1940

# Condensation of mercaptans with chloral in the gaseous phase

Francis Bertram Moore
*Iowa State College*

## Recommended Citation

Moore, Francis Bertram, "Condensation of mercaptans with chloral in the gaseous phase " (1940). *Retrospective Theses and Dissertations*. 12983.
https://lib.dr.iastate.edu/rtd/12983

# CONDENSATION OF MERCAPTANS WITH CHLORAL IN THE GASEOUS PHASE

by

Francis B. Moore

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Physical-Plant Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1940

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

## ACKNOWLEDGMENT

The author wishes to express his sincere appreciation for the assistance given by Dr. I. B. Johns in carrying out this investigation, and for the suggestions given by Dr. H. A. Wilhelm during the construction and testing of the apparatus.

# TABLE OF CONTENTS

Use of Gauge

# INTRODUCTION

## HISTORICAL

In earlier studies it has been shown that a relationship exists between the polar properties of a number of series of organic compounds and an empirically determined property of organic radicals, the electron sharing ability (12) (1) (15) (14) (9) (26) (11) (13) (4) (20) (17).

Among the many series studied were the ionizations of the carboxylic acids and the primary amines in water, methanol and ethanol. When the values for log $K_{\text{dissoc.}}$ for these series are plotted against the electron sharing ability of the radicals, smooth curves are obtained which may be represented by exponential equations (11). For the series of acids the equation is

$$\log K = 20e^{0.5x - 5.6} - C$$

where K is the dissociation constant for the acid, x is the electron sharing ability and C is a constant, which has the value 4.8 when water is the solvent. For methanol and ethanol as solvents the value of C is 9.64 and 10.64, respectively.

There thus seems to be a constant difference between the value for log K in any two solvents. This difference is expressed by the constant C in these equations since for a given series the rest of the equation remains identical as the solvent is changed from water to methanol and ethanol.

It therefore is possible to predict the dissociation constant for a substance from the value of the constant for its dissociation in a different solvent.

This is quite contrary to the views of Conant (5) since he believes that in many cases the solvent effect is large enough to mask the true characterists of the equilibrium. In his studies of the free energy of the reduction of a series of substituted quinones, (6) (7) he has shown the values for the free energies referred to the gaseous state decrease in a regular fashion as each chlorine atom is introduced. On the other hand the free energy values for the solutions are irregular, first increasing as chlorine atoms are introduced and then decreasing. The results of this investigation are given in Table 1, and are for the reaction

$$\text{quinone} + H_2 \rightarrow \text{hydroquinone}$$

TABLE 1

Free Energy of Reduction of Quinones in Different Standard States at 20° C.

| Quinone | $F^o_g$ Gaseous State | $F^o_{alc.}$ Dil. Alc. | $F^o_{H_2O}$ Dil. Acq. |
|---|---|---|---|
| | Calories | sol. Calories | sol. Calories |
| Benzoquinone | -26,300 | -32,800 | -32,200 |
| Chloroquinone | -28,200 | -34,000 | -32,900 |
| 2,6-dichloroquinone | -29,350 | -34,500 | -33,300 |
| Trichloroquinone | -29,950 | -33,500 | ------- |
| Tetrachloroquinone | -30,300 | -32,500 | ------- |
| P-Xyloquinone | -22,400 | -27,200 | -27,550 |

The free energies of enolization of a series of substituted acetoacetic esters and related compounds have been studied by Conant and Thompson (8), in different standard states. A comparison was made between the free energies for the compounds as determined by equilibria in the gaseous, liquid and dissolved states. The free energy values obtained in the different standard states are shown in Table 2.

TABLE 2

Free Energy of Enolization in Different Standard States

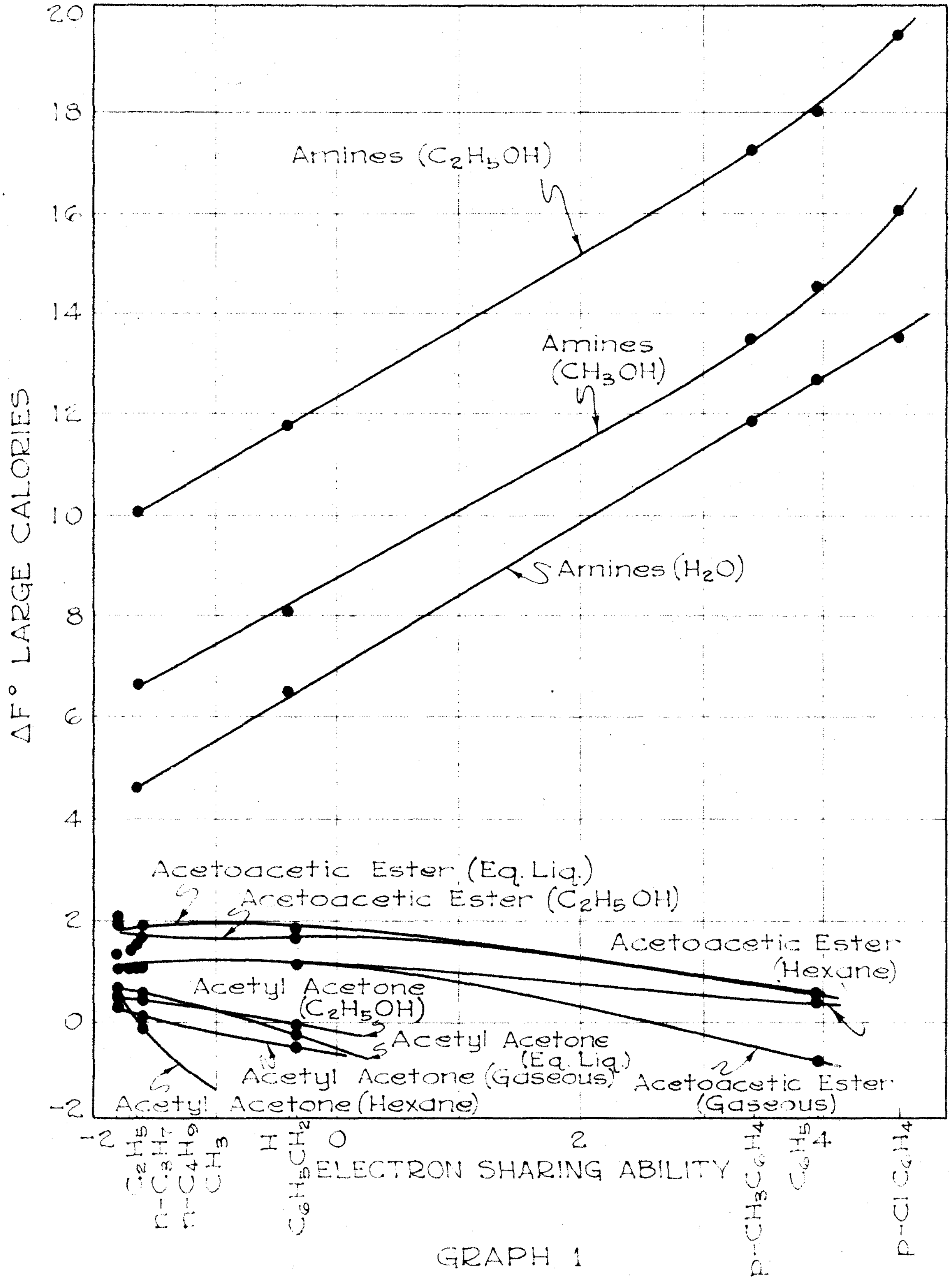
$\Delta F^{\circ} = -RT\ln K$ Free Energy of enolization at 25°

| Substituted Groups | Gaseous phase Large Calories | Equilibrium liquid Large Calories | 0.1M hexane sol. Large Calories | 0.1M abs. alcohol sol. Large Calories |
|---|---|---|---|---|
| Acetoacetic ester group | | | | |
| H | 0.1 | 1.5 | 0.0 | 1.2 |
| $(CH_3)$ | 1.1 | 1.9 | 1.1 | 1.7 |
| $(C_2H_5)$ | 1.3 | 2.1 | 1.1 | 2.0 |
| $(C_3H_7n)$ | 1.1 | 1.5 | 1.1 | ---- |
| $C_4H_9n$ | 1.1 | 1.6 | 1.3 | 1.6 |
| $C_3H_7i$ | 1.6 | 1.8 | 1.6 | ---- |
| $C_6H_5$ | -0.8 | 0.5 | 0.4 | 0.5 |
| $CH_2C_6H_5$ | 1.2 | 1.8 | 1.2 | 1.7 |
| Acetyl Acetone Group | | | | |
| H | -1.3 | -0.7 | -1.3 | -1.0 |
| $CH_3$ | 0.1 | 0.5 | -0.2 | 0.4 |
| $C_2H_5$ | 0.3 | 0.6 | 0.6 | 0.5 |
| $CH_2C_6H_5$ | -0.5 | -0.25 | ---- | -0.1 |

The similarities in the substituted groups is best shown in the results in the gaseous phase, although in many instances the values for the dilute hexane solution are approximately the same. The divergence was greatest between the values for the equilibrium liquid and the gaseous phase, inmany cases being equivalent to a power of ten in the equilibrium constant. According to the results obtained in the gaseous phase the alkyl groups are practically equivalent and the benzyl radical is very like the alkyls. The secondary alkyl is more effective in decreasing enolization than the primary group, while the phenyl group has a decided tendency to increase enolization.

