls on the crystal oscillator; one tunes the resonant circuit, the other controls the amplitude of oscillation.

(d) The Capacity Controlled Oscillator comprises a simple inductively coupled regenerative oscillator circuit a part of the tuning capacity of which is furnished either

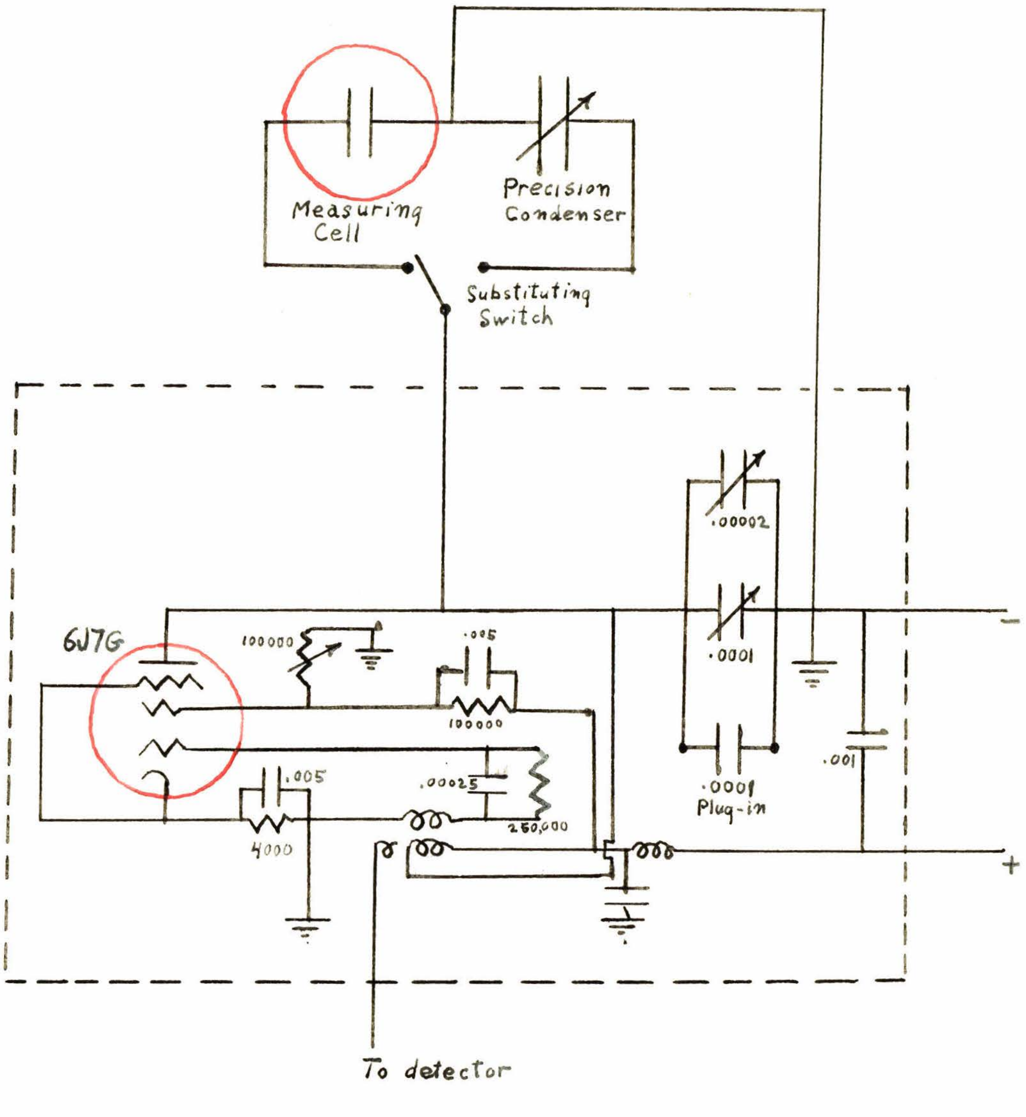


Fig. 4b. Capacity-Controlled Oscillator and Measuring Circuit

by the precision condenser or by the measuring cell. This capacity is connected in parallel with two variable tuning condensers and with a plug-in fixed condenser. By changing the plug-in tuning coil and the plug-in tuning condenser a large flexibility in frequency and capacity measuring range is available. The desirability of mechanical rigidity in this oscillator was borne in mind. The ungrounded connection from the oscillator to the external capacity circuit is shielded and fastened solidly in place. In addition to the two tuning condenser controls there is an amplitude control and a switch which changes the capacity of the resonant circuit by a small, fixed amount. This switch may be used to check the balancing of the precision condenser against the measuring cell at a different frequency from that at which it was carried out. Such a check is useful inasmuch as the oscillator frequency is a double valued function of the beat note produced. Each oscillator, the power supply, the detector and the precision condenser are enclosed in electrically shielding boxes.

(e) The Measuring Cell is shown in Fig. 1. The construction with the electrodes outside the glass was chosen because it was originally intended to use the cell with solutions containing iodine. That procedure was abandoned for reasons that will be mentioned. There are, however, certain possible advantages to the use of such a cell. As implied, it can be used with metal corroding liquids. It can be cleaned with less precaution than might be required by a condenser with metal immersed in the liquid. It can be designed to cover a range of dielectric constants from one to infinity within a finite capacity range. The disadvantages are that it is less sensitive to dielectric constant changes, it requires more liquid for a given capacitance (with any reasonable sensitivity), its calibration is less straight forward.

The cell is enclosed in a brass tube with stoppers at the top and bottom arranged to permit the circulation of thermostating water. The brass tube is grounded.

(f) The Precision Condenser is a General Radio Type 722-D Serial No. 420.

It has two capacity ranges, one from 100 to 1100 mmfd and the other from 25 to 110 mmfd. The lower range is used. The smallest division on the worm dial represents .02 mmfd. Usually readings are make to the nearest .01 mmfd. Because of small deviations from linearity of capacity against scale reading, it was found desirable to calibrate the condenser. The condenser can be set extremely accurately by matching of beat notes, but it was found that these settings are not exactly reproducible from day to day. The maximum variation observed in precision condenser reading corresponding to an air-filled measuring cell was about one small division, i.e. about .02 mmfd. It seems probable that this small change which corresponds to a fractional change in capacity of less than .001 could be attributed to a small temperature or humidity coefficient in the condenser;

it was not quartz insulated.

(g) Circuit and Operation. The method of comparing the capacities of the cell and the precision condenser is essentially a null method in that it involves replacing the cell capacity by the precision condenser capacity in an oscillating circuit which is otherwise kept constant. The precision condenser is then adjusted until this substitution causes no alteration in frequency of the oscillation. Since the substitution involves the throwing of a single switch, it is very rapid and it was found quite satisfactory to compare the two beat notes by memory, i.e. it was not found necessary to have any fixed standard of pitch. It is because the dielectric constant determination depends only on constancy of beat note before and after a rapid substitution of capacities, that slow creep in the frequency of the oscillators caused by gradual voltage or temperature fluctuations is not detrimental.

Some experimentation in selecting a switch for capacity substitution was necessary. It was found that some switches would not always come to rest in exactly the same position. This would cause a slight change in capacity and would make accurate capacity determinations impossible. The switch finally used is a small rotary single-pole double-throw type which was slightly modified with stops to assure reproducibility of the rest positions. This switch was mounted directly on the precision condenser near the terminals and as far as possible from the operator. It is operated by a knob connected to the switch through a six-inch glass rod. The grounded sides of the precision condenser, measuring condenser and capacity controlled oscillator are permanently connected together. The ungrounded end of the oscillator's resonant circuit is connected to the center of the substituting switch, and the ungrounded sides of the cell and precision condenser are connected respectively to the two outside electrodes of the switch. The parts are arranged so as to make these ungrounded leads as short as possible. Shielding was made as complete as necessary.

Unless stated to the contrary all measurements of dielectric constant were made at 25° C. To make a measurement the liquid is drawn into the measuring cell by sucking through a $CaCl_2$ tube. The pump for circulating thermostat water is turned on. The substituting switch is turned to the cell position and then any suitable audio beat note is produced in the earphone of the detector by tuning the variable condensers in the capacity controlled oscillator. (Theoretically, the lower the beat note, the more precise may be the capacity matching). The substituting switch is now thrown to the precision condenser position and the precision condenser adjusted until a beat note is obtained which is not altered by throwing the substituting switch. The oscillator tuning condenser may now be slightly changed to give a different beat note and then if on throwing the substituting switch no change in tone is produced, it may be assumed that the capacities of the two circuits are equal. After the measurement the liquid is rinsed out of the cell with a volatile solvent which is then evaporated by blowing air through the cell with an atomizer bulb.

Calibration of the Precision Condenser

The makers guarantee the precision condenser readings on the lower range (25-110 micromicrofarads) to be accurate to within ± 0.2 mmfd. Since it was desired to measure small differences in capacity with an error considerably less than this figure a calibration was necessary. This was made in the following way:

A second variable condenser, which happened in this case to be an older General Radio Precision Condenser Type 222 No. 482, was connected into the dielectric constant apparatus in parallel with the condenser to be calibrated. By means of a switch it was possible to connect in parallel with these two condensers a third small fixed condenser, or to disconnect it. The procedure was to start with one of the precision condensers at minimum capacity and the other at high capacity setting. The small fixed capacity would be out of the circuit at this point. The total capacity of the parallel condensers was now matched with a standard capacity which standard was then unchanged throughout the calibration and served, therefore, as a means of bringing the total capacity of the parallel precision condenser circuit back to its initial value while varying the values of the individual precision condensers. The readings of the precision condensers were recorded. The switch was now thrown to add to the sum of the capacities of the precision condensers that of the small fixed condenser. Now the total capacity of the parallel circuit would not equal that of the standard. To regain the equality one of the precision condensers was changed. The two precision condenser readings were again recorded. The switch was now turned back to remove the small fixed capacity and the parallel capacities returned to the standard value by varying the other precision condenser setting. After recording the readings the fixed capacity switch is again thrown and the process repeated.

This stepwise procedure of varying the two precision condensers, one from a low to a high and the other from a high to a low capacity, while keeping the total capacity constant is the basis of the calibration. The difference between any two consecutive different readings of either of the precision condensers should be the same and equal to the value of the small added (or subtracted) fixed capacity. By dividing the total capacity change indicated by the precision condenser by the number of steps in bringing about this change a value for the capacity of the small fixed condenser may be obtained which should not be in error by a greater percentage than the percent error in the measured total capacity change. If the precision condenser is good and the total change is a fairly large fraction of its total capacity, this latter error should be very small.

Calling the thus determined value of the capacity of the little fixed condenser x it should be possible to construct a set of values $Nx - C$ which would represent the true values of the capacity corresponding to consecutive readings of the precision condenser obtained in the calibration experiment. N assumes consecutive integral values and C is a constant. The value of N for the first reading and the approximate value of C are to be chosen so that the differences between the values of Nx - C and the recorded condenser readings are as small as possible throughout the series. If now the value Nx - C is subtracted in every case from the corresponding condenser reading, a set of values will be obtained the irregularities of which will correspond approximately to deviations from a linear relationship between condenser reading and capacity.

After tabulating the values of Nx - C, the condenser readings R, and the differences between these two quantities, it might be observed that by readjusting the values of C and x the averages of the absolute values of the differences would be decreased. One should then make this readjustment. That this step is justified may be seen by considering its implications. The readjustment of x to give smaller values of R - Nx - C means that the original value assumed for x was obtained by using a somewhat incorrect value for the total capacity change. This incorrect value could have arisen because of the fact that the error in capacity indicated by the initial reading was not the same as that of the capacity of the final reading. Then by readjusting x at the present stage one is essentially using an average value rather than a value obtained from the difference of but two readings. That C should be readjusted to give as small deviations as possible is only to say that the most probable average deviation over the whole range is zero.

Assuming that the deviations of the capacity from the condenser reading could be attributed to a periodic deviation due to irregularities in the driving worm superimposed on an irregularity in the worm gear or condenser plates, a separate calibration was made for the worm correction and for the other correction.

The worm calibration was carried out as described above. The computed deviations were plotted against the readings of the worm dial. The curves obtained appeared approximately sinusoidal, and it was assumed that the periodic error in the worm could best be approximated by a sine function and that the deformation in the curves obtained experimentally was largely due to the superimposition of errors in the worm gear and condenser plates. Accordingly, a true sine curve was plotted with amplitude and phase corresponding approximately to the averages of these quantities indicated in the experimental curves. Worm corrections determined from this idealized curve were then added to the deviations observed in the long-range calibration. This should make the resulting long-range deviations independent of the periodic worm errors. This treatment made plotting much easier since the long-range correction curve was thus made comparatively smooth.

