mole) of $C_3F_3Cl_5$, liquid at room temperature; and 49 g. of residual material computed as 0.17 mole of $C_3F_2Cl_6$.

Zinc Dehalogenations.—A 20-g. portion of tetrafluoride was placed in a steel vessel with three times its volume of absolute ethanol and 10% excess of granular zinc. This bomb was rocked for 12 hours at a temperature of 100°. The material was poured into water and decanted; the aqueous layer was diluted to 500 cc. and a 50-cc. aliquot was titrated with silver nitrate, indicating the presence of 0.0154 g. atom of chloride which corresponded well with the observed zinc consumption of 0.077 g. atom. A qualitative test for fluoride ion was negative. About 0.6 g. of the original paraffin was recovered and, after purification, 10 g. of olefin $C_3F_4Cl_2$, b.p. 42–48°, $n^{20}\text{D}$ 1.3490, and 2 g. of tar were collected; possible amount of olefin would have been 14 g.

A similar zinc treatment was applied to the difluoride $C_3F_2Cl_6$, to show the formation of 0.15 g. equivalent of chloride corresponding to the 0.077 g. atom of zinc consumed. A qualitative test for F^- proved negative. The olefin was dark and tar-like and was not treated further.

The trifluoride, when treated with zinc and alcohol at 100° gave a high boiling polymerized material. When the solvent was shifted to dioxane, satisfactory results were obtained at 100°; at higher temperature the dioxane is affected by the generated zinc chloride and becomes tarry. It is more convenient to carry the reaction under a dephlegmator and slowly distil a mixture of olefin and dioxane; this gave about half olefin, $C_3F_3Cl_3$, and half unreacted paraffin to be retreated. The chloride ion titration corresponds to the zinc consumption, and a fluoride ion test proves negative.

Oxidation of the Olefins.—$C_3F_2Cl_4$ was oxidized with basic permanganate by our previously described procedure.[8] The reaction mixture was continuously extracted with ether, and the ether extract was distilled until a temperature of 105° was passed, to ensure the removal of any possible $CF_3CO_2H + H_2O$ azeotrope. Alcohol, benzene and a few drops of sulfuric acid were added to the residue. Distillation through a dephlegmator was then performed until the boiling point of the alcohol/benzene binary azeotrope (68.2°) was reached; this procedure collected as distillate the azeotropes of water, benzene, alcohol and all of the ester. The distillate was washed with water to remove the alcohol; the benzenic solution of the ester was then subjected to a stream of dry ammonia. After distilling off most of the benzene, the amide crystallized out, with a m.p. of 78°. A known sample of CF_2ClCO_2H was then transformed into its amide by the same procedure, and a m.p. of 78° was observed. A mixed m.p. gave 77.5°. The m.p. would have been 126° if the sample had been a monofluoride, $CFCl_2CONH_2$, instead of the difluorinated compound. The yield of purified amide from crude olefin was 62%.

$C_3F_4Cl_2$ was similarly treated and gave, in similar yield, only $CF_2ClCONH_2$, m.p. 78°, mixed m.p. 77.5°. A search for possible CF_3CO_2H in the oxidation products proved negative.

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[8] Henne and Trott, THIS JOURNAL, **69**, 1820 (1947).

COLUMBUS, OHIO

RECEIVED MAY 15, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, AND THE NAVAL MEDICAL RESEARCH INSTITUTE]

Electrostatic Interactions in Aliphatic Dicarboxylic Acids and the Kirkwood–Westheimer Theory[1]

BY H. MILTON PEEK[2] AND TERRELL L. HILL

Dissociation constants of some of the saturated aliphatic dicarboxylic acids from four carbon atoms to fourteen carbon atoms have been determined at 25.0° in 20 wt. per cent. methanol–water solution by the method of Speakman. These experimental results and also the available constants for water as solvent are analyzed in terms of the theory of Kirkwood and Westheimer. It is found that the theory gives quite satisfactory agreement with the experimental results.