The values for free energy shown in Table 2 are plotted against the electron sharing ability in Graph 1. In the acetoacetic ester series the general trend of the curves for the different standard states is qualitatively the same, any differences being in degree of displacement. In the alkyl part of the series the points fall closest to the curve for the gaseous reactions and the hexane solution reactions.

In all instances the hydrogen substitution compound was far below the curve. In the acetyl acetone series the points are too few to well characterize the curves but it is apparent that there is little to choose between them. Since the curve for the hexane solution is established by only two points, it is of little significance. The curve for the amines by which the electron sharing ability values of the radicals are established is shown as a basis for comparison. The curves for the amines in methanol and ethanol are also shown.


ΔF° LARGE CALORIES
20
18
16
14
12
10
8
6
4
2
0
-2
Amines ($C_2H_5OH$)
Amines ($CH_3OH$)
Amines ($H_2O$)
Acetoacetic Ester (Eq. Liq.)
Acetoacetic Ester ($C_2H_5OH$)
Acetoacetic Ester (Hexane)
Acetyl Acetone ($C_2H_5OH$)
Acetyl Acetone (Eq. Liq.)
Acetyl Acetone (Gaseous)
Acetoacetic Ester (Gaseous)
Acetyl Acetone (Hexane)
-2
0
2
4
$C_2H_5$
$n-C_3H_7$
$n-C_4H_9$
$CH_3$
H
$C_6H_5CH_2$
$p-CH_3C_6H_4$
$C_6H_5$
$p-Cl\,C_6H_4$
ELECTRON SHARING ABILITY

GRAPH 1

## THEORETICAL DISCUSSION

The difference between the conventional equilibrium constants as determined for a reaction in the gaseous phase and in solution lies in the effect of the solvent upon the solutes.

The equilibrium constant for a gaseous reaction is determined solely by the free energy change for the reaction whereby the reactants in their standard states form the products in their standard states. The constant for the same reaction carried out in solution will be affected by an additional factor, the effect of the solvent molecules upon the escaping tendency of the components.

Consider the equilibrium reaction in the gaseous phase where A dissociates into B and C according to the equation

$$A_{(v)} = B_{(v)} + C_{(v)}$$

where the notation (v) indicates that the gaseous phase is the standard state.

The standard state for a gas is chosen so that the activity approaches the pressure as the latter approaches zero, so in dilute gaseous systems pressures may be substituted for activities. This leads to the equation

$$K_{P(v)} = \frac{P_{B(v)} \times P_{C(v)}}{P_{A(v)}}$$

where $P_{A(v)}$, $P_{B(v)}$, $P_{C(v)}$ are the pressures of components A, B, C measured in atmospheres and $K_{P(v)}$ is the dissociation constant in the vapor state calculated from actually measured pressures.

When the equilibrium is established in solution we have

$$A_{(1)} = B_{(1)} + C_{(1)}$$

where the notation (1) indicates that the dissolved state is the standard and the same three components exist in a hypothetically ideal solution.

The standard state for a solute is chosen so that the activity equals the mol fraction as the mol fraction approaches zero. This leads to the equation

$$K_N = \frac{N_{B(1)} \times N_{C(1)}}{N_{A(1)}} \qquad \text{where}$$

$N_{A(1)}$, $N_{B(1)}$, $N_{C(1)}$ are the mol fractions of components A, B, C in the solution and $K_N$ is the dissociation constant determined in a sufficiently dilute solution. In this range of concentrations, Henry's Law gives

$$P_A = kN_A \quad \text{or} \quad N_A = \frac{P_A}{k}$$

where P is the pressure of substance A above the solution, $N_A$ is the mol fraction of A in the solution and k is a constant characteristic of the escaping tendency of the solute A.

The substitution of this value leads to the equation

$$K_{P(1)} = \frac{\frac{P_{B(1)}}{k_B} \times \frac{P_{C(1)}}{k_C}}{\frac{P_{A(1)}}{k_A}}$$

$$\text{or } K_{p(1)} = \frac{P_{B(1)} \times P_{C(1)}}{P_{A(1)}} \times k_D$$

where $P_{B(1)}$ is the pressure of B in the vapor above the liquid,

$$k_D = k_B \times k_C/k_A \quad \text{and}$$

$K_{P(1)}$ is the dissociation constant for the dissolved state as determined in the solution.

Since at equilibrium $P_{A(v)} = P_{A(1)}$, $P_{B(v)} = P_{B(1)}$ and $P_{C(v)} = P_{C(1)}$, it is apparent that $K_{P(1)} = K_{P(v)} \times k_D$.

Since the above equation requires the equilibrium to be established in perfect solution, the value for the dissociation constant determined in solution will vary as the solution deviates from Henry's Law. A change of solvent should change the value of the constant.

The solution may deviate from Henry's Law in several ways. The chemical nature of one or more components may be changed by reaction with the solvent, such as hydration, or the solvent may cause association or dissociation. These possibilities will be considered briefly.

In the case in which combination occurs between the solute and the solvent, two equilibria must be considered. The first exists between the uncombined solute molecules and molecules in the vapor state; the second exists between the combined and uncombined solute molecules.

Since Henry's Law applies to the first equilibrium

$$\frac{P}{N_1} = k$$

where P is the pressure of the uncombined solute molecules above the solution, $N_1$ is the mol fraction of uncombined molecules in the solution and k is the constant characteristic of the escaping tendency.

The second equilibrium is governed by the mass law and

$$\frac{N_1 \text{ x } (N_s)^n}{N_2} = K_1$$

where $N_s$ is the mol fraction of the solvent molecules, n is number of solvent molecules combining with one solute molecule, $N_2$ is the mol fraction of solvated molecules, and $K_1$ is the equilibrium constant. Since the mol fraction of solvent molecules is very large and does not vary appreciably in a dilute solution, $(N_s)^n$ is a constant and the above equation becomes

$$\frac{N_1}{N_2} = \frac{K_1}{(N_s)^n} \quad \text{or} \quad \frac{N_1}{N_2} = K_2$$

Inverting this equation and adding 1 to each member gives

$$\frac{N_2 + N_1}{N_1} = \frac{1 + K_2}{K_2}$$

The equation for the first equilibrium is divided by the above equation and

$$\frac{\frac{P}{N_1}}{\frac{N_2 + N_1}{N_1}} = \frac{k}{\frac{1 + K_2}{K_2}} \quad \text{or} \quad \frac{P}{N_2 + N_1} = k_3$$

where $k_3$ has the value $k \times K_2/1 + K_2$, and $N_2 + N_1$, is the total mol fraction of the solute as it would be determined by analysis.

It is therefore apparent that the only effect due to solvation would be a change in the value of the characteristic constant, k, which relates the pressure above the solution to the mol fraction of the solute in the solution, and a resultant change in the numerical value of the equilibrium constant for the reaction in the dissolved state.

The cases in which a solvent causes association or dissociation of one of the components are considered in a similar manner and therefore only the case of dissociation will be considered. Again in this case Henry's Law applies to the equilibrium between the undissociated molecules in the solution and the molecules in the vapor phase. Accordingly

$$P = N_1 k_1$$

where P is the pressure of the solute molecules above the solution, $N_1$ is the mol fraction of the undissociated molecules in the solution and $k_1$ a constant characteristic of the solute and solvent.

In the case of a substance which dissociates to form two products the equilibrium between the undissociated molecules and the products of the dissociation may be expressed by the mass law equation.

$$K_d = \frac{(N_2\,\alpha)^2}{N_2\,(1-\alpha)} = \frac{N_2\alpha^2}{1-\alpha}$$

where $K_d$ is the dissociation constant, $N_2$ is the total mol fraction of the solute as it would be determined by analysis, and   is the degree of dissociation.

