

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

## Evidence for Ring Structure in Certain Aliphatic Organic Compounds

BY HILTON A. SMITH AND J. P. McREYNOLDS

In connection with the study of the rate of esterification of organic acids, the postulation has been made that acids with a chain involving four or more carbon atoms have a ring structure. The purpose of this paper is to use this as a basis for explaining a number of properties of organic acids and other organic compounds which might have such a structure.

## I. Esterification

The rates of the catalyzed esterification of normal aliphatic acids in methyl alcohol have been studied recently.<sup>1</sup> Figure 1 shows the effect of the length of the carbon chain on the values of the rate constant at 25°. From this figure, it is obvious that increasing the chain length of the acid produces a definite effect when there are less than four carbon atoms in the chain. Starting with butyric acid, however, lengthening of the chain produces no effect. These facts were explained by postulating that the chain of butyric and higher acids was not straight, but that the first four carbon atoms including that in the carboxyl group formed a ring.

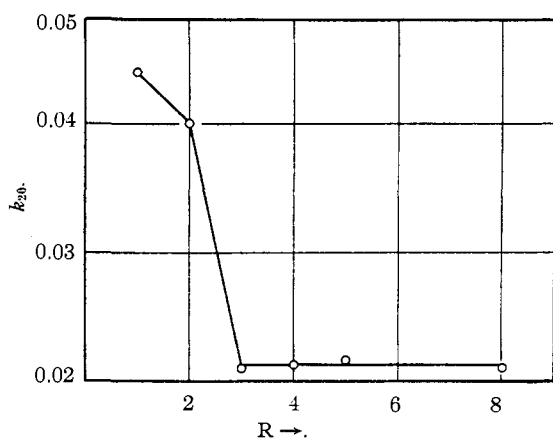


Fig. 1.—Effect of acid chain length on the reaction  $\text{CH}_3\text{OH}_2^+ + \text{RCOOH} \rightarrow \text{CH}_3\text{COOR} + \text{H}_3\text{O}^+$ .

In a subsequent paper<sup>2</sup> it was shown that the rates of the catalyzed esterification of methyl and phenyl substituted acids in methanol substantiated this theory.

(1) Smith, *THIS JOURNAL*, **61**, 254 (1939).

(2) Smith, *ibid.*, **61**, 1176 (1939).

## II. Saponification

The effect of the length of the carbon chain of the acid group on the rate of the alkaline hydrolysis of saturated aliphatic esters was studied by Evans, Gordon and Watson.<sup>3</sup> These workers found that the values of the reaction rate constants decreased with increasing chain length until ethyl butyrate was reached. Further increase in the chain length had no effect. They attributed the decreasing values of  $k$  in the early members of the series to an increase in the activation energy of the reaction. This idea has been modified<sup>4</sup> and it has been shown that within experimental error the activation energy does not change with increasing chain length. The change is rather a change in the steric factor in the equation  $k = sZe^{-E/RT}$ .

Figure 2 shows the effect of the length of the carbon chain on the reaction velocity constants for the saponification of the ethyl esters of normal aliphatic acids at 25°. The data of Smith and Levenson were used for the first three points on this graph, while subsequent points were obtained from the data of Evans, Gordon and Watson.

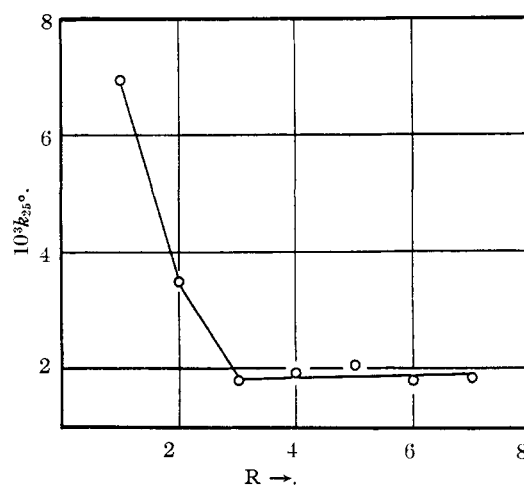


Fig. 2.—Effect of acid radical chain length on the reaction  $\text{NaOH} + \text{RCOOC}_2\text{H}_5 \rightarrow \text{RCOONa} + \text{C}_2\text{H}_5\text{OH}$ .