Introduction

The purpose of this work is to provide a further test of the Kirkwood–Westheimer theory[3] of the electrostatic influence of substituents on dissociation constants. Aside from its applications to physical and organic chemistry, the theory has important biological implications in its relation to the behavior of amino acids, proteins and polyelectrolytes in solution.

Since publication of the original work[3] a number of applications and discussions of the subject have appeared.[4–13] In particular, Westheimer and Kirkwood[13] have given an extensive review of the successes and limitations of the theory. One aspect of their treatment not tested in much detail by Westheimer and Kirkwood,[3,13] or by Wynne-Jones and Rushbrooke,[12] pertains to the predicted effective dielectric constant in a series of long ellipsoidal molecules, for example the aliphatic dicarboxylic acids. Dissociation constants of these acids are available in the literature[14] up to $C = 9$ (C = number of carbon atoms in the molecule), with water as solvent. Decreasing solubility is the limiting factor in extending these measurements to larger values of C. In this paper we report measurements to $C = 14$, made possible by use of 20% (by weight) methyl alcohol as solvent. As will be seen below, the Kirkwood–Westheimer theory is in satisfactory agreement with both sets of experimental dissociation constants.

Experimental

Method.—If the ratio of the successive thermodynamic dissociation constants K_1 and K_2 of a dicarboxylic acid is of the order 10^3 or greater, then it is sometimes possible to obtain quite accurate values for the dissociation constants by

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[1] From part of a Ph.D. thesis submitted by H. M. Peek to the University of Rochester (further details are available in this thesis). Supported in part by the Dreyfuss Foundation, University of Rochester. The opinions contained herein are those of the authors and do not necessarily reflect the views of the Navy Department.

[2] P. O. Box 1663, Los Alamos, New Mexico.

[3] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

[4] F. H. Westheimer and M. W. Shookhoff, THIS JOURNAL, **61**, 555 (1939); **62**, 269 (1940).

[5] F. H. Westheimer, *ibid.*, **61**, 1977 (1939); **62**, 189 (1940).

[6] F. H. Westheimer, W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942).

[7] J. H. Elliott and M. Kilpatrick, *ibid.*, **45**, 454, 466, 472, 485 (1941).

[8] J. H. Elliott, *ibid.*, **46**, 221 (1942).

[9] M. Kilpatrick, *Chem. Revs.*, **30**, 159 (1942).

[10] T. L. Hill, *J. Chem. Phys.*, **11**, 545, 552 (1943); **12**, 56, 147 (1944); THIS JOURNAL, **65**, 1564, 2119 (1943); *J. Phys. Chem.*, **48**, 101 (1944).

[11] J. N. Sarmousakis, *J. Chem. Phys.*, **12**, 277 (1944).

[12] W. F. K. Wynne-Jones and G. S. Rushbrooke, *Trans. Faraday Soc.*, **40**, 99 (1944).

[13] F. H. Westheimer and J. G. Kirkwood, *ibid.*, **43**, 77 (1947).

[14] R. Gane and C. K. Ingold, *J. Chem. Soc.*, 2153 (1931).

several methods.[15] If the ratio K_1/K_2 is less than 10^3 but larger than, say 10^2, one can obtain accurate constants by procedures[16] involving successive approximations with data obtained by the above methods.[15] For the acids used in this work the ratio K_1/K_2 lies in the range 35 to 5. For such low values of K_1/K_2 the above mentioned procedures become very tedious. We therefore adopt a somewhat less refined method, which gives values of the ratio K_1/K_2 accurate to about 4%.

