[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Distillation of Methylchlorosilanes

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The distillation of methylchlorosilane crudes to yield the principal components in high purity is a difficult process that is complicated by the presence of extraneous materials in small amounts. Methyltrichlorosilane is the principal component most difficult to obtain pure in this way, but this isolation has been accomplished. It has been shown that the separation by distillation of pure methyltrichlorosilane from its binary mixture with dimethyldichlorosilane is a less difficult problem. Provisional normal boiling points are dimethyldichlorosilane, 70.2 ± 0.1°; and methyltrichlorosilane, 66.1 ± 0.1°.

Subsequent laboratory and industrial experience indicates clearly that the appreciable boiling-point ranges of (approximately) pure dimethyldichlorosilane (DDS) and methyltrichlorosilane (MTS) as first prepared[1] are traceable to the difficulty of isolating these silicone intermediates by distillation. These first preparations were made by the Grignard reaction, which yields a less complex mixture of products than does the reaction between methyl chloride and silicon.[2] Distillation is by far the most attractive way of isolating these reaction products on an industrial scale. Consequently, the problems involved in such distillations have been the subject of several laboratory investigations,[3] of which the results of one are given here.

Distillation of a Crude Fraction.—The nature of the distillation problem is indicated by Fig. 1, which contains approximate boiling points and hydrolyzable chlorine contents obtained in 1941 on a fraction boiling between 48 and 60° of a methylchlorosilane crude (*i.e.*, a mixture of products from the reaction of methyl chloride and silicon). The distillation of the fraction was carried out at 2 and 5% take-off during a period of 241 hours on a column later shown to have 88 theoretical plates.[4] Similar preliminary distillations had shown that plateaus as well defined as those in Fig. 1 did not occur at 10% take-off.

Three conclusions may be drawn from Fig. 1: (1) Although the cut that constituted the charge had been made between 48 and 60°, it contained materials boiling between 24 and 70°. (2) Silicon tetrachloride (b.p. 57.6°) was not isolated because an excess of trimethylchlorosilane was present. These two substances form the azeotrope[3b] that was found near 54°. (3) MTS is the only methylchlorosilane isolated whose chlorine content was never in satisfactory agreement with the theoretical value, but the other chlorine contents were often low also.

On the basis of Fig. 1 and of other experience, the situation may be summarized as follows. It is difficult to obtain any methylchlorosilane of theoretical chlorine content by the fractionation of a methylchlorosilane crude. The difficulty is greatest when MTS is sought.

Distillations Involving MTS and DDS.—Even before 1943, pure DDS had frequently been obtained here in distillations resembling those of Fig. 1, but pure MTS had not. The following experience of C. E. Reed and W. J. Scheiber is typical. An extended distillation of a methylchlorosilane mixture in a pilot-plant Stedman[5] column having about 35 theoretical plates was carried out in the hope of obtaining pure MTS and DDS. Average hydrolyzable chlorine contents for a large number of the best samples were: DDS, 54.96% (theor. 54.95%); MTS, 71.00% (theor. 71.17%). Although the determination of hydrolyzable chlorine is more difficult for MTS than for other methylchlorosilanes, the detailed analytical data for this and other distillations showed clearly that the low result for MTS was not due to analytical errors.

Accordingly, three painstaking distillation experiments were planned on a laboratory scale: (1) redistillation of "pure" MTS obtained by distillation from a methylchlorosilane crude, the object being to establish whether pure MTS can be obtained in this way. (2) Redistillation of pure DDS similarly derived, mainly in order to test the experimental methods. (3) Distillation of a mixture of the products from the first two experiments for the purpose of discovering whether these pure methylchlorosilanes can be recovered by distillation from their binary mixture. Extreme precautions were to be taken against hydrolysis during distillation and analysis. The constancy of corrected specific gravity readings on sensitive sealed-in hydrometers was to be taken as the ultimate criterion of purity on a distillate of satisfactory chlorine content. Such readings could be made to 0.01% on material never exposed to air.

