

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Molecular State of the Vapor of Acetic Acid at Low Pressures at 25, 30, 35 and 40°

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Introduction

In a previous publication² it was pointed out that our knowledge of the equilibrium between single and double molecules of acetic acid in the vapor phase at room temperatures was far from being exact. The published data were discordant and could lead to only a very rough estimate of the equilibrium constants. It seemed desirable to undertake an accurate investigation of the behavior of acetic acid vapor at room temperatures and under pressures ranging from that of the saturated vapor to three or four millimeters of mercury.

The Preparation of Acetic Acid

The method of Chandlee and Hutchison³ was employed in the purification of glacial acetic acid. A tail fraction from the final distillation was further purified by fractional crystallization until an acid melting at $16.60 \pm 0.01^\circ$ was obtained. Two samples prepared by Dr. Fuller had melting points of 16.612° (sample A) and 16.616° (sample B), respectively. These were used in the final measurements. The "International Critical Tables"⁴ give 16.60° as the melting point of the pure acid.

In order to free the acid from dissolved gases, a 200-ml. sample was introduced into a small flask, which had been cleaned previously, dried and filled with dry nitrogen. The flask was fitted with two glass break-off seals. After the introduction of the acid, the flask was sealed and was then attached to the distillation system shown in Fig. 1 by means of one of the break-off joints. The flask in question is shown at A, Fig. 1. When the entire system had been evacuated and flamed out, so that over a period of twenty-four hours it was able to maintain a vacuum of the order of 10^{-5} mm. of mercury as read on the McLeod gage G, the break-off seal was broken, and the acid was distilled into one of the bulbs B. The distillation was accomplished by freezing the acid into B by means of a bath of ether and solid carbon dioxide. After the residual nitrogen had been pumped off, the acid was sublimed repeatedly in the evacuated system back and forth between the two bulbs B. After each sublimation the residual pressure due to permanent gases was read on the McLeod gage, and the system was again exhausted to 10^{-4} mm. This procedure was repeated until the residual pressure

after a sublimation did not exceed 10^{-5} mm. Finally about one-half of the sample was collected in the original flask and sealed off from the distillation system. It was then ready to be connected by means of the second break-off joint to the apparatus for determining the pressure-volume data, Fig. 2.

The Experimental Apparatus for Obtaining the Density Data

The Specific Information to be Obtained.—By a suitable manipulation of this apparatus and by means of certain auxiliary operations it was possible to obtain the following three pieces of information about each sample of acetic acid employed in these experiments: (1) the pressure and (2) the volume at three different pressures at a given constant temperature and (3) the absolute quantity of acetic acid in the sample.

General Plan of the Apparatus.—In Fig. 2 there is a diagrammatic sketch of the apparatus used in making the density measurements. The three glass bulbs, A, B, C, of known volume, part of one of which, A₁, also served as

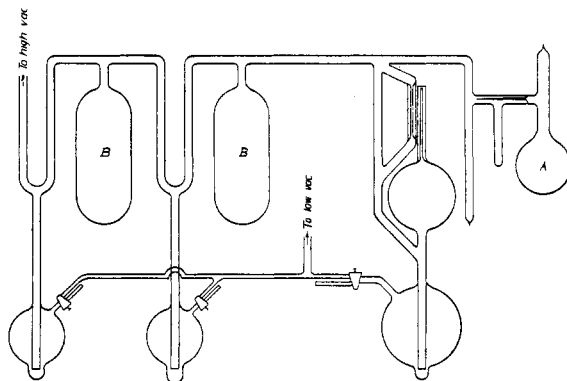


Fig. 1.—Distillation system.

one arm of a U-type differential mercury manometer, were connected to each other in series by mercury Y-seals of the usual type. Thus if B were evacuated and if A contained a sample of gas, the opening of the seal between A and B would allow free expansion of the gas from A into B. These bulbs were set into a water-bath in which the temperature could be controlled to within 0.05° between 25 and 40° . The water-bath, which was $36'' \times 18'' \times 18''$ ($91 \times 46 \times 46$ cm.) and was made of galvanized iron, contained a large glass window on one side, through which the operation of the mercury seals could be observed. Holes were punched in the bottom of the bath for the tubes for the control of the mercury seals and for the manometer, the other arm of which was outside of the bath, and the cracks about these holes were sealed with picein wax. The metal walls of the bath were insulated with heavy felt.