The method used here is due to Speakman.[17] The necessary equations are

$$X = K_1Y + K_1K_2 \tag{1}$$

$$X = a^2_{\mathrm{H}^+}L\gamma_{\mathrm{A}^-}/N\gamma_{\mathrm{H_2A}} \tag{2}$$

$$Y = a_{\mathrm{H}^+}M\gamma_{\mathrm{A}^=}/N\gamma_{\mathrm{HA}^-} \tag{3}$$

$$L \equiv B + m_{\mathrm{H}^+} - m_{\mathrm{OH}^-} = m_{\mathrm{HA}^-} + 2m_{\mathrm{A}^-} \tag{4}$$

$$M \equiv A - B - m_{\mathrm{H}^+} + m_{\mathrm{OH}^-} = m_{\mathrm{H_2A}} - m_{\mathrm{A}^=} = A - L \tag{5}$$

$$N \equiv 2A - B - m_{\mathrm{H}^+} + m_{\mathrm{OH}^-} = 2m_{\mathrm{H_2A}} + m_{\mathrm{HA}^-} = A + M \tag{6}$$

where

a_{H^+}	is the hypothetical hydrogen ion "activity"
γ_i	is the activity coefficient of the species i
m_i	is the molar concentration of the species i
A	is the total molar concentration of acid
B	is the molar concentration of an added, strong, monoprotic base

The experimental scheme is as follows. A measured volume of acid solution of known concentration is titrated with a standard base solution; *p*H measurements are made for various volumes of added base. *p*H values are determined in the following cell

glass electrode | solution under investigation || satd. KCl || KCl(0.1 *m*), AgCl–Ag

using a Beckman model G *p*H meter. The quantity *B* is determined from the volume of base added; a_{H^+} is assumed to be given by

$$p\mathrm{H} = -\log a_{\mathrm{H}^+} \tag{7}$$

The quantities *L*, *M* and *N* are then calculated assuming (1) m_{OH^-} is negligible and (2) m_{H^+} is equivalent to a_{H^+}. In calculating the quantities *X* and *Y* the activity coefficients γ_i are calculated by the Debye–Hückel limiting law; $\gamma_{\mathrm{H_2A}}$ is assumed to be unity. For a large number of pairs of *X* *Y* values, the constants K_1 and K_2 are computed from Eq. (1) by the method of least squares.

Solvent.—The solvent used was 20% methanol–80% water by weight. Solvent was prepared in one-liter lots, as needed, in a calibrated flask (25.0°) designed for the purpose. Methanol was Baker C.P. analyzed, special, absolute. Water was high purity, distilled, having a conductance of 2×10^{-6} mho or less.

Acids.—Succinic and sebacic acids were obtained from the Matheson Co. Glutaric, adipic, pimelic and azelaic acids were Eastman Kodak Co. "white label." Dodecanedioic and tetradecanedioic acids were obtained from the University of Illinois. Succinic, adipic, pimelic, azelaic and sebacic acids were purified by repeated recrystallization from water until titration analyses showed approximately 100% purity. Glutaric acid was recrystallized several times from thiophene-free benzene according to Marvel and Tuley.[18] Dodecanedioic and tetradecanedioic acids were recrystallized several times from 75:25 ethyl alcohol:water. Acid solutions were prepared by solution of weighed samples of dried acids in the solvent.

***p*H Measurements.**—*p*H measurements were made as mentioned above. The glass electrode was obtained from the National Technical Laboratories. The AgCl–Ag electrodes were prepared as follows: platinum electrodes of the spiral type were (1) cleaned by electrolysis as anode in 6 *N* $\mathrm{HNO_3}$, (2) washed thoroughly in distilled water, (3) electrolyzed as cathode in 3% $\mathrm{KAg(CN)_2}$ solution for 6 hours at 0.1 milliampere current density in a low light-level room, (4) washed and allowed to stand in distilled water for 6 to 10 hours in a light-protected vessel and (5) chloridized by electrolysis as anode in 0.1 *N* HCl solution for 30 minutes at 0.5 milliampere current density in a darkened room. The silver deposit was always white and the silver chloride deposit was a pink to purple color. Electrodes were replated if any color changes were noted during use. Electrodes prepared in this way were found to be quite stable in the methanol–water solvent for an indefinite length of time provided light was excluded from the electrode vessels.