This figure shows that, as in the case of esterification, the effect of increasing the length of the

(3) Evans, Gordon and Watson, *J. Chem. Soc.*, 1439 (1938).

(4) Smith and Levenson, *THIS JOURNAL*, **61**, 1172 (1939).

carbon chain is quite different before and after a total of four carbon atoms are present. These results readily may be explained on the basis of the ring theory. The ring will be formed in the ethyl esters of butyric and higher acids.

Evans and co-workers included in their studies the rate of saponification of the ethyl esters of several methyl-substituted acids. Here also the results are readily explainable on the basis of the ring theory. Thus, substitution of a methyl group on the third carbon of butyric acid gives a smaller rate constant than the substitution of a similar group on the second carbon of propionic acid. This is evidenced by the fact that the values of  $k$  for ethyl isovalerate are lower than the corresponding values for ethyl isobutyrate.<sup>5</sup> Also the values of  $k$  for the saponification of the ethyl ester of methylethylacetic acid are smaller than the corresponding values for isobutyric acid. This shows the effect of the ring formation caused by completion of the four carbon atom chain.

The saponification of the ethyl ester of diethylacetic acid is particularly interesting. This ester gives the lowest values of  $k$  and also the highest activation energy of any of the esters studied by Evans, Gordon and Watson. It behaves very similarly to trimethylacetic acid ester. Evans and co-workers were unable to offer any explanation of the results with ethyl diethylacetate. The postulation of a ring structure gives such an explanation. In this ester, there are two rings formed, and the terminal methyl groups are brought into such a position that the screening of the carboxyl group is even greater in the case of the diethylacetate than in that of the trimethylacetate. Evans and co-workers found that branching on the  $\alpha$ -carbon atom leads to a lower probability factor in the case of the ethyl esters of isobutyric and trimethylacetic acids. While their conclusion is correct, their low value of the activation energy of isobutyric acid<sup>5</sup> is responsible for their very low value of " $s$ " for this acid.

Hinshelwood and Legard<sup>6</sup> demonstrated that substitution in the  $\alpha$ -position often causes an in-

(5) In this connection, Evans and co-workers state among other conclusions that "ethyl isobutyrate gives a value of  $E$  which is smaller than that for ethyl  $n$ -butyrate." This conclusion apparently results from a mistake in calculation. A re-plotting of their reaction rate constants against inverse temperature resulted in an activation energy of 15,000 cal. per mole in each case. These values were checked by the method of least squares. The results gave 15,023 for isobutyric acid and 14,968 for its normal isomer. These are certainly the same within experimental error.

(6) Hinshelwood and Legard, *J. Chem. Soc.*, 587, 1588 (1935).

crease in the activation energy. While this increase is found for the esters of trimethylacetic acid, methylethylacetic acid, and isovaleric acid, it is not found for the isobutyric ester. This same effect was found in esterification studies.<sup>7</sup> It may be that in the case of trimethylacetic and diethylacetic acids the reacting molecules must possess an added amount of energy at the time of collision in order to break through the force field set up around the carboxyl group by the several close methyl groups.

#### Acid Dissociation Constants

The dissociation constant of an organic acid may be considered as the representation of an equilibrium between the release of protons by the acid and the reaction between the  $H_3O^+$  ion and the acid radical. The effect of increasing the chain length of the acid may have a different effect on each of these, thus causing a shift in the value of the dissociation constant. The latter reaction is very similar to the catalyzed esterification of an acid with an alcohol. One might, therefore, expect to find much the same results when the effect of chain length on the two properties is studied.