Experimental.—The Stedman column (total-condensation head) used for this work was rated at 108 theoretical plates and found to contain 72 theoretical plates when tested with *n*-heptane–methylcyclohexane.[4a] With the still-head set for total reflux, 0.35% take-off actually occurred; the distillations were carried out under these conditions. The receiver for the still is shown in Fig. 2, which is self-explanatory. Dry nitrogen at a rate near 12 bubbles per minute was fed into the line connecting the stillpot to the mercury manometer instrumental in the automatic control of pressure. This nitrogen protected the mercury from chlorosilane vapors and aided in keeping moist air out of the system. As is indicated in Fig. 2, both outlets of the receiver were also protected to prevent hydrolysis.

Concomitant hydrometer and temperature readings were taken when sufficient distillate to float the hydrometer had accumulated. Transfer of distillate from the receiver into a glass-stoppered erlenmeyer flask positioned within the dry box (Fig. 3) was accomplished by siphoning, which was initiated and maintained by closing and then opening the stopcock of Fig. 2.

The manipulations within the dry box were performed in the following sequence. The manipulator E was used to

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(1) Gilliam, Liebhafsky and Winslow, THIS JOURNAL, **63**, 801 (1941).

(2) Rochow, *ibid.*, **67**, 963 (1945).

(3) (a) Sauer, Scheiber and Hadsell, *ibid.*, **70**, 4254 (1948); (b) Sauer and Hadsell, *ibid.*, **70**, 4258 (1948).

(4) A *n*-heptane–methylcyclohexane mixture was used to test our 56-inch column (*cf.* (a) Beatty and Calingaert, *Ind. Eng. Chem.*, **26**, 504 (1934). The prototype of our column, a 28-inch section similarly packed, was found to contain 55 theoretical plates by (b) Whitmore, Fenske, *et al.*, THIS JOURNAL, **62**, 795 (1940). In our (total-condensation, partial-take-off type) column, constant reflux ratio was maintained at all through-puts by use of a modified automatic reflux-ratio still-head.

(5) Bragg, *Ind. Eng. Chem., Anal. Ed.*, **11**, 283 (1939).