Following recommendations of Dole[19] and of Bates[20] the *p*H meter was standardized with the following buffer solutions: (1) at *p*H 4.01 at 25.0°–0.05 molar potassium acid phthalate; (2) at *p*H 9.18 at 25.0°–0.01 molar borax. No account was taken of the effect of the methyl alcohol on *p*H values. All electrode leads were electrically shielded.

Titrations.—The concentration of NaOH was such that not more than 5 ml. were required for titration of 200 ml. of acid solution. The buret used was a 5 ml. "Normax" grade microburet calibrated in hundredths of a milliliter. All solutions were prepared, and titrations run, utilizing dry nitrogen to exclude $\mathrm{CO_2}$. The temperature of titrations was maintained at 25.0 ± 0.1°.

Results

In Table I we give the computed thermodynamic dissociation constants as determined in this work. ΔpK_m is defined as

$$\Delta pK_m = \Delta pK - \log 4 = \log (K_1/4K_2) \tag{8}$$

We include the values of ΔpK_m for water as solvent.[14] The values of K_1 and K_2 obtained in this research are accurate to about 2% and the uncertainty in ΔpK_m is about 0.02 *pK* unit. The values for tetradecanedioic acid are somewhat less accurate than for the other acids owing to its very low solubility.

Because of the lower dielectric constant of the methanol solution we expect $\Delta pK_m > \Delta pK_m(\mathrm{H_2O})$ in Table I. The exceptions at $C = 6$ and $C = 7$ in the table may be due to experimental error in either or both of the sets of dissociation constants, or could originate in some question of detailed molecular structure of the solvent molecules in the neighborhood of acid molecules and ions (hydrogen bonds, etc.).

We have not included $C = 2$ and $C = 3$ in this work because of the likelihood[10] of important non-electrostatic effects in these cases; also the ellipsoidal model used below becomes questionable for *C* too small.

TABLE I

DISSOCIATION CONSTANTS IN 20% METHANOL[21]

Acid	*C*	No. of *X*-*Y* values	10^5K_1	10^6K_2	ΔpK_m	ΔpK_m $(\mathrm{H_2O})^{14}$
Succinic	4	191	2.60	0.796	0.913	0.682
Glutaric	5	150	1.90	1.44	.519	.474
Adipic	6	190	1.34	1.43	.370	.392
Pimelic	7	180	1.19	1.43	.318	.338
Suberic	8	...	...	...	...	.284
Azelaic	9	258	1.00	1.22	.312	.261
Sebacic	10	209	0.911	1.15	.297	...
Dodecanedioic	12	168	.843	1.17	.256	...
Tetradecanedioic	14	54	.789	1.22	.207	...

Discussion and Theory

In their second paper,[3] Kirkwood and Westheimer computed the effective dielectric constant D_E, defined by

$$2.303\,\Delta pK_m = e^2/D_ERkT \tag{9}$$

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[15] See, for example, H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publishing Corp., New York, N. Y., 1950.

[16] See, for example, W. J. Hamer and S. F. Acree, *J. Research Natl. Bur. Standards*, **35**, 381 (1945).

[17] J. C. Speakman, *J. Chem. Soc.*, 855 (1940).

[18] H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 289.

[19] M. Dole, "The Glass Electrode," J. Wiley and Sons, Inc., New York, N. Y., 1941.

[20] R. G. Bates, *Chem. Revs.*, **42**, 1 (1948).

[21] All values are on a molar concentration scale at 25°. The NaOH concentration was 0.02866 molar and the acid concentrations used varied from 2.1×10^{-4} to 7.8×10^{-4} molar.

for a molecule with the shape of a prolate ellipsoid of revolution and having charges at the foci, the interfocal distance being R. The theory gives D_E as a function of λ_0, as shown in Fig. 1, where $\lambda_0 = d/R$ and d is the length of the major axis of the ellipsoid.

In order to test the theory, we use experimental values of ΔpK_m and estimate R and λ_0 from structural considerations, thus allowing a computation of D_E as a function of λ_0 to be compared with the Kirkwood–Westheimer theoretical curve in Fig. 1.