The acid dissociation constants of a number of aliphatic acids have been studied by Dippy.<sup>8</sup> The effect of the length of the carbon chain on the dissociation constant of a normal aliphatic acid is shown in Fig. 3. It will be noted that the general effect of increasing the carbon chain is to lower the value of the dissociation constant. In the case of the shift from propionic to butyric acids, however, there is an increase in the value of  $K$ . The recent work of Belcher<sup>9</sup> is in accord with Dippy's findings. Bennett and Moses<sup>10</sup> compared the dissociation constants of propionic, butyric, and heptonic acids; they attributed the high value in the case of butyric acid to the fact that the end methyl in this group, being free to move, occasionally came into close proximity to the carboxyl group and facilitated ionization. Dippy, on the

(7) The activation energy of the catalyzed esterification of isobutyric acid with methyl alcohol was found to be the same as that for normal acids. " $E$ " for the same reaction with methylethylacetic acid was higher. In the case of trimethylacetic acid the activation energy is also greater. The results with this latter acid have not yet been published. In the case of isovaleric acid, the activation energy had about the same value (10,000 cal./mole) as that for normal acids. The value of  $k$  at 50° for this acid appears to be somewhat low, and may account for this result. However, this point was checked several times, all runs agreeing within the limits of experimental error.

(8) Dippy, *J. Chem. Soc.*, 1222 (1938).

(9) Belcher, *THIS JOURNAL*, 60, 2744 (1938).

(10) Bennett and Moses, *J. Chem. Soc.*, 2364 (1930).

other hand, explains the high dissociation constant of butyric acid by stating that after the proton has left the acid, the anion forms a ring of the type here postulated for the acid itself. The idea that the ring is present in the anion only seems untenable for two reasons. In the first place, the same general effect is found in the study of esterification of the acids, and also of saponification of the corresponding esters. In neither instance is the ion involved in the reaction, but rather the acid or ester molecule itself. In the second place, butyric acid hardly can be regarded as an exception. The dissociation constant of valeric acid is also higher than that of propionic acid, while that of hexoic acid is almost the same. It appears that butyric and higher acids follow one curve, while acids of shorter chain length follow another. Evidently the same effect which is found in butyric acid persists in higher normal acids. These facts can be explained by postulating ring formation for butyric and higher acids both in the undissociated molecule and in the anion. Of course, the ring must be more stable in the anion than in the acid.

Dippy feels that the possibility of explaining the dissociation constants by steric hindrance is rendered less likely by the absence of abnormality in the phenyl-substituted acids.<sup>11</sup> This already has been discussed in connection with the esterification of these acids<sup>2</sup> where it has been shown that the lack of such an abnormality may be readily accounted for by ring structures.

It would appear that the change in the dissociation constants of normal aliphatic acids may be explained on the assumption that increase in the chain length involves two opposing factors. The first may be assigned to a decrease in the ability of the proton to leave the acid when chain length is increased, and results in a decrease in the dissociation constant. This effect becomes smaller with increasing chain length. The second may be due to the fact that the number of effective collisions between the  $H_3O^+$  ion and the  $COO^-$  group of the anion is lessened with increasing chain length up to butyric acid. This results in an increase in the value of the dissociation constant. The shape of this curve will be essentially the inverse of that shown in Fig. 1 for the case of esterification. The shape of the curve in Fig. 3 results from the combination of these two curves. The sudden drop in the dissociation constant

from octoic to nonoic acids was not explained by Dippy, nor can it be explained here.

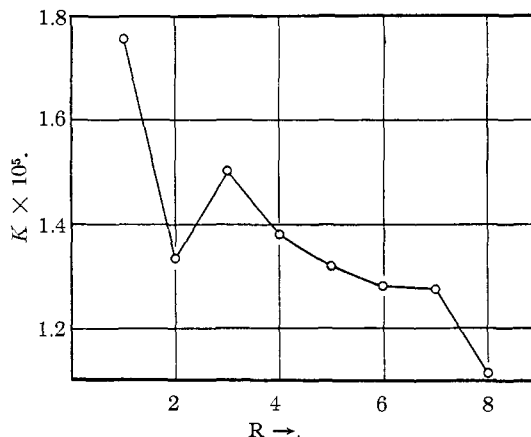


Fig. 3.—Effect of acid chain length on ionization constants.