It might be well at this point to recapitulate the significance of capacity values obtained from precision condenser readings with the use of these correction plots. Since the calibration was made without any capacity standard but the condenser being calibrated itself, it cannot be expected to have given curves from which absolute values may be obtained. What it should be possible to obtain by correcting the condenser readings by the values shown on the calibration curves is a quantity which varies linearly with the capacity and which never differs from it by more than the maximum error in the capacity read from the condenser. Actually, the maximum error in the corrected values of capacity should be considerably less than the maximum inaccuracy of the precision condenser, more nearly equal to the average inaccuracy. For any use to which the precision condenser in the dielectric apparatus has been put, the absolute capacity values are of no consequence, only linearity of capacity with corrected reading being essential.

The experimental calibration data are given on the following pages. The worm calibration data are first. The first column gives the precision condenser reading, R, at each step of the calibration. The second column gives the difference between consecutive readings. The third column is N and the fourth R - Nx - C where the significance of these quantities is that already discussed. The last column contains the actual reading on the worm dial. (One revolution of the dial corresponds to a change in reading of 5.00 mmfd.)

The long-range calibration data are included in the next table. Column 1 gives the consecutive readings of the dielectric constant apparatus precision condenser. Column 2 contains the readings of the other condenser. These readings are irrelevant to the calibration of the first condenser but are included in the data since from them could be obtained a calibration of the other condenser if that should ever be desired. In the third column an x indicates that the small fixed condenser was in the circuit and an o that it was disconnected. Column 4 is N, column 5 a preliminary value of Nx. Column 6 is the worm correction for the given reading. The next column is the condenser reading corrected for the worm error. The eighth column is R - Nx - f(Θ) - C and the last column is the same thing where x and C have been readjusted (see discussion). The calibration plot is a plot of the values in this last column against the values of R in the first column. In this plot the axis corresponding to o correction has been placed so that the curve falls about equally above and below it.

The experimental worm fluctuation data (column 4 vs column 5) are plotted in Fig. 5. The following two graphs are respectively the idealized worm correction plot and the long-range correction plot. **To correct a condenser reading both the correction indicated by Fig. 5a , and that indicated by Fig. 6, should be added to the reading.**

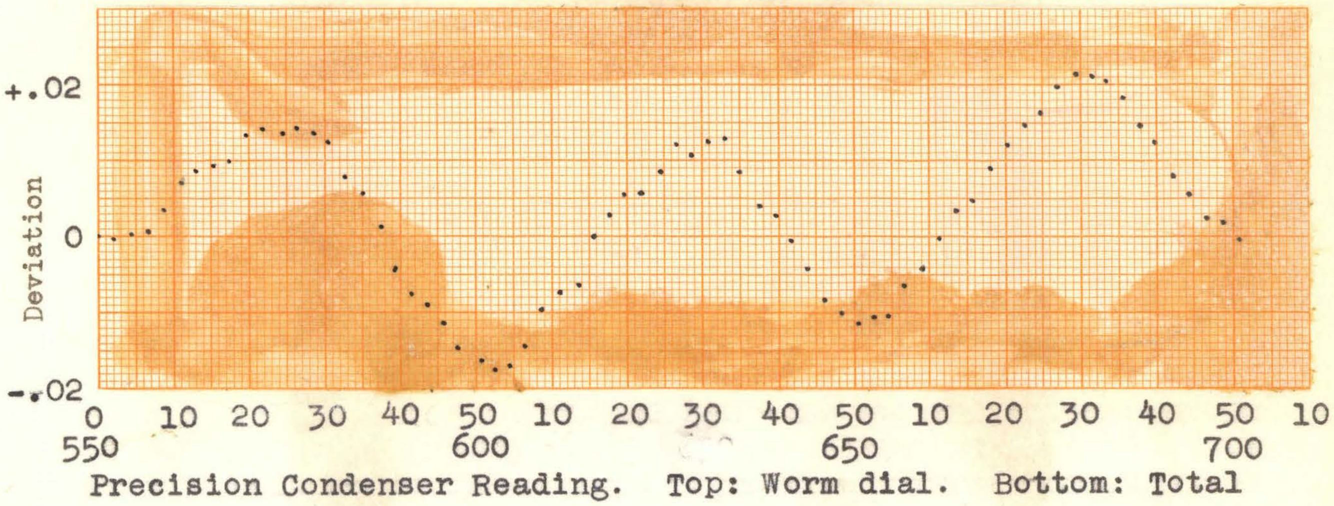


Fig. 5. Precision Condenser Worm Error Correction Data

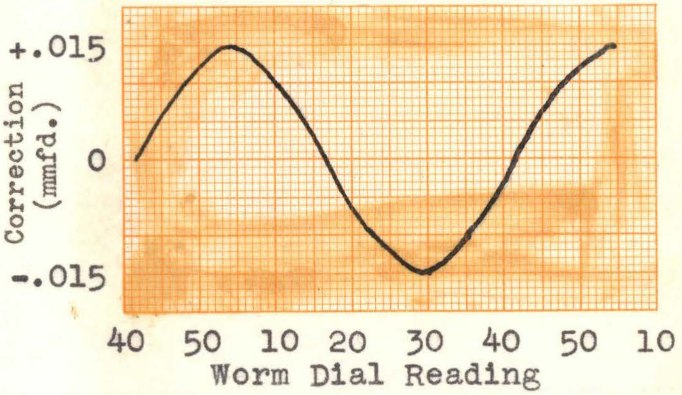


Fig. 5a. Idealized Worm Correction Curve

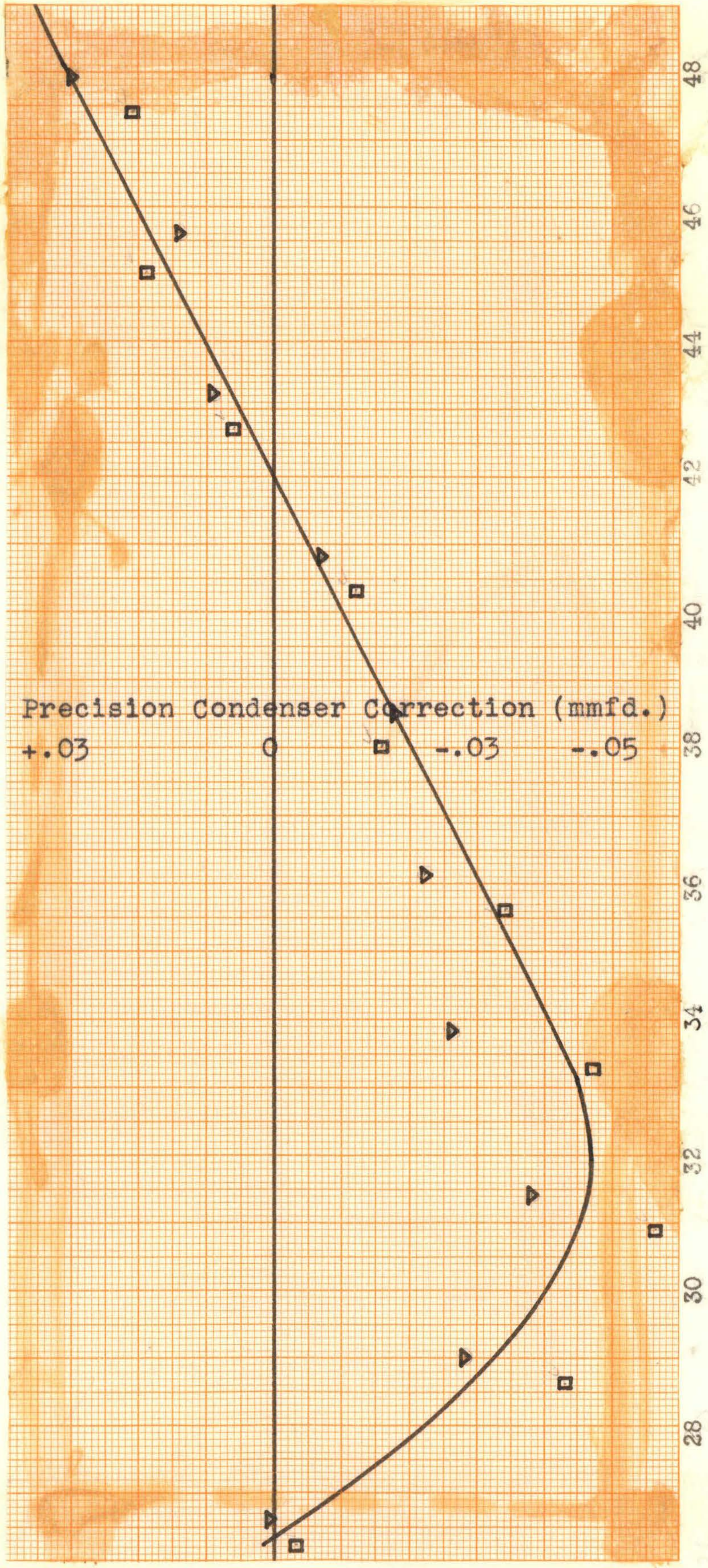

Precision Condenser Correction (mmfd.)
+.03
0
-.03
-.05
Precision Condenser Reading
28
30
32
34
36
38
40
42
44
46
48

Fig. 6. (begun)

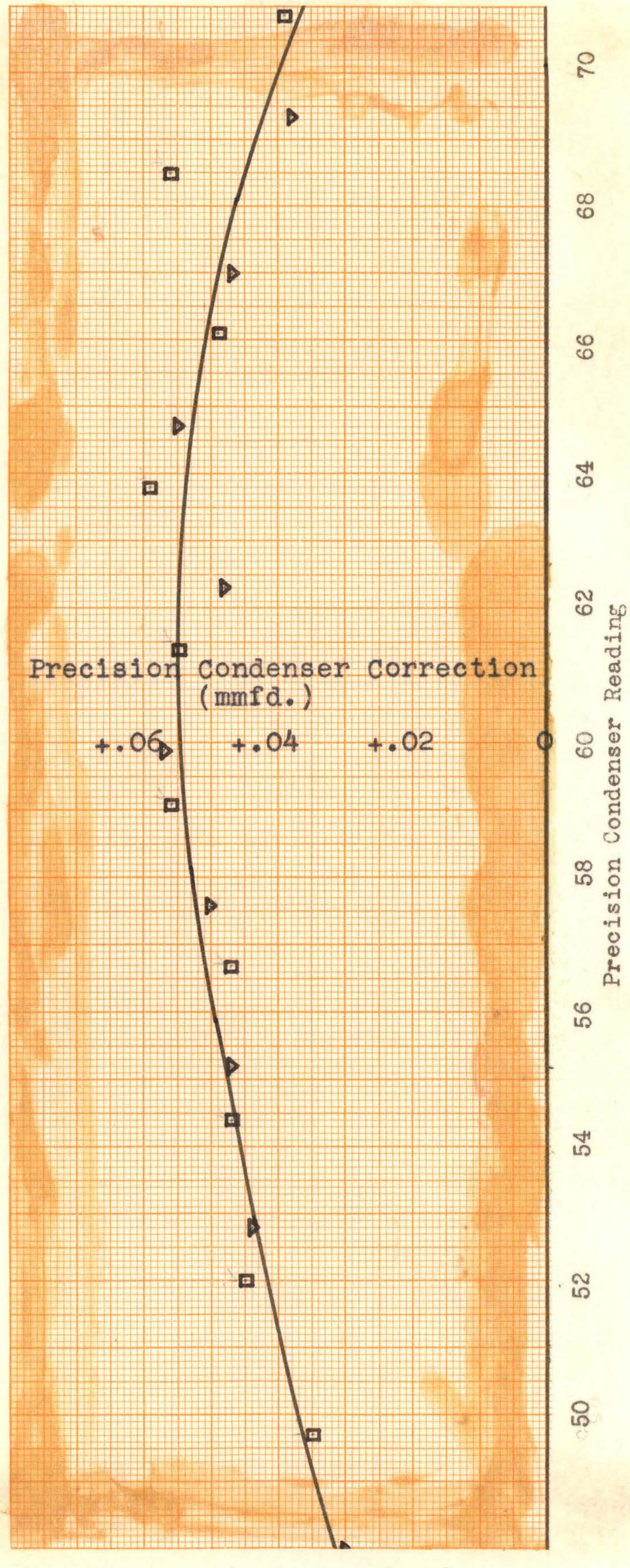


Fig. 6. (continued)

