THE VAPOR PRESSURE OF ACETIC ACID AND ACETIC-d_3 ACID-d. THE LIQUID DENSITY OF ACETIC-d_3 ACID-d

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The vapor pressures of CH_3COOH and CD_3COOD have been measured by a static method from 25 to 125° and the data fitted to an Antoine equation. The liquid density of CD_3COOD has been measured in the same temperature range and the data fitted to a cubic function of the temperature.

In the course of a study in this Laboratory on the vapor density of CD_3COOD, it became necessary to know the vapor pressure and liquid density of this substance over a considerable range of temperature. Data available[2,3] on the vapor pressure of CD_3COOD are discordant, and having been determined by comparison with CH_3COOH, depend on a knowledge of the vapor pressure of the ordinary acid. The vapor pressure of ordinary acetic acid itself does not seem to be accurately known, however, as normal boiling points reported in the literature,[4-6] range from 117.75 to 118.6°. It was therefore decided to remeasure the vapor pressure of CH_3COOH as well. This article reports the results of these measurements together with measurements of the density of liquid CD_3COOD.

Materials. Acetic-d_3 Acid-d.[2,3]—Thirty-five grams of carbon suboxide,[7] prepared from diacetyl tartaric anhydride and purified by several bulb-to-bulb distillations *in vacuo*, were introduced into a vacuum system and condensed by liquid air into a 500-cc. reaction tube equipped with a breakable joint. The tube was then charged with 300 cc. of CCl_4 and 20 g. of 99.5% D_2O, and sealed off under vacuum with the contents frozen.[8] The reaction tube was allowed to warm to room temperature and shaken for 48 hours. The reaction proceeded smoothly with no parasitic decomposition of the carbon suboxide. The tube was then sealed to the vacuum line through the breakable joint, the solvent distilled out, and the remaining malonic-d_2 acid-d_2 baked under vacuum for one hour at 100°. The temperature was then raised to 160° for decarboxylation, the resulting CD_3COOD being collected in a Dry Ice trap. The crude acid was distilled twice through a Piros-Glover microstill operating at about 25 theoretical plates and then fractionally crystallized three times. The melting point remained at 15.92 ± 0.07° after the last two fractional freezings. The final yield was 18 g. of acetic-d_3 acid-d (53% based on the carbon suboxide). Mass spectrographic analysis of a sample of hydrogen prepared by reaction of the acid with magnesium showed a deuterium content of 95% ± 3%.

Acetic Acid.—Reagent grade acetic acid was fractionally crystallized twenty times. The melting point of the final residue was 16.54 ± 0.07°, and it was used without further purification.

Both materials were stored under vacuum in tubes equipped with several breakable joints for removal of partial samples.

Vapor Pressure.—Vapor pressures were measured by the simple static method. The pressure exerted by acetic acid vapor in equilibrium with liquid acetic acid was observed on a manometer connected to the vapor chamber. To avoid distillation of acetic acid from the hot vapor chamber to the cold manometer, a small differential manometer was interposed between them. In our adaptation, the sample bulb is connected to a small mercury manometer. Both are contained in a thermostated oil-bath having a plate glass window through which the manometer may be observed. The small manometer is connected to a large manometer outside the oil-bath by a tube fitted with a 3-way stopcock. As the bath is coming to temperature, the pressure in the connecting tube between the manometers is regulated, by pressure or vacuum connections to the stopcock, so that the mercury in the two arms of the small manometer remains at about the same level. A half hour at constant temperature was found sufficient for attaining vapor–liquid equilibrium. The small manometer is read by a telescopic cathetometer outside the bath. The large manometer is read by a steel scale graduated in 0.5 mm., readily estimated to 0.1 mm. by a parallax-eliminating mirror-reading device. Both manometers were constructed of 22 mm. i.d. tubing, large enough to eliminate errors arising from differences in capillary depression and meniscal shape. A small amount of sample always distilled from the sample bulb to the mercury surface in the small manometer during the runs. Manometer measurements were corrected for the weight of this layer which never amounted to more than 0.2 mm. mercury equivalent. The total pressure in the sample bulb was obtained as the algebraic sum of the two manometer heights and was reduced to mm. of mercury at 0° and normal gravity. Corrections for the vapor pressure of mercury were applied where necessary.

