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Liquid and Vapor Densities of Aluminum Chloride

LOWELL A. KING[1] and DAVID W. SEEGMILLER
Frank J. Seiler Research Laboratory (Air Force Systems Command) and Department
of Chemistry, United States Air Force Academy, USAF Academy, Colo. 80840

The liquid and vapor densities of aluminum chloride were measured from 188°–296° C. A very precise and rapid method of simultaneously determining liquid and vapor densities was used. The method should be applicable for almost any volatile material and should be especially useful for those that are also highly reactive. Least-squares fit cubic polynomials were derived which represent the liquid and vapor densities, each within a standard deviation of ±0.1%.

The densities of pure aluminum chloride liquid and vapor were required as part of our study on molten salt electrolytes which contain aluminum chloride. The values which exist in the literature are of relatively poor precision and/or cover only a narrow temperature range (*1, 2, 4, 6-8*). Precise data, especially for vapor over a wide temperature span, were needed as part of the information required to calculate compositions of volatile $AlCl_3$-containing melts enclosed in vessels of known vapor volume.

EXPERIMENTAL

Procedure. Liquid and vapor densities were determined by measuring the volumes of each phase in sealed dilatometric tubes having a calibrated graduated region at the phase boundary and a known total volume. The total mass of $AlCl_3$ in each tube also was known. The experimental procedure followed was suggested by the method of Quinn and Wernimont (*9*), and modified to yield considerably more precise results. Data were obtained from two sets of four borosilicate tubes, each tube being similar to that shown in Figure 1. Two sets of tubes were used so that the entire temperature region of interest could be covered in overlapping temperature spans. Two sets also provided an internal check in the overlapping regions on the accuracy of the calibration methods.

A set of four tubes was immersed in a well-stirred bath of the ternary eutectic $NaNO_3$-$NaNO_2$-KNO_3 [mp 142° C (*5*)]. The bath temperature was controlled with a Leeds and Northrup Precision Set Point Control System, which operated a magnetic amplifier power supply. The bath temperature was determined by measurement of the emf of a Chromel-Alumel thermocouple with a Leeds and Northrup type K-3 potentiometer and type 9834 electronic dc null detector. The thermocouple was calibrated at the melting points of benzoic acid, tin-lead eutectic, tin, and cadmium. For convenience, the thermocouple was frequently checked with Sn-Pb eutectic, for which a melting point of 183.0° C was assigned (*3*).

Each tube contained a known mass of $AlCl_3$. At a given temperature, the height of the liquid in the graduated stem was measured with a cathetometer. The volume of liquid was calculated from the cathetometer reading and known calibration data for each tube. The total enclosed volume of each tube also was known. For any two tubes in a set, at any given temperature, the densities of liquid and vapor could be calculated by solving the simultaneous equations:

$$W_1 = V_1 D + (T_1 - V_1) d$$

$$W_2 = V_2 D + (T_2 - V_2) d$$

where

D = density of $AlCl_3$ liquid
d = density of $AlCl_3$ vapor
W_1 and W_2 = mass of $AlCl_3$ in tubes 1 and 2
V_1 and V_2 = volume of liquid in tubes 1 and 2
T_1 and T_2 = total enclosed volume in tubes 1 and 2

In every case, volumes were corrected for the thermal expansion of Pyrex glass. This correction was less than 0.3% at the highest temperatures reached.

In practice, the six possible sets of simultaneous equations arising from four tubes were solved, and average D and d reported. This method also provided an internal check on the reliability of the method. Whenever the average deviation of each D or d from the mean exceeded a preselected (arbitrary) limit, all four cathetometer readings were rejected, and reread after allowing a more extended time for equilibrium to be established. This was not a frequent occurrence.

Pyrex glass evidently does not expand significantly owing to the pressure of the aluminum chloride vapor. Measurements were taken with both ascending and descending temperature with no mismatch of the data. Individual tubes were kept at elevated temperatures (up to 325° C) for two to three months without changes in the liquid volumes. When these same tubes were cooled to temperatures just above the triple point, the same densities were calculated as were obtained with these tubes when they were heated for the first time.

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[1] To whom correspondence should be addressed.