The high dissociation constants found for isovaleric and diethylacetic acids are readily explainable on the basis of the ring theory; also the fact that isobutyric acid has essentially the same  $K$  as propionic acid. The very low value of the dissociation constant for trimethylacetic acid is unexpected, and can be explained only by assuming that some factor comes into play here which decreases the ability of the proton to leave the acid.

Dippy and Lewis<sup>11</sup> also find that the dissociation constant for *cis*-cinnamic acid is considerably higher than that for the *trans* form. This is readily explainable on the basis of the ring theory. In the *cis* isomer the ring will be formed, while in the *trans* isomer this is structurally impossible. For this reason, the solid angle within which  $H_3O^+$  ions may approach the carboxyl group in order to have reaction occur is much greater in the *trans* than in the *cis* form. In fact, it is often found that when organic acids are capable of existing in two geometrical isomers of this type, the *cis* form will have the higher dissociation constant. This generality may be explained by the fact that in the *trans* form the solid angle from which  $H_3O^+$  ions may approach the anion in order to collide with the carboxyl group, is considerably greater than the corresponding solid angle for the *cis* form.

Certain recent evidence may be considered to be opposed to this theory. For instance, dielectric constant data indicate that the length of an amino acid increases regularly with the number of carbon atoms between the charged groups, despite the

(11) Dippy and Lewis, *J. Chem. Soc.*, 1008 (1937).

fact that these groups are of opposite sign.<sup>12</sup> Nevertheless, the dipole distances calculated assuming a zig-zag chain structure are considerably larger than those actually found, thus indicating that the charged portions of the molecule actually are closer than might be expected. Then, too, the effect of ring formation has not been observed either for the saponification of the esters of dibasic acids,<sup>13</sup> or in the ionization constants of certain substituted acids.<sup>14</sup> This is, however, not surprising since the effect of substitution of  $-\text{COOH}$ ,  $-\text{Cl}$  or similar groups gives rise to changes which are of a completely different type and order of magnitude from the effects under consideration here. For instance, substitution of a chlorine atom, or carboxyl group in the alpha position changes the dissociation constant of acetic acid from  $1.8 \times 10^{-5}$  to about  $10^{-3}$ , while the corresponding substitution of a methyl group causes a change which is not only of smaller magnitude ( $K$  for propionic acid is approximately  $1.3 \times 10^{-5}$ ) but is also in the opposite direction. The work of Ingold<sup>15</sup> when compared with that of Evans, Gordon and Watson<sup>3</sup> also shows that the effects due to increasing chain length are quite different when one is dealing with a dibasic acid as compared to a monobasic acid.

### Optical Rotatory Power

The preceding three sections have dealt with the explanation of the effect of the length of the carbon chain of an acid or related compound on certain chemical reactions. The argument may be raised that all of these may be explained on some other basis than that of physical structure. In order to forestall such criticism, a study has been made of the correlation of optical rotatory power of acids and related compounds with their structures as predicted by the ring theory already outlined. This property is known to depend on molecular structure.

Pickard and Kenyon<sup>15</sup> found evidence of irregularities in optical rotatory power for the series of alcohols  $\text{EtCHOHR}$  which could be interpreted as evidence for the suggested spiral structure of Frankland.<sup>16</sup> This scheme indicates an irregularity when  $R = 5$  or  $6$ , and again when  $R = 9$  or  $10$ .

The explanation of irregularities in a homologous series of optically active compounds is

(12) Cf. Cohn, *Ann. Rev. Biochem.*, **4**, 93 (1935).

