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RECEIVED for review November 11, 1971. Accepted March 31, 1972. This work was partly supported by the National Space and Aeronautics Administration under contract NAS-8-26760.

# Liquid and Vapor Densities of Aluminum Chloride

## II. Extension to the Critical Temperature

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**The orthobaric liquid and vapor densities of aluminum chloride were measured from 197°C to the critical point. A single empirical equation was derived which was symmetrical about the rectilinear diameter and which represented both the liquid and vapor densities. This method yielded  $t_c = 355.2 \pm 0.3^\circ\text{C}$  and  $\rho_c = 0.5073 \pm 0.0004 \text{ g/cm}^{-3}$ .**

In a recent publication from our laboratory (2), the densities of pure aluminum chloride liquid and vapor were reported from 188–296°C. The experimental method used was rapid, and gave extremely precise results. The aluminum chloride was contained in pyrex vessels which were designed with relatively large enclosed volumes. The measurements were not continued above 300°C because of the safety hazard associated with the containment of high pressures in glass apparatus. The present paper describes a modification of the apparatus which permitted the extension of the measurements up to the critical point of aluminum chloride.

### EXPERIMENTAL

**Density Tubes.** Eleven heavy-wall pyrex tubes,  $\frac{3}{8}$  in. o.d. and about 25 cm long were used. The density tubes were

calibrated and liquid  $\text{AlCl}_3$  volumes measured by the method used for density tubes A, B, C, and D of ref. 2. Calibration data are given in Table I. The manner in which  $\text{AlCl}_3$  was purified and the procedure used to load the density tubes with  $\text{AlCl}_3$  also were the same as used before.

**Procedure.** Density tubes were immersed in the molten salt bath described earlier (2). The bath temperature was determined by measurement of the resistance of a Leeds and Northrup Model 8163 platinum resistance thermometer with the aid of a Data Technology Corp. Model 370 digital volt meter. The platinum thermometer was an Air Force Reference Standard Thermometer, calibrated at the freezing point of zinc, freezing point of tin, boiling point of water, triple point of water, and the boiling point of oxygen by the U.S. Air Force Measurement Standards Laboratory, Aerospace Guidance and Metrology Center, Newark Air Force Station, OH.

Experimental values of  $\text{AlCl}_3$  liquid volume were obtained by measuring with a cathetometer the distance from the bottom of the  $\text{AlCl}_3$  meniscus to an arrow etched on the tube.

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Table I. Calibration of Density Tubes

Tube	Vol. to arrow, cm <sup>3</sup>	Vol. of capillary, cm <sup>3</sup> /cm	Total enclosed vol., cm <sup>3</sup>	Mass of $\text{AlCl}_3$ in tube, g
I	2.211 ± 0.003	0.2575 ± 0.0006	6.17 ± 0.05	4.794
II	2.174 ± 0.003	0.2477 ± 0.0008	5.91 ± 0.05	3.922
III	2.189 ± 0.004	0.2479 ± 0.0004	5.92 ± 0.05	2.977
IV	2.234 ± 0.008	0.2544 ± 0.0008	6.05 ± 0.05	2.046
V	2.257 ± 0.002	0.2550 ± 0.0006	5.84 ± 0.05	1.925
VI	2.389 ± 0.007	0.256 ± 0.002	5.93 ± 0.05	2.435
VII	2.238 ± 0.004	0.254 ± 0.001	6.07 ± 0.05	2.933
VIII	2.122 ± 0.006	0.249 ± 0.002	5.47 ± 0.05	3.338
IX	2.366 ± 0.004	0.249 ± 0.002	5.87 ± 0.05	3.812
X	2.234 ± 0.005	0.256 ± 0.002	5.90 ± 0.05	4.285
XI	2.176 ± 0.005	0.250 ± 0.002	5.93 ± 0.05	4.762

From this measurement and the calibration data, the liquid volume was calculated. Meniscus corrections were made in the manner described previously (2).