The manometer used to obtain the pressure data was of the differential U type. One arm, A₁, was inside the bath,

(1) This research has been made possible by grants from the Research Fund of the Graduate School of the University of Minnesota. Credit for the devising, constructing and testing of the apparatus should go chiefly to Dr. C. P. Roe. Dr. Donald Fuller prepared several samples of very pure acetic acid. Mr. Herbert Sargent carried out the final series of measurements.

(2) MacDougall and Blumer, *THIS JOURNAL*, **55**, 2242 (1933).

(3) Chandlee and Hutchison, *ibid.*, **53**, 2881 (1931).

(4) "International Critical Tables," Vol. IV, p. 6.

and the other arm, M, was outside. The inside arm was considerably larger than the outside one, so that most of the movement took place in the outside arm. The reading of the mercury level in the latter was accomplished by means of a traveling microscope which could be focused alternately on the meniscus or on a steel meter bar which was graduated in 0.5-mm. divisions and which was rigidly fixed with respect to the manometer. The microscope also contained a scale on which it was found that 13.3 divisions were equal to 0.5 mm. on the steel meter bar. Thus the position of the meniscus could be estimated to 0.004 mm., but in practice it was found that results which were reproducible to 0.01 mm. were the best that could be obtained. In order to obtain consistent results with the manometer it was found necessary to surround the greater part of the outside arm with a wooden jacket lined with wax, through which a stream of water from the bath was kept moving by means of a circulating pump. In this way the temperature of the manometer was kept constant. The manometer was calibrated for the reading of absolute pressures against the McLeod gage, G, with help of pure nitrogen as a permanent gas.

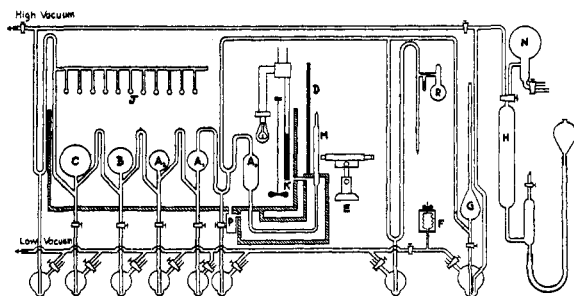


Fig. 2.

Between the bulb C and the pumps there was inserted a line of small sample bulbs of 1 to 2 ml. each. These bulbs were blown on the ends of stubs of heavy-walled Pyrex tubing of about 4 mm. inside diameter. A sample of acetic acid, following the taking of pressure readings on it, was frozen into one of the sample bulbs, sealed off from the line and subsequently analyzed for its acetic acid content by titrating with a standard barium hydroxide solution.

The remainder of the apparatus consisted of a mercury condensation pump, an oil pump, a glass reservoir N for nitrogen and the necessary mercury traps for the control of the McLeod gage and the mercury seals.

Details of the McLeod Gage.—This instrument, shown at G in Fig. 2, served the two-fold purpose, (1) of testing the state of evacuation of the entire density apparatus, and (2) of calibrating the differential manometer so that readings taken directly from the manometer could be converted to absolute pressure. In order to gain the necessary precision for the latter purpose, two unusual features in the construction of the gage were introduced.

The first was that the capillary tube of the ordinary McLeod gage was replaced by a tube some 30 cm. long and of approximately 6 mm. inside diameter. By means of hydrofluoric acid three fine scratches were etched on this tube, and the volume from each scratch to the sealed-off end of the tube was determined by finding its mercury capacity.

The total volume of the gage was also determined with mercury. The scratches were so located that when the instrument was in use for the measurement of pressures lying in the range from 1–15 mm., the meniscus in the gage could always be set on one of the scratches and the pressure could then be read on the special comparison barometer for the gage, which was taken from the same piece of stock as the etched tube. A cathetometer with scale and vernier attached was used for this purpose. It should be noted that the special barometer, although drawing on the same mercury well as the gage, had no connection with the gage. The necessity for this arrangement is obvious when one considers the magnitude of the pressures to be measured. The high pressure readings on the gage always lay in the range from 8 to 45 cm., and it is to be noted that the precision of the gage was always much greater than that of the manometer.