The constant temperature bath was regulated by a continuously operating electronic control and was reliable to within 0.01° at all temperatures at which measurements were made. Temperatures were measured by means of a platinum resistance thermometer calibrated by the National Bureau of Standards.

The entire apparatus was tested by measuring the vapor pressure of water up to 100°. The results obtained showed an average deviation of less than 0.25 mm. from the values given by Osborne and Meyers.[9]

Vapor pressures of the two acids were obtained by successive equilibrations at a series of six to twelve temperatures, each higher than the preceding, and then spotting in about an equal number of points at decreasing temperatures in the same range. Self-consistency between both sets of readings was taken as indicating that equilibrium was reached. At the conclusion of such a run, about 80% of the sample in the bulb was distilled out through the attached breakable seal and sealed off. A new series of vapor pressures was taken on the remaining 20%. Consistency of the observed vapor pressures between the 20% sample and the total sample was taken as indicative of the purity of the sample and of the absence from the system of permanent gases.

The vapor pressures observed for CH_3COOH and CD_3COOD are listed in Tables I and II.

On fitting to an Antoine equation in the form

$$\log P_{\mathrm{mm}} = A - B/(C + t)$$

the following values were obtained

	CH_3COOH	CD_3COOD
A	7.4275	7.4397
B	1558.03	1556.17
C	224.79	224.82

for pressures expressed in mm. of Hg. The tables

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[2] C. L. Wilson, *J. Chem. Soc.*, 492 (1935).

[3] J. O. Halford and L. C. Anderson, *J. Am. Chem. Soc.*, **58**, 736 (1936).

[4] N. Alpert and P. H. Elving, *Ind. Eng. Chem.*, **41**, 2864 (1949).

[5] R. R. Dreisbach and S. A. Schrader, *ibid.*, **41**, 2897 (1949).

[6] W. Ramsay and S. Young, *J. Chem. Soc.*, **47**, 640 (1885).

[7] C. D. Hurd and F. D. Pilgrim, *J. Am. Chem. Soc.*, **55**, 757 (1933).

[8] Prof. J. O. Halford in a private communication has called the authors' attention to the explosion hazard involved if this reaction is not carried out at high dilution. Heavy-walled bomb tubing should be used and the concentration of C_3O_2 should not exceed 1.5 molar.

[9] N. S. Osborne and C. H. Meyers, *J. Research Natl. Bur. Standards*, **13**, 1 (1934).

TABLE I

VAPOR PRESSURE OF ACETIC ACID

Temp., °C.	Obsd. vapor pressure, mm. Total sample	20% sample	Calcd. vap. press.
29.80	20.0		20.3
40.25	35.2		35.3
51.08	60.1		60.1
55.54	74.1		73.9
60.93	94.5		94.1
65.50		115.0	114.8
71.04	145.1		144.7
75.50		173.3	173.3
80.41	210.3		210.2
85.69		256.7	256.6
90.59	307.0		307.1
95.66		367.4	367.7
100.29	431.2		431.2
105.45		512.4	512.4
110.00	594.0		593.9
115.12		697.5	697.9
118.41	772.4		772.2
122.44		871.1	871.8
123.86	909.5		909.5
126.45		980.1	981.0

TABLE II

VAPOR PRESSURE OF ACETIC-d_3 ACID-d

Temp., °C.	Obsd. vapor pressure, mm. Total sample	20% sample	Calcd. vap. press.
24.34	15.6		15.6
30.42	22.0		22.0
40.27	37.1		37.1
50.27	60.7		60.7
55.39	77.1		77.1
60.04	94.8		94.8
60.06		95.1	94.9
65.11	118.2		118.1
69.85	144.2		144.2
74.83		176.6	176.4
75.32	179.6		179.8
80.18	217.0		217.5
84.82	258.8		259.4
89.92		312.8	312.9
90.10	315.2		314.9
94.95	374.0		374.3
99.89	443.8		443.8
103.97		508.9	509.0
104.73	522.0		521.9
109.80	615.3		615.4
114.59		715.3	715.8
114.86	721.0		721.8
116.61	761.3		761.9
118.88	815.7		816.6
119.52		832.3	832.4
121.21	876.0		876.0
122.44	908.7		908.8
124.39		962.3	962.4

also give the vapor pressures calculated from these equations for the temperatures observed. The average deviation observed from calculated values is less than 0.25 mm. The computed normal boiling points are: for CD_3COOD, 116.53°; for CH_3COOH, 117.89°. The uncertainty in both boiling points, estimated by a propagation of the average deviation in vapor pressure, is ±0.01°.