It was not possible to immerse simultaneously all 11 density tubes in the bath. Therefore measurements were taken in two groups. Tubes III-VII inclusive contained the least amounts of  $\text{AlCl}_3$ , and could be heated to the critical temperature. These five tubes were handled together. The remaining six tubes contained larger masses of  $\text{AlCl}_3$  than could be contained at the higher temperatures. These tubes were handled together, and were removed from the bath, one by one, as the liquid volume approached the total enclosed volume.

## CALCULATIONS

Results of the liquid volume measurements are shown in Table II. The data were not all taken in the order listed; measurements were made with both ascending and descending temperature. Hand-fitted curves of liquid volume vs. temperature were constructed for each density tube. Unlike the earlier study (2), we found no empirical equations for this relationship which would reproduce the data as closely as did hand-drawn curves.

The liquid volumes for all 11 tubes were read from the curves at convenient temperature intervals (every  $5^\circ\text{C}$  from  $190$ – $320^\circ\text{C}$ , then every  $2^\circ$  until  $338^\circ$ , and every  $1^\circ$  thereafter). All liquid volumes and total enclosed volumes were corrected for the thermal expansion of pyrex glass before any calculations were performed. The data were analyzed by two quite different mathematical approaches.

**Least-Squares Matrix Method for Overdetermined Variables.** At a given temperature, liquid and vapor densities are related to tube volume and mass of  $\text{AlCl}_3$  by the set of equations

$$DV_i + d(T_i - V_i) - m_i = z_i \quad (1)$$

where each density tube contributes one equation. At each temperature selected, the set of equations was solved for  $D$  and  $d$  by a least-squares treatment which minimized the sum

$$\sum_{i=1}^N (z_i)^2$$

The computational technique was adapted from the method described by Margulis (3).

Densities were computed with all equations in each set given equal weights in the least-squares calculations. Standard deviations in mass were calculated from

$$\sigma = \left[ \frac{1}{N-2} \sum_{i=1}^N (z_i)^2 \right]^{1/2} \quad (2)$$

Estimated errors in  $D$  and  $d$ ,  $\sigma_D$  and  $\sigma_d$  are the changes in density for a mass change of one standard deviation,  $\sigma$ .

Some of the parameters which describe this data-reduction method are given in Table III.

**Tube Pair Simultaneous Equations.** Densities were also calculated by the same method as used in the previous report (2), by solving pairs of simultaneous equations and averaging the different values at each temperature. Eleven tubes yield 55 different pairs of simultaneous equations. In practice the number of usable pairs seldom exceeded 40. The principal reason for rejecting a particular pair of equations is that the more nearly the two equations become identical, the less reliable are the calculated densities. This situation was common with consecutively numbered tubes, as these tubes contained similar masses of  $\text{AlCl}_3$ . Since total enclosed volumes were almost the same for all 11 tubes, the liquid volumes were also similar for consecutively numbered tubes.

An arbitrary process was used to reject pairs of equations. At each temperature, all 55 pairs of equations were solved for  $D$  and  $d$ . If either  $D$  or  $d$  for a particular pair differed by more

