Phase Equilibria Data for Helium–Methane in the Vapor-Liquid and Fluid-Fluid Region

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Phase compositions for 12 isotherms from 94° to 192° K, including four in the fluid-fluid region, are presented for the helium-methane system at pressures from 1000 to 3800 psia. The critical temperature and pressure of the methane was 190.53° ± 0.02° K and 668.9 ± 0.2 psia. A windowed phase equilibria cell with a vapor recirculating pump was used for the determinations.

In recent years, the helium-methane system has been studied to 188° K and 3000 psi by several investigators (*3, 5, 7*). This work is part of our program to study the helium-nitrogen-methane system. Also we wanted to resolve a minor disagreement between the data of Heck and Hiza (*3*) and that of Sinor *et al.* (*7*) on the 2000 psia T-x diagram. Three reports (*4, 8, 10*) of phase separations of helium-containing systems at supercritical temperatures prompted us to examine the phase behavior above and below the critical temperature of methane.

In 1967, Kaplan (*4*) used Kreglewski's (*6*) D^2 method ($D^2 = 3RT_c/2V_c$) to predict that helium-methane would exhibit limited equilibrium solubility above the critical temperature of the pure methane. Streett (*8*) used one 2000 psia data point of Sinor *et al.* (*7*) to illustrate the possibility of a fluid-fluid separation for this system.

Sinor *et al.* (*7*) used 99+ mole % methane in their mixtures. Heck and Hiza (*3*) found their results were not affected by using either 99.8 or 99.95% purity methane. We investigated the distribution of oxygen, nitrogen, and ethane impurities in helium-methane vapor-liquid equilibria using feed gases with different contamination levels. Results are shown in Table I.

We used 99.99% methane containing oxygen and nitrogen impurities, but no ethane. Consequently, our thermal conductivity analyses were for methane only. The critical temperature and pressure of the methane were 190.53° ± 0.02° K and 668.9 ± 0.2 psia.

EXPERIMENTAL

The experimental apparatus and procedures used in this investigation were the ones previously described (*2, 9, 11*), with three minor exceptions. The lower fine mesh copper screen, used in the helium-nitrogen study to break up bubbles from the recirculating pump, was removed because it tended to trap gas beneath it, rather than to disperse it. The copper-constantan differential thermocouple in the cell was replaced by one of gold-cobalt for greater sensitivity (0.03° K). Temperatures are reported on the 1968 IPTS, by comparison to a recent NBS calibrated platinum resistance thermometer. The constants A_4 and C_4 that were calculated are used in the deviation function in the interpolation formula for IPTS. Pressure measurements were made using a strain gage pressure transducer which was calibrated against a dead weight piston gage traceable to NBS. The statement of accuracy by the vendor was made in May 1968 for piston area and April 1969 for the masses of the weights used for this dead weight tester. The equilibration procedure and thermal conductivity analyses described by Tully *et al.* (*11*) are a vapor recirculating method, with a windowed phase cell suspended in a gas bath cryostat capable of a precise temperature control (±.001° K) of a point in the phase cell. Feed gases were charged into the system and circulated for a period required to stabilize the pressure which usually requires 2 hours. The system is then isolated from the charge gas regulator and the vapor is recirculated until the pressure is constant for 30 min. The phases are then analyzed using a thermal conductivity apparatus described by Rhodes and Tully (*9*). The accuracy of this apparatus is better than 0.02% and is calibrated using weighed primary standards with composi-