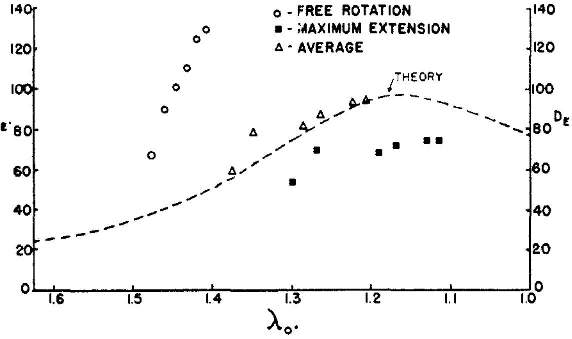

Fig. 1.—Effective dielectric constants for water as solvent, for C = 4 to 9 (in order from left to right).

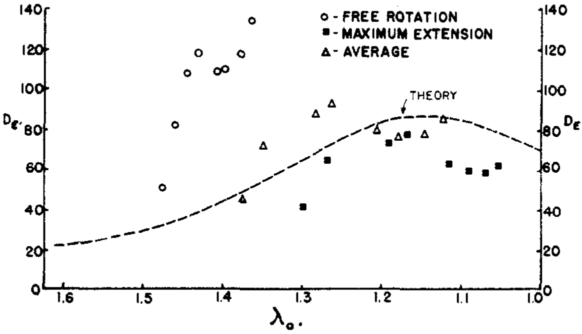

Fig. 2.—Effective dielectric constants for 20% methyl alcohol as solvent for C = 4, 5, 6, 7, 9, 10, 12, 14 (in order from left to right).

The volume V of the ellipsoid is estimated (for both solvents) using Traube's rule.[22] For R, we use the free rotational (root mean square) and maximum extension distances between protons, R_{fr} and R_{max}, as representing lower and upper limits[3,23] on R. In obtaining R_{fr} and R_{max} we locate[3] the protons at a distance of 1.45 Å. from the respective carboxyl carbon atoms on the extensions of the terminal carbon to carbon bonds. Owing to the repulsion between charges, the "correct" (if a single intercharge distance is to be used) average value of R, $\bar{R}$, lies somewhere between R_{fr} and R_{max} but would be extremely difficult[24] to compute for $6 \leqslant C \leqslant 14$ (see below for a discussion of the C = 4 case). We shall use as a ***rough*** guess, $\bar{R} = (R_{fr} + R_{max})/2$. In any case, for particular values of R and V, λ_0 may be found using

$$\lambda_0^3 - \lambda_0 = (6/\pi)(V/R^3) \qquad (10)$$

and D_E calculated from Eq. (9) using R and the experimental value of ΔpK_m.

Table II

Interproton Distances[25]

C	V, Å.^{3}/molecule	R_{fr}, Å.	R_{max}, Å.	$\bar{R}$, Å.
4	137.8	5.33	6.65	5.99
5	164.5	5.75	7.40	6.57
6	191.3	6.15	9.03	7.59
7	218.0	6.52	9.92	8.22
8	244.7	6.87	11.46	9.17
9	271.5	7.21	12.43	9.82
10	298.2	7.53	13.93	10.73
12	351.7	8.14	16.40	12.27
14	405.1	8.70	18.89	13.80

In Table II we give the values of V, R_{fr}, R_{max} and $\bar{R}$, and in Figs. 1 and 2 the "experimental" points D_E *versus* λ_0 are plotted using the three different values of R. The theoretical curve D_E *versus* λ_0 in Fig. 1 was computed by Kirkwood and Westheimer for water as solvent, D = 78. With 20% methyl alcohol as solvent,[26] D = 69.2. In view of the small difference in D and the approximate nature of the theory we have not considered it worthwhile to repeat the lengthy theoretical calculation of D_E for D = 69.2 but instead simply estimate the position of this curve, shown in Fig. 2, by multiplying each value of D_E in Fig. 1 by 69.2/78, without changing λ_0.