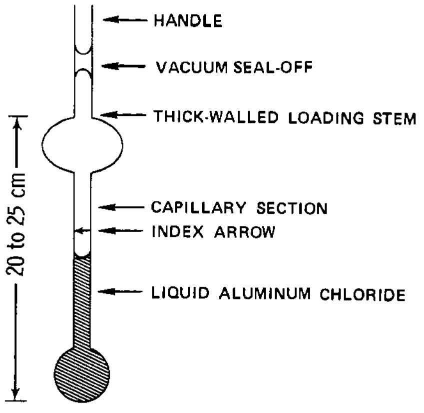

Figure 1. Density tube

Purification of Aluminum Chloride. "Baker Analyzed" aluminum chloride was purified by repetitive sublimation in a stream of argon. Approximately 500 grams of $AlCl_3$ was loaded in one end of a 55-mm od Pyrex tube approximately 60 cm long. Over a period of about 8 hr, the tube was passed through a furnace maintained at about 200° C. The final sublimate was collected in a water-cooled receiving tube, which was transferred into a glove box for further $AlCl_3$ transfer. The box atmosphere was nitrogen, dried by recirculation over a molecular sieve. The white, free-flowing $AlCl_3$ powder was transferred as quickly as possible into the density tubes, which were then stoppered and removed from the box for weighing and sealing under vacuum.

The aluminum chloride melted into a clear, colorless liquid.

Calibration and Filling of Density Tubes. Tubes *A*, *B*, *C*, and *D* were prepared with an arrow etched midway along the capillary. Each tube was calibrated in the following manner: Distilled water was added to a preweighed tube with a long-needled syringe (to avoid water touching the upper walls of the capillary and loading stem) until the meniscus was within the capillary section. The distance from the bottom of the meniscus to the arrow was measured with a cathetometer, and the tube with water was weighed on an analytical balance. This procedure was repeated at least twice more, with the meniscus at different regions of the capillary. From these measurements, it was possible to calculate the volume to the arrow, and the volume per unit length of capillary. The tube was filled with water to a mark on the loading stem at which the tube ultimately would be sealed, and was weighed to determine the total tube volume. In all cases, weights were corrected for the buoyancy of air.

Cathetometer readings were made while the tubes were immersed and equilibrated in a water bath thermostated at 20° C. Meniscus corrections were made by assuming the volume of water contained in the meniscus was calculated correctly assigning an exactly hemispherical shape to the meniscus surface. This assumption was verified by carefully measuring enlargements of photographs of the meniscus. Any error in assigning meniscus shape will tend to cancel out in the final density calculations. The calibration data for tubes *A*, *B*, *C*, and *D* are given in Table I.

The other set of density tubes, *S*, *T*, *U*, and *V*, were made with larger diameter capillaries to enable their use at higher temperatures, where the densities are changing more rapidly with temperature. In this case, we used the stems of measuring pipets. These capillaries were factory-marked at 0.1 cm^3 per division, with divisions approximately 0.36 cm apart. The upper and lower bulb volumes of *S*, *T*, *U*, and *V* corresponded closely with those of *A*, *B*, *C*, and *D*. The calibration method was similar to that just described, although somewhat simpler, for we accepted the manufacturer's claim on capillary volume between graduation marks on each tube.

After the tubes were calibrated they were cleaned, then dried under vacuum overnight at 350° C. The tubes were weighed on an analytical balance, passed into a glove box for loading with $AlCl_3$, then removed, evacuated, sealed, and reweighed to determine the mass of $AlCl_3$. The initial weight was corrected for the mass of the air enclosed in the tube. As before, all weights were corrected for the buoyancy of air.

The experimental measurements of $AlCl_3$ liquid volume were made by measuring with a cathetometer the distance of the bottom of the $AlCl_3$ mensicus from the arrow (tubes *A*, *B*, *C*, *D*) or the nearest graduation mark (tubes *S*, *T*, *U*, *V*). From this measurement and the calibration data, the liquid volume could be calculated. As described above, on the strength of enlargements of photographs of the $AlCl_3$ menisci, an exactly hemispherical shape was assumed.

RESULTS

Results of the density measurements are shown in Table II. These are unsmoothed data, and, in each instance, are averages of the densities calculated from the six sets of simultaneous equations. The uncertainties shown are calculated from

$$\text{uncertainty} = \left[\tfrac{1}{6} \sum_{i=1}^{6} (\text{individual value} - \text{average value})^2 \right]^{1/2}$$

It was decided to smooth these data in a rather involved way before calculating final empirical equations for density. Our first step was to compute a least-squares polynomial equation for the liquid volume in each density tube *vs.* temperature.