It is of interest to compare the vapor pressure difference (CH_3COOH minus CD_3COOD) obtained by the differential method employed by Wilson[2] and Halford and Anderson[3] with that obtained by subtracting the independent measurements of this research. Table III lists the vapor pressure difference obtained by these authors at a number of temperatures compared with corresponding data from the present research.

TABLE III

DIFFERENCE IN VAPOR PRESSURE OF ORDINARY AND DEUTEROACETIC ACID IN MM.

Temp., °C.	V.P. of CH_3COOH minus V.P. of CD_3COOD according to Wilson[2]	Halford–Anderson[3]	This research
21.0	0.7	0.6	0.7
35.8	1.6	0.9	1.1
41.7	2.1	1.3	1.8
48.6	2.9	1.8	2.5
54.6	3.7	2.4	3.2
59.7	4.7	2.8	4.1
65.9	6.0	3.4	5.6
74.3	8.3	4.7	7.2
83.6	11.8	6.5	10.4

The results of this research fall everywhere between those of the earlier authors. Halford and Anderson stated in effect that they were uncertain of the adequate purification of their material. They do not report the deuterium content of their deuteroacid. Wilson reports a m.p. of 15.75° for his deuteroacid compared to 15.92° for ours. Our acid, known to contain 95% deuterium melts 0.68° lower than the ordinary acid. Since CD_3COOD and CH_3COOH surely form solid solutions, it seems unlikely that an additional 5% of deuterium would lower the m.p. by as much as 0.17° more. There is thus considerable reason to believe that Wilson's acid was less pure than ours.

Attempts were made to prepare CH_3COOD for a study of its vapor pressure. The most successful method was similar to that employed by Engler,[10] and involved the hydrolysis of CH_3COCl with D_2O, followed by treatment of the crude hydrolysate with CH_3COOAg in order to remove dissolved DCl.

Lewis and Shutz[11] failed to find evidence of methyl–carboxyl hydrogen exchange in CH_3COOD, but later work by Herman and Hofstadter[12] indicates that exchange may occur. In view of the conflicting evidence it was thought advisable to investigate the possibility of exchange before proceeding with the vapor pressure measurements.

The infrared spectrum of one portion of a sample of CH_3COOD was obtained. Another portion of the same sample was sealed in a glass tube, held at 100° for two days, and then examined by the infrared spectrometer. Parts of the resulting spectra are reproduced in Fig. 1. Comparison of the two spectra shows an unequivocal increase in absorption in the O–H**O region and decrease in the O–D**O region. W. C. Child of this Laboratory has

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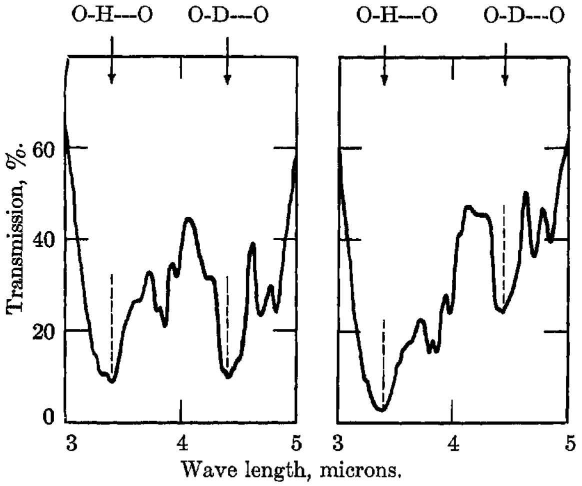
(10) W. Engler, *Z. physik. Chem.*, **B32**, 471 (1936).

(11) G. N. Lewis and P. W. Shutz, *J. Am. Chem. Soc.*, **56**, 493 (1934).