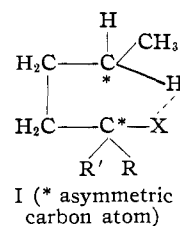
(13) Ingold, *J. Chem. Soc.*, 2170 (1931).

(14) Cf. Westheimer and Shookhoff, *THIS JOURNAL*, **61**, 555 (1939).

(15) Pickard and Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

(16) Frankland, *ibid.*, **75**, 368 (1899).

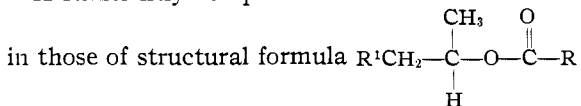
much more satisfactory when these irregularities are interpreted in the light of a ring formed through a hydrogen bond. The introduction of such a ring into a compound already containing an asymmetric atom should produce certain effects upon the optical activity. (1) The increment of change  $\Delta[M]_D$  in the molecular rotation for added  $\text{CH}_2$  groups should show a variation when enough groups are added to close a ring. The effect of the added  $\text{CH}_2$  group and the effect of the ring closure are superimposed. That ring closure does have a marked effect upon optical activity is well known from the lactones of sugar acids. (2) The introduction of a further  $\text{CH}_2$  group after the ring is closed will introduce an asymmetric carbon atom into the ring as shown in I. Due to this increase in the number of asymmetric carbon atoms a change in  $\Delta[M]_D$  should be found for the addition of this group. (3) Additional  $\text{CH}_2$  groups should show uniform effects. The increment may well be quite small since the change in structure is so far removed from the center



of asymmetry that it should show little effect.

The introduction of an asymmetric atom into such a ring does not necessarily demand that such an ester as methyl *n*-valerate be resolvable into optical antipodes. The ring must, by its very nature, be quite unstable. This would prevent isolation of the two diastereoisomers by use of an active resolving agent. A kinetic resolution would occur yielding only one diastereoisomer, followed by immediate racemization upon liberation of the free compound. Thus, the esterification of *n*-valeric acid with an optically active alcohol would direct the structure of the asymmetric carbon in the acid ring preferentially to one or the other possible asymmetric structures.

A sufficiently complete series of esters is found



( $\text{R}^1$  from  $\text{CH}_3$  through  $\text{C}_6\text{H}_{13}$ , and  $\text{R}$  from  $\text{CH}_3$  through  $\text{C}_8\text{H}_{17}$ ). The values for the specific rotation were taken from the "International Critical Tables"<sup>17</sup> and converted to molecular rotation through multiplication by one-hundredth of the molecular weight. The molecular rotations are given in Table I. Figure 4 makes use of the data

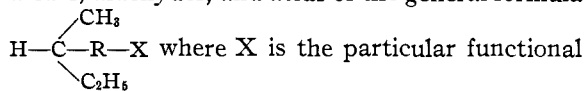
(17) "International Critical Tables," Vol. V11, pp. 360-1.





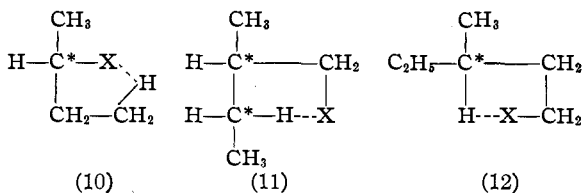
only one asymmetric carbon atom, and the ring structure is much the same as that in the normal series. Figure 6 shows the results of these structures on the optical rotatory power.

That this type of ring formation is quite general seems fairly well supported by the curves in Fig. 7. These represent optical activities of azides, aldehydes, and acids of the general formula



The values used for acids are by Levene, Rothen and Marker<sup>19</sup>; those for aldehydes by Levene and Rothen<sup>20</sup>; and those for the azides are by the same authors.<sup>21</sup> The three examples of each type contain the same ring structures.