A digital computer program was used which automatically assigned weights to each point; the weight depended on the distance of that point to the calculated line. The computer carried out the following sequence: A least-squares cubic polynomial was calculated for a given tube from the volume *vs.* temperature data, with each point assigned a weight of unity. Then the observed volume at each temperature was compared to the volume calculated from the newly generated equation. The difference was used to calculate a new weight for that point, equal to exp $[-(\text{difference})^2]$. The new weights were compared with the old weights, point by point. If any weight changed by 10^{-6} or more, a new least-squares equation was computed using these weights, and the sequence just described was repeated. Five of the tubes required two iterations, and three tubes required three iterations.

The quality of fit of the observed volumes to the empirical equations is indicated in Table III. The liquid volume in a density tube may rise, fall, or pass through a maximum as the temperature is increased, depending upon the relative sizes of the upper and lower bulbs.

Table I. Calibration of Tubes

Tube	Vol to arrow, cm^3	Vol of capillary[a], cm^3/cm	Total enclosed vol, cm^3
A	9.735 ± 0.002	0.066 ± 0.002	24.56 ± 0.05
B	10.338 ± 0.009	0.064 ± 0.002	34.45 ± 0.05
C	10.898 ± 0.003	0.066 ± 0.002	56.45 ± 0.05
D	12.798 ± 0.004	0.066 ± 0.001	84.54 ± 0.05

[a] Tubes *A*, *C*, and *D* were made from the same piece of capillary; *B* was made from a different piece.

Table II. Unsmoothed Liquid and Vapor Densities

Temp, °C	Liquid density, D, g-cm^{-3}	Uncertainty in D, g-cm^{-3}	Vapor density, d, g-cm^{-3}	Uncertainty in d, g-cm^{-3}
		Tubes *A*, *B*, *C*, *D*		
188.8	1.2958	0.0004	0.0151	0.0001
189.1	1.2935	0.0008	0.0155	0.0002
189.6	1.293	0.001	0.0156	0.0003
190.1	1.290	0.004	0.0157	0.0003
190.4	1.291	0.001	0.0160	0.0003
190.7	1.291	0.001	0.0159	0.0004
191.2	1.290	0.001	0.016	0.004
192.5	1.2867	0.0001	0.0167	0.0004
193.6	1.2855	0.0009	0.0162	0.0004
193.6	1.2833	0.0005	0.0172	0.0002
197.7	1.274	0.006	0.019	0.002
198.1	1.2738	0.0005	0.0189	0.0002
201.8	1.2655	0.0004	0.0204	0.0001
206.0	1.2561	0.0003	0.0222	0.0001
206.3	1.2552	0.0008	0.0224	0.0003
206.4	1.253	0.005	0.022	0.001
208.6	1.250	0.004	0.023	0.001
209.9	1.245	0.003	0.0240	0.0008
211.4	1.2430	0.0008	0.0250	0.0003
211.7	1.243	0.002	0.0250	0.0006
213.3	1.238	0.005	0.0255	0.0008
213.6	1.238	0.002	0.0260	0.0006
215.0	1.2353	0.0008	0.0260	0.0004
215.1	1.2351	0.0006	0.0266	0.0002
215.6	1.234	0.002	0.0270	0.0006
217.1	1.230	0.003	0.0280	0.0007
217.2	1.229	0.004	0.027	0.001
217.7	1.2291	0.0009	0.0276	0.0006
218.7	1.226	0.002	0.0288	0.0005
218.9	1.226	0.002	0.0290	0.0006
221.0	1.220	0.002	0.0302	0.0007
221.5	1.220	0.001	0.0293	0.0009
222.1	1.220	0.009	0.029	0.002
222.4	1.218	0.002	0.0304	0.0006
223.0	1.216	0.003	0.0314	0.0007
224.9	1.211	0.003	0.0325	0.0007
226.2	1.2106	0.0008	0.0313	0.0004
226.5	1.211	0.005	0.032	0.001
227.5	1.205	0.003	0.0342	0.0007
227.6	1.206	0.002	0.0336	0.0005
228.8	1.201	0.003	0.0353	0.0007
		Tubes *A*, *B*, *C*, *D* (*Continued*)		
230.0	1.203	0.006	0.034	0.001
230.1	1.1988	0.0008	0.0358	0.0003
230.2	1.199	0.001	0.0357	0.0004
230.2	1.199	0.002	0.0357	0.0006
230.3	1.202	0.006	0.034	0.002
231.0	1.198	0.001	0.0360	0.0004
232.2	1.196	0.004	0.0367	0.0009
232.2	1.196	0.004	0.036	0.001
233.7	1.191	0.004	0.038	0.001
235.4	1.191	0.009	0.037	0.002
235.9	1.191	0.009	0.037	0.002
237.2	1.182	0.003	0.040	0.001
237.3	1.182	0.003	0.040	0.001
237.7	1.184	0.002	0.0397	0.0007
		Tubes *S*, *T*, *U*, *V*		
201.0	1.268	0.004	0.019	0.002
204.4	1.260	0.001	0.0209	0.0007
211.4	1.241	0.002	0.024	0.002
215.2	1.232	0.002	0.026	0.001
221.5	1.218	0.003	0.029	0.002
226.6	1.206	0.002	0.033	0.001
231.2	1.1954	0.0002	0.0358	0.0001
236.4	1.1820	0.0002	0.03962	0.00008
241.5	1.1687	0.0009	0.0433	0.0006
246.1	1.1557	0.0009	0.0475	0.0005
251.2	1.142	0.002	0.0520	0.0008
256.3	1.1293	0.0005	0.0566	0.0002
260.7	1.115	0.003	0.062	0.002
265.0	1.103	0.002	0.067	0.001
265.0	1.100	0.002	0.068	0.001
266.0	1.099	0.002	0.0680	0.0006
269.6	1.089	0.004	0.073	0.002
270.2	1.086	0.002	0.074	0.001
272.2	1.082	0.005	0.076	0.002
275.3	1.070	0.003	0.081	0.001
281.4	1.051	0.005	0.089	0.002
286.4	1.035	0.004	0.096	0.002
291.5	1.017	0.003	0.106	0.002
296.1	1.000	0.003	0.115	0.002