The second unusual feature of the gage was an arrangement for making fine adjustments of the meniscus near the scratches. Credit is due to Dr. George Glockler for suggesting the method of doing this. The essential part of this arrangement was a short length, 13 cm., of semi-collapsible corrugated brass tubing about 2.5 cm. in diameter which was mounted between two rigidly connected brass plates. One end of the tube was soldered to one of the plates, while the other end was closed up and attached to a screw which operated in the other plate as a base. A small outlet tube, which was cemented to a suitable glass connection, was inserted in the brass plate which was fixed to the collapsible tube. This arrangement was sealed to the low vacuum side of the mercury well controlling the gage. By suitable operation of the screw, the brass tubing could be expanded or collapsed within certain limits, and corresponding changes could thus be produced in the menisci of the gage and its barometer.

In the calibration of the etched tube on the gage it was necessary to hold the tube in a position which was just inverted from that which it occupied when in use. Thus each of the volumes determined from the mercury calibration had to be given a positive correction of twice the volume of the meniscus. The data on this point were obtained in the "International Critical Tables."⁵

Details of Calibration and Use of Manometer.—The manometer, the arms of which are shown at A₁ and M in Fig. 2, was of the differential U-type; but it was unusual in that the two arms were of different diameters. This had the effect of confining the movement resulting from changes in pressure on the meniscus in the larger arm, A₁, largely to the meniscus in the smaller arm, M. The diameter of the larger arm was approximately 6 cm., while that of the smaller arm was 16 mm. The considerable size of the larger arm had the advantage of reducing the relative importance of edge effects, which presumably varied with varying conditions, to a negligible order of magnitude. The manometer was prepared by evacuation and suitable flaming out of the glassware, and subsequent vacuum distillation of the mercury into the U. When the distillation had proceeded far enough, the arm M was sealed off permanently from the still and from the high vacuum system.

Since the position of the meniscus in the smaller arm had to be read with an accuracy of 0.01 mm., if possible, a

(5) "International Critical Tables," Vol. I, p. 72.

small traveling microscope which magnified to the extent of about twenty-five diameters was mounted on a wooden frame at a convenient place in front of M. The immediate standard of comparison in the reading of heights with microscope was a steel meter bar prepared by the Gaertner Scientific Corporation of Chicago, and graduated in 0.5-mm. divisions. This was mounted rigidly just behind the smaller manometer arm as referred to the microscope. The microscope could be focused either on the meniscus or on the steel meter bar by means of a screw adjustment, and the vertical motion was controlled by a similar device.

The calibration of the manometer between 1 and 15 mm. was accomplished by admitting pure nitrogen to the system up to the desired pressure and then reading both the rise in the manometer column and the absolute pressure as indicated by the McLeod gage. The upper reaches of the manometer were calibrated after the volumes of the density bulbs had all been determined. When these volumes were known, it was necessary only to allow a sample of nitrogen to expand from one bulb to another and measure the change in the manometer and repeat the process as often as it seemed desirable in order to complete the calibration.

In the manipulation of the manometer the following procedure was used. The microscope was first set at approximately the level of the meniscus and was then focused on the steel scale. A given mark on the microscope scale, in practice 6.00, was set on the nearest scratch on the steel scale. The microscope was then focused on the meniscus. In order to get a sharp image of the latter the aid of a strip of black paper with a slit in it was required. The paper was wrapped and pasted about the tube M so that the slit was in a horizontal position and so that the whole strip could be moved up and down the tube at will. When the meniscus was under observation, the slit, which was about 2 mm. in width, was so placed with respect to the meniscus that the band of light between the meniscus and the upper edge of the slit as seen in the field of the microscope always had the same width. The position of the meniscus could then be read, and its displacement from the zero position, which was determined in the same manner, could be calculated from a direct count of the number of scratches on the steel scale past which the reference mark on the microscope scale had been moved and from the displacements of the meniscus from the reference mark. It should be mentioned that the vertical carriage of the microscope carried a small light, so that optical effects in the microscope were always the same.

Details of Temperature Control.—The temperature of the water thermostat was controlled by the suitable turning on and off of a bank of several 100-watt light bulbs, connected in parallel and immersed in the water. A small telephone relay was used to open and close the tilting mercury switch which controlled the power circuit upon which the heater lamps drew. The relay was in turn operated by the grid circuit of a Commander 71a power vacuum tube, the circuit being opened and closed by the thermal contraction and expansion of a standard mercury control placed in the bath.