Although there is some scatter in Fig. 2, it is clear in both figures that: (1) the Kirkwood–Westheimer theoretical curve falls ***between*** the limiting R_{fr} and R_{max} sets of "experimental" points, as it should; (2) the $\bar{R}$ "experimental" points are in rather satisfactory agreement with the theoretical curves; and (3) values of $D_E > D$ (for $\bar{R}$) are obtained for $\lambda_0 > 1$, and hence, since $D_E \rightarrow D$ as $\lambda_0 \rightarrow 1$, the maximum in the D_E *versus* λ_0 curve predicted by the theory is confirmed by the present approximate analysis.

It is possible to give an alternative and more detailed discussion of the C = 4 case (succinic acid). Here we compute various theoretical values of ΔpK_m (with water as solvent), using structural information and allowing rotation about the central carbon–carbon bond. These values may be compared with the experimental value ΔpK_m = 0.682.

Let θ be the rotational angle around the central carbon–carbon bond, with $\theta = 0$ when the protons are at their distance of nearest approach. Let $F(\theta)$ be the electrostatic free energy of interaction of the protons in the configuration θ. That is

$$F(\theta) = e^2/D_E(\theta)R(\theta) \qquad (11)$$

where, from the geometry,

$$R^2(\theta) = 12.485 + 31.787 \sin^2(\theta/2)(\text{in Å.}^2) \qquad (12)$$

For a given value of θ, we calculate $R(\theta)$ from Eq. (12) and hence $\lambda_0(\theta)$ from Eq. (10), using V =

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[22] E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943, p. 157.

[23] As pointed out by Kirkwood and Westheimer, in computing the electrostatic repulsion in the doubly ionized ion, $A^=$, the use of the proton–proton distance instead of the distance between negative charges compensates approximately for our neglect of the O–H dipole–dipole interaction in H_2A and the charge–dipole interaction in HA^-.

[24] For much larger values of C, one can use the probability distribution functions employed for high polymers. Intermediate values of C, such as $6 \leqslant C \leqslant 14$, are the most awkward to handle.

[25] The quantities in this table are used for both solvents.

[26] G. C. Akerlof, This Journal, **54**, 4125 (1932).

137.8 Å.[3] (Table II). The corresponding value of $D_E(\theta)$ is then read off of the theoretical D_E *versus* λ_0 curve in Fig. 1.

The rotation about the carbon–carbon bond is hindered not only by $F(\theta)$ but presumably also[10] by a potential energy $U(\theta)$ of the type which exists in gaseous ethane and related compounds. We can approximate $U(\theta)$ by

$$U(\theta) = (U_0/2)(1 + \cos\theta) \tag{13}$$

The minimum in U is undoubtedly at $\theta = \pi$; hence both $U(\theta)$ and $F(\theta)$ tend to emphasize the "maximum extension" ($\theta = \pi$) configuration. U_0 is not known but we make the calculation for U_0 = 0, 1, 2 and 3 kcal./mole.

We calculate ΔpK_m here from[10]

$$\Delta pK_m = \log(\alpha/\beta) \tag{14}$$

$$\alpha = \int_0^{2\pi} \exp(-U/kT)d\theta \tag{15}$$

$$\beta = \int_0^{2\pi} \exp[-(U + F)/kT]d\theta \tag{16}$$

using numerical integration. Experimental and theoretical values are compared in Table III. We include also, for comparison, theoretical values of ΔpK_m calculated in the same way except that only a single configuration (value of R) is considered, using R_{fr}, R_{max} and $\bar{R}$ from Table II (C = 4). In this case Eq. (14) reduces to Eq. (9).