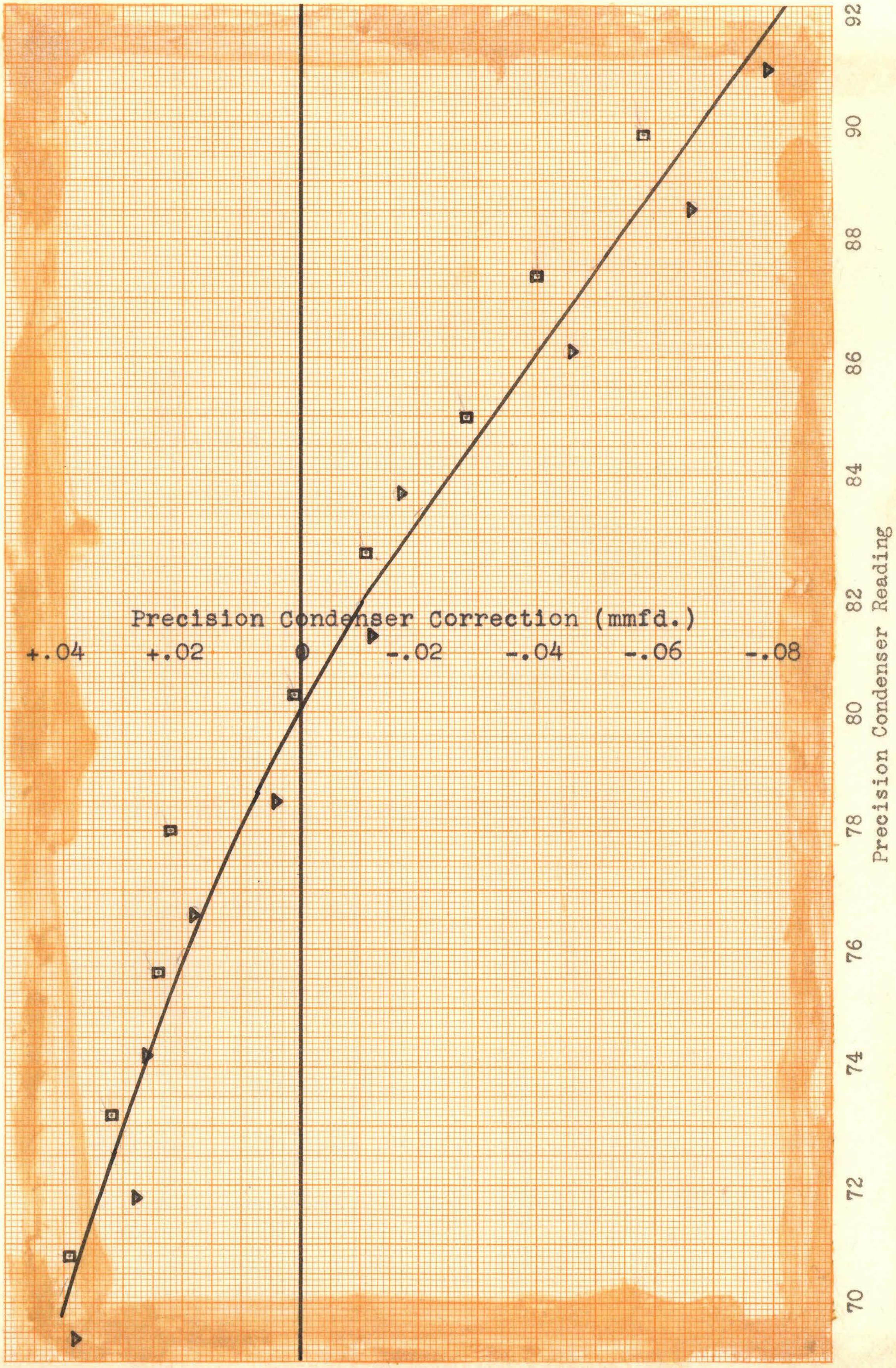


Fig. 6. (continued)

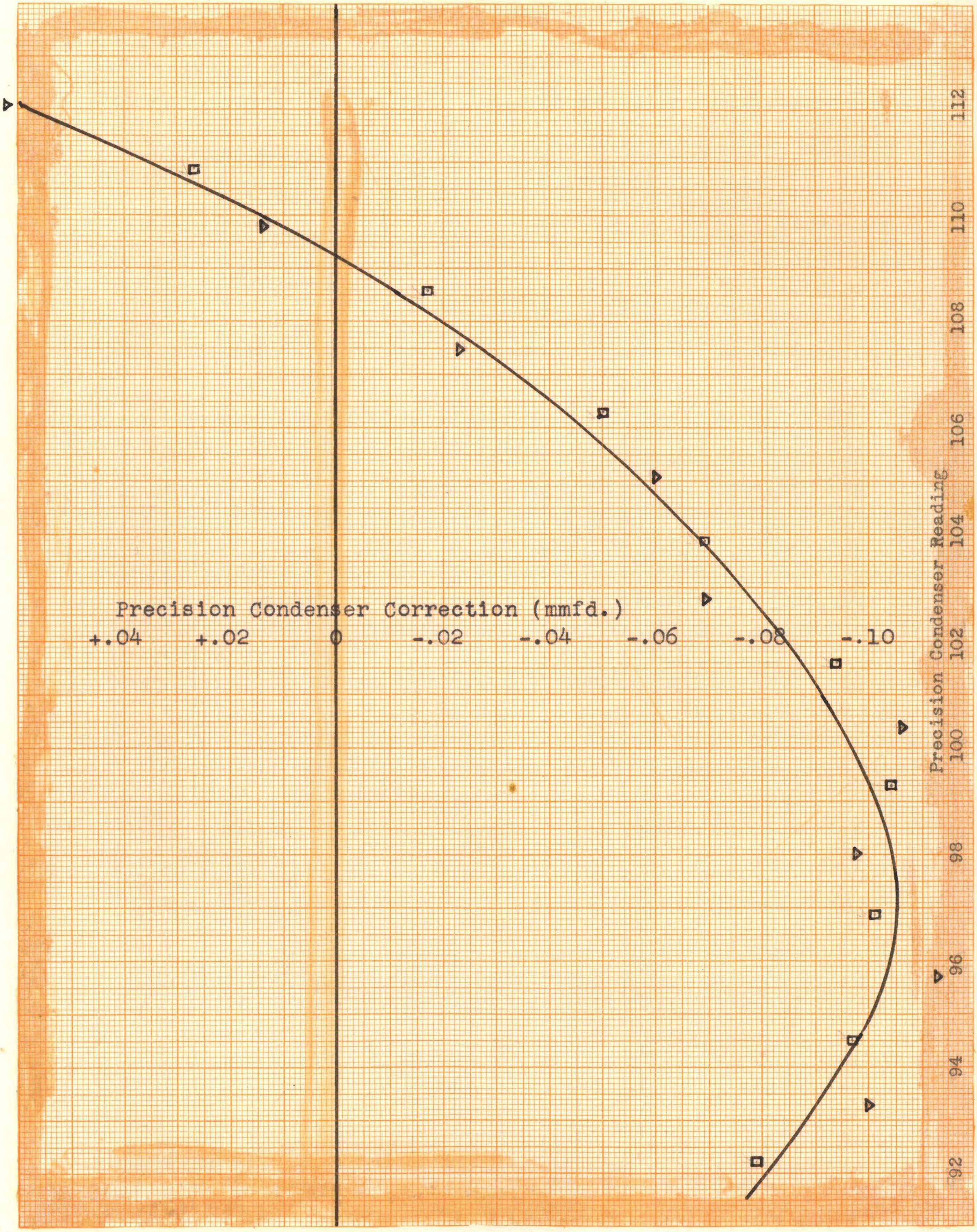


Fig. 6 (concluded)

Table 1

Worm Calibration Data

1	2	3	4	5
55.000		0	.0000	0.00
	.218			
55.218		1	-.0004	2.18
	.219			
55.437		2	+.0002	4.37
	.219			
55.656		3	+.0008	6.56
	.221			
55.877		4	+.0034	8.77
	.222			
56.099		5	+.0070	10.99
	.220			
56.319		6	+.0086	13.19
	.219			
56.538		7	+.0092	15.38
	.219			
56.757		8	+.0098	17.57
	.222			
56.979		9	+.0134	19.79
	.219			
57.198		10	+.0140	21.98
	.218			
57.416		11	+.0136	24.16
	.219			
57.635		12	+.0142	26.35
	.218			
57.853		13	+.0138	28.53
	.217			
58.070		14	+.0124	30.70
	.214			
58.284		15	+.0080	32.84
	.216			
58.500		16	+.0056	35.00
	.214			
58.714		17	+.0012	37.14
	.213			
58.927		18	-.0042	39.27
	.215			
59.142		19	-.0076	41.42
	.217			
59.359		20	-.0090	43.59
	.216			
59.575		21	-.0114	45.75
	.215			
59.790		22	-.0148	47.90
	.217			

Table 1 (continued)

1	2	3	4	5
60.007		23	-.0162	0.07
	.217			
60.224		24	-.0176	2.24
	.219			
60.443		25	-.0170	4.43
	.221			
60.664		26	-.0144	6.64
	.223			
60.887		27	-.0098	8.87
	.221			
61.108		28	-.0072	11.08
	.219			
61.327		29	-.0066	13.27
	.225			
61.552		30	-.0000	15.52
	.221			
61.773		31	+.0026	17.73
	.221			
61.994		32	+.0052	19.94
	.219			
62.213		33	+.0058	22.13
	.221			
62.434		34	+.0084	24.34
	.222			
62.656		35	+.0120	26.56
	.217			
62.873		36	+.0106	28.73
	.220			
63.093		37	+.0122	30.93
	.218			
63.311		38	+.0118	33.11
	.215			
63.526		39	+.0084	35.26
	.214			
63.740		40	+.0040	37.40
	.217			
63.957		41	+.0026	39.57
	.215			
64.172		42	-.0008	41.72
	.215			
64.387		43	-.0042	43.87
	.214			
64.601		44	-.0086	46.01
	.217			
64.818		45	-.0100	48.18
	.217			
65.035		46	-.0114	0.35
	.219			

Table 1 (continued)

1	2	3	4	5
65.254		47	-.0108	2.54
	.219			
65.473		48	-.0102	4.73
	.222			
65.695		49	-.0066	6.95
	.221			
65.916		50	-.0040	9.16
	.222			
66.138		51	-.0004	11.38
	.222			
66.360		52	+.0032	13.60
	.220			
66.580		53	+.0048	15.80
	.223			
66.803		54	+.0094	19.03
	.221			
67.024		55	+.0120	20.24
	.221			
67.245		56	+.0146	22.45
	.220			
67.465		57	+.0162	24.65
	.222			
67.687		58	+.0198	26.87
	.220			
67.907		59	+.0214	29.07
	.218			
68.125		60	+.0210	31.25
	.218			
68.343		61	+.0206	33.43
	.216			
68.559		62	+.0182	35.59
	.215			
68.774		63	+.0148	37.74
	.216			
68.990		64	+.0124	39.90
	.214			
69.204		65	+.0080	42.04
	.216			
69.420		66	+.0056	44.20
	.215			
69.635		67	+.0022	46.35
	.218			
69.853		68	+.0018	48.53
	.216			
70.069		69	-.0006	0.69

Table 2a

Precision Condenser Calibration Data
First Run

1	2	3	4	5	6	7	8	9
121.340	0.00	0	51	120.717	+.005	121.345	.372	.427
119.035	0.00	x		118.350	-.003	119.032	.318	.368
119.035	7.40	0	50					
116.735	7.40	x		115.983	.000	116.735	.248	.293
116.735	9.15	0	49					
114.420		x		113.616	+.005	114.425	.191	.231
	10.20	0	48					
112.110		x		111.249	-.008	112.102	.147	.182
	11.00	0	47					
109.770		x		108.882	+.009	109.779	.104	.134
	11.67	0	46					
107.455		x		106.515	-.012	107.443	.072	.097
	12.30	0	45					
105.095		x		104.148	+.013	105.108	.040	.060
	12.89	0	44					
102.760		x		101.781	-.015	102.745	.036	.051
	13.43	0	43					
100.395		x	42	99.414	+.015	100.410	.004	.014
	13.97	0						
98.045		x	41	97.047	-.015	98.030	.017	.022
	14.50	0						
95.660		x	40	94.680	+.013	95.673	.007	.007
	15.01	0						
93.300		x	39	92.313	-.012	93.288	.025	.020
	15.52	0						
90.885		x	38	89.946	+.010	90.895	.051	.041
	16.02	0						
88.520		x	37	87.579	-.010	88.510	.069	.054
	16.50	0						
86.110		x	36	85.212	+.008	86.118	.094	.074
	16.98	0						
83.725		x	35	82.845	-.008	83.717	.128	.103
	17.44	0						
81.335		x	34	80.478	+.005	81.340	.138	.108
	17.90	0						
78.955		x	33	78.111	-.003	78.952	.159	.124
	18.34	0						
76.570		x	32	75.744	+.001	76.571	.173	.133
	18.78	0						
74.185		x	31	73.377	+.001	74.186	.191	.146
	19.22	0						
71.815		x	30	71.010	-.003	71.812	.198	.148
	19.64	0						
69.425		x	29	68.643	+.005	69.430	.213	.158
	20.07	0						