Calibration of the Density Bulbs.—The final calibrations of the bulbs A₂, B, C, were made during a period when the apparatus was temporarily dismantled, but after it had

once been set in place. Hence the validity of the various water and mercury calibrations was only negligibly affected by subsequent glass blowing operations which were necessary to make the seals between the various parts of the apparatus. The explanatory material in connection with the presentation of the data is sufficient to indicate the details of these calibrations.

Since the volume of A₁ or of A taken as a whole could be found only after the whole system was in place (this was on account of the impossibility of controlling precisely the amount of mercury distilled into the manometer) it was necessary to resort to the use of the expansion of pure nitrogen for this purpose. The procedure was as follows. A sample of nitrogen was admitted to A₁, the seal between A₁ and the nitrogen reservoir was closed and the pressure was read by means of the manometer. Then the seal between A₁ and A₂ was opened, and the pressure was again read. It was necessary in making calculations to take account of the change in capacity of A with pressure. This change was due to the vertical movement of the large meniscus in the manometer, and could be found directly from the movement in the small one, the diameter of which was known to be 16 mm. Now let R₁ and R₂ be the rises observed on the manometer when the gas occupies A₁ and the whole of A, respectively. From the known diameter of the outside manometer tube, a 1-mm. rise produces an increase in the volume of A of 0.2 ml. Let V_{A₂} and V_A be the zero pressure volumes of A₂ and A, respectively. Then

$$V_A = V_{A_2} \left(\frac{R_1}{R_1 - R_2} \right) - 0.2(R_1 + R_2)$$

The Experimental Procedure

The entire system was exhausted to a point where no pressure could be detected on the McLeod gage. A sample of acetic acid vapor from the reservoir of liquid acid at R was then admitted to the bulb A, and when the desired pressure was approximately reached, the mercury seal between A and R was closed. The mercury levels in the seals confining the vapor to the bulb A were adjusted to their proper marks, and after sufficient time had elapsed to ensure that the vapor had come to the temperature of the bath, the change in the manometer meniscus from its zero position was read and recorded. The seal between bulbs A and B was then opened, so that the vapor occupied the combined volumes of these two bulbs. The manometer was again read and recorded. When this procedure had been repeated for the bulb C, the seal leading to the line of sample bulbs was opened, and the vapor in the apparatus was condensed into one of them by means of liquid air. The liquid air was allowed to remain on the sample bulb for at least fifteen minutes after the meniscus in the manometer had returned to its zero position. The sample

bulb was then sealed off and detached from the line. The bulb was broken while submerged in a weighed amount of barium hydroxide solution. The broken bulb was then rinsed with distilled water and the acid yet unneutralized was titrated with standard base using phenol red as indicator. The solution was boiled when near the end-point and was then cooled to room temperature under a soda-lime tube. The titration was completed under a stream of nitrogen.

Barium acetate, purified by recrystallization, was dissolved in carbon dioxide-free water, phenol red was added and the volume and concentration were adjusted to the conditions obtaining

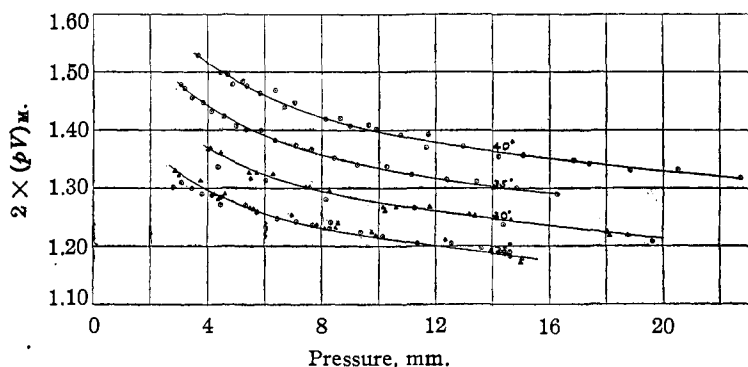


Fig. 3.—Isothermals of acetic acid vapor.

at the end-point of the titrations. This solution was stored under carbon dioxide-free air and was used in estimating end-points.