Table II. Unsmoothed Liquid  $\text{AlCl}_3$  Volumes

Temp, $^\circ\text{C}$	Liquid volume, $\text{cm}^3$					
	Tube III	Tube IV	Tube V	Tube VI	Tube VII	
197.2	2.2745	1.5280	1.4272	1.8385	2.2378	
207.5	2.3055	1.5446	1.4374	1.8578	2.2645	
217.4	2.3340	1.5548	1.4463	1.8808	2.2925	
227.5	2.3625	1.5675	1.4578	1.8987	2.3205	
237.1	2.3935	1.5738	1.4616	1.9141	2.3472	
247.0	2.4245	1.5827	1.4680	1.9295	2.3739	
256.8	2.4555	1.5853	1.4692	1.9461	2.4006	
266.2	2.4803	1.5815	1.4603	1.9512	2.4261	
275.9	2.5100	1.5764	1.4514	1.9615	2.4553	
285.5	2.5348	1.5497	1.4259	1.9627	2.4706	
295.7	2.5708	1.5319	1.4080	1.9704	2.5036	
305.3	2.6030	1.4975	1.3724	1.9653	2.5278	
314.8	2.6365	1.4492	1.3252	1.9499	2.5494	
320.0	2.6526	1.4123	1.2844	1.9269	2.5571	
324.8	2.6687	1.3640	1.2410	1.9013	2.5660	
329.5	2.6823	1.3131	1.1888	1.8731	2.5723	
333.8	2.6612	1.2075	1.0702	1.8027	2.5291	
336.7	2.6625	1.1464	1.0230	1.7656	2.5176	
338.8	2.6662	1.1057	0.9835	1.7323	2.5087	
340.8	2.6749	1.0587	0.9313	1.6964	2.4960	
343.0	2.6674	1.0180	0.8866	1.6619	2.4769	
345.1	2.6588	0.9633	0.8407	1.6106	2.4540	
347.9	2.6526	0.9060	0.7821	1.5492	2.4197	
350.8	2.6327	0.8323	0.7171	1.4647	2.4019	
353.2	2.5559	0.7394	0.6176	1.3187	2.3192	
354.9	2.4567	0.6249	0.5016	1.2419	2.1958	
357.5	2.2745	0.4863	0.3117	1.1049	2.0445	
359.8	2.2126	0.2955	0.0452	0.9974	1.8804	
360.1		0.2484	0.0070	0.8642	1.8613	
361.5	1.9622	0.0334	<sup>a</sup>	0.7963	1.8804	
362.5	2.0477	<sup>a</sup>		0.6965	1.8384	
	Tube I	Tube II	Tube VIII	Tube IX	Tube X	Tube XI
197.3	3.7071	3.0137	2.5631	2.9273	3.3139	3.6829
207.0	3.7689	3.0657	2.6043	2.9697	3.3614	3.7441
217.2	3.8268	3.1115	2.6417	3.0121	3.4139	3.8067
227.1	3.8950	3.1574	2.6767	3.0582	3.4691	3.8704
236.6	3.9659	3.2094	2.7153	3.1031	3.5268	3.9367
249.6	4.0573	3.2812	2.7740	3.1729	3.6114	4.0367
259.3	4.1423	3.3382	2.8189	3.2253	3.6806	4.1205
269.8	4.2350	3.4001	2.8625	3.2876	3.7537	4.2118
278.8	4.3405	3.4744	2.9224	3.3524	3.8421	4.3219
288.5	4.4641	3.5562	2.9760	3.4235	3.9383	4.4432
298.3	4.6186	3.6491	3.0671	3.5096	4.0537	4.5945
303.1	4.6946	3.6974	3.0783	3.5594	4.1190	4.6720
307.9	4.7860	3.7593	3.1170	3.6118	4.1896	4.7708
311.5	4.8671	3.8076	3.1519	3.6654	4.2460	4.8496
322.0	5.1761	3.9896	3.2692	3.8163	4.4767	5.1584
327.1	5.3757	4.1023	3.3440	3.9210	4.6229	5.3710
332.0	5.6448	4.2510	3.4363	4.0470	4.8113	5.6286
334.6	5.8353	4.3674	3.4949	4.1317	4.9357	<sup>b</sup>
337.0	<sup>b</sup>	4.4764	3.5723	4.2365	5.0882	
339.5		4.6200	3.6571	4.3711	5.2600	
342.0		4.7971	3.7781	4.5469	5.4664	
343.5		5.0560	3.9004	4.7153	<sup>b</sup>	
344.3		5.0845	3.8791	4.6941		
344.9		5.3223	4.0051	4.8686		
345.0		5.2269	3.9515	4.8038		
345.8		5.3929	4.0238	4.9135		
346.2			4.1947	5.1292		
346.4		5.5885	4.1049	5.0307		
346.8		<sup>b</sup>	4.1648	5.1105		
347.0			4.1548	5.1180		
347.3			4.2022	5.1729		
347.6			4.2347	5.2402		
348.2			4.3719	5.4372		
348.8			4.5290	<sup>b</sup>		
349.1			4.5465			
349.2			4.6638			

<sup>a</sup> Liquid all volatilized. <sup>b</sup> Liquid volume approached total tube volume, and tube removed from bath.