Table 2a (continued)

1	2	3	4	5	6	7	8	9
67.055		x	28	66.276	-.006	67.049	.227	.167
	20.49	0						
64.660		x	27	63.909	+.009	64.669	.240	.175
	20.90	0						
62.315		x	26	61.542	-.011	62.304	.238	.168
	21.32	0						
59.910		x	25	59.175	+.013	59.923	.252	.177
	21.72	0						
57.570		x	24	56.808	-.013	57.558	.250	.170
	22.13	0						
55.175		x	23	54.441	+.014	55.189	.252	.167
	22.54	0						
52.835		x	22	52.074	-.015	52.820	.254	.164
	22.96	0						
50.190		x	21	49.707	+.014	50.204	.503	
	23.39	0						
47.945		x	20	47.340	-.015	47.930	.410	.150
	23.80	0						
45.560		x	19	44.973	+.014	45.574	.399	.134
	24.21	0						
43.220		x	18	42.606	-.013	43.207	.399	.129
	24.62	0						
40.840		x	17	40.239	+.011	40.851	.388	.113
	25.03	0						
38.500		x	16	37.872	-.010	38.490	.382	.102
	25.45	0						
36.120		x	15	35.505	+.008	36.128	.377	.092
	25.87	0						
33.760		x	14	33.138	-.006	33.754	.384	.094
	26.29	0						
31.390		x	13	30.771	+.004	31.394	.377	.082
	26.70	0						
29.015		x	12	28.404	-.003	29.012	.392	.092
	27.10	0						
26.610		x	11	26.037	+.001	26.611	.426	.121
	27.50	0						
24.035		x	10	23.670	-.003	24.032	.638	.328
	27.90	0						
18.445		x	9	21.303	-.012	18.433	3.870	3.555
	28.30	0						

Table 2b

Precision Condenser Calibration Data
Second Run

1	2	3	4	5	6	7	8	9
10.000	27.94	x	9	21.177	+.012			11.574
23.560		0	10	23.530	-.009			.389
	27.56	x						
26.170		0	11	25.883	+.007			.117
	27.16	x						
28.580		0	12	28.236	-.009			.077
	26.76	x						
30.925		0	13	30.589	+.013			.064
	26.34	x						
33.295		0	14	32.942	-.012			.073
	25.94	x						
35.610		0	15	35.295	+.014			.086
	25.52	x						
37.975		0	16	37.648	-.015			.104
	25.11	x						
40.295		0	17	40.001	+.015			.108
	24.71	x						
42.660		0	18	42.354	-.014			.126
	24.60	x						
44.975		0	19	44.707	+.012			.139
	23.89	x						
47.350		0	20	47.060	-.011			.141
	23.49	x						
49.670		0	21	49.413	+.009			.155
	23.08	x						
52.030		0	22	51.766	-.007			.165
	22.68	x						
54.370		0	23	54.119	+.005			.167
	22.27	x						
56.730		0	24	56.472	-.001			.167
	21.87	x						
59.075		0	25	58.825	-.001			.176
	21.47	x						
61.425		0	26	61.178	+.004			.175
	21.04	x						
63.785		0	27	63.531	-.006			.179
	20.63	x						
66.135		0	28	65.884	+.008			.169
	20.22	x						
68.500		0	29	68.237	-.010			.176
	29.81	x						
70.850		0	30	70.590	+.011			.159
	19.39	x						
73.235		0	31	72.943	-.013			.152
	18.96	x						
75.570		0	32	75.296	+.014			.144
	18.52	x						

Table 2b (continued)

1	2	3	4	5	6	7	8	9
77.955		0	33	77.649	-.015			.142
	18.09	x						
80.300		0	34	80.002	+.015			.121
	17.63	x						
82.695		0	35	82.355	-.014			.109
	17.19	x						
85.040		0	36	84.708	+.012			.092
	16.71	x						
87.430		0	37	87.061	-.012			.080
	16.23	x						
89.780		0	38	89.414	+.010			.062
	15.74	x						
92.175		0	39	91.767	-.010			.041
	15.24	x						
94.530		0	40	94.120	+.007			.023
	14.74	x						
96.900		0	41	96.473	-.005			.019
	14.23	x						
99.250		0	42	98.826	+.002			.016
	13.70	x						
101.595		0	43	101.179	+.001			.026
	13.16	x						
103.930		0	44	103.532	-.005			.051
	12.60	x						
106.255		0	45	105.885	+.005			.070
	12.01	x						
108.590		0	46	108.238	-.009			.103
	11.37	x						
110.880		0	47	110.591	+.011			.147
	10.63	x						
113.205		0	48	112.944	-.013			.200
	9.76	x						
115.490		0	49	115.297	+.015			.241
	8.50	x						
117.810		0	50	117.650	-.014			.304
	5.96	x						
120.060		0	51	120.003	+.015			.379

Calibration of the Measuring Cell

Figure 1 is a diagram of the measuring cell. It has already been partially described on page 26. The liquid-containing part of it was about 20 cm long and 3 cm in diameter. In making measurements it was filled completely which required about 13cc of fluid. The silvering on the outside, which was reinforced by a heavy coating of electrically plated copper, covered the condenser completely extending a distance on the fluid inlet and outlet tubes. The silvering on the inside extended only partly up the cell as indicated in the diagram and was electrically connected to the circuit by a rod extending through the top center tube and connected through a length of flexible wire to the silvering by low melting solder. The silvering on the inside was protected by a coat of clear laquer. The cell was rigidly fastened in the apparatus and neither it nor its connecting wires were ever changed in position.

The equation that was assumed to relate the electrical capacity, R, of the cell as measured on the precision condenser to the dielectric constant, ε, of the fluid in it is

$$R = A - \frac{BC\varepsilon}{B - C\varepsilon}$$

Where R is the capacity as measured by the precision condenser, ε is the dielectric constant of the fluid and A, B, and C are constants which were determined by calibration with fluids of known dielectric constant. This equation represents the capacity of a circuit containing three condensers, two of which are in series, the third being in parallel with the series circuit. The capacity of the third condenser is A, that of the first and second being B and $C\varepsilon$ respectively. In applying this equation to the cell A is the lead capacity, B is the capacity of a hypothetical condenser containing only glass as dielectric, and $C\varepsilon$ is the capacity of a hypothetical condenser containing only a fluid of dielectric constant ε, these two hypothetical condensers being in series. The approximation involved in assuming the validity of the above equation for expressing the capacity of the measuring cell is that the inner and outer boundaries between glass and fluid in the cell are each equipotential surfaces. This approximation seems reasonable because the thickness of glass and liquid layers is quite uniform and small compared to their length. In any case, this equation is probably the best simple equation that could be used for interpolating between calibration points. Actually, for the purposes of the research dealt with in this thesis no known relationship between dielectric constant and cell capacity is required. It is only necessary that the capacity vary smoothly with the dielectric constant, a condition hard to be avoided. This is true because empirical curves were drawn relating the composition of the different solutions directly to the corrected precision condenser reading when the cell was filled with these solutions.

However, it seemed desirable to calibrate the cell in terms of the dielectric constant of the filling fluid because by so doing it would be possible to obtain from the recorded solution data dielectric constants for the solutions, which will make it possible to use the data with a different cell or measuring apparatus.

To determine the constants in the capacity equation it is evident that at least three calibrating fluids of known dielectric constant are necessary. By determining the precision condenser reading when the measuring cell is filled with each of these fluids three simultaneous equations in terms of A, B, and C may be set up, and values for these parameters may be obtained. Preliminary evaluations of A, B, and C were made in this way. The three calibrating fluids used were air, benzene, and chlorobenzene. (Care was taken, of course, to purify and dry the liquids). After these preliminary values had been derived they were used in the equation to calculate the dielectric constant of other liquids that had been measured in the cell, and then by comparing these calculated ε's with the best values obtainable from the literature, the parameters A, B, and C were slightly adjusted to distribute the deviations over all the reliable liquids.

Actually, since the dielectric constant is the quantity desired to be calculated, an equivalent of the above equation in the form

$$\varepsilon = \frac{L(R - M)}{1 - N(R - M)}$$

was the one for which the parameters were determined in the way described. The finally accepted values were L = 0.02506, M = 3.090, N = 0.006890. The following tabulation exhibits I the fluid, II the experimental value of (R - 3.090), i.e. (R - M), III the dielctric constant of the fluid calculated using these accepted values of L, M, and N, IV the reported ε, V the literature reference from which these values were obtained.

I	II	III	IV	V
air	31.311	1.0004	1.0006	25
CCl_4	55.100	2.225	2.227	26
C_6H_5Cl	88.021	5.605	5.612	27
C_2H_5Br	104.275	9.281	9.21	28
$C_2H_4Cl_2$	107.440	10.36	10.36	29
C_6H_6	55.795	2.271	2.272	30

To facilitate dielectric constant determinations the values of ε corresponding to corrected condenser readings was calculated at a number of points along the complete range of the precision condenser, and through these points an ε vs R graph was plotted. By the same procedure a magnified portion of this curve was plotted for a short range of ε values in the region in which the common non-polar liquids lie. These two graphs are reproduced in Fig. 8a and Fig. 8b.

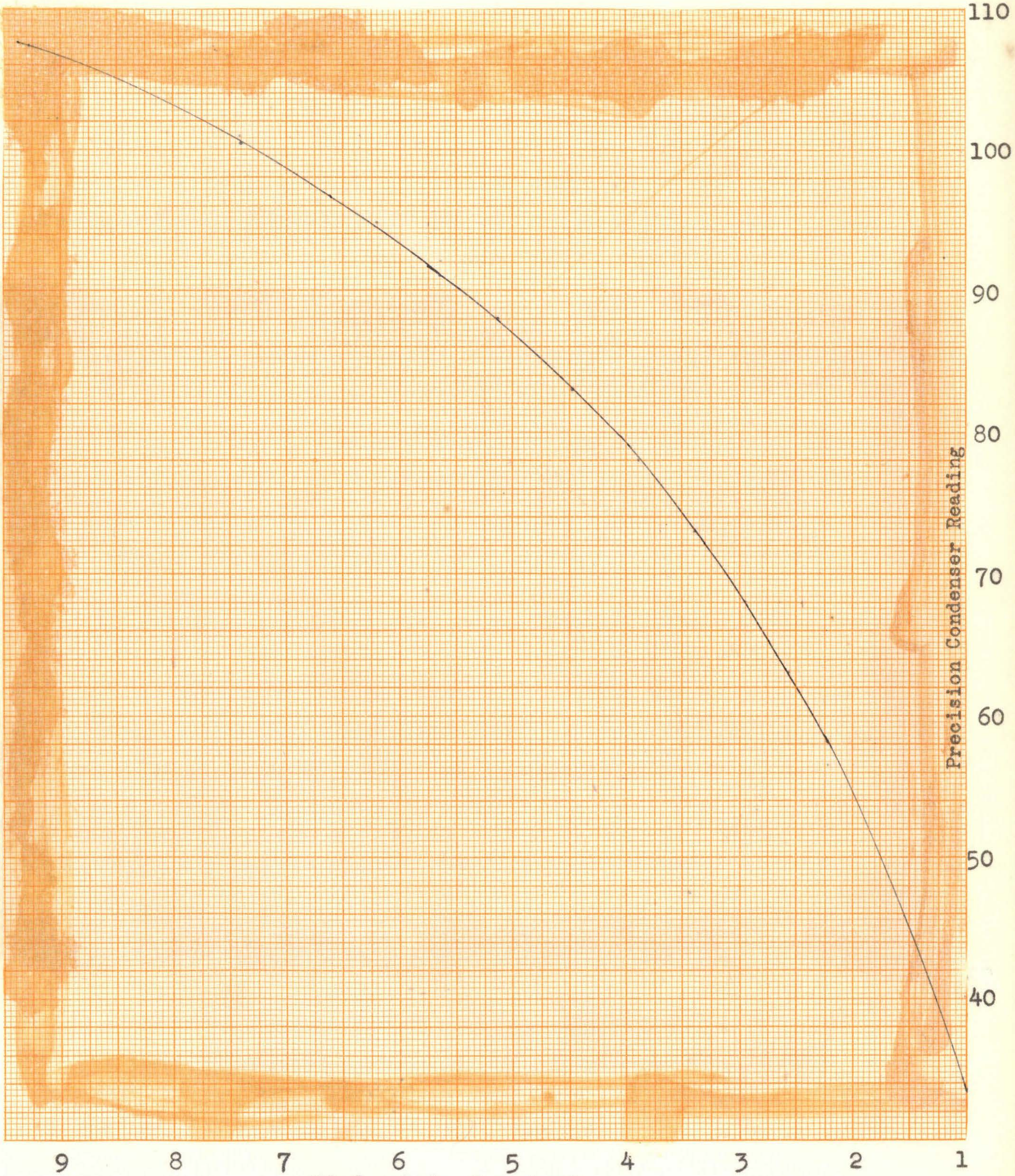

110
100
90
80
70
60
50
40
Precision Condenser Reading
9
8
7
6
5
4
3
2
1
Dielectric Constant

Fig. 8a.