Calibration of the McLeod Gage

V_4 = total volume
 V_1 = volume from uppermost scratch to the top
 V_2 = volume from middle scratch to the top
 V_3 = volume from lowest scratch to the top

These volumes were determined with mercury at 25°. The values obtained (corrected for inversion of meniscus by adding 0.023 ml.) were $V_4 = 326.4$, $V_1 = 3.804$, $V_2 = 7.700$, $V_3 = 11.734$ ml. The factors, $V_1/V_2 = 0.01165$, $V_2/V_4 = 0.02359$ and $V_3/V_4 = 0.03595$ are needed. These factors are represented by the symbol F .

Calibration of Manometer by Means of the McLeod Gage at 25° Using Nitrogen

R = manometer rise in millimeters
 P' = pressure observed on McLeod gage in millimeters of mercury at 25° after the nitrogen in the gage had been compressed from the volume V_4 to the volume V_3 or V_2
 $F = V_3/V_4$ or V_2/V_4 (see preceding section)

P = pressure of the gas in the system in mm. at 0° before being compressed in the gage. $P = P' \times F \times 0.9955$

$f = P/R$ = factor used to convert manometer rise to pressure in mm. at 0°

From seventeen determinations of the value of the factor f at 25°, we obtain an average value of 1.0956. The average value of the deviations was ± 0.0014 . The accepted value of f at 25° was 1.096. The values of f at 30, 35 and 40° are calculated to be 1.095, 1.094 and 1.093, respectively.

Experimental Data

In the following tables, R is the rise in the manometer, p is the pressure in mm., V is the volume in ml. of the bulb or bulbs containing the acetic acid vapor, g is the weight in grams of barium hydroxide solution (0.007925 equivalent per kilogram of solution) required to neutralize the sample of acetic acid, and $(pV)_M$ is the pressure-volume product for 60.03 g. of acetic acid when 760 mm. \times 22,414 ml. is taken as unity. It will be evident that

$$2(pV)_M = (1 + \alpha)T/273.1 \quad (1)$$

where α is the degree of dissociation of $(\text{HOAc})_2$ into HOAc.

In Table I are given the complete data for two runs, one at 25° and the second at 35°. In the presentation of the rest of the experimental results we give the number of the run, the temperature, the pressure and the value of $2(pV)_M$. The work at 25 and at 35° was carried out with sample A, that at 30 and 40° with sample B of the acid prepared by Dr. Fuller.

TABLE I

Run	t , °C.	R	p	V	g	$2(pV)_M$
I	25	10.38	11.38	652.5	91.32	1.204
		5.88	6.44	1194		1.248
		3.16	3.46	2315		1.300
VIII	35	11.32	12.39	652.8	91.14	1.314
		6.47	7.08	1194		1.374
		3.52	3.85	2315		1.448

In Fig. 3 we have plotted the experimental values of $2(pV)_M$ against p for each of the four temperatures, 25, 30, 35 and 40°. Included in the figure are values (indicated by triangles) obtained by Dr. Roe at 25 and 30°. From curves drawn on a large scale plot, we have read off the "best" values of $2(pV)_M$ for integral values of the pressure. These values are given in Table IV.

From the chemical equation $(\text{HOAc})_2 = 2\text{HOAc}$ we find for the dissociation constant, K_p ,

$$K_p = 4\alpha^2 p / (1 - \alpha^2) \quad (2)$$
 where α , the degree of dissociation, is given by the equation

$$\alpha = 2(\rho V)_M \times (273.1/T) - 1 \quad (3)$$

In Table V are given values of α corresponding to the data of Table IV and the values of X_p calculated by means of equation 2.

TABLE II

Runs I to VII at 25°; VIII to XIV at 35°

Run	p	$2(\rho V)_M$	Run	p	$2(\rho V)_M$
II	10.15	1.216	IX	16.25	1.289
	5.73	1.258		9.24	1.340
	3.08	1.310		5.01	1.408
III	12.56	1.204	X	13.43	1.311
	7.09	1.242		7.65	1.366
	3.80	1.290		4.14	1.433
IV	13.59	1.196	XI	14.83	1.300
	7.68	1.236		8.44	1.353
	4.13	1.288		4.58	1.423
V	9.38	1.224	XII	11.16	1.324
	5.32	1.270		6.37	1.383
	2.81	1.302		3.46	1.456
VI	14.59	1.182	XIII	10.28	1.337
	8.31	1.230		5.88	1.400
	4.44	1.272		3.19	1.473
VII	14.61	1.190	XIV	5.33	1.401
	8.33	1.240		3.07	1.478
	4.45	1.284		1.68	1.568