**Table III. Standard Deviations in Densities Calculated by Least-Squares Matrix Method for Overdetermined Variables<sup>a</sup>**

Std dev	190–330°C <sup>b</sup>	190–350°C <sup>c</sup>
$\bar{\sigma}$	0.011	0.043
$\bar{\sigma}_D$	0.0016	0.0045
$\bar{\sigma}_d$	0.0016	0.0048

<sup>a</sup> In each case the quantity given is the average of the values taken at all of the different temperatures in the temperature range indicated. <sup>b</sup> Thirty-two different temperatures. <sup>c</sup> Fifty-two different temperatures.

**Table IV. Standard Deviations in Densities Calculated from Pairs of Simultaneous Equations<sup>a</sup>**

Std dev	190–330°C <sup>b</sup>	190–350°C <sup>c</sup>
$\bar{\delta}_D$ (All possible combinations)		0.015
$\bar{\delta}_D$ (After rejection of similar equations)	0.003	0.007
Average change in $\bar{D}$ after rejection of similar equations		0.002
$\bar{\delta}_d$ (All possible combinations)		0.013
$\bar{\delta}_d$ (After rejection of similar equations)	0.003	0.008
Average change in $\bar{d}$ after rejection of similar equations		0.002

<sup>a</sup> In each instance the quantity given is the average of the values taken at all of the different temperatures in the temperature range indicated. <sup>b</sup> Thirty-two different temperatures. <sup>c</sup> Fifty-two different temperatures.

than one standard deviation,  $\delta$ , from the respective means,  $\bar{D}$  or  $\bar{d}$ , that pair of equations was not used. The remaining pairs of equations were solved and new means and deviations calculated. Standard deviations were calculated from

$$\delta_{D \text{ or } d} = \left[ \frac{1}{n} \sum_{i=1}^n (\text{individual value} - \text{mean value})^2 \right]^{1/2}$$

Some of the parameters which describe this data-reduction method are given in Table IV.

## RESULTS

Clearly the least-squares matrix method leads to less uncertainty in calculated densities, and it was these values which were used to calculate the final empirical equation described below.

According to the law of the rectilinear diameter, the mean of the orthobaric densities of a substance is a linear function of temperature. Stated another way, the liquid and saturated vapor densities of a substance should describe a symmetrical function about the rectilinear diameter. The liquid and vapor densities obtained in the manner described above were least-squares fit to the function

$$t = t_c + a_2(\rho - \rho_m)^2 + a_4(\rho - \rho_m)^4 \quad (3)$$

where

$$\rho_m = b_0 + b_1 t \quad (4)$$

and  $t_c$ ,  $a_2$ ,  $a_4$ ,  $b_0$ , and  $b_1$  are all adjustable constants, the first of which is the critical temperature. In Equation 3 both  $D$  and  $d$  were substituted for  $\rho$  in making the fit.

Equation 4 was obtained by a least-squares fit of the mean densities at the 35 temperatures lying between 190° and 336°C, inclusive. An automatic weighting procedure was followed, where each point was given the weight

$$\text{weight} = 1/(\text{residual in } \rho_m + 0.0006)^2$$

The term 0.0006 in the denominator was introduced to prevent

**Table V. Empirical Equation for AlCl<sub>3</sub> Density<sup>a</sup>**

$$\rho(\text{g/cm}^3) = b_0 + b_1 t \pm \left\{ \frac{-a_2 - [a_2^2 - 4a_4(t_c - t)]^{1/2}}{2a_4} \right\}^{1/2} \quad (5)$$

$$t_c = 355.2 \pm 0.3^\circ\text{C}$$

$$a_2 = -181 \pm 3$$

$$a_4 = -546 \pm 7$$

$$b_0 = 0.8279 \pm 0.0003$$

$$b_1 = -(9.02 \pm 0.01) \times 10^{-4}$$

<sup>a</sup> Obtained by solving Equation 3 for  $\rho$ ; + root yields  $D$  and - root yields  $d$ .