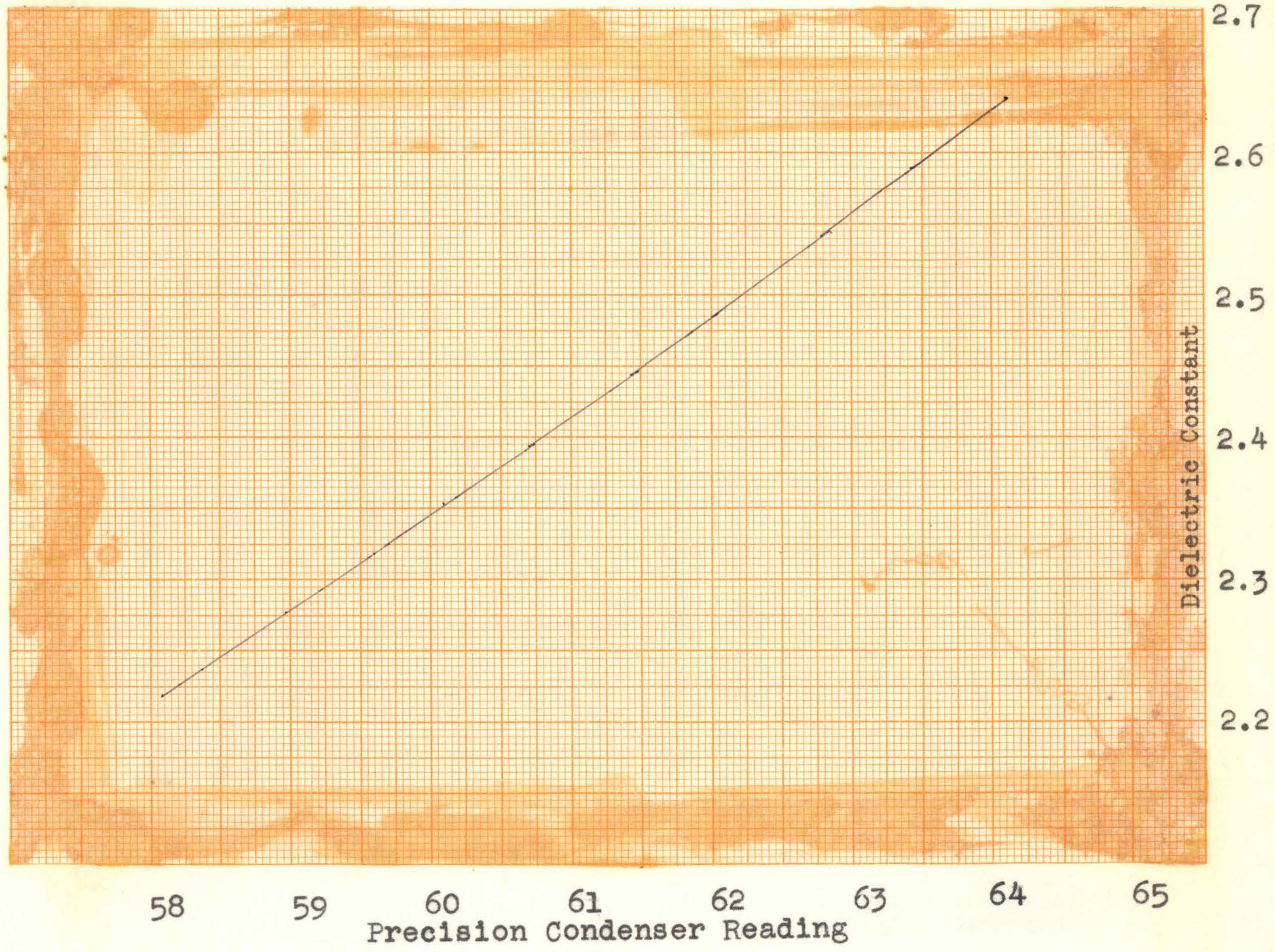

2.7
2.6
2.5
2.4
2.3
2.2
Dielectric Constant
58
59
60
61
62
63
64
65
Precision Condenser Reading

Fig. 8b.

Materials

The cis and trans dichlorethylenes were prepared by fractional distillation of a mixture of the isomers obtained from Eastman Kodak Company. It was found desirable to carry out the distillation under CO_2 to avoid oxidation by air. Pure trans dichlorethylene was noticeably subject to air oxidation. The fractional distillations were carried out with a five foot column filled with glass helices, and it was found possible to obtain large fractions boiling at a constant temperature and having identical dielectric constants at the beginning and end of the fraction. After purification the liquids were stored under CO_2 in flasks having delivery tubes sealed with mercury to prevent access to air. The same method of storage was applied to the stock solutions of dichlorethylene in the solvents, benzene and cyclohexane. Liquid for use was forced out by CO_2. The liquids thus stored were found to retain their original dielectric constant throughout the series of experiments (several months).

Thiophene-free benzene was fractionally crystallized, dried, and distilled.

Eastman Practical cyclohexane was shaken with fuming sulfuric acid, washed with sodium hydroxide solution, then with water, dried, and distilled.

The iodine used in these experiments was sublimed from potassium iodide-iodine mixture, resublimed, powdered, and then stored in a desiccator

Procedures

The considerations which should underlie choices of experimental procedures in any kinetic studies of this kind are (1) the physical and chemical characteristics of the reactants, (2) the available apparatus, (3) the degree of precision required, (4) the interdependence of the proposed procedures. In the present research the primary procedure-determining factors were the analytical method and the reaction temperature and pressure.

At the outset a method of analysis based on dielectric constant measurement was chosen. The chemical properties of cis-trans isomeric pairs are usually so similar that estimation methods based on differences in physical properties are often to be preferred. The difference between the dielectric constants of cis- and trans-dichlorethylene is large and offers convenient analytical method. This method requires a calibration of the composition of the dichlorethylene solutions with respect to their dielectric constants. It will only be possible to determine compositions in this manner in two-component liquids, e.g. solutions of the dichlorethylenes in each other, or in more-component systems in which the concentrations of all but two of the components are known on other grounds, e.g. solutions of the dichlorethylenes in which the total $C_2H_2Cl_2$ concentration is known. In this latter case the complete calibration graph would be a surface in n dimensional space where n is the number of components. A calibration of this kind for a three component system would be inconvenient to carry out and was avoided in these experiments by making a whole series of experiments with solutions having nearly constant total dichlorethylene concentrations.

Calibrations were made by mixing in various proportions two solutions, one of a known concentration of cis$C_2H_2Cl_2$ in the solvent, and the other of nearly the same concentration of trans$C_2H_2Cl_2$ in the solvent. The corrected readings of the precision condenser when filled with these mixtures was determined and these readings plotted against composition, as a rule, against the mol % cis$C_2H_2Cl_2$ present. These same two calibrating solutions were then used in the subsequent reaction experiments. The reason for plotting the data in terms of the mol fraction cis$C_2H_2Cl_2$ present is that if the two calibrating standard solutions were of nearly but not exactly the same $C_2H_2Cl_2$ concentration, mixtures resulting from the isomerization of the dichlorethylene in one of the standard solutions will be of nearly but not exactly the same total $C_2H_2Cl_2$ concentration as that of mixtures so obtained from the other stock solution, and these concentrations will be nearly but not exactly the same as the total $C_2H_2Cl_2$ present in any of the calibrating mixtures. However, because of the near equality of the dielectric constant of trans$C_2H_2Cl_2$ and that of benzene or cyclohexane, $\left(\frac{\partial \varepsilon}{\partial(\text{trans}C_2H_2Cl_2)}\right)_{\text{cis}\,C_2H_2Cl_2}$ will be small and as an approximation may be neglected. If this is done the plot of condenser reading vs mol percent cis$C_2H_2Cl_2$ will be valid for isomerized mixtures obtained from either stock solution.

The calibration data for the dichlorethylene, benzene, and cyclohexane solutions is given in the following pages in tabular and graphic form. Originally the composition vs condenser reading data was plotted directly on a large scale graph. In order to reduce the plots to a size convenient to be included in this thesis without sacrificing accuracy, the data was here plotted as deviation from linearity between cell capacity and composition. Data for solutions of dichlorethylene in CCl_4 and in dibutyl phthalate is also set forth. These datawere obtained in contemplation of isomerization studies in these solvents. These studies were abandoned, however, in the case of dibutyl phthalate because a reaction between this substance and iodine appeared to occur at 150° , and in the case of the CCl_4 because an as yet unexplained reaction occurred in CCl_4-$C_2H_2Cl_2$ in the absence of I_2. This reaction seemed not to be a simple isomerization since the expected equilibrium for that case seemed not to be obtained.

The isomerizations were carried on in thick glass ampoules. As a rule the stock solutions were transferred to the ampoules from which the air had been dispelled by a stream of CO_2. This was not always done, however, since no appreciable difference in rate of reaction was observed between experiments from which air had presumably been excluded by considerable boiling and sealing off under CO_2 , and those in which steps were taken only to keep the partial pressure of air low. This latter precaution was always observed except in preliminary qualitative experiments.

Iodine was introduced in weighed amounts in weighed glass capsules which were broken into the ampoules. The compositions were determined by weighing the ampoules empty and after they were filled and sealed off. Sealing off was done in the experiments in $C_2H_2Cl_2$ solutions under CO_2, and in the solvent experiments was done while the ampoules, cooled in CO_2 snow, were being pumped on to remove air. Blank experiments were made to prove that the fractional distillation of the components of these frozen solutions did not appreciably alter their compositions. In all manipulations care was exercised to keep moisture from the solutions because it was known that traces of water were very effective in altering the dielectric constants.

The sealed ampoules were preheated in boiling liquids (usually cyclohexanol) for a time estimated to bring their temperature to approximately the reaction temperature. They were quickly transferred from the preheating baths to the thermostat. In the case of the rate experiments conducted at 160° the thermostat was a cyclohexanol vapor bath and in these cases no separate preheating step was involved. At other temperatures the thermostat was an electric tubular furnace controlled by a mercury regulator. Because of lag the average temperature control was probably not better than 0.1° ; short time fluctuations considerably greater than this were observed.

The reason for using the boiling cyclohexanol vapor bath at 160° was to reduce the uncertainty in time required for the ampoules to be brought to temperature, this being more important in these experiments where the rates were fast and reaction times correspondingly short.

After the reaction had run for the desired length of time the ampoules were removed from the thermostat, cooled quickly. The stems were broken open, and cleaned, dried helical copper coils were inserted into the solutions to remove the iodine. (The probable validity of this method is shown by experiments in which to a standard dichlorethylene solution of known composition iodine was added and allowed to remain in the room light at room temperatures for periods longer than would be the case in actual experiments. The iodine then was removed by a copper wire, and by dielectric constant analysis no change in composition from that of the original solution was indicated.)

When the iodine color was gone the wires were removed, the solutions drawn into the dielectric measuring cell, the precision condenser adjusted and read, and then the composition of the reaction mixture deduced with the aid of the condenser correction graphs and the calibration graph for the solution involved. Since a blank run (#49) with benzene containing no dichlorethylene showed a change in dielectric constant which would correspond to a small increase in cis$C_2H_2Cl_2$ in a solution of it in benzene, in treating regular experiments in these solutions .02 was always subtracted from the final precision condenser reading before the corresponding composition was read from the calibration curve.