As shown by Fig. 7, the trend of the three curves is quite analogous in all respects, except that the azide curve is inverted. Such inversion offers no difficulties, since an asymmetric carbon may contribute either a positive or negative effect to the total rotation. Whatever structure is used to explain the trend in one series must be used to explain the trend in all three. Possible structures for these series are given by 10, 11, and 12, where X may represent  $-\text{COOH}$ ,  $-\text{CHO}$ , or  $-\text{CH}_2\text{N}_3$ .



In 10, there is but one asymmetric atom. In 11, there are two such atoms. In 12, there is still the same ring as in 10 and 11, but it contains only one asymmetric carbon.

Unquestionably other data related to optical activity may be explained on the basis of ring structure. However, in most cases, insufficient data are available to warrant further discussion.

It is thus possible to explain not only the effect of the character of the carbon chain on esterification, saponification, and dissociation constants, but also its effect on optical activity, by assuming that certain ring structures may be formed. Probably this type of ring structure may explain other anomalies which now appear in the literature, particularly the peculiar effect which the ethyl group often exerts. This anomaly has been pointed out by Evans and co-workers.<sup>3</sup> The ef-

(19) Levene, Rothen and Marker, *J. Chem. Phys.*, **1**, 662 (1933).

(20) Levene and Rothen, *ibid.*, **4**, 48 (1936).

(21) Levene and Rothen, *J. Org. Chem.*, **1**, 76 (1936).

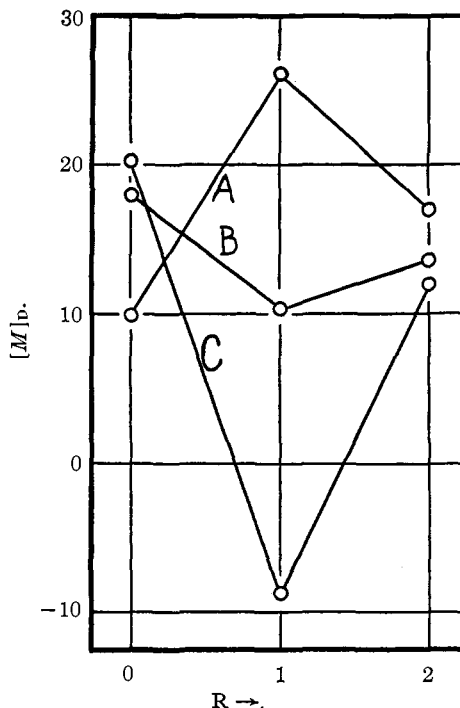


Fig. 7.— $[M]_D$  for  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2)_n\text{X}$  from

$n = 0$  to  $n = 2$ ; X =  $\text{COOH}$ ,  $\text{CHO}$ , or  $\text{CH}_2\text{CN}_3$ ; A, azides; B, acids; C, aldehydes.

fect of the nature of the carbon chain on the rate of both the base catalyzed<sup>22</sup> and the acid catalyzed<sup>23</sup> prototropy of phenyl alkyl ketones may be explained by the formation of a ring containing four carbons quite as easily as by the three carbon containing ring postulated by the authors. The three-carbon ring must be under a great strain, while that containing four C atoms would be essentially strainless. In this connection, Huggins<sup>24</sup> has pointed out that in general hydrogen bonds are more stable when distances through which the bond operates are small.

It is probably unnecessary to point out that the ortho effect found in many organic compounds is probably due to this same type of ring formation. That such rings are formed in salicylic acid, *o*-toluic acid, *o*-chlorobenzoic acid, and similar compounds has already been postulated.<sup>25</sup> In all these cases the bonding hydrogen atom completes

(22) Evans and Gordon, *J. Chem. Soc.*, 1434 (1938).

(23) Evans, *ibid.*, 785 (1936).

(24) Huggins, *J. Org. Chem.*, **1**, 407 (1936).