TABLE III

Runs I and II at 30°; III to XI at 40°

Run	p	$2(\rho V)_M$	Run	p	$2(\rho V)_M$
I	19.63	1.208	VII	16.85	1.348
	11.25	1.265		9.63	1.409
	6.03	1.313		5.24	1.485
II	14.38	1.237	VIII	15.08	1.357
	8.14	1.280		8.63	1.402
	4.37	1.333		4.69	1.495
III	20.52	1.332	IX	14.19	1.355
	11.74	1.392		8.13	1.419
	6.39	1.468		4.43	1.499
IV	22.74	1.318	X	11.66	1.370
	12.97	1.372		6.70	1.440
	7.06	1.447		3.67	1.429
V	18.85	1.331	XI	8.50	1.407
	10.78	1.391		4.88	1.479
	5.85	1.463		2.66	1.563
VI	17.37	1.343			
	9.92	1.402			
	5.39	1.476			

Since the saturated vapor pressures of acetic acid (see a later section of this paper) are 15.5 at 25°, 20.6 at 30°, 27.0 at 35° and 35.2 at 40°, it will be observed that the pressures recorded in Tables II and III for 25 and 30° approach quite

closely the saturation pressures whereas for 35 and 40° the highest pressures measured are approximately 60% of the saturation pressures. It will be noticed that at 25 and 30° the calcu-

TABLE IV

p	Values of $2(\rho V)_M$ Obtained from Graphs			
	25°	30°	35°	40°
3	1.319		1.471	
4	1.295	1.369	1.442	1.516
5	1.272	1.342	1.413	1.484
6	1.255	1.321	1.390	1.458
7	1.242	1.306	1.372	1.438
8	1.231	1.294	1.357	1.421
9	1.222	1.284	1.345	1.407
10	1.214	1.275	1.334	1.396
11	1.208	1.267	1.325	1.386
12	1.201	1.260	1.317	1.378
13	1.194	1.253	1.310	1.370
14	1.188	1.248	1.303	1.364
15	1.182	1.242	1.297	1.358
16		1.236	1.292	1.351
17		1.230		1.346
18		1.225		1.340
19		1.219		1.335
20		1.213		1.330
21				1.325
22				1.320
23				1.316

lated values of K_p fall off rapidly as the saturated pressure is approached. This may be due to an increasing deviation from ideal behavior, but whatever the reason may be, it seems plausible to derive the best value of K_p for 25° from the values for pressures in the range 3 to 9 mm. and the best value of K_p for 30° from the values for pressures in the range 4 to 11 mm. For 40° the best value of K_p was taken to be the average of the values corresponding to pressures from 10 to 23 mm. On this basis, we obtain

$$K_p \text{ at } 25^\circ = 0.547 \text{ mm.} \quad K_p \text{ at } 35^\circ = 1.37 \text{ mm.}$$

$$K_p \text{ at } 30^\circ = 0.909 \text{ mm.} \quad K_p \text{ at } 40^\circ = 2.08 \text{ mm.}$$

When $\log_{10} K_p$ is plotted against $1/T$, the points obtained fall, within the experimental error, on a straight line given by the equation

$$\log_{10} K_p = 11.789 - (3590/T) \quad (4)$$

The values of K_p calculated by means of equation (4) for 25, 30, 35 and 40° are, respectively, 0.557, 0.881, 1.37 and 2.10 mm.

The Measurement of the Saturated Vapor Pressure of Acetic Acid

The density bulbs and the line leading to the mercury seal separating the reservoir R from the density bulbs were exhausted as completely as possible. After the temperature of the bath had been constant for fifteen minutes, the height of the mercury meniscus in the manometer was read. With the pump going, the mercury seals separating