If the above equation is solved for   the result is

$$= \frac{-K_d \pm \quad K_d^2 + 4KN_2}{2N_2}$$

Since $N_1 = N_2 (1 - \quad)$ and the value of   is given above we have

$$N_1 = \frac{2N_2 + K_d \pm \quad K_d^2 + 4K_dN_2}{2}$$

If this value of $N_1$ is substituted in the equation for the first equilibrium

$$P = N_1k_1$$

the result is

$$P = (2N_2 + K_d \pm \quad K_d^2 + 4K_dN_2)\frac{k_1}{2} =$$

$$N_2k_1 + K_d\frac{k_1}{2} \pm \frac{k_1}{2} \quad K_d^2 + 4K_dN_2$$

From this equation it is apparent that the pressure of the solute above the solution will be influenced by the equilibrium constant for the dissociation occurring in the solution, as well as the mol fraction of the solute in the solution and the constant characteristic of the escaping tendency of the solute.

The electron sharing ability of an organic radical is a measure of the influence of that radical upon the polar characteristics of compounds. The numerical value of the electron sharing ability for a radical is arbitrarily established from the best values obtainable for the dissociation constant of its amine, and these values were measured in solution. If the solvent effect upon the value of the dissociation constant is large in proportion to its value, the true polar characteristics of the compounds would be masked by the solvent effect. From the work of Goodhue (11) the effect of the solvent is seen to be purely additive. Results obtained in the vapor phase should therefore show an equally good relationship between F and the electron sharing ability. This concept permits the dissociation constant of a member of any series to be calculated from the corresponding member of another series providing the characteristic equations for the two series are known. It should then be possible to calculate the value for the dissociation constant for a reaction in the vapor phase if the equations for its series are known as determined in the vapor phase and in a solution.

The determination of gaseous equilibria is a tedious and time-consuming matter at best and is further complicated by the limited number of possible reactions, since in many cases the equilibrium is not established at ordinary temperatures in any reasonable length of time. The problem may be attacked by either of two methods as illustrated by the work of Conant (6) and Conant and Thompson (8). A modification of the second method to permit the direct measurement of the pressures in a gaseous equilibrium is of great interest and constitutes the method employed in the present investigation.

The dissociation constants in benzene for a series of hemimercaptals had been determined in this laboratory (13). These hemimercaptals seemed to be adapted to a determination of the equilibrium in the gaseous phase since their vapor pressures were moderately high, their equilibrium in the gaseous phase was established in a reasonable time, and their reaction had been shown to be free of complications.

The method selected consisted in releasing a trace of dry hydrogen chloride, in an evacuated reaction flask and determining the pressure. Known weights of chloral and mercaptan were then released and their pressures measured. When equilibrium was established and its pressure measured the dissociation constant could be calculated.

## THE GAUGE PROBLEM

The nature of the pressure measurements attempted required a gauge with very definite characteristics. Since the reactants and products were liquids or solids the range of pressures used must fall below the vapor pressure of the least volatile constituent. The accuracy and reproducibility of the measuring device must be good over the entire range since the change in pressure due to reaction is the significant factor. Very few of the gauges described in the literature are capable of operating conveniently over the desired range with the necessary accuracy. If the reacting substances are to be weighed accurately so that nearly equal molar quantities may be provided, the resultant pressures may go as high as 1-2 mm. In order to calculate satisfactory equilibrium constants these pressures must be measured to 0.001 mm.

The McLeod gauge cannot be used to measure these equilibrium reactions. The pressure recorded would not be the pressure of the reaction mixture. The equilibrium would be shifted to counteract the compression and the liquid or solid phase would separate.

The Pirani gauge operates in a slightly lower pressure range and depends for its action upon the proportionality between the pressure of gases at low pressure and thermal conductivity. It must be calibrated for each gas used and the presence of a heated wire in a reaction chamber would disturb the established equilibrium.

An oil manometer described by Burch (3) makes use of a U-tube having one limb larger than the other. The meniscus in the small arm is read with a microscope. This manometer operates over the desired range and has the required sensitivity but cannot be used in many instances because the oil absorbs many gases and as a result the pressures read would not be significant.

Many modifications of the Bourdon gauge (18) (15) are described. These gauges register pressure changes through the movement of a thin glass diaphragm. Various means are used to record this movement, one of the more recent being to make the diaphragm the moving plate of a variable condenser, and to measure pressure changes by the change in capacity of the condenser (19) (21). These gauges are all fragile and as their sensitivity is increased their accuracy is seriously affected by vibration.

The accuracy of all direct reading mercury manometers is limited by the tendency of mercury to stick to glass. The simplest type consists of inclined limbs, the pressure change being proportional to the movement of the mercury in the limb. A modification of this type is described by Smith (25). A second type is constructed by joining the two limbs of a U-tube with a horizontal capillary tube containing a bubble of air (or sulfuric acid) which separates the mercury in the two limbs. The pressure change is magnified according to the ratio of the areas of the limb and the capillary tube (23).

Viscosity gauges of numerous types are described but find their usefulness in a lower range of pressures. They are very sensitive to vibrational influences.

The Rayleigh gauge (22) consists of two wide limbs in which the mercury just touches glass points. Pressure changes are counterbalanced by tilting the gauge to restore contact between the mercury surfaces and the glass points. The extent to which the gauge must be tilted is a measure of the pressure change. A modification of this gauge (24) is less cumbersome since the gauge remains fixed and the displacement of the mercury is measured by a float which rotates a mirror as the mercury level changes. The deflection of the mirror is a measure of the pressure change. Vibration affects these gauges to a marked degree.

The first device tested was a direct reading type which consisted of a calibrated vernier screw mounted in the closed end of a mercury manometer. One division on the vernier was equivalent to a pressure difference of 0.02 mm., and an estimation could be made to 0.2 of a division giving a measurement to 0.004 mm. A platinum needle attached to the screw made contact with the mercury surface and acted as a switch in the circuit of a dry cell. The deflection of the galvanometer indicated when contact had been made. A change in pressure could be measured directly by re-establishing contact.

The fundamental inaccuracy in this device was due to variation in the contact made with the mercury surface. Its accuracy was considerably less than the 0.004 mm. calculated for it. Several trials indicated that it could measure pressure changes of about 0.02 mm.

An attempt was made to construct a modification of the optical lever manometer described by Shrader and Ryder (24) which would have the desired characteristics. A mercury manometer was equipped with a vertical plane glass window just above the mercury surface. This arm of the manometer was attached to the balance chamber. The other arm was attached to the reaction chamber. A hair like quartz fiber was sealed with selenium to two glass rods extended over the mercury surface. These rods were cemented into sockets ground in the glass window. A light glass lever arm was sealed to the fiber with selenium so that its length was perpendicular to the fiber and the window. A light mirror made from a microscope cover glass was mounted vertically upon the lever at the point of contact with the fiber. The free end of the lever contacted the center of the mercury surface through a small glass bubble. Rotation of the mirror due to movement of the mercury surface was measured by means of the telescope and scale from a wall type galvanometer.

One difficulty with this manometer was its extreme sensitivity to shock and to vibration. The extent to which the movement of the mercury surface is magnified is determined by the ratio between the length of the lever arm and the distance between the mirror and the scale. The movements due to causes other than pressure change were magnified to the same degree. The agreement between the zero points established at the beginning and conclusion of a reaction was poor. Since a vibrationless pier and constant temperature room were not available this difficulty could not be eliminated. A second difficulty was the variation in the effective length of the lever arm over the range of pressures to be measured. The desired sensitivity required a short lever arm. The effective lever arm length is determined by the cosine of the angle of rotation of the mirror, and this angle can only be small if the lever arm is long in comparison to its vertical displacement. The desired sensitivity required a ratio of 4 - 5 to 1 between the lever arm length and the vertical displacement. Due to these difficulties the use of this gauge was impractical.

The gauge finally chosen consisted of a modified, direct reading, mercury U-tube manometer. The limbs of the U-tube were large to decrease the tendency of the mercury to stick to the walls. A non-volatile, non-viscous liquid, dicyclohexyl was placed above one mercury surface and allowed to extend into a horizontal capillary tube. The magnification of the movement of the mercury surface due to a change in pressure is determined by the ratio of the areas of cross section of the limb of the manometer and the capillary tube.

# STATEMENT OF THE PROBLEM

The purpose of this investigation was:

1. To determine the relationship which exists between the electron sharing ability of the radicals and the dissociation constants in the gaseous phase for a series of hemimercaptals formed by the condensation of chloral with a series of mercaptans.

2. To compare the free energies of the reaction in the gaseous phase with those previously obtained in benzene solution.

3. To design an apparatus and a pressure measuring device to permit the determination of the dissociation constants.

4. To determine, if possible, the role of the catalyst in the reaction.

## EXPERIMENTAL

### MATERIALS

Chloral was prepared in an apparatus consisting of a U tube joined through a stopcock to small distilling flask and condenser. The condenser delivered into a "multiple receiver" so constructed that weighed capillary tubes could be placed open end down in one arm. The entire apparatus was thoroughly dried by passing dry air through it. Chloral hydrate was trapped in the closed arm of the U tube by concentrated sulfuric acid. When dehydration was complete the chloral was pulled by gentle suction into the distilling flask. The chloral was then distilled and a small portion boiling at 97° was caught in the arm containing the capillary tubes.