Having obtained the fractional isomerization, x, the rate constant, k, was obtained from the integrated form of the rate expression discussed in the Preliminary Discussion on page 12. This form is, for experiments started from the cis side of equilibrium,

$$k = \frac{-\ln\left\{1 - (1 - K)x\right\}}{K\tau} \quad ;$$

and for experiments starting from the trans side,

$$k = \frac{-\ln\left\{1 - (1 - \frac{1}{K})x\right\}}{K\tau}$$

Table 3.

Calibration Data for CisC_2H_2Cl--Trans$C_2H_2Cl_2$ Solutions

Composition (% cis$C_2H_2Cl_2$) C	Condenser Reading (corrected) R	(R-56.82)	d
100.0	107.11	50.29	0
86.4	102.96	46.14	5.35
75.4	99.23	42.41	8.93
59.8	93.00	36.18	12.14
43.7	85.38	28.56	13.09
0	56.82	0	0

d is the deviation from linearity and is defined by the equation:

$$C = 1.989\ (R - 56.82) - d$$

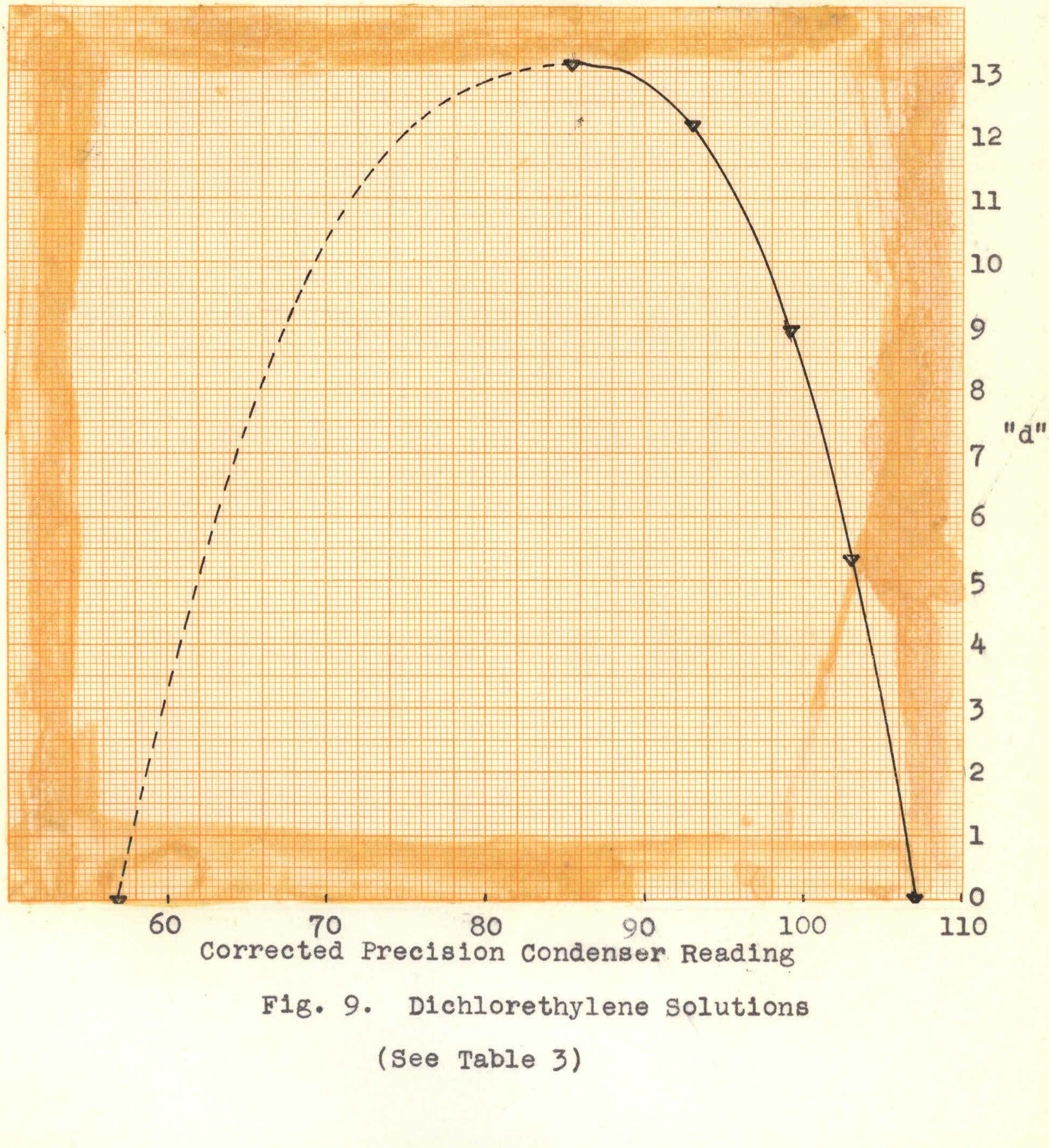


Fig. 9. Dichlorethylene Solutions

(See Table 3)

Table 4.

Calibration Data for Benzene Solutions of Cis and Trans Dichlorethylene

Composition (% cis$C_2H_2Cl_2$) C	Condenser Reading (corrected) R	(R-58.65)	d
0	58.65	0	0
2.301	60.21	1.56	.115
4.288	61.53	2.88	.169
4.243	61.50	2.85	.167
6.017	62.64	3.99	.158
7.659	63.67	5.02	.108
9.890	65.04	6.39	0

$$C = 1.548\ (R - 58.65) - d$$

These are three component solutions. They contain cis$C_2H_2Cl_2$, trans$C_2H_2Cl_2$ and benzene. They are made by mixing in various proportions a stock solution containing 10.00 mol percent trans$C_2H_2Cl_2$ in benzene with a stock solution containing 9.89 mol percent cis$C_2H_2Cl_2$ in benzene.

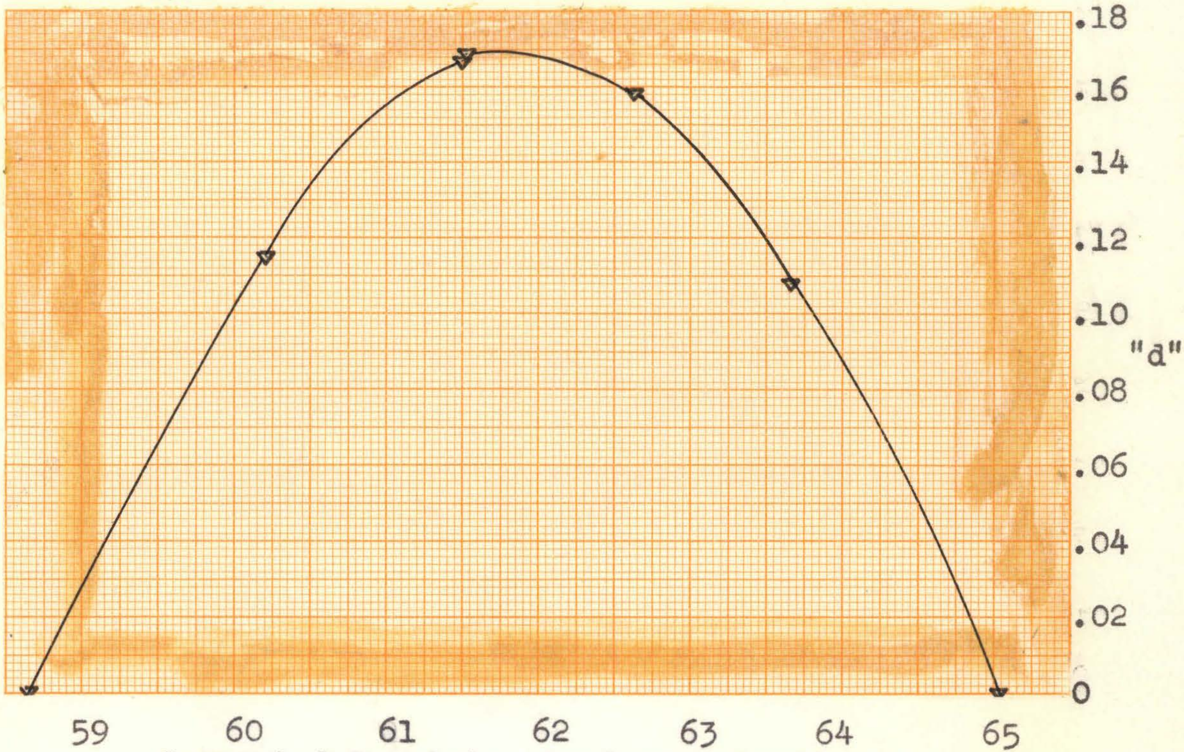
Table 5.

Calibration Data for Cyclohexane Solutions
of Cis and Trans Dichlorethylene

Composition (% cis$C_2H_2Cl_2$) C	Condenser Reading (corrected) R	(R-54.88)	d
0	54.88	0	0
3.52	56.85	1.97	.04
5.37	57.88	3.00	.05
4.73	57.52	2.64	.04
6.93	58.73	3.85	.02
10.02	60.43	5.55	0

$$C = 1.807\ (R - 54.88) - d$$

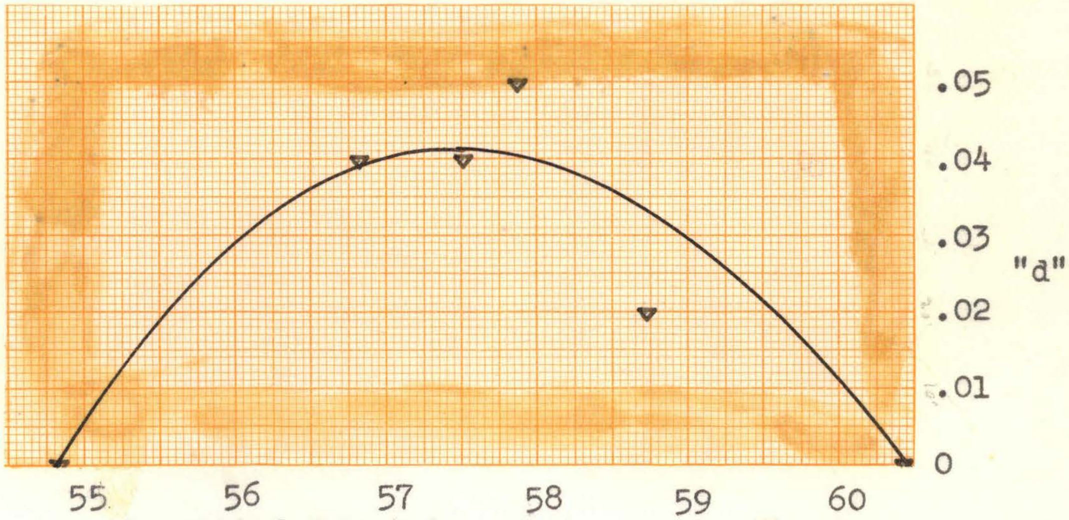
These are three component solutions. They contain cis$C_2H_2Cl_2$, trans$C_2H_2Cl_2$, and cyclohexane. They are made by mixing in various proportions a stock solution containing 9.99 mol percent trans$C_2H_2Cl_2$ in cyclohexane with a stock solution containing 10.02 mol percent cis$C_2H_2Cl_2$ in cyclohexane. R for the cyclohexane used in these solutions is 54.79.



Corrected Precision Condenser Reading

Fig. 10. Benzene Solutions

(See Table 4.)



Corrected Precision Condenser Reading

Fig. 11. Cyclohexane Solutions

(See Table 5.)

Table 6.

Calibration Data for Carbon Tetrachloride Solutions of Cis- and Trans-Dichlorethylene

Composition (Fraction Cis$C_2H_2Cl_2$ of Total $C_2H_2Cl_2$) C	Condenser Reading (corrected) R	(R-58.06)	d
0	58.06	0	0
.1709	59.03	0.97	.0039
.2969	59.73	1.67	.0040
.4456	60.58	2.52	.0089
.4104	60.38	2.32	.0078
.5649	61.24	3.18	.0086
.7908	62.48	4.42	.0057
1.0000	63.61	5.55	0

$$C = .1802\ (R - 58.06) - d$$

These are three component solutions. They contain Cis$C_2H_2Cl_2$, Trans$C_2H_2Cl_2$, and CCl_4. They are made by mixing in various proportions a stock solution containing 9.25 mol percent cis$C_2H_2Cl_2$ in CCl_4 with a stock solution containing 9.25 mol percent trans$C_2H_2Cl_2$ in CCl_4.

Table 7.