TABLE V
Degree of Dissociation and Dissociation Constant

P, mm.	25°		30°		35°		40°	
	α	K_p	α	K_p	α	K_p	α	K_p
3	0.208	0.543			0.304	1.22		
4	.186	.573	0.233	0.919	.278	1.34	0.322	1.85
5	.165	.560	.209	.914	.252	1.36	.294	1.89
6	.150	.552	.190	.899	.232	1.37	.272	1.92
7	.138	.544	.177	.906	.216	1.37	.254	1.93
8	.128	.533	.166	.907	.203	1.38	.239	1.94
9	.120	.526	.157	.910	.192	1.38	.227	1.96
10	.112	.508	.149	.908	.182	1.37	.218	2.00
11	.107	.510	.142	.906	.174	1.37	.209	2.01
12	.100	.485	.135	.891	.167	1.38	.202	2.04
13	.094	.464	.129	.880	.161	1.38	.195	2.06
14	.088	.437	.124	.875	.155	1.38	.190	2.10
15	.083	.416	.119	.862	.150	1.38	.185	2.13
16			.114	.843	.145	1.37	.178	2.09
17			.108	.802			.174	2.12
18			.104	.787			.169	2.12
19			.098	.737			.164	2.10
20			.093	.696			.160	2.16
21							.156	2.10
22							.151	2.05
23							.148	2.06

(1) the line of sample bulbs from the high vacuum line, and (2) the line of sample bulbs from density bulb C, were closed. Acetic acid vapor from the reservoir R was admitted to the bulbs by opening the seal between the reservoir and the line leading to the density bulbs. Cold water was allowed to run over bulb C until a sufficient amount of acetic acid had condensed and collected above the mercury surface of the seal separating bulb C from the line of sample bulbs. The seal between the line leading to the reservoir and the bulb A₁ was then closed. The bath was again brought to the original temperature, and, after thirty minutes had elapsed to allow the system to become uniform and constant in temperature, the height of the manometer meniscus was read.

The seal separating the line of sample bulbs from the bulb C was opened and the acetic acid in the bulb system was frozen into one of the sample bulbs by means of liquid air. After the sample bulb had been cooled for fifteen minutes the height of the manometer meniscus was again read as a check on the original reading.

Subsequent runs were made using this same sample of acid. The acid was frozen into a sample bulb and, while it remained cooled by the liquid air, the seal separating the system from the high vacuum line was opened and the entire sample bulb and density bulb system was subjected to evacuation for thirty minutes, although the manometer readings taken during this time showed negligible changes. The seal separating the system from the vacuum line was closed, and the sample of acid was transferred from the sample bulb to the density bulbs by removing the liquid air and running cold water over one of the density bulbs. The seal between the density bulb system and the sample bulbs was then closed, confining the vapor to the bulbs inside the water bath.

In each run enough acid was condensed into the system so that a visible amount of liquid was present after equilibrium had been established. In practice it was found

that liquid acetic acid collected on the surface of the mercury in the inner manometer arm, causing an indeterminate error in the manometer reading. It was impossible to avoid this entirely, although it was minimized by using as little excess acid as possible. The maximum thickness of this layer of liquid on the surface of the mercury was estimated to be 1 mm. and the usual thickness much less than 1 mm.

The thermometer used in these experiments was compared with thermometer 40316 in Bureau of Standards set 19691, marked C343, and was found to require a correction of -0.06° at 25 and 30° , of -0.03° at 35° and of -0.07° at 40° .

TABLE VI
Data on Vapor Pressure of Acetic Acid

$t = 24.94$		$t = 29.94$	
Manometer rise	Vapor pressure	Manometer rise	Vapor pressure
14.20	15.56	18.90	20.70
14.13	15.48	18.84	20.63
14.09	15.44	18.76	20.54
Average 15.49		18.71	20.49
$t = 34.97$		18.70	20.48
Manometer rise	Vapor pressure	Average 20.57	
24.75	27.08		
24.72	27.04		
24.56	26.87		
24.58	26.89		
24.50	26.80		
24.60	26.91		
24.65	26.97		
Average 26.94			
		$t = 39.93$	
		Manometer rise	Vapor pressure
		32.20	35.19
		32.19	35.18
		31.95	34.92
		31.95	34.92
		Average 35.05	

In Table VI are given the results obtained for the vapor pressure of acetic acid at 24.94, 29.94, 34.97 and 38.93° . We readily obtain for 25.00° , 15.54 mm., for 30.00° , 20.64 mm., for 35.00° ,

26.98 mm. and for 40.00°, 35.18 mm. The "International Critical Tables"⁶ give for these temperatures 15.6, 20.6, 26.9, 34.8. The equation

$$\log_{10} p_s (\text{in mm.}) = 8.5723 - (2200/T) \quad (5)$$

reproduces our results very accurately, the average deviation corresponding to ± 0.04 mm., which is well within the experimental error.