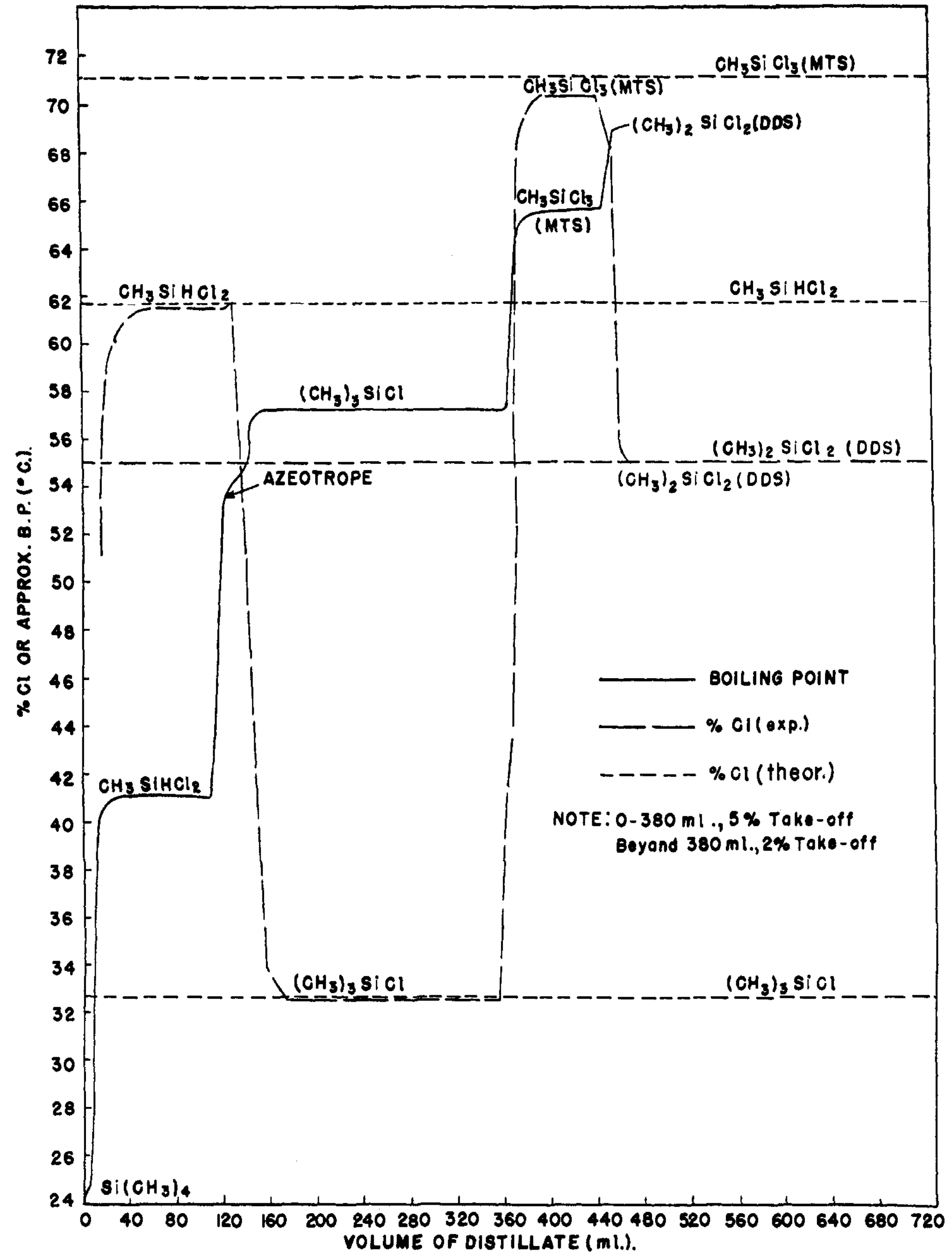

Fig. 1.—Distillation curve for a fraction from a methylchlorosilane crude. True plateaus are obtained only at low take-off. The silicon tetramethyl was identified only by boiling point and density.

open the end of the tube A, and to unstopper the erlenmeyer flask, which was then raised to receive the distillate. When the discharge was complete, the flask was lowered and stoppered. With the manipulator, the rubber tube attached to C was joined to A, so that the receiver could be purged with dry nitrogen. While this purging was in progress, the door was opened and an empty erlenmeyer flask put in place of the one containing distillate, which was taken to a second dry box for sampling. The door remained open no longer than necessary. When the purging was finished the drying tube was again connected to A, and the collection of the next distillate was begun.

The precision of the titration for hydrolyzable chlorine may be judged from data in Table I and from the following results on the starting material for Experiment 1: Sampled in laboratory, 70.64, 70.75, 70.75% Cl; sampled in second dry box, 70.66, 70.84, 70.76% Cl. Though these results do not prove the occurrence of appreciable hydrolysis during sampling in the laboratory, all sampling of distillates was nevertheless carried out in the second dry box.

Results.—Table I describes the three distillations, each uninterrupted, and gives the results. Owing to uncontrollable losses during flooding, distillation and purging, the weights in Column 2 cannot yield a material balance. The over-all average chlorine contents and the over-all average specific gravities (Table I, notes) were computed by giving equal weight to the average values for each fraction considered pure. Densities based on these over-all averages have already been reported.[6]

Discussion.—We have concluded from the data in Table I that (1) pure MTS can be prepared by distillation from a methylchlorosilane crude, (2) a binary mixture of DDS and MTS can be

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(6) Balis, Gilliam, Hadsell, Liebhafsky and Winslow, THIS JOURNAL, 70, 1654 (1948).

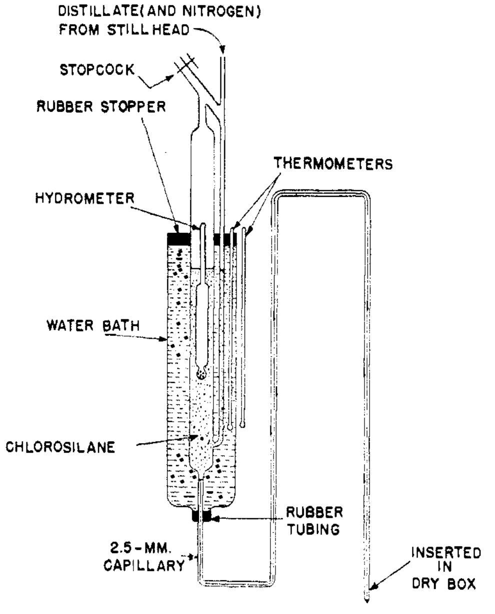

Fig. 2.—Receiver for final distillations. Note sealed-in hydrometer and precautions taken to prevent hydrolysis.