Calibration Data for Dibutyl Phthalate Solution of Cis- and Trans-Dichlorethylene

Composition (% cis$C_2H_2Cl_2$) C	Condenser Reading (corrected) R	(R-95.27)	d
0	95.27	0	0
2.50	95.75	.48	.20
4.56	96.12	.85	.23
7.50	96.63	1.36	.16
9.98	97.04	1.77	0

$$C = 5.64\ (R - 95.27) - d$$

These are three component solutions. They contain cis$C_2H_2Cl_2$, trans$C_2H_2Cl_2$, and benzene. They are made by mixing in various proportions a stock solution containing 9.98 mol percent cis$C_2H_2Cl_2$ in dibutyl phthalate with a stock solution containing 9.89 mol percent trans$C_2H_2Cl_2$ in dibutyl phthalate. R for the dibutyl phthalate used in these solutions is 96.00.

Discussion of Individual Experiments

1. Experiments in Dichlorethylene

The experiments through #26 were made with solutions in the dichlorethylenes without any other solvent.

(a) #6, #25 are blanks containing no iodine. Over the comparatively long heating periods (115 hours and 67 hours) the observed change in dielectric constant was very small. On the basis of these experiments it was concluded that neglect of possible uncatalyzed isomerization would not introduce any serious error into the treatment of rate experiments on the catalyzed isomerization.

(b) #7, #8, #24 are equilibrium experiments. #7 and #8 started with cis$C_2H_2Cl_2$, #24 with trans$C_2H_2Cl_2$. The equilibrium constants are in good agreement. The value 2.43 for K was used in calculations of rate constants for the rate experiments in Table 8.

(c) #9, #10, #11, #12 are rate experiments starting with cis$C_2H_2Cl_2$ solutions of iodine. The apparent increase in the values of $k/\sqrt{(I_2)}$ shown in Column XI for these experiments is probably not significant. This seems likely because of the lack of corresponding observed trends in other sets of experiments. The trend could be due to having preheated the ampoules to a temperature higher than the reaction temperature. If this had occurred, it would be expected that the largest error would be in the shortest run, and the error would correspond to a too-high rate constant.

(d) #19, #23, #26 are rate experiments starting with trans$C_2H_2Cl_2$. The values in Column XI for this set are in very good agreement. They are slightly lower than the set for the experiments starting with cis$C_2H_2Cl_2$, but this difference, too, seems of doubtful significance. It could be explained by the same assumption as was suggested for explaining the trend in set (c).

2. Experiments in Benzene

Table 9 includes the equilibrium and blank experiments conducted with benzene solutions of cis- and trans-$C_2H_2Cl_2$.

(a) #34, #40, #43, #49 are blank experiments. #34, #40, #43 are experiments on benzene solutions of dichlorethylene which contained no iodine. All these experiments showed an apparent increase in cis$C_2H_2Cl_2$, although an actual increase in cis-$C_2H_2Cl_2$ is obviously impossible in #40 which began with cis-$C_2H_2Cl_2$. It seems probable that the small change in dielectric constant was due to some change in the benzene or in some contaminant in it. #49 is a blank which contained benzene and iodine but no dichlorethylene. It is noted that here, too, an increase in dielectric constant occurred. #49 was made from the same benzene as the solution of #46, and in computing k from #46 the change observed in #49 was subtracted from that observed in #46.

(b) #41, #42 are equilibrium experiments in benzene solutions at 150°. The K's are in good agreement and here, as in 1(b) the average value 2.43 was accepted for purposes of calculation of the rate data.

(c) #50, #51, #55, #57, #58 are equilibrium experiments at 185°. All these except #51 are in good agreement. The cause of #51's deviation was not determined. The value accepted was 2.19. For K's between 140° and 185° linear interpolations or exterpolations were used.

3. Experiments in Benzene

Table 10 is made up of the rate experiments in benzene solutions.

(a) #35 is a preliminary experiment made before the standard $C_2H_2Cl_2$ solutions were prepared. Since it is an odd concentration at which no calibration of composition vs dielectric constant was made, no exact value can be put in Column IV.

(b) #44, #45, #46, #47, #48 are rate experiments at 150°. The deviation between the lowest and highest value in Column XI, the 150° values of $k/\sqrt{(I_2)}$, is about 3%. They are very similar to the corresponding values in Table 8, the difference between the averages of these two tables being 2 or 3 percent. Since the K's for Table 8 and Table 10 are the same, the corresponding values in Column XIII will agree as well as those in Column XI.

(c) #52, #56 are rate experiments at 140.5°.

(d) #53, #54 are rate experiments at 158.9° and 159.5°. The plot of 1/T vs ln k, (Fig. 12) for the rate data in benzene solutions shows all these data to fall quite well on a straight line.

4. Experiments in Cyclohexane

Table 11 exhibits the cyclohexane solution data.

(a) #64, #65, #66 are blanks without iodine. Apparently something went awry in #65. The changes in #64 and #66 are higher than those in the benzene series, but not very serious.

(b) #60, #61, #67, #68, the 150° equilibrium data, and #71, #72, the 185° equilibrium data are definitely different from the corresponding data in Tables 8 and 9. However, the

ΔH's from the temperature coefficients of the K's in Tables 9 and 11 are the same, as can be seen by comparing Figs. 12 and 13. The difference in the K's in Tables 8 and 9 and those in Table 11 must be attributed to differences in the vapor pressure-composition relations of at least one of the isomers in the different solvents.

(c) #62, #63, #69, #70 are the rate experiments at 150° in cyclohexane. It is to be observed that the values of $k/\sqrt{(I_2)}$ in Column XI are noticeably higher than the corresponding ones in Tables 8 and 10. It will also be observed, however, that the values of $Kk/\sqrt{(I_2)}$ in Column XIII are very similar to the corresponding values in Tables 8 and 10. From these facts it might be concluded that the cis$C_2H_2Cl_2$ has different vapor pressure-composition relations in cyclohexane than in benzene or $C_2H_2Cl_2$, whereas these relations of trans-$C_2H_2Cl_2$ are about the same in the different solvents. Cis-$C_2H_2Cl_2$ being a polar liquid might be expected to behave less regularly than trans$C_2H_2Cl_2$, but why this difference should occur in going from C_6H_6 to C_6H_{12} is not clear. The average values in Column XIII for Table 8, 10, and 11 respectively are the same to within about 2%.

Explanation of Experiment Tables

On the following pages are tabulated the individual experiments. Table 8 contains the experiments done with the pure liquids cis- and trans-$C_2H_2Cl_2$. Table 9 is a list of the blank and equilibrium experiments done with benzene solutions of $C_2H_2Cl_2$. Table 10 contains rate experiments done with benzene solutions. Table 11 lists the experiments using cyclohexane as a solvent.

The data tabulated in the various columns is as follows:

I. The experiment number.

II. The isomer originally present in the reaction solution. No experiments are listed which began with a mixture of isomers. Experiment #49 contained no $C_2H_2Cl_2$, only benzene.

III. The total mol percent $C_2H_2Cl_2$ before adding I_2. This column is omitted from Table 8 in which the composition was always 100% $C_2H_2Cl_2$, and from Table 11 in which the concentration was always 10.02 mol percent $C_2H_2Cl_2$ in the cis- solutions and 9.99 mol percent $C_2H_2Cl_2$ in the trans solutions.

IV. The composition in mol percent cis-$C_2H_2Cl_2$ found at the end of the experiment by dielectric constant analysis. In case of the blank (iodineless) experiments the values are usually given in terms of the apparent <u>increase</u> in mol percent cis-$C_2H_2Cl_2$. In equilibrium experiments #71 and #72 the measured value has been corrected by an amount calculated to correspond to the distance those solutions would have been from equilibrium after the seven hour heating period. For experiments #34 and #35 since these were done with total $C_2H_2Cl_2$ concentrations at which a calibration of mol percent cis$C_2H_2Cl_2$ vs condenser reading had not been made, no exact value could be put in this column.

V. Temperature of the experiment, °C.

VI. Duration of experiment in hours, τ.

VII. Mol fraction $I_2 \times 10^3$.

VIII. Square root of mol fraction $I_2 \times 10^2$, i.e. $100\sqrt{(I_2)}$.

IX. The rate constant, k, calculated from this experiment as described on page 61, at the temperature of the experiment. In Tables 8 and 11 these values are multiplied by 10^3.

X. $k/\sqrt{(I_2)}$.

XI. The value of column X calculated to the standard temperature by means of the rate constant temperature coefficient data. The standard temperature for experiments done at about 150° was 150° . For those at about 160° was taken as 159°. At the lowest temperature it was 140.5°.

XII. The equilibrium constant, K, at the temperature of the experiment.

XIII. For experiments at 150°. The 150° equilibrium constant times the values in Column XI. The values in Column XIII represent 150° rate constants for the reaction trans$C_2H_2Cl_2$ $\longrightarrow$ cis$C_2H_2Cl_2$.

XIV. The uncorrected precision condenser reading corresponding to the reaction mixture at the end of the experiment.

The precision condenser readings corresponding to the liquids from which the various reaction solutions were made up are as follows:

Liquid	Uncorrected Precision Condenser Reading
cis$C_2H_2Cl_2$	107.20
trans$C_2H_2Cl_2$	56.81
Benzene	58.81
Cyclohexane	54.74
9.89% cis$C_2H_2Cl_2$ in benzene	64.97
10.00% trans$C_2H_2Cl_2$ in benzene	58.60
10.02% cis$C_2H_2Cl_2$ in cyclohexane	60.36
9.99% trans$C_2H_2Cl_2$ in cyclohexane	54.82

Experiments in Dichlorethylene Solutions

I	II	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
6	c	98.8	150	115	0	0						106.88
25	t	0.3	150	67.2	0	0						57.05
7	c	70.8	150	495	3.16	5.62				2.42		97.74
8	c	71.1	150	239	7.1	8.43				2.46		97.83
24	t	70.6	150	281	3.59	5.99				2.40		97.63
9	c	87.6	150	31.15	1.103	3.321	5.19	.156	.156		.378	103.47
10	c	83.3	150	30.40	2.718	5.21	8.16	.157	.157		.380	102.08
11	c	83.3	150	18.60	7.22	8.44	13.33	.158	.158		.382	102.09
12	c	83.2	150	13.00	14.57	12.07	19.27	.160	.160		.387	102.05
19	t	39.4	149.7	22.80	6.86	8.28	12.46	.151	.154		.373	85.55
23	t	34.3	149.7	24.76	2.704	5.20	7.84	.151	.155		.375	80.14
26	t	44.1	149.7	53.20	1.261	3.553	5.37	.151	.155		.375	85.60

Table 8.

Experiments in Benzene Solutions

I	II	III	IV	V	VI	VII	VIII	XII	XIV
34	t	14.04	*	150	20	0	0		58.60
40	c	9.89	+.05	150	ca21	0	0		65.00
41	t	10.00	7.07	150	252	3.0	5.5	2.41	63.28
42	c	9.89	7.03	150	252	4.0	6.3	2.46	63.25
43	t	10.00	+.03	150	ca22	0	0		58.62
50	c	9.89	6.78	185	ca21	4.3	6.5	2.18	63.10
51	t	10.00	7.01	185	ca21	4.3	6.5	2.34	63.24
55	t	10.00	6.78	185	ca7.5	5.9	7.7	2.165	63.10
57	c	9.89	6.89	185	ca5.8	6.0	7.7	2.210	63.17
58	t	10.00	6.85	185	ca21.5	5.7	7.5	2.175	63.14
49	Benzene	0	#	150	37.5	4.0	6.3		58.845

* Initial no. = 58.57
\# Initial no. = 58.825

Table 9.

Experiments in Benzene Solutions

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XIII	XIV
35	c	20.34		149.6	18.0	3.43	5.85	Initial no. = 71.00				69.58
44	t	10.00	3.76	149.5	40.0	1.403	3.746	.00553	.1476	.154	.374	61.14
45	t	10.00	4.90	149.5	20.8	12.62	11.24	.01653	.1470	.154	.374	61.90
46	t	1.09	0.570	150.0	37.5	4.82	6.95	.0105	.1510	.151	.368	59.200
47	c	9.89	8.18	150.0	17.5	9.44	9.72	.91485	.1527	.153	.372	63.96
48	c	9.89	8.30	150.0	47.2	1.104	3.32	.0496	.1493	.149	.362	64.03
52	t	10.00	4.44	140.5	91.0	2.237	4.73	.00305	.0645	.0645		61.58
53	t	10.00	3.58	158.9	7.3	8.01	8.95	.0290	.3240	.326		61.02
54	t	10.00	4.28	159.5	28.3	0.854	2.92	.00989	.3390	.325		61.48
56	t	10.00	4.20	140.5	42.6	8.39	9.16	.00595	.0650	.0650		61.43

Table 10.