Thermochemical Calculations

Heat of Dissociation.—Representing by ΔH the heat absorbed in the dissociation of a mole of $(\text{HOAc})_2$ into two moles of HOAc, we find from equation (4) for a temperature between 25 and 40°

$$\Delta H = 16,400 \text{ cal.} \quad (6)$$

We judge that this value may be in error by as much as 800 cal.

Heat of Vaporization.—If we assume that the saturated vapor of acetic acid does not deviate much from an ideal gas, we can calculate the latent heat of vaporization of one mole (120 g.) of acid by means of the equation

$$L = -(1 + \alpha)R \frac{d \log_e p_s}{d(1/T)} \quad (7)$$

In view of equation (5), we obtain

$$L = 10,060(1 + \alpha) \quad (8)$$

Inserting in equation (2) the measured values of K_p and of p_s , we find for 25°, $\alpha = 0.093$; for 30°, $\alpha = 0.104$; for 35°, $\alpha = 0.112$ and for 40°, $\alpha = 0.121$. From equation (8) we obtain

$$L \text{ at } 25^\circ = 11,000 \text{ cal.}$$

$$L \text{ at } 30^\circ = 11,110 \text{ cal.}$$

$$L \text{ at } 35^\circ = 11,190 \text{ cal.}$$

$$L \text{ at } 40^\circ = 11,270 \text{ cal.}$$

(6) "International Critical Tables," Vol. III, p. 217.

Brown⁷ obtained by direct measurement at 117.4° a value of 97.05 calories per gram, equivalent to 11,650 calories per 120 g. of the acid.

From Ramsay and Young's⁸ measurements of the saturated vapor pressure, p_s , at 100, 110, 120 and 130°, we readily find for 118°, assuming the vapor to be ideal, $L = 9344(1 + \alpha)$. Combining this result with that of Brown we infer that at 118° and 1 atm. the value of $(1 + \alpha)$ is 1.247. On the other hand, the value of pV at 118° and 1 atm. obtained by Ramsay and Young⁹ is about 0.319 liter-atm. per gram which leads to a value of $(1 + \alpha)$ equal to 1.194. The difference in the calculated values of $(1 + \alpha)$ is probably due to an appreciable departure from ideal behavior when the vapor is saturated.

Summary

1. Values of pV have been determined for the vapor of very pure acetic acid at 25, 30, 35 and 40° and at pressures as low as 3 mm.

2. The equilibrium constant for the reaction: $(\text{HOAc})_2 \rightleftharpoons 2\text{HOAc}$, has been determined for 25, 30, 35 and 40°. The heat of dissociation is calculated to be about 16,400 cal.

3. The vapor pressure of acetic acid has been measured at 25, 30, 35 and 40°. The heat of vaporization per 120 g. of acid at these temperatures is calculated to be 11,000, 11,110, 11,190 and 11,270 cal.

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(7) Brown, *J. Chem. Soc.*, **88**, 987 (1903).

(8) Landolt-Börnstein, "Tabellen," 1912, p. 388.

(9) "International Critical Tables," Vol. III, p. 437.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Use of Chromous Sulfate in the Removal of Oxygen from a Stream of Gas. A Comparison with Other Oxygen Absorbents

BY HOSMER W. STONE

The frequent need of a stream of inert gas of low oxygen content led the author to the observation that not only did the commercial nitrogen contain appreciable quantities of oxygen, but even the gas from the liquid carbon dioxide was contaminated. The usual methods of purifying the nitrogen proved unsatisfactory. This, together with the lack of data on the relative effectiveness of oxygen-absorbing reagents, led to the work reported in this paper.

A cylinder of commercial nitrogen, containing 0.3% oxygen, was chosen for reference. This gas was passed through the apparatus containing the absorbent to be tested, at a constant rate. The time which elapsed before sufficient oxygen escaped the absorbing reagent to color a very sensitive oxygen indicator has been taken as a measure of the effectiveness of that absorbent for removing oxygen from the stream of nitrogen. All of the reagents allowed detectable quantities