The tubes were filled by evacuating the system and admitting dry air at atmospheric pressure. They were then removed and warmed to expel a small amount of liquid at the tip. When the tube cooled an empty space at the tip permitted better sealing. A piece of cold metal was touched to this space and the hair like tip sealed in the edge of a micro flame. The tubes were then washed with alcohol, allowed to dry, and reweighed on the micro balance.

The capillary tubes were prepared by drawing six millimeter tubing down to three or four tenths of a millimeter.

This tubing was cut into convenient lengths, and one end was sealed. The other end was pulled to hair like dimensions in a soft flame and cut off to leave a two or three millimeter projection.

*Butyl mercaptan* was prepared by the method described by Ellis and Reid (10). Its boiling point was 97°.

*Ethyl mercaptan* was obtained from the Eastman Kodak Co. and fractionally distilled. Its boiling point was 36°.

*Methyl mercaptan* was obtained from the Eastman Kodak Co. and fractionally distilled. Its boiling point was 6-7°. In order to fill the capillary tubes it was necessary to cool the receiver in an acetone-dry ice bath. The filled tubes were then transferred rapidly to a second bath, where the open ends were sealed as described above.

*Allyl mercaptan* was first prepared by the general method described by Ellis and Reid (10). Instead of boiling at 90° as expected, the product obtained distilled over a range of 80-139°, leaving a residue which decomposed. This behavior has been reported by Brown and Murjahn (5) who prepared allyl mercaptan by saponifying the urethan, and obtained a product boiling at 67-68°. The allyl mercaptan used was prepared by their method, had the reported boiling point, and when used in the experimental work produced pressures which compared favorably with those produced by equimolar quantities of the other mercaptans.

Thiophenol was obtained from the Eastman Kodak Co. and fractionally distilled. Its boiling point was 168°.

APPARATUS

A top view of the apparatus is shown in Fig. 1. It consists of two one liter round bottom flasks, A and B, which are connected through a stopcock, C. The reaction chamber, A, is joined to the capillary tube breaker, D, by means of a standard taper number 19/38 Pyrex ground glass joint, F. The balance flask, B, is connected to a McLeod gauge at J and to a Cenco Hyvac pump through a stopcock, G. A by-pass containing a stopcock, H, is built around a hair-like capillary, I, sealed in tube K.

The capillary tube breaker consists of a horizontal tube, L, to which are joined three sidearms, M, which slant downward at a slight angle. The breakers, N, slide in these sidearms and consist of iron rods sealed in glass. The capillary tube, O, is slipped through the glass loop on the breaker and is held firmly against the wall of tube L by the weight of the breaker.

The energy for breaking a capillary tube is furnished by an electromagnetic coil which operates on 110 Volts and is

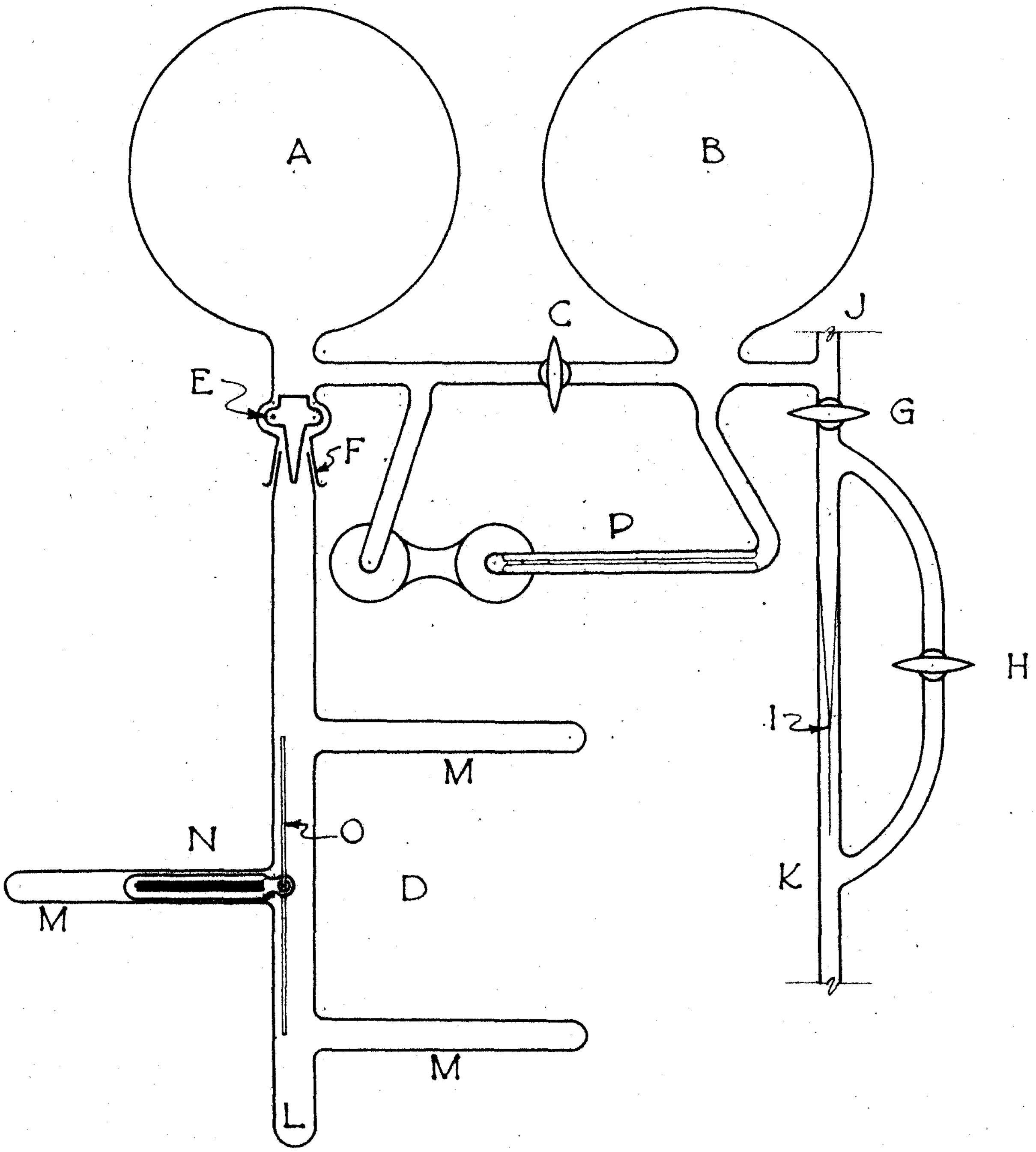


Figure 1

wound from 28 B. and S. gauge lacquered magnet wire. The field strength is regulated by a variable resistance connected in series. The opening in the center of the breaker coil just fits the sidearm, M. When the center of the coil is approximately one half inch from the center of the iron core in the breaker, the switch is thrown and the breaker is jerked into the magnetic field. An efficient switch must be used or the breaker may be thrown from the field with sufficient force to injure the apparatus.

The glass plug, E, is placed in the cup of the joint, F, to prevent the passage of a broken capillary into the reaction chamber. Before this precaution was taken one capillary tube acquired sufficient velocity, due to the rapid vaporization of the liquid content, to break a chip from the back of the reaction flask.

The McLeod gauge which is attached at J is so constructed that each scale division measures a pressure of 0.008091 millimeters of mercury. Readings of the scale were made to 0.2 of a division.