Experiments in Cyclohexane Solutions

I	II	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
60	c	6.74	150.7	308	6.7	8.2				2.07		58.59
61	t	6.89	150.7	308	7.7	8.8				2.22		58.67
62	t	4.91	150.7	21.0	11.27	10.62	19.8	.187	.176		.370	57.58
63	t	3.14	150.7	21.2	2.503	5.01	9.47	.189	.178		.374	56.59
64	c	-.05%	150	55	0							60.39
65	t	-.44%	150	55	0							55.07
66	t	-.08%	150	24	0							54.87
67	c	6.77	150	92	11	10				2.12		58.63
68	t	6.81	150	92	13	11				2.10		58.60
69	t	4.29	150	21.1	7.29	8.54	1.53	.179	.179		.376	57.24
70	c	8.06	150	22.0	5.21	7.22	13.40	.186	.186		.390	59.30
71	c	*6.58	185	7	6.4	8				1.92		58.53
72	t	6.50	185	7	6.0	7.7				1.86		58.40
73	t	3.58	159.2	8.3	5.91	7.69	29.4	.383				56.85
74	t	4.40	159.2	8.3	11.73	10.82	42.0	.388				57.30

Table 11.

Table 12.

Rate Experiments in Benzene Solutions
Temperature Coefficient Data

Expt. No.	$k/\sqrt{(I_2)}$	T °C	1/T °K	log $k/\sqrt{(I_2)}$	2.303 log $k/\sqrt{(I_2)}$
44	.148	149.5	.0023658	$\bar{1}.17026$	-1.912
45	.147	149.5	.0023658	$\bar{1}.16732$	-1.918
48	.149	150.0	.0023629	$\bar{1}.17319$	-1.905
47	.153	150.0	.0023629	$\bar{1}.18469$	-1.877
52	.0645	140.5	.0024171	$\bar{2}.80956$	-2.741
56	.0650	140.5	.0024171	$\bar{2}.81291$	-2.735
53	.324	158.9	.0023144	$\bar{1}.51055$	-1.128
54	.339	159.5	.0023110	$\bar{1}.53020$	-1.082

See Fig. 12.

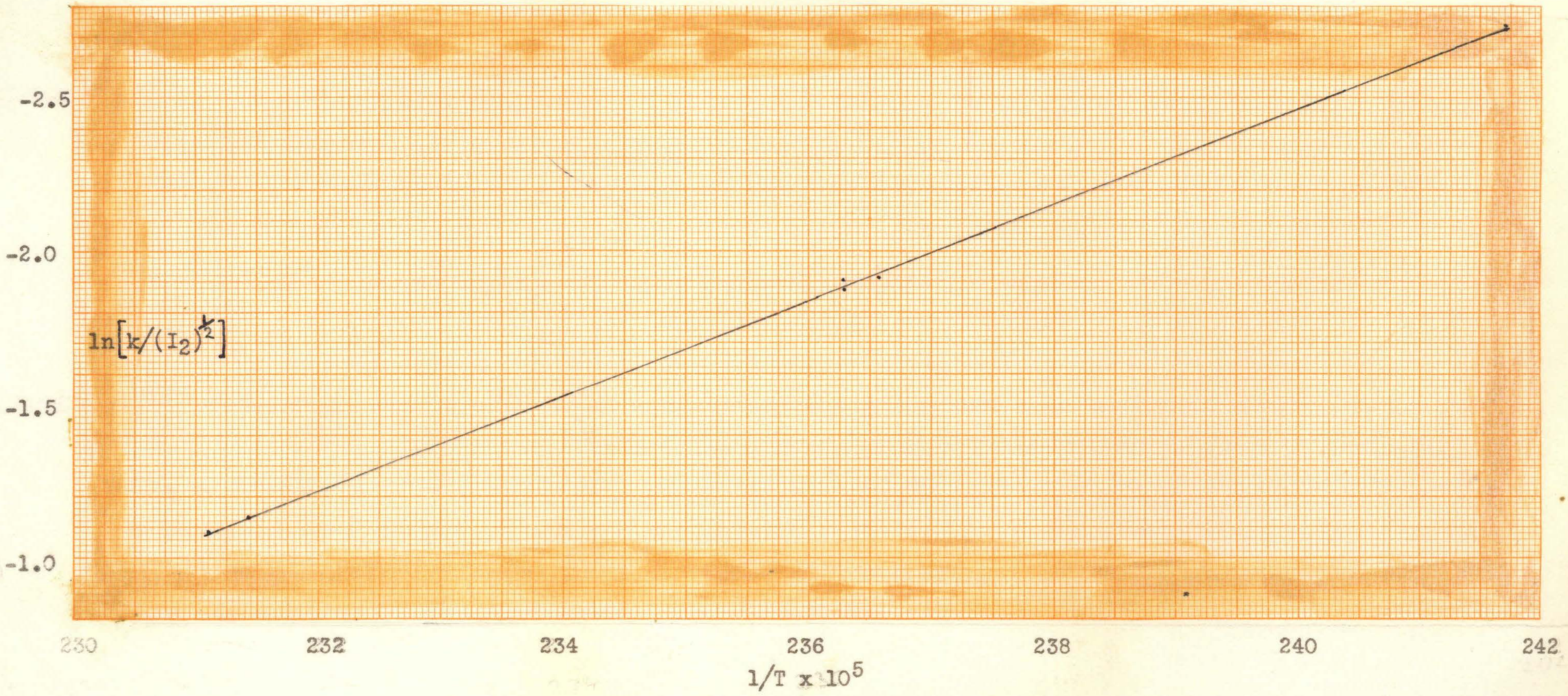


Fig. 12. Benzene Solutions
Rate-constant temperature coefficient

Table 13.

Rate Experiments in Cyclohexane
Temperature Coefficient Data

Expt. No.	$k/\sqrt{(I_2)}$	T °C	1/T °K	log $k/\sqrt{(I_2)}$	2.303 log $k/\sqrt{(I_2)}$
62	.187	150.7	.0023591	$\bar{1}.27184$	-1.678
63	.189	150.7	.0023591	$\bar{1}.27646$	-1.667
69	.179	150.0	.0023630	$\bar{1}.25285$	-1.721
70	.186	150.0	.0023630	$\bar{1}.26951$	-1.682
73	.383	159.2	.0023126	$\bar{1}.58320$	-0.960
74	.388	159.2	.0023126	$\bar{1}.58883$	-0.947

See Fig. 13.

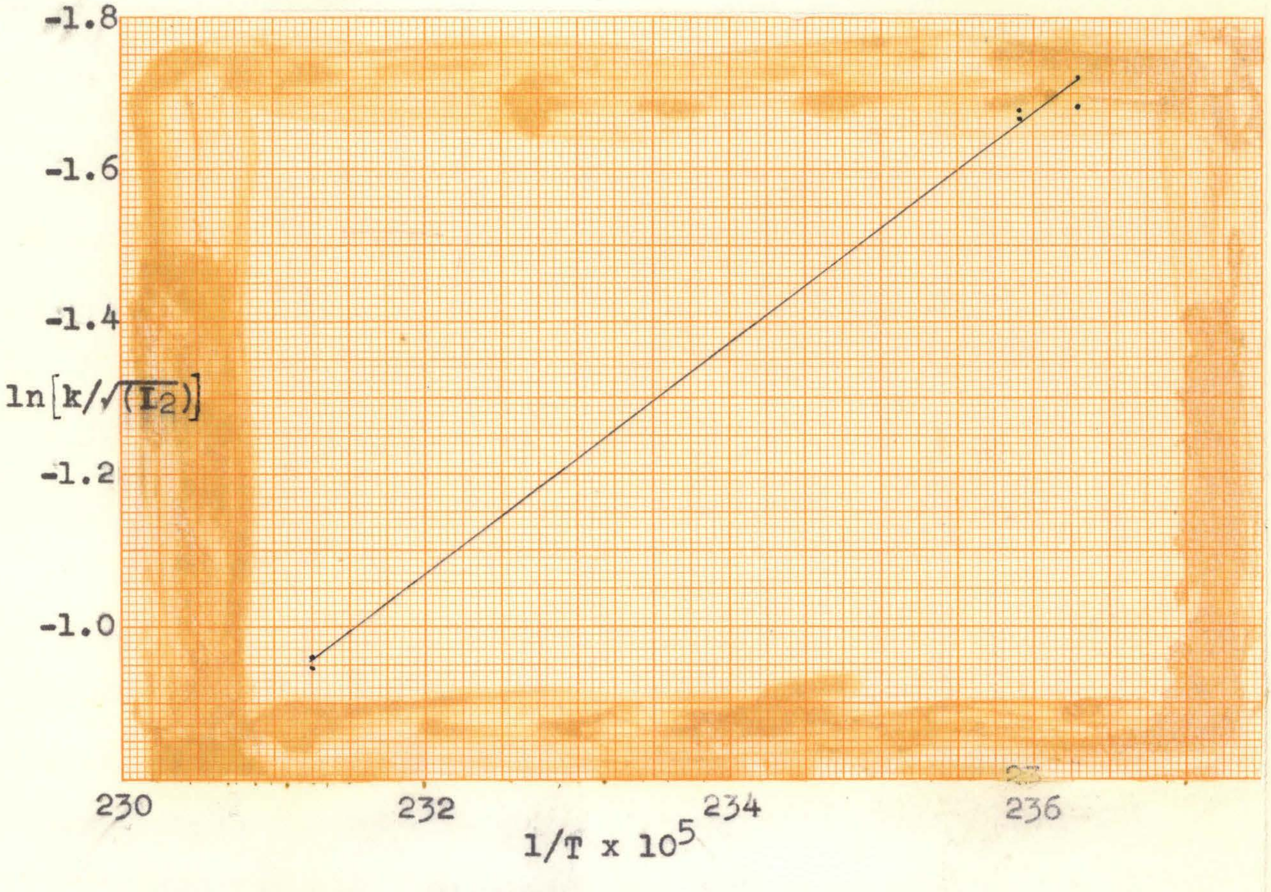


Fig. 13. Cyclohexane Solutions
Rate-constant temperature coefficient

Average Values

In the following table (Table 14) are presented the average values of rate and equilibrium constants found for the studied isomerization referred to 150°. In all computations have been expressed in mol fractions. This has been primarily because data concerning the densities of the solutions at the temperatures of the experiments have not been available. In Table 14 an attempt has been made to translate, approximately, the rate constants for the reaction trans$C_2H_2Cl_2 \longrightarrow$ cis$C_2H_2Cl_2$ (Column 4) expressed for concentrations in terms of mol fractions to corresponding values (Column 7) expressed for concentrations in terms of mols per cubic centimeter. The factor 1/3600 has also been applied, so that rates calculated using the values in Column 7 together with concentrations expressed in mols per cubic centimeter should have the conventional units, mols cc^{-1} sec^{-1}. The bases for these translations are the values of the molal volumes at 150° shown in Column 5, and these, in turn, represent approximate values obtained (a) assuming volume additivity in the solutions, (b) neglecting the iodine concentration, and (c) using empirical density-temperature equations for $C_2H_2Cl_2$ (31), C_6H_6 and C_6H_{12} (32). A similar translation of the values in Column 3 to those in Column 6 has been made.

Next to the very close agreement of the values in Column 4, already referred to, probably the most striking exhibit in the table is the fact that the agreement of the values in Column 7 is considerably poorer. The values in Column 6 also deviate

1	2	3	4	5	6	7
Solvent	k $/\sqrt{(I_2)}$	K	Kk $/\sqrt{(I_2)}$	$\tilde{V}$	$\frac{\sqrt{\tilde{V}}\ k \times 10^4}{\sqrt{(I_2)}}$	$\frac{\sqrt{\tilde{V}}\ Kk}{\sqrt{(I2)}}$
$C_2H_2Cl_2$	.156	2.43	.379	92.5	4.15	10.1
C_6H_6	.153	2.43	.372	102.0	4.30	10.4
C_6H_{12}	.179	2.10	.376	122.0	5.50	11.5

Table 14--Average Values at 150°

from each other more than those in Column 2. However, because of the smallness of the differences between values of $\sqrt{\tilde{V}}$ for the three solutions, and because of the approximations involved in arriving at these values, it would seem well to defer the drawing of conclusions based on a comparison of Column 4 with Column 7 or Column 3 with Column 6 until experiments have been done in a solution with a considerably different $\tilde{V}$. Such experiments are contemplated.

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