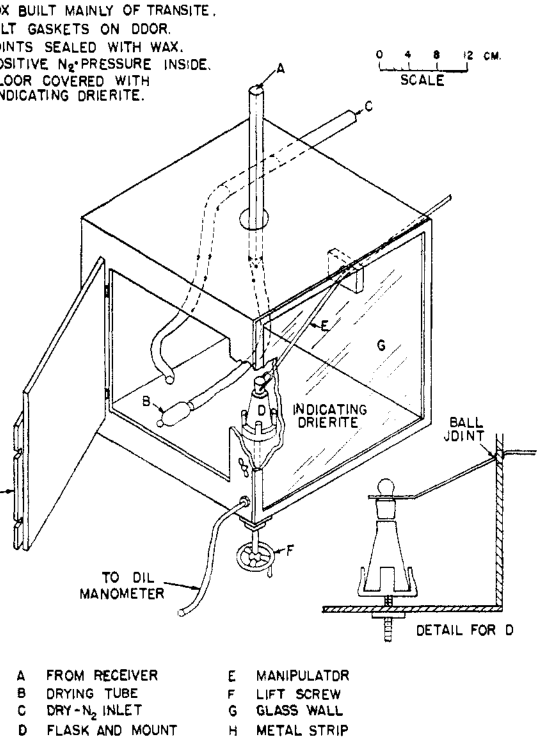

Fig. 3.—Dry box containing flask for removal of distillate from receiver of Fig. 2. Note precautions taken to prevent hydrolysis.

fractionated to give the pure components, (3) extraneous substances in small amount are ordinarily responsible for failures to recover pure MTS from methylchlorosilane crudes (in this connection, compare the progress of chlorine contents and specific gravities in Experiment 1 and in the initial part of Experiment 3). Figure 1 and other experiences indicate that the third conclusion applies (though less forcibly) to other methylchlorosilanes also. The presence of these extraneous materials[3a] (some as yet unidentified) is evidence that the interaction of methyl chloride and silicon is accompanied by complex reactions.

TABLE I

REDISTILLATION OF "PURE" METHYLCHLOROSILANES

a. Experiment 1. Aug. 5-30, 1943. Charge, 1932 g. "pure" MTS

		Chlorine by hydrolysis		Specific gravity	
Fraction	Weight, g.	No. of titrations	Average % Cl	No. of readings	d^{27}_{27} (cor.)
347·1	132.0	5	70.7_6	..	
·2	37.5	4	70.7_5	..	
-3	39.5	4	70.9_0	..	
·4	90.7	2	70.9_5	..	
·5	157.0	4	71.0_7	6	1.268_0
·6	128.5	4	71.0_7	9	1.268_9
-7	133.0	4	71.1_1	19	1.268_5
-8	130.0	7	71.1_5	19	1.269_6
·9	117.0	4	71.2_4	9	1.270_2
·10	156.0	8	71.1_6	9	1.270_0
·11	133.8	4	71.1_9	14	1.270_3
·12	39.3	3	71.1_6	..	