The gauge, P, is used to establish a balance between the pressures in flasks A and B. It is shown in detail in Fig. 2. The gauge is joined to the apparatus by ground glass joints, A, which permit its removal for cleaning and refilling when necessary. All ground glass joints in the apparatus are sealed in with a beeswax-rosin cement. The arms of the mer-

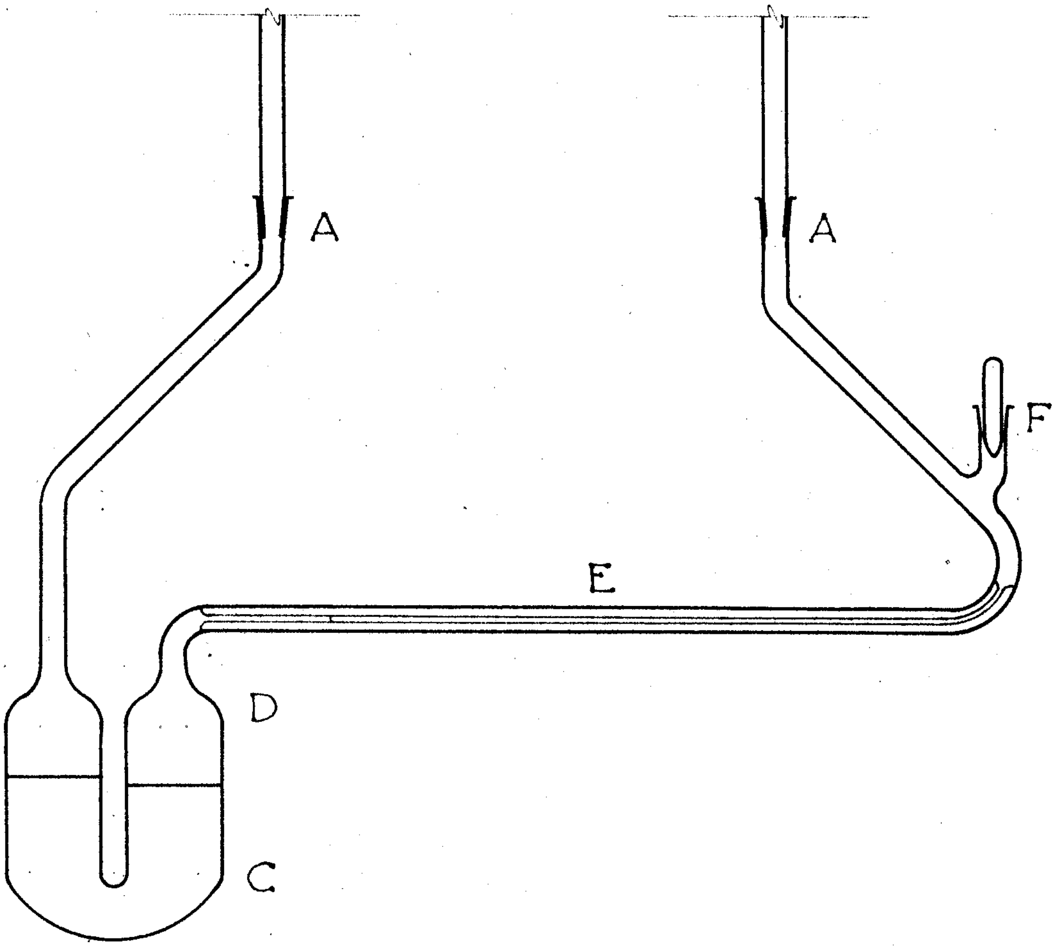


Figure 2

cury manometer, C, are constructed of uniform glass tubing and joined to a capillary tube, E, which is provided with a millimeter scale and kept horizontal by leveling screws attached to the apparatus. Sufficient dicyclohexyl is added through the opening provided by the ground glass stopper, F, to fill the space above the mercury and extend into the capillary tube. The stopper furnishes a convenient means of replacing the dicyclohexyl which is lost during the evacuation of the apparatus. Three reactions may be run before additional liquid is required.

The sensitivity of the gauge is determined by two factors, the ratio of the area of cross section of tube C to that of tube E, and the resistance to the liquid flow through the capillary, E. If the area of cross section of tube C is 200 times that of tube E, the deflection in tube E will be 100 times as great as the change in the levels of the mercury surfaces. A change in pressure of 0.01 mm. would move the meniscus 1 mm.

The liquid used in the gauge must wet the tube and be non-viscous. Since its vapor pressure must be very low the possibilities were limited. The first substance investigated, n-butyl phthalate, failed to flow with sufficient freedom, and as a result small inequalities in pressure were not registered. In a private communication Dr. Willard Ruby of the Eastman

Kodak Co. suggested the use of dicyclohexyl. The compound was obtained from the Eastman Kodak Co., and was purified by shaking with a mixture of concentrated sulfuric and nitric acids, washing with distilled water and distilling over sodium.

Changes in temperature have a very noticeable effect upon the zero point of the gauge. Due to the difference between mercury and dicyclohexyl as to their coefficients of thermal expansion and their change in density per degree variation in temperature the zero point will remain constant only if the temperature is constant. To determine the magnitude of this effect the zero point of the gauge was recorded over a range of temperatures from 20° to 30° C. It was found that a one degree rise in the temperature shifted the zero point 8 mm. to the right. It was, therefore, necessary to place the apparatus in an air bath in which the temperature could be controlled within 0.1° C.

If the apparatus is allowed to stand for some time at pressures above two or three millimeters, nitrogen is dissolved by the gauge liquid. Unless this gas is boiled out under good vacuum the horizontal liquid column may break after the apparatus is evacuated for the next reaction. If the apparatus is kept at low pressure between reactions this difficulty is eliminated.

The effective area of cross section of the horizontal capillary will depend upon the thickness of the liquid film left upon it. For this reason the rate at which the dicyclohexyl drains back to the zero point must be constant. This was accomplished by the use of capillary I, Fig. 1, which provided a constant slow admission of dry nitrogen to the balance chamber.

The gauge as described could be used as a direct pressure measuring device by calibrating it against the McLeod gauge. It could also be used as a null instrument, permitting the use of the McLeod gauge as the indirect measuring device. A study was undertaken to determine the relative merits of the methods.

## USE OF GAUGE AS A DIRECT MEASURING INSTRUMENT

The apparatus was pumped down to a convenient pressure, the zero point of the gauge established, and the reading of the McLeod gauge recorded. Stopcock C, Fig. 1, was then closed and pumping resumed. When sufficient pressure differential had been reached, the new readings were established and recorded. Typical results are shown in Table 3, Group 1.

Here $P_{Bal.\ gauge}$ is the change in the reading of the balance gauge in millimeters and $P_{McL.}$ is the change in the reading of the McLeod gauge.

The actual volume of the reaction chamber was determined

TABLE 3

Calibration of the Balance Gauge

| Group | $\Delta P_{Bal. Gauge}$ | $\Delta P_{McL.}$ | $\Delta P_{McL.}/\Delta P_{Bal. Gauge}$ |
|---|---|---|---|
| 1 | 107.6 | 81 | 0.753 |
| | 108.4 | 82 | 0.757 |
| | 200.8 | 151 | 0.752 |
| 2 | 152.2 | 107.6 | 0.707 |
| | 151.0 | 108.8 | 0.721 |
| | 158.6 | 113.8 | 0.718 |
| 3 | 146.4 | 100.4 | 0.686 |
| | 164.6 | 112.4 | 0.683 |
| | 161.4 | 112.4 | 0.696 |

as 1130 ml. from the weight of distilled water required to fill it. The volume was also determined by liberating in it known quantities of the non polar compounds, carbon tetrachloride, benzene, chloroform and measuring the resulting pressure increase.

The procedure was as follows: The breaker device was loaded with three capillary tubes and prepared for the determinations in the manner described above. A tube was broken and the resulting deflection of the gauge recorded. The process was repeated with the other two capillary tubes. Typical results are shown in Table 4.

TABLE 4

Determination of Reaction Chamber Volume at 25°C. Using Deflection Method

| Group | Compound | $M \times 10^5$ | $\Delta P_{Bal.Gauge}$ | $\Delta P_{atm.} \times 10^4$ | $V_{(ml)}$ |
|---|---|---|---|---|---|
| 1 | $CCl_4$ | 3.754 | 98.8 | 7.93 | 1,158 |
|  | " | 4.424 | 116.0 | 9.31 | 1,162 |
| 2 | $CHCl_3$ | 6.979 | 185.2 | 14.85 | 1,148 |
|  | " | 4.777 | 127.6 | 10.24 | 1,141 |
|  | " | 1.427 | 38.0 | 3.05 | 1,145 |
| 3 | $C_6H_6$ | 3.730 | 104.8 | 8.22 | 1,085 |
|  | " | 4.452 | 126.2 | 10.13 | 1,075 |
| 4 | $C_6H_6$ | 2.052 | 58.0 | 4.66 | 1,078 |
|  | $CHCl_3$ | 0.778 | 22.0 | 1.77 | 1,078 |
|  | $CCl_4$ | 6.332 | 173.6 | 13.93 | 1,111 |

In group one the first tube contained $3.754 \times 10^{-5}$ mols of carbon tetrachloride and deflected the balance gauge 98.8 units. Each of these units is equivalent to 0.754 McLeod gauge units as shown in column 3 of Table 3, group 1. The deflection is therefore equivalent to 98.8 x 0.754 or 74.5 McLeod units. To secure the actual pressure change in atmospheres this value must be multiplied by 0.008091 to change it to millimeters, and divided by 760. This gives the value $7.93 \times 10^{-4}$ recorded in column 2. Substituting in the gas law equation V = MRT/P, we get $V = 3.754 \times 10^{-5} \times 82.06 \times 298/7.93 \times 10^{-4}$ or V = 1158 cc. Each group in Table 4 represents the results obtained from an individual loading of the apparatus.