(12) R. C. Herman and R. Hofstadter, *J. Chem. Phys.*, **6**, 538 (1938).



Unheated portion Heated portion

Fig. 1.—Part of the infrared spectrograms of fresh "CH_3-COOD" and the same material heated in glass at 100° for two days. The principal bonds ascribed to hydrogen bond and deuterium bond absorption are marked. The decrease in hydrogen bond and increase in deuterium bond absorption on heating indicates an exchange between methyl hydrogen and carboxyl deuterium.

carried out a similar experiment using CH_3CH_2-COOD with similar results.

Apparently then there is no stable compound of formula CH_3COOD under the conditions obtaining in our vapor pressure apparatus, and the question of its vapor pressure has no clearly definable meaning. No attempt was made to investigate the exchange equilibrium nor to make measurements of vapor pressure on the equilibrium mixture.

Liquid Density.—The liquid density of CD_3-COOD was measured using a weight dilatometer similar to that of Gibson and Loeffler,[13] but differing from the cited design in having its only opening through the capillary tip. The thermal expansion and volume of the dilatometer were determined by a calibration run using water. The observed liquid densities are shown in Table III.

TABLE III

LIQUID DENSITY OF ACETIC-d_3 ACID-d

Temp., °C.	Density, g./cc. Obsd.	Density, g./cc. Calcd.	Temp., °C.	Density, g./cc. Obsd.	Density, g./cc. Calcd.
28.70	1.1091[a]	1.1091	74.80	1.0528	1.0528
29.86	1.1075	1.1077	79.77	1.0466	1.0467
34.84	1.1013	1.1016	84.98	1.0402	1.0402
39.75	1.0956	1.0955	89.90	1.0340	1.0341
44.52	1.0898	1.0897	94.85	1.0278	1.0279
49.81	1.0833	1.0833	99.98	1.0213	1.0213
54.85	1.0772	1.0772	105.05	1.0148	1.0149
59.40	1.0716	1.0717	109.51	1.0090	1.0091
64.77	1.0650	1.0651	113.32	1.0041	1.0042
69.88	1.0588	1.0588			

[a] Determined independently by pycnometer.

The above data were fitted to a cubic polynomial in temperature (t = °C.) by means of least squares, the result being

$$1.1450 - (1.2807 \times 10^{-3})t + (1.218 \times 10^{-6})t^2 - (7.84 \times 10^{-9})t^3$$

with an average deviation of 0.7×10^{-4} g./cc. The densities calculated from this equation are also listed in Table III.

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[13] R. E. Gibson and O. H. Loeffler, *J. Am. Chem. Soc.*, **61**, 2515 (1939).

THE STANDARD POTENTIAL OF SILVER–SILVER CHLORIDE ELECTRODE IN ETHANOL

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The standard potential of silver–silver chloride electrode in spectroscopically pure and dry ethanol has been determined with the help of two types of cells without junction, one of which involves a metallic contact. The value +0.00977 volt of the potential (in molar scale) so obtained for the reaction $AgCl + 0.5H_2 \rightarrow Ag + Cl^-_{EtOH}H^+_{EtOH}$, not only differs in magnitude but also in sign from those reported by previous workers. The discrepancy is perhaps ascribable to the presence, however small, of accidental impurities and/or moisture in the alcohol. In the spectroscopically pure alcohol used in this work the presence of the above was scrupulously guarded against.

Introduction

Suitable reference electrodes for electro-chemical work in the non-aqueous solvents offer special problems and hence they cannot be easily made. In this paper, silver–silver chloride electrode has been used as a reference in connection with certain measurements in ethanol as solvent. For this purpose, its standard potential in this medium in terms of hydrogen electrode as zero, was determined. The value so obtained has been compared with those reported by previous workers.[1–5]

Apparatus and Method.—The following two types of cells were set up: Cell A.

$$\bar{P}t, H_2;\ HCl/EtOH;\ AgClAg^+$$

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(1) P. S. Danner, *J. Am. Chem. Soc.*, **44**, 2832 (1922).

(2) H. S. Harned and M. H. Fleysher, *ibid.*, **47**, 82 (1925).

(3) J. W. Woolcock and H. Hartley, *Phil. Mag.*, [7] **5**, 1133 (1928).