Notes: Distillation completed. Ranges in % Cl: minimum, Fraction 347-4, 70.9_4–70.9_5; maximum, Fraction 347-8, 70.9_0–71.2_4. For pure MTS (Fraction 347-8 to 347-11 inclusive) av. % Cl, 71.1_9; av. d^{27}_{27} 1.270_0

b. Experiment 2. Sept. 25-Oct. 23, 1943. Charge, 1614 g. "pure" DDS

		Chlorine by hydrolysis		Specific gravity	
Fraction	Weight, g.	No. of titrations	Average % Cl	No. of readings	d^{27}_{27} (cor.)
367·1	225.0	6	54.7_1	..	
-2	145.4	4	54.7_5	11	1.069_3
-3	50.0	..		..	
-4	130.0	2	54.7_1	9	1.066_5
·5	126.0	4	54.8_5	6	1.066_8
·6	113.0	3	54.9_1	6	1.066_9
-7	151.0	5	54.9_8	10	1.067_1
-8	125.0	3	54.9_1	10	1.067_2
·9	111.0	3	54.9_1	7	1.067_1
-10	...	2	54.9_6	..	

Notes: Distillation suspended. Ranges in % Cl: minimum, Fraction 367-8, 54.9_1–54.9_1; maximum, Fraction 367-7, 54.8_7–55.1_0. For pure DDS (Fractions 367-6 to 367-9 inclusive) av. % Cl 54.9_3; av. d^{27}_{27} 1.067_1

c. Experiment 3. Dec. 8-23, 1943. Charge, 525 g. MTS (Fractions 347·8 to 347·11 inclusive) and 482 g. DDS (Fractions 367·6 to 367·10 inclusive)

		Chlorine by hydrolysis		Specific gravity	
Fraction	Weight, g.	No. of titrations	Average % Cl	No. of readings	d^{27}_{27} (cor.)
460-1	40.1	2	70.8_0[a]	..	
-2	139.8	4	71.1_4	11	1.270_0
-3	134.5	3	71.1_3	8	1.270_0
-4	135.5	4	68.4_0	..	
-5	16.9	4	55.0_5	..	
·6	70.0	3	54.8_0	..	
·7	126.5	4	54.9_3	..	
·8	35.8	4	54.8_5	..	

[a] Contains material transferred during initial flooding.

Notes: Distillation suspended. Ranges in % Cl: minimum, Fraction 460-8, 54.8_3–54.8_6; maximum, Fraction 460-5, 55.0_2–55.1_0. For pure MTS (Fractions 460-2 and 460-3) av. % Cl, 71.1_4; av. d^{27}_{27} 1.270_0. For pure DDS (Fractions 460-5 to 460-8 inclusive) av. % Cl, 54.9_1. No d^{27}_{27} for DDS because MTS hydrometer was sealed in.

Boiling Points.—Inasmuch as Martin[7] did not isolate or identify MTS or DDS, his work yielded

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[7] Martin, *Ber.*, **46**, 2442 (1913).

no boiling points for these chlorosilanes. The first values reported for these substances have been superseded by better data.[8] After carefully reviewing the literature and considering the evidence available to us here, we have selected the following provisional normal boiling points: DDS, 70.2 ± 0.1°; MTS, 66.1 ± 0.1°. In selecting these values, we have assigned the greatest weight to determinations on both compounds by R. O. Sauer (one of these having been made on Fraction 460–6, Table I) and to the difference (4.0 ± 0.1°) in the boiling points of DDS and MTS, which was established by Experiments 1 and 2, Table I.

We wish to thank our colleagues A. L. Marshall, C. E. Reed, R. O. Sauer, W. J. Scheiber, A. E. Schubert and E. H. Winslow for helping in various ways with the work reported here.

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[8] (a) Gilliam and Sauer, THIS JOURNAL, **66**, 1793 (1944); (b) Booth and Martin, *ibid.*, **68**, 2655 (1946); (c) Booth and Suttle, *ibid.*, **68**, 2658 (1946); (d) Lewis and Newkirk, *ibid.*, **69**, 701 (1947); (e) Stull, *Ind. Eng. Chem.*, **39**, 517 (1947); (f) Burkhard, Rochow, Booth and Hartt, *Chem. Revs.*, **41**, 97 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Differential Diffusion Coefficient of Lanthanum Chloride in Dilute Aqueous Solution at 25°

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The differential diffusion of lanthanum chloride in water at 25° has been determined by the conductometric method through a concentration range of 0.00093 to 0.026 molar. The results are all somewhat lower than those computed by the theory of Onsager and Fuoss but appear to approach the limiting law of the theory in a satisfactory manner.