The results in Table 3, Group 2, were obtained immediately following the completion of the work described above. The use of 0.715, the average ratio thus obtained, in recalculating the volume for group 4, Table 4, gave the value 1139 cc. which agrees with the actual volume.

It was evident that the decrease in the calculated volumes must be due to a shift in the calibration ratio of the balance gauge. The results shown in Table 3, Group 3, were obtained as further evidence of this shift.

The difficulty encountered above might be due to the fact that the motion of the mercury in manometer C, Fig. 2, varied with the exact section of the tube at which the dicyclohexyl contacted the mercury. The width of the strip below the mercury wet by the dicyclohexyl and the thickness of the adhering film could also cause the observed variance. These variables could be eliminated during a run by making all gauge readings as nearly identical as possible and using the McLeod gauge to register the pressure changes in the balance flask. Due to these variables the above described method of using the gauge as a direct reading instrument is not advisable.

## USE OF GAUGE AS NULL INSTRUMENT.

An investigation was made similar to the above but using the gauge as a null instrument. In Table 5, $P_0$ Reaction Fl. is the pressure in the reaction chamber in millimeters of mercury as measured by the McLeod gauge at the beginning of the experiment, when the zero point of the balance gauge was $G_0$. The gauge shift, D, was caused by evacuating the balance chamber. Its pressure was then increased to $P_{McL.}$ causing the balance gauge reading to shift back to $G_F$. The correction of $P_{McL.}$ for the difference between $G_0$ and $G_F$ gives P Calcd., the measured value of the pressure in the reaction flask. The

TABLE 5

Comparison of Actual and Measured Pressures

| $P_0$(mm) Reaction Fl. | $G_0$ | $G_F$ | $P_{McL.}$(mm) | Balance Gauge Shift | $P_0$(mm)[(a)] Calcd. |
|---|---|---|---|---|---|
| 0.850 | 4.0 | 0.0 | 0.889 | 135.4 | 0.866 |
| 0.808 | 9.0 | 1.8 | 0.850 | 114.2 | 0.804 |
| 0.890 | 5.0 | 13.2 | 0.857 | 140.0 | 0.905 |
| 0.887 | 10.6 | 5.8 | 0.929 | 142.0 | 0.901 |

(a) This value is $P_{McL.}$ corrected for the difference between $G_0$ and $G_F$.

actual pressure and the measured pressure agree within less than 2 per cent.

The results obtained in the determination of the reaction chamber volume by the null method are shown in Table 6. In the first experiment 5.395 x $10^{-5}$ moles of carbon tetrachloride were released into the reaction flask when its pressure was 0.008 mm. The zero point of the balance gauge was 3.0 and a pressure of 0.882 mm. in the balance flask was required to return the meniscus to the reading 4.0, near the original value. To correct for the difference in zero points, 0.006 mm. was added, giving the value 0.888 mm. for the final pressure in the reaction flask. The difference between the original and final pressure was converted to atmospheres,

TABLE 6

Determination of Reaction Chamber Volume at 25°C. Using the Null Method

| Compound | M x $10^5$ | $G_0$ | $G_F$ | $P_0$(mm) | $P_{McL.}$(mm) | $P_F$(mm)[(a)] | $P_{atm}$x$10^4$ | V(ml) |
|---|---|---|---|---|---|---|---|---|
| $CCl_4$ | 5.395 | 3.0 | 4.0 | 0.008 | 0.882 | 0.887 | 11.58 | 1140 |
| " | 5.434 | 5.4 | 1.4 | 0.019 | 0.938 | 0.913 | 11.76 | 1131 |

(a) This value is $P_{McL.}$ corrected for the difference between $G_0$ and $G_F$.

giving the value $11.58 \times 10^{-4}$. The volume was calculated from this pressure as shown above.

The null method for using the gauge was chosen on the basis of the evidence given above. The results recorded in Table 5 show a satisfactory agreement between the actual and measured pressures, while the results in Table 6 show that a definite weight of material will register its correct pressure.

## DETERMINATION OF EQUILIBRIUM CONSTANTS

The method of procedure is perhaps best presented by the following description of a typical reaction between chloral and ethyl mercaptan.

Dry nitrogen was admitted to the apparatus until it was at atmospheric pressure. The ground joint F, Fig. 1, was warmed and the capillary tube breaker removed. Capillary tubes containing 6.026 mg. of chloral, dry hydrogen chloride and 2.548 mg. of ethyl mercaptan were placed in the loops of the breakers, N. The capillary tube breaker was then replaced and the apparatus pumped down to a reading of 0.0 on the McLeod gauge. The zero reading of the balance gauge was established as 28.0 and the chloral tube broken. The meniscus of the gauge was deflected to 125.0. Dry nitrogen was slowly admitted to the balance flask through the capillary, (I), until the meniscus had moved back to 30.8. After two hours the final reading was

28.0. The McLeod gauge reading was then 72.6.

The ethyl mercaptan tube was then broken and the gauge meniscus moved to 130.0. Thirty minutes later the reading was 124.0. After an additional two hours the reading was 112.0. Ten hours later the final reading of 100.4 was obtained.

The hydrogen chloride tube was then broken. This increased the reading to 101.4, and caused no subsequent decrease in gauge reading.

The pressure in the balance flask was again increased until the balance gauge reading was 30.8. One hour later it had decreased to 30.0 and no further shift occurred. The Mc Leod gauge reading was 123.8. This reading corrected, to the original zero of the balance gauge, 28.0, was 125.2.

Since each division of the McLeod gauge is equal to 0.008091 mm. of mercury, the pressure of the chloral was 0.587 mm. The pressure produced by the ethyl mercaptan was calculated to be 0.617 mm. The equilibrium pressure was 1.013 mm.

If no combination took place, the pressure would have been 1.204 mm., therefore the change in pressure due to combination between chloral and ethyl mercaptan was 0.191 mm. This is the pressure of the hemimercaptal. The pressure of the uncombined chloral and ethyl mercaptan would be 0.396 and 0.426 mm. respectively. From these values the equilibrium constant was calculated to be 1.16 x $10^{-3}$. The data obtained are given in Table 7.

## TABLE 7

### The Dissociation Constants of a Series of Hemimercaptals in the Gaseous Phase

| M x $10^5$ RSH | M x $10^5$ Chloral | $P_{chl}$ (mm) | $P_{RSH}^{(a)}$ (mm) | $P_{Total}$ (Initial) (mm) | $P_{Total}$ (final) (mm) | $\Delta P^{(b)}$ due to reaction (mm) | $P_{chl}$ final (mm) | $P_{RSH}$ final (mm) | $K_p$ (atm.) (25°C) |
|---|---|---|---|---|---|---|---|---|---|
| $C_2H_5SH$ | | | | | | | | | |
| 4.102 | 4.089 | 0.587 | 0.617 | 1.204 | 1.013 | 0.191 | 0.396 | 0.426 | $1.16 \times 10^{-3}$ |
| 4.238 | 4.083 | 0.667 | 0.696 | 1.363 | 1.152 | 0.211 | 0.456 | 0.485 | $1.38 \times 10^{-3}$ |
| 0.898 | 0.990 | 0.125 | 0.116 | 0.241 | 0.228 | 0.013 | 0.112 | 0.103 | $1.17 \times 10^{-3}$ |
| $C_4H_9SH$ | | | | | | | | | |
| 2.290 | 2.311 | 0.340 | 0.345 | 0.685 | 0.372 | 0.313 | 0.027 | 0.032 | $3.63 \times 10^{-6}$ (c) |
| 1.169 | 1.200 | 0.163 | 0.163 | 0.325 | 0.228 | 0.097 | 0.065 | 0.066 | $5.82 \times 10^{-5}$ |
| 0.887 | 0.826 | 0.120 | 0.131 | 0.251 | 0.184 | 0.067 | 0.053 | 0.064 | $6.66 \times 10^{-5}$ |
| $CH_3SH$ | | | | | | | | | |
| 0.877 | 0.995 | 0.139 | 0.136 | 0.275 | 0.217 | 0.058 | 0.081 | 0.078 | $1.43 \times 10^{-4}$ |
| 6.769 | 6.598 | 0.982 | 1.071 | 2.053 | 1.282 | 0.771 | 0.211 | 0.300 | $1.08 \times 10^{-4}$ |
| $C_3H_5SH$ | | | | | | | | | |
| 1.984 | 2.145 | 0.298 | 0.280 | 0.578 | 0.443 | 0.135 | 0.163 | 0.145 | $2.30 \times 10^{-4}$ |
| 2.799 | 2.895 | 0.419 | 0.421 | 0.840 | 0.520 | 0.320 | 0.099 | 0.101 | $4.11 \times 10^{-5}$ (c) |
| 1.547 | 1.519 | 0.226 | 0.226 | 0.452 | 0.341 | 0.111 | 0.115 | 0.115 | $1.57 \times 10^{-4}$ |

(a) This value was read from the gauge as follows: the deflection produced by the chloral was measured five minutes after the compound had been released. The deflection produced by the RSH compound was similarly measured. From the ratio of these deflections and the measured pressure of the chloral, the pressure of the RSH compound was calculated.