(25) See, for instance, Dippy, Evans, Gordon, Lewis and Watson, *J. Chem. Soc.*, 1421 (1937). It should be noted that these authors postulate that this ring formation takes place only in the anion of the acid. It seems preferable to consider that the bond is also present in the un-ionized acid since reactions such as esterification do not depend on ionization of the acid, but show a marked dependence on the ortho effect.

a six-membered ring similar to that postulated for the normal acids.

### Summary

The effect of the character of an alkyl side chain on the processes of esterification and saponification, on acid dissociation constants, and on optical activity has been discussed. It has been shown that ring formation similar to that already

postulated to explain the effect of the alkyl chain length of normal aliphatic acids on their velocity of esterification in methanol gives a satisfactory explanation of these phenomena.

The same structure may be used to explain other reactions. It is pointed out that the ortho effect is unquestionably due to the same type of structure.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## Chlorine. The Heat Capacity, Vapor Pressure, Heats of Fusion and Vaporization, and Entropy

BY W. F. GIAUQUE AND T. M. POWELL

This paper presents the results of a low temperature calorimetric investigation of chlorine. The entropy of chlorine has been calculated previously<sup>1</sup> from band spectrum data and the principal purpose of the present work is to compare the value obtained by means of the third law of thermodynamics with the accurately known spectroscopic value. No difficulty with false equilibrium at low temperatures, such as has been found with a few other substances, was anticipated in the case of a molecule like chlorine. Thus it was expected and has been found that the two methods of obtaining the entropy are in excellent agreement.

The measurements were made in a calorimeter which has been described as Gold Calorimeter II.<sup>2</sup> A detailed description of a similar calorimeter has been given previously.<sup>3</sup>

Chlorine reacts slowly with gold at ordinary temperatures and before the gold calorimeter was used for chlorine the reactivity was investigated by immersing a sheet of gold in liquid chlorine at its boiling point. The sheet had an area of 58.5 cm.<sup>2</sup> and was boiled in nitric acid, washed in alcohol and heated before weighing after each removal from the chlorine. During the first twenty-four hours the gold lost 0.0140 g. but subsequent immersion for four days caused an additional decrease of only 0.0087 g. Since the calorimetric investigation required that the liquid chlorine be at temperatures near the boiling point for a comparatively short period, the reaction

could not occur to any appreciable extent. Moreover, the data on the rate of solution of gold were obtained with undried commercial liquid chlorine whereas the chlorine used to fill the gold calorimeter was carefully dried and purified. Presumably the reaction between gold and very dry chlorine would be much slower than that recorded above. When measurements were not in progress, the chlorine was solidified and kept near the temperature of liquid air.

The resistance thermometer was calibrated during the measurements against a copper-constantan thermocouple with the laboratory designation W.<sup>4</sup> Small corrections to this standard thermocouple were recently determined by Stephenson and Giauque.<sup>5</sup> Following the present research the standard thermocouple was compared with the vapor pressures of hydrogen and agreement with the corrections of Stephenson and Giauque was found.

**Preparation of the Chlorine.**—The chlorine was prepared by dropping 3 *M* HCl on manganese dioxide. The small amount of hydrogen chloride in the gas was removed by water and the chlorine was dried with concentrated sulfuric acid and finally with phosphorus pentoxide.

Chlorine prepared as above was placed in the calorimeter and measurements of the heat effect associated with premelting in the solid showed it to contain an impurity of about 5 parts in 10,000 on a molal basis. The material was removed from the calorimeter and fractionated in a vacuum jacketed column. Subsequent premelting

(1) Giauque and Overstreet, *THIS JOURNAL*, **54**, 1731 (1932).

(2) (a) Giauque and Wiebe, *ibid.*, **50**, 101 (1928); (b) Blue and Giauque, *ibid.*, **57**, 991 (1935).

(3) Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(4) Giauque, Buffington and Schulze, *THIS JOURNAL*, **49**, 2343 (1927).

(5) Stephenson and Giauque, *J. Chem. Phys.*, **5**, 149 (1937).