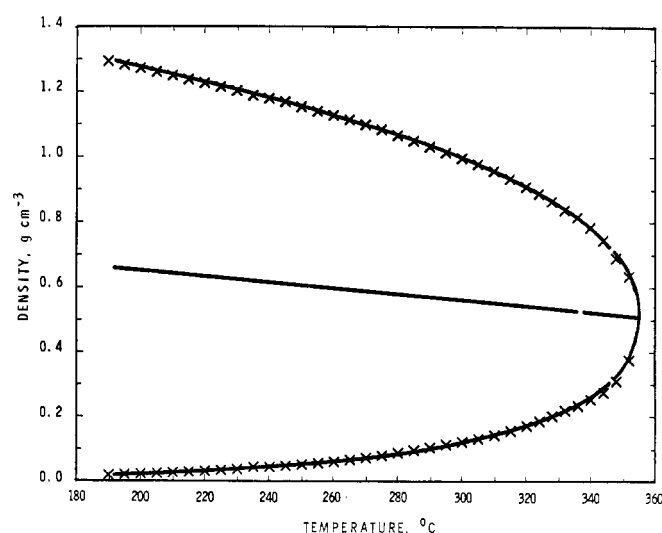
the possibility of some individual point accidentally dominating the fit. The term was equal to the final standard deviation in  $\rho_m$  in an analogous least-squares fit in which all points were given equal weight.

The final standard deviation in  $\rho_m$ , calculated from an equation analogous to Equation 2, was 0.0004.

Equation 3 was obtained by a least-squares fit of the 86 calculated density values which lay between 190° and 345°C. Each point was weighted equally. The final standard deviation in  $t$ , calculated from an equation analogous to Equation 2, was 0.7. The values of the adjustable constants are given in Table V, together with Equation 5, which is useful for calculating densities at a particular temperature. Equation 5 was obtained by solving Equation 3 for  $\rho$ .

## DISCUSSION

The experimental method is essentially the same as that employed by Quinn and Wernimont (5). The large bulbs used in our previous study (2) were not employed in the present work because of the high internal pressures generated. Denisova and Baskova (1) reported a critical pressure of 26 atm. It is obvious that the present method will not yield the precision of our previous work (2), which extends over a smaller temperature region. The least-squares matrix method for density calculation gave estimated liquid and vapor density uncertainties of  $\pm 0.1\%$  and  $\pm 3\%$ , respectively, over the temperature range 190–330°C, and  $\pm 0.4\%$  and  $\pm 6\%$ , respectively, over the temperature range 190–350°C. Calculated values are compared with Equation 5 in Figure 1.



**Figure 1. Liquid and vapor densities of aluminum chloride**

X, calculated from least-squares matrix method (only points at 4°C intervals plotted above 320°C, for purposes of clarity); — calculated from Equations 4 and 5. The breaks in the curves occur at the highest temperature used in fitting the equations: 336°C for Equation 4 and 345°C for Equations 3 and 5

The rapidly deteriorating precision at the highest temperatures is attributable mostly to those density tubes which contained the least  $\text{AlCl}_3$ . That this is so was demonstrated by using Equation 1 to calculate  $V_i$  at various temperatures, using  $T_i$  and  $m_i$  from Table I and  $D$  and  $d$  from Equation 5. Appropriate corrections for thermal expansion were made. This procedure reproduced the 11 liquid volumes in Table II at 197°C with a  $\pm 0.2\%$  average deviation, the nine volumes from 197–337°C with a  $\pm 0.7\%$  average deviation, and the eight volumes over the temperature range 197–345°C with an average deviation of  $\pm 2.6\%$ . The maximum expected error arising from the uncertainties in the calibration data and cathetometer readings was about  $\pm 0.5\%$  to  $\pm 1.0\%$ . At the higher temperature it was evident that the tubes with the least  $\text{AlCl}_3$ , and most especially tubes IV and V, were the sources of most of the uncertainty. On the other hand, the liquid volume in tube III, whose overall density of  $\text{AlCl}_3$  was very nearly the critical density, could be calculated to within  $\pm 1.5\%$  of the observed value at temperatures as high as 355°C.