(b) This value is the pressure due to the hemimercaptal formed.

(c) These values were discarded because the equilibrium was not homogeneous.

## DISCUSSION OF RESULTS

Since the dissociation constants shown in Table 7 must be calculated on the basis that all three components of the reaction are at equilibrium in the gaseous phase, it was necessary to show that a homogeneous equilibrium had been established. This was found to be particularly necessary because of the unexpected behavior of the hemimercaptal of thiophenol which was the second member of the series to be investigated.

When $2.4 \times 10^{-5}$ mols of chloral and thiophenol had been released, the total initial pressure was 0.695 mm. If complete combination had occurred, the final pressure would have been 0.348 mm. Before the reaction had reached equilibrium, the pressure had decreased to 0.220 mm., a value which could not well be explained except by the separation of a liquid or solid phase. This behavior was contrary to that predicted by an earlier determination of the vapor pressure of this hemimercaptal (13), and prevented the measurement of the dissociation constants for the aromatic members of the series since these vapor pressures fall below the range which can be accurately measured.

As a result only the low molecular weight aliphatic members of the series could be investigated and care had to be taken to keep the reactions homogeneous. Accordingly determinations were made for all members of the series at varying pressures and values accepted only when checks were obtained at significantly different pressures. The evidence from Table 7 indicates that the hemimercaptal of butyl mercaptan cannot exist entirely in the vapor phase at a pressure of 0.685 mm. At a slightly higher pressure considerable condensation occurred. In the case of the allyl hemimercaptal condensation occurred in the case where the total initial pressure was 0.840 mm.

The free energies of dissociation in benzene and in the gaseous phase are shown in Table 8. The first column shows

TABLE 8

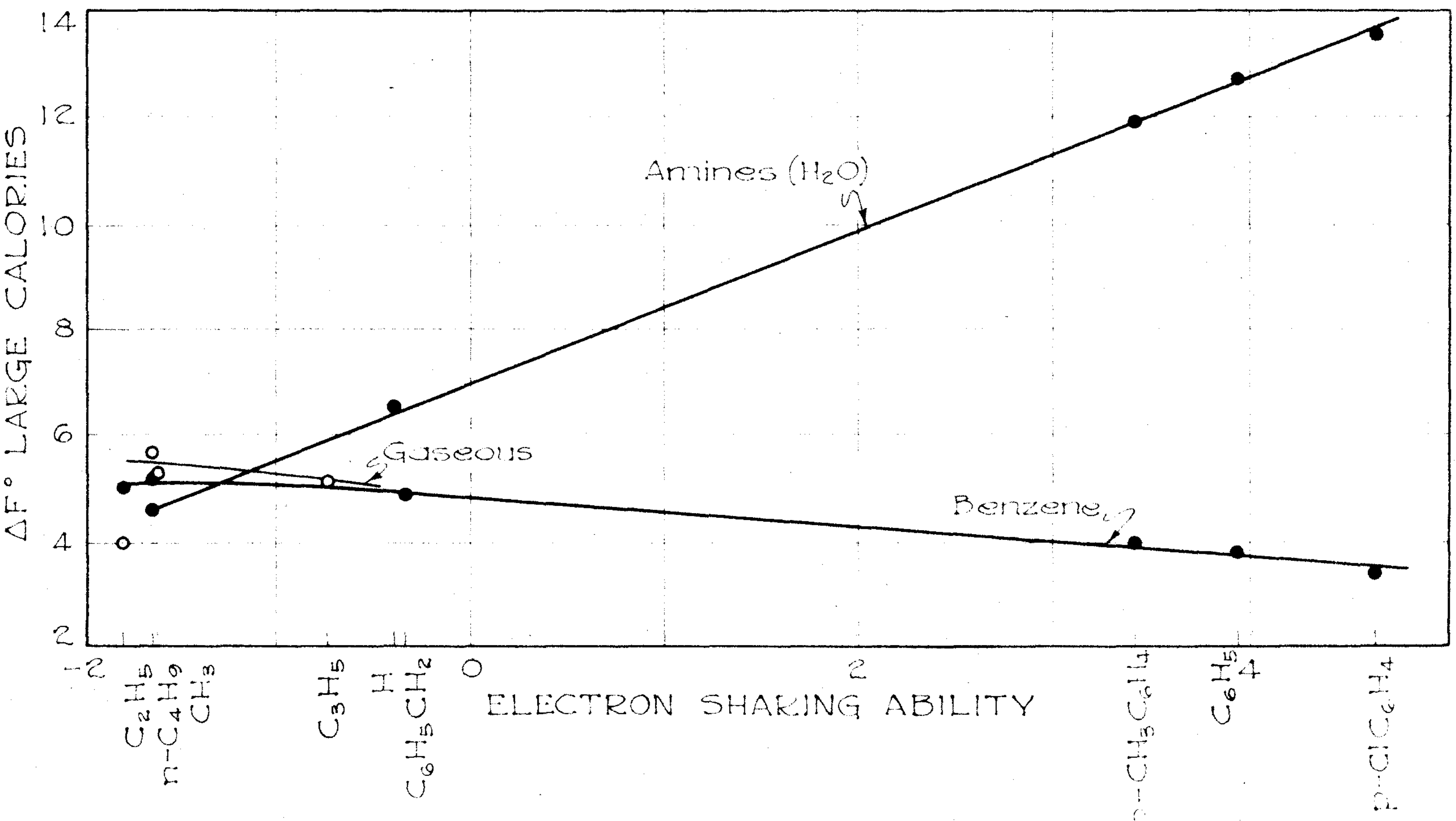
Free Energies of Hemimercaptals in Benzene and the Gaseous Phase

| Hemi-mercaptal | $K_{dissoc}$ Benzene | $K_x$ Benzene | $K_p$ atm Gaseous | $\Delta F°$Cal. Benzene | $\Delta F°$Cal. Gaseous |
|---|---|---|---|---|---|
| n-$C_4H_9$ | $2.0 \times 10^{-3}$ | $1.5 \times 10^{-4}$ | $6.24 \times 10^{-5}$ | 5.2 | 5.7 |
| $C_2H_5$ | $2.35 \times 10^{-3}$ | $2.1 \times 10^{-4}$ | $1.24 \times 10^{-3}$ | 5.0 | 4.0 |
| $CH_3$ | | | $1.26 \times 10^{-4}$ | | 5.3 |
| $C_3H_5$ | | | $1.94 \times 10^{-4}$ | | 5.1 |
| $C_6H_5CH_2$ | $2.8 \times 10^{-3}$ | $2.4 \times 10^{-4}$ | | 4.9 | |
| p-$CH_3C_6H_4$ | $1.55 \times 10^{-2}$ | $1.2 \times 10^{-3}$ | | 4.0 | |
| $C_6H_5$ | $2.1 \times 10^{-2}$ | $1.63 \times 10^{-3}$ | | 3.8 | |
| p-$ClC_6H_4$ | $4.1 \times 10^{-2}$ | $3.2 \times 10^{-3}$ | | 3.4 | |

the values determined previously in this laboratory (13). These constants were calculated at that time in terms of mols per 1000 g. of benzene. Column two shows these constants recalculated in terms of mol fractions while in column three are the average values from the present work taken from Table 7. In columns four and five are the values for the free energy of the reactions calculated from the relationship $\Delta F° = -RT \ln K_a$. With the exception of the value for the ethyl hemimercaptal the trend in the gaseous phase seems to differ little from that in the benzene solution, indicating but little solvent effect.

The free energies from Table 8 are plotted in Graph 2 together with the amine curve which determines the position of the radicals on the x-axis. Due to the short range covered by the aliphatic members of the series, the curve for the gaseous phase free energies is of little value and should be considered as a group of points. It seems probable, however, that no significant differences exist between the curves for the two phases.