Accurate measurements of the conductance,[1,2] transference numbers[3] and activity coefficient[4] of lanthanum chloride at 25° in dilute aqueous solutions provide the necessary data for the theoretical computation of the diffusion coefficient according to the theory of Onsager and Fuoss.[5] It is to be noted that the conductance of this salt approaches the limiting law of the Onsager theory normally as its concentration approaches zero. This evidence indicates that it is a strong electrolyte. Shedlovsky's calculation of the thermodynamic data yields 6.8 Å. for the "mean distance of approach" of the Debye and Hückel theory. Although this value indicates high dissociation, it does not exclude the formation of ions such as $LaCl_2^+$, etc.

The 2–1 salt, calcium chloride, shows analogous characteristics. Similar agreement with theory occurs with both the conductance and the activity coefficient. On the other hand, the cation transference members of both calcium and lanthanum chlorides show no tendency to approach the limiting law of the theory at 0.01 molar.[6] Since the diffusion coefficient of calcium chloride[7] exhibits the largest deviation from theory of any of the salts yet investigated, it is a matter of considerable interest to investigate the diffusion coefficient of a salt whose other properties parallel those of calcium chloride.

Experimental Results and Theoretical Calculations

Anhydrous lanthanum chloride of high purity was obtained from the Atomic Energy Commission. Upon dissolving this salt in water at room temperature, heat was evolved and hydrolysis occurred. The *p*H of this solution was 5.0. Accordingly, 20 g. was dissolved slowly in ice-water and the solution was filtered. Crystallization was effected by slow evaporation in a vacuum desiccator over concentrated sulfuric acid. After 48 hours, the crystals were dried by centrifuging. The *p*H of a 0.005 molar solution was found to be 5.6. This process of crystallization was repeated and the crystals dried in air. Assuming the composition to be $LaCl_3 \cdot 7H_2O$, a 0.2 molar stock solution was prepared. A 0.005 molar solution prepared from this stock solution was found to have a *p*H of 5.9.

The technique of measurement and the method of computation of the diffusion coefficient from the observed conductances were essentially the same as those previously employed and described in detail.[8] Examination of the specific conductance of lanthanum chloride showed that, over the concentration ranges employed, the assumption that the differences in conductances between the bottom and top electrodes of the cell are proportional to the differences in concentrations between the bottom and top of the cell is valid within the required limits.

The theoretical equations for computing the diffusion coefficients[9,10] may be written

$$\mathfrak{D} = K \times 10^{13} \left(\frac{\overline{\mathfrak{M}}}{c}\right)\left[1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right] \qquad (1)$$

$$\left[1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right] = 1 - \frac{E\sqrt{c}}{(1 + A'\sqrt{c})^2} + Fc - c\psi(\mathrm{d}) \qquad (2)$$

$$c\psi(\mathrm{d}) = \frac{Gc - Hc^{3/2}}{d_0 + Gc - Jc^{3/2}} \qquad (3)$$

$$\left(\frac{\overline{\mathfrak{M}}}{c}\right) \times 10^{20} = P - Q\,\frac{\sqrt{}}{(1 + A'\sqrt{c}} + R'\phi(A'\sqrt{c}) \qquad (4)$$

where

$$K = 1000\,RT(\nu_1 + \nu_2) \qquad (5)$$

$$E = 1.15148_{(f)} \qquad (6)$$

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[1] Jones and Bickford, THIS JOURNAL, **56**, 602 (1934).

[2] MacInnes, *J. Franklin Institute*, **225**, 661 (1938).

[3] Longsworth and MacInnes, THIS JOURNAL, **60**, 3070 (1938).

[4] Shedlovsky, *ibid.*, **72**, 3680 (1950).

[5] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[6] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950, Fig. (6-6-2), p. 164.

[7] Harned and Levy, THIS JOURNAL, **71**, 2781 (1949).

[8] Harned and Nuttall, *ibid.*, **69**, 736 (1947).

[9] Ref. 6, pp. 89, 90; Harned, *Chem. Revs.*, **40**, 461 (1947).

[10] Harned and Blake, Jr., THIS JOURNAL, **73**, 2448 (1951).