There were three likely contributors to this observation. Any temperature gradients or temperature uncertainties in the bath would affect most the location of the meniscus of tubes with the least  $\text{AlCl}_3$ . Any impurities in the  $\text{AlCl}_3$  would become more and more concentrated as the liquid volume decreased and therefore most profoundly affect the vapor densities of these tubes. Finally, as a meniscus would approach either end of a density tube it would eventually enter a region where the volume of capillary per unit length would deviate from the calibration value.

Nisel'son and Sokolova (4) obtained a critical temperature of 354.0°C from plots of orthobaric densities and the mean density. They reported a critical density of 0.505 g/cm<sup>3</sup>. Denisova and Baskova (1) reported 352.5°C as the critical temperature and a critical density of 0.510 g/cm<sup>3</sup>. Our critical temperature was an adjustable parameter in Equation 3 and had the value 355.2  $\pm$  0.3°C. Equation 4 yields a critical density of 0.5073  $\pm$  0.0004 g/cm<sup>3</sup>.

## NOMENCLATURE

- $a_i, b_i$  = empirical coefficients  
 $d$  = density of  $\text{AlCl}_3$  vapor  
 $D$  = density of  $\text{AlCl}_3$  liquid  
 $m_i$  = mass of  $\text{AlCl}_3$  in  $i$ th tube  
 $n$  = number of pairs of equations solved for density  
 $N$  = number of density tubes used at each temperature  
 $t$  = temperature in degrees centigrade  
 $t_c$  = empirical coefficient; critical temperature  
 $T_i$  = total enclosed volume in  $i$ th tube  
 $V_i$  = volume of liquid in  $i$ th tube  
 $z_i$  = residual in mass  
 $\delta_D, \delta_a$  = standard deviation in calculated liquid or vapor density  
 $\rho$  = orthobaric density  
 $\rho_m$  = mean density  
 $\sigma$  = standard deviation in mass  
 $\sigma_D, \sigma_a$  = estimated error in calculated liquid or vapor density

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RECEIVED for review January 3, 1972. Accepted March 2, 1972.

# Low-Frequency Dielectric Constant of Methylamine, *n*-Propylamine, and Isopropylamine

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**The dielectric constants of liquid methylamine, *n*-propylamine, and isopropylamine have been measured at 0.1 MHz over a wide range of low temperatures. The data are accurate to 3%. The dielectric constants at 0°C and the linear temperature coefficients are computed for each amine by least-squares analysis.**

Recent studies of solvation effects in ammonia and ammonia-like solvents have produced a need for low-frequency dielectric constant data for liquid alkyl amines over a wide temperature range (4, 6, 12). Currently available data do not allow accurate extrapolation to low temperatures. The present work reports measurements of the low-frequency dielectric constants of methylamine, *n*-propylamine, and isopropylamine over an extended range of low temperatures and presents linear temperature coefficients computed for each amine.

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## METHOD

The dielectric constants of the liquids were measured by a conventional liquid substitution procedure using an all-glass capacitance cell and a Boonton 74C-S8 capacitance bridge operating at 0.1 MHz (11, 14, 15).

The capacitance cell was made of concentric thin-walled glass cylinders with cylindrical electrodes plated on the inside surfaces in contact with the dielectric fluid after the design of Sayce and Briscoe (9). An alternative design used electrodes plated on the outside of the glass surface. End-effect correction expressions were computed by calibration with analytical grades of benzene, carbon tetrachloride, chloroform, and