It is therefore apparent that the vapor phase measurements in this case have no particular advantage over the measurements made in solution. They have, however, shown that the free energy difference due to the solvent is not large. The disadvantages of the method are the characteristic inaccuracy

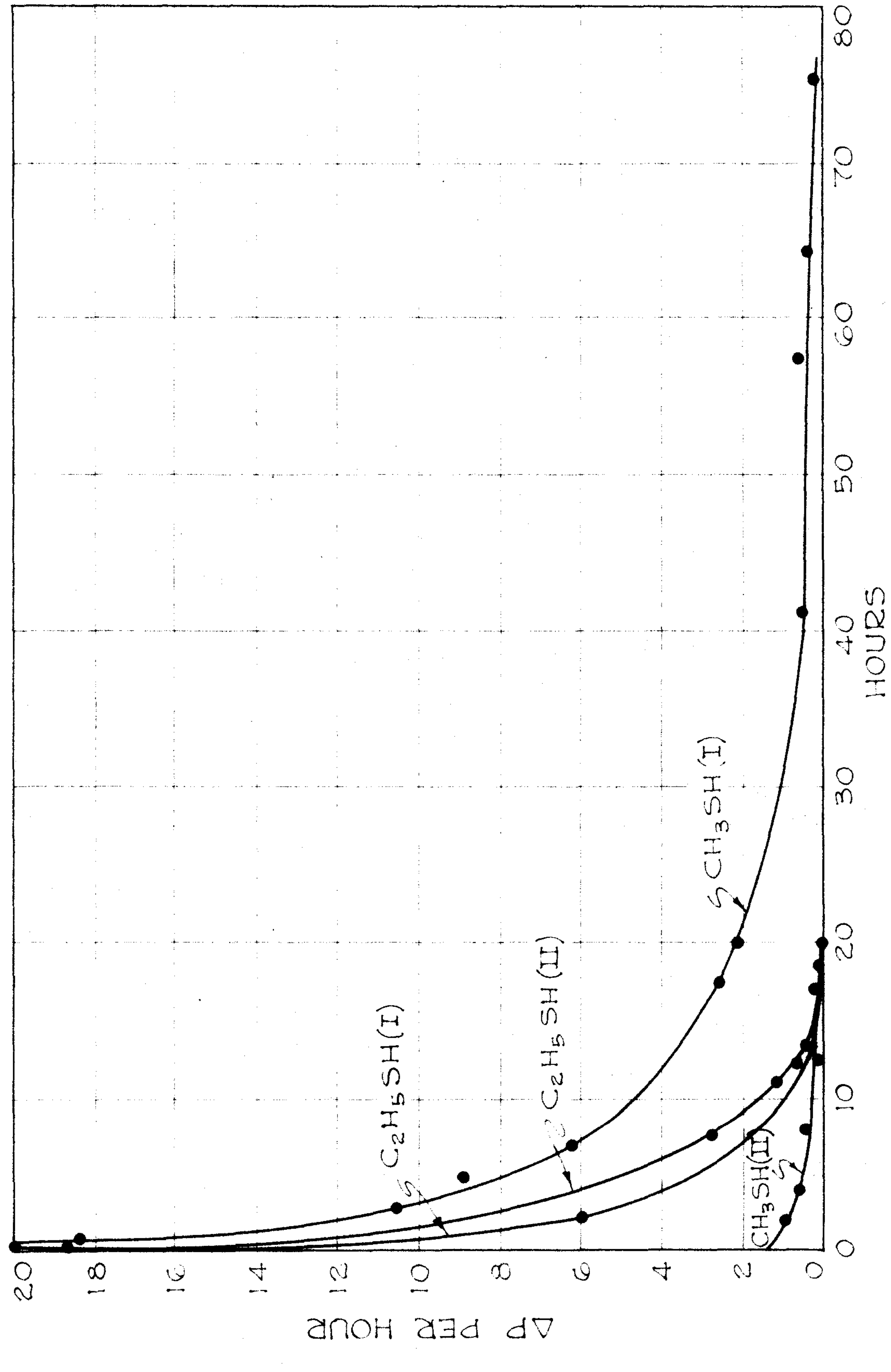

ΔF° LARGE CALORIES
14
12
10
8
6
4
2
Amines ($H_2O$)
Gaseous
Benzene
-2
0
2
4
ELECTRON SHAKING ABILITY
$C_2H_5$
n-$C_4H_9$
$CH_3$
$C_3H_5$
H
$C_6H_5CH_2$
p-$CH_3C_6H_4$
$C_6H_5$
p-$ClC_6H_4$

GRAPH 2

of measurements at low pressure, and the time-consuming nature of the work.

The velocity with which equilibrium is attained is shown in Graph 3. Curve $C_2H_5SH$(I) represents the reaction between 4.1 x $10^{-5}$ mols each of chloral and ethyl mercaptan. In this reaction the HCl catalyst was added at the end of the reaction time and caused no additional pressure decrease. Curve $C_2H_5SH$ (II) represents the reaction between 4.1 x $10^{-5}$ mols of chloral and 4.2 x $10^{-5}$ mols of ethyl mercaptan. In this reaction the HCl was added before the reactants were released in the reaction flask. It is obvious that in the gaseous phase the reaction proceeds with the same velocity with or without the catalyst. As additional evidence a reaction was run qualitatively in the presence of a high concentration of catalyst without appreciably increasing the velocity with which equilibrium was attained.

Curve $CH_3SH$(I) represents the reaction between 6.6 x $10^{-5}$ mols of chloral and 6.8 x $10^{-5}$ mols of methyl mercaptan, while in curve $CH_3SH$(II) the quantities were 1.0 x $10^{-5}$ and 0.9 x $10^{-5}$ mols respectively. It is evident that the time required to attain equilibrium varies as the initial concentrations. The time required also varies with the reacting substances, since the equilibrium is established in approximately the same time for 4.1 x $10^{-5}$ mols of ethyl and 0.9 x $10^{-5}$ mols of


ΔP PER HOUR
20
18
16
14
12
10
8
6
4
2
0
HOURS
0
10
20
30
40
50
60
70
80
$C_2H_5SH$(I)
$C_2H_5SH$(II)
$CH_3SH$(I)
$CH_3SH$(II)

GRAPH 3

methyl mercaptan.

Curves of this type offer additional proof of the establishment of equilibrium in the reaction, since the general shape of the curve indicates the approach of equilibrium. If two pressure readings erroneously indicate establishment of equilibrium, the curve would show a sudden change of slope.

## SUMMARY

1. An apparatus for measuring the dissociation constants of gaseous equilibria has been described.
2. The dissociation constants of the hemimercaptals formed by the condensation of chloral with butyl, ethyl, methyl, and allyl mercaptan have been determined.
3. It has been shown that the free energies of dissociation of the aliphatic hemimercaptals in the vapor phase differ to no significant extent from those in benzene solution.
4. There is no evidence here shown to indicate that the gaseous phase has marked advantages over the dissolved state for the determination of the influence of radicals on polar groups.
5. The catalyst has little if any influence upon the velocity with which equilibrium is attained in the gaseous phase.

## LITERATURE CITED

1. Allison and Hixon, J. Am. Chem. Soc., 50, 168 (1928).
2. Braun and Murjahn, Ber., 59B, 1202 (1926).
3. Burch, Proc. Roy. Soc., A, 123, 271 (1929).
4. Carr, Johns and Hixon, J. Am. Chem. Soc., 60, 891 (1938).
5. Conant, Ind. Eng. Chem., 24, 466 (1932).
6. Conant, J. Am. Chem. Soc., 49, 293 (1927).
7. Conant and Feiser, ibid., 45, 2194 (1923).
8. Conant and Thompson, ibid., 54, 4039 (1932).
9. Craig and Hixon, ibid., 53, 4367 (1931).
10. Ellis and Reid, ibid., 54, 1674 (1932).
11. Goodhue and Hixon, ibid., 56, 1329 (1934).
12. Hixon and Johns, ibid., 49, 1786 (1927).
13. Johns and Hixon, ibid., 56, 1333 (1934).
14. Johns and Hixon, J. Phys. Chem., 34, 2226 (1930).
15. Johns, Peterson and Hixon, ibid., 34, 2218 (1930).
16. Johnson and McIntosh, J. Am. Chem. Soc., 31, 1138 (1909).
17. Kirchner and Johns, ibid., (to appear August 1940).
18. Ladenburg and Lehmann, Verh. d. deut. phys. Gesell., 8, 20 (1906).
19. Lind and Livingston, J. Am. Chem. Soc., 54, 94 (1932).
20. Oldham and Johns, ibid., 61, 3289 (1939).
21. Olson and Hirst, ibid., 51, 2378 (1929).

22. Rayleigh, Phil. Trans., A, 196 205 (1901).

23. Roberts, Proc. Roy. Soc., A, 78, 410 (1906).

24. Shrader and Ryder, Phys. Rev., 13, 321 (1919).

25. Smith, Rev. Sci. Inst., 7, 157 (1936).

26. Starr, Bulbrook and Hixon, J. Am. Chem. Soc., 54, 3971 (1932).