The next step in smoothing the data was to again solve six sets of simultaneous equations at each experimental temperature, this time, however, using liquid volumes calculated from the empirical cubic polynomials. This step also was performed with a digital computer.

Table III. Fit of Empirical Volume Equations to Observed Values[a]

Tube	Standard deviation, cm^3
A	0.005
B	0.007
C	0.005
D	0.016
S	0.015
T	0.011
U	0.008
V	0.022

[a] Throughout this paper, the term standard deviation will be defined by the equation

$$\sigma = \left(\frac{1}{N}\sum_{i=1}^{N}\epsilon_i^2\right)^{1/2}$$

where σ = standard deviation and ϵ = difference between an observed value and the corresponding value calculated from an empirical equation.

All of the liquid densities and vapor densities thus obtained were fit to least-squares cubic polynomials. This time, the automatic weighting of points was not considered to be necessary. The final empirical equations are given in Table IV, together with the standard deviations of both the original unsmoothed densities and of the calculated densities (as described in the previous paragraph). Also given is an empirical equation for the mean of the liquid and vapor densities, which is useful for application of the law of Cailletet and Mathias.

Original data and the empirical equation for vapor density are plotted in Figure 2. Also shown are the vapor densities which other workers obtained (*2*, *8*).

The only vapor pressure data which cover the entire temperature span of the present work are those of Denisova and Baskova (*2*). Compressibility factors calculated from their pressure measurements and our density values range from 0.64 at 195° C to 0.41 at 295° C. A totally dimeric aluminum chloride species was assumed.

DISCUSSION

Our experimental method is an improvement over that of Quinn and Wernimont (*9*), which is in turn a modification of a one-tube technique first described by Young (*10*). In each of these accounts, constant diameter tubes were used. Our use of bulbs in the liquid and vapor phase

Table IV. Empirical Equations for $AlCl_3$ Density

	$Y = a_0 + a_1t + a_2t^2 + a_3t^3$ (188.8° C $\leq t \leq$ 296.1° C)				Standard deviation	
Y, g-cm^{-3}	a_0	$a_1 \times 10^{-3}$	$a_2 \times 10^{-5}$	$a_3 \times 10^{-8}$	Original data, g-cm^{-3}	Calcd densities, g-cm^{-3}
D	1.9089	−5.5242	1.8584	−3.474	0.002[a]	0.001
d	−0.25748	3.7958	−1.92624	3.6065	0.0007[b]	0.0002
(D + d)/2	0.8270	−0.9125	...	...	...	0.0005