TABLE III

CALCULATION OF ΔpK_m FOR SUCCINIC ACID IN WATER AT 25°

Source	ΔpK_m
Experimental[14]	0.682
$U_0 = 0$	.924
U_0 = 1 kcal./mole	.725
U_0 = 2 kcal./mole	.624
U_0 = 3 kcal./mole	.576
R_{fr} only	1.184
R_{max} only (or $U_0 = \infty$)	.492
$\bar{R}$ only	.728

In Table III, the four values of ΔpK_m allowing for rotation all fall between the R_{fr} and R_{max} values, as expected. It is apparent from the table that the Kirkwood–Westheimer theory, together with a not unreasonable value of U_0, is again in satisfactory agreement with experiment even in this more detailed calculation.

In conclusion, although we are aware of the approximate nature of both the Kirkwood–Westheimer model and of the present calculations, we feel that the analysis given here furnishes additional[13] evidence that the theory does succeed in taking into account the dominant features of the problem.

We are indebted to Professors W. D. Walters and H. E. Gunning for a number of very helpful suggestions.

BETHESDA, MD. RECEIVED MAY 25, 1951

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

The Densities of Liquid Tritium, 20.6 to 29°K.[1]

BY E. R. GRILLY

Most of a 70 cc. (S.T.P.) sample of tritium (containing 2.0% HT) was liquefied in a Pyrex bulb of 58 mm.^{3} capacity between two fixed marks. The amount of gas used for this filling gave the difference between liquid and gas density. The results were corrected for gas density and for the presence of HT.

The Tritium Sample.—For this work 70 cc. (S.T.P.) of tritium was used. The source, purification, and storage have been described elsewhere.[2] The gas used in the present work contained 2.0% HT and negligible amounts of other constituents, such as H_2, air, and tritocarbons, all determined mass spectrometrically.

The Apparatus.—This was essentially the same as that used in the vapor pressure measurements.[2] In addition, there were provisions for measuring accurately the amounts of gas and of liquid. For the former, the gas was kept under constant volume, constant temperature and variable pressure, or approximately 255 cc., 25°, and 0 to 230 mm., respectively. The Pyrex liquid bulb consisted of a 17 mm. length of 2 mm. i.d. tubing, above and below which were regions narrowed down to 0.4 mm. i.d. Inked reference marks for the liquid levels, "empty" and "full," were put on the narrow regions. The bulb was observed through a traveling microscope. The bulb volume was calibrated with liquid hydrogen at 19.50°K., the average of six determinations giving a volume of 57.80 mm.^{3} with a mean deviation of ±0.06%. Volume determinations were also made between 14 and 22.8°, but no consistent variation was observed. The liquid hydrogen molar volumes below 20.4° were taken from Scott and Brickwedde,[3] and those above 20.4°, from Woolley, Scott and Brickwedde,[4] who recomputed the results of Mathias, Crommelin and Onnes.[5] At 19.500°K. the value used was 28.021 cc./mole.

Procedure.—The Toepler pump was used to transfer low-pressure gas into the condensing tube so that the liquid level just came to the bottom mark. The amount of gas left on the other side of the pump was measured by noting the pressure. More gas was liquefied until the upper mark was reached. Bulb immersion in the bath was kept 1 cm. above the mark by raising the dewar. Again the amount of gas left was measured. The amount of gas (in moles) used to fill the liquid bulb divided by the bulb volume (between the marks) gives the difference between liquid and gas densities. The gas densities were calculated as previously[2] and amounted to a maximum correction of 3.6%. To make a slight (0.3%) correction for the 2.0% HT, linearity between mole fraction and molar volume was assumed, and the molar volume of HT was taken equal to that of D_2.

Results.—As a check, the density of deuterium at 19.48°K. was determined (after correcting for 0.72% HD) to be 42.89 mole/liter, 0.2%

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[1] This paper is based on work performed under University of California contract with the Atomic Energy Commission.

[2] E. R. Grilly, THIS JOURNAL, **73**, 843 (1951).

[3] R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **19**, 237 (1937).

[4] H. W. Woolley, R. B. Scott and F. G. Brickwedde, *ibid.*, **41**, 379 (1948).

[5] E. Mathias, C. A. Crommelin and H. Kamerlingh Onnes, *Comm. Leiden*, **154b** (1921).