[a] ABCD data only; $\sigma = 0.002$, STUV data only; $\sigma = 0.001$. [b] ABCD data only; $\sigma = 0.0006$, STUV data only; $\sigma = 0.0007$.

regions which are connected by a capillary magnifies the movement of the meniscus as the temperature is changed. Furthermore, we thereby provide a considerably larger space to be occupied by vapor, which increases the precision of measurements at low vapor densities. Quinn and Wernimont (*9*) measured liquid and vapor densities of N_2O, and reported experimental errors of ±0.25%, and ±2.0%, respectively. Our method gave approximately equal experimental errors for each phase of ±0.1%. Inspection of Table II reveals no trend to lesser precision at low vapor densities.

The previously reported aluminum chloride vapor densities (*2, 8*) were determined by heating known masses of sample in sealed ampules of known volumes. One density values are represented by least-squares fit cubic polynomials over temperature ranges similar to our work with a standard pear or appear in the condensed phase. These experimental values are represented by least squares fit cubic polynomials over temperature ranges similar to our work with a standard deviation 6.3 (*8*) or 13.5 (*2*) times as large as ours. Over the entire temperature ranges reported by those workers, their standard deviations are approximately 30 times larger than ours. Their data are compared with the results of the present work in Figure 2.

The same workers measured liquid densities using pycnometers with measuring capillaries. As expected, their results have about the same uncertainty as ours in the same temperature region. However, their overall standard deviations are 14 times larger than ours.

The present method clearly gives vapor densities for aluminum chloride with greater precision than other workers have found, and is at least as good for liquid measurements. The method also permits sweeping a temperature range with as small a temperature increment between measurements as desired, with the same sample and enclosure. Furthermore, there is no apparent reason why the technique should be less precise at higher temperatures than it is in the temperature region studied.

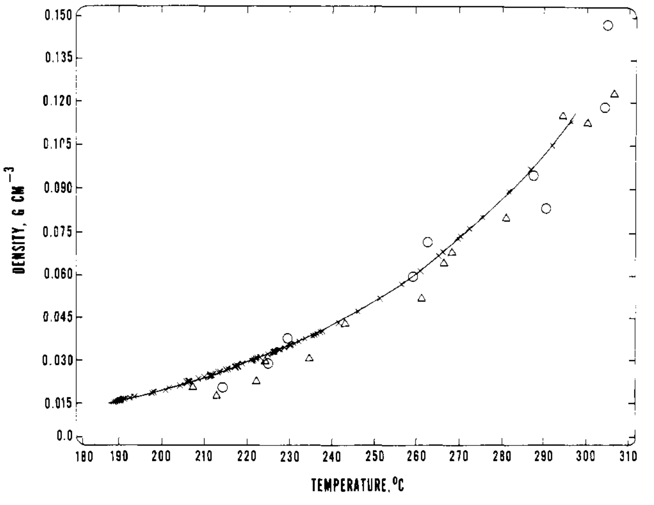

Figure 2. Vapor density of aluminum chloride

×, this work; ○, Denisova and Baskova (*2*); Δ, Nisel'son and Sokolova (*8*); —, plot of the empirical equation from present work

In using this method it is necessary to avoid having any two tubes in a set possess a similar liquid phase to vapor phase volume ratio. If this does occur, the accuracy of the densities calculated from the corresponding pair of simultaneous equations suffers. We found it convenient to use sets of four tubes with similar liquid volumes in which the enclosed vapor volumes were in the approximate ratio 1:2:3:4.

Our experimental approach is particularly well suited for volatile substances, for substances reactive with air or moisture, and for substances which are reactive with manometric fluids. The feature of simultaneously determining both liquid and saturated vapor densities should have applicability in studies of liquid structure, studies of behavior near the critical point, and for determinations of the critical constants.

SAFETY

The containment in glass vessels of liquids at temperatures above their normal boiling points is hazardous. There is not only the possibility of flying glass, but if the vessel breaks below the surface of a high temperature bath, the sudden expansion of the volatile liquid will tend to direct the hot bath fluid upward. Our apparatus was set up in a conventional laboratory hood. A dike was built across the front to prevent the possibility of spilled bath fluid from escaping through the seam between the closed hood window and floor.

In practice, we were able to work up to 325° C with well-annealed density tubes. Internal pressures would have reached nearly 20 atm (*2*).

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