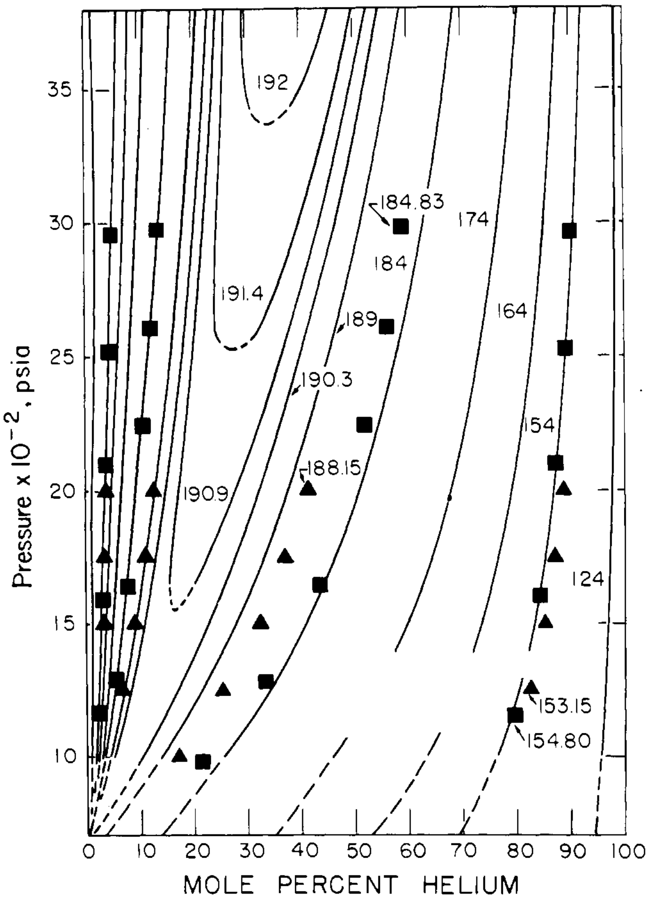

Figure 1. Pressure-composition diagram

▲ Sinor *et al.* (*7*)
■ Heck and Hiza (3)
— This work

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Table I. Distribution of Impurities in Helium–Methane Equilibria

Impurities in feed gas			Pressure, psia	Temp., °K	Liquid, ppm			Vapor, ppm		
O_2	N_2	C_2H_6			O_2	N_2	C_2H_6	O_2	N_2	C_2H_6
20	55	15	2600	191.4	30	30	40	30	30	0
50[a]	190		1000	188		145			165	
30[a]	115		1000	164		135			180	
	2278		1000	165		1700			2900	
	2278		1000	178		1282			2311	

[a] Second and third feed gases contained oxygen and nitrogen in an air ratio, but in the liquid and vapor samples only the nitrogen concentration was determined.

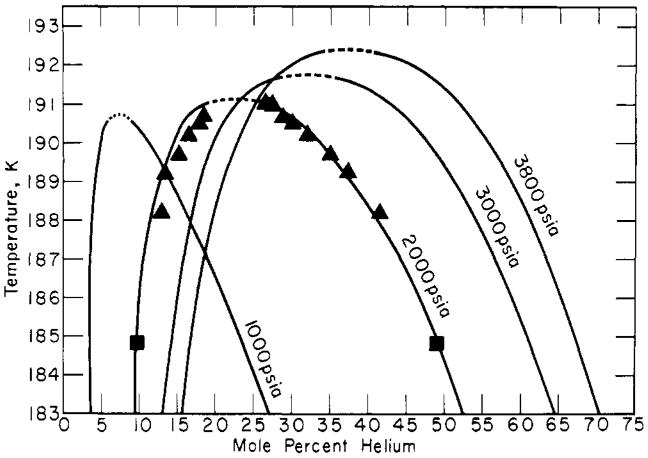

Figure 2. Temperature-composition diagram
▲ Sinor *et al.* (7)
■ Heck and Hiza (3)
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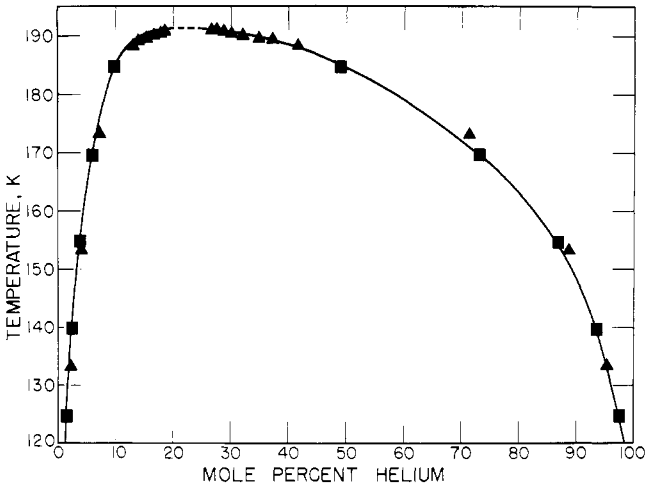

Figure 3. 2000 psia isobaric temperature-composition diagram
▲ Sinor *et al.* (7)
■ Heck and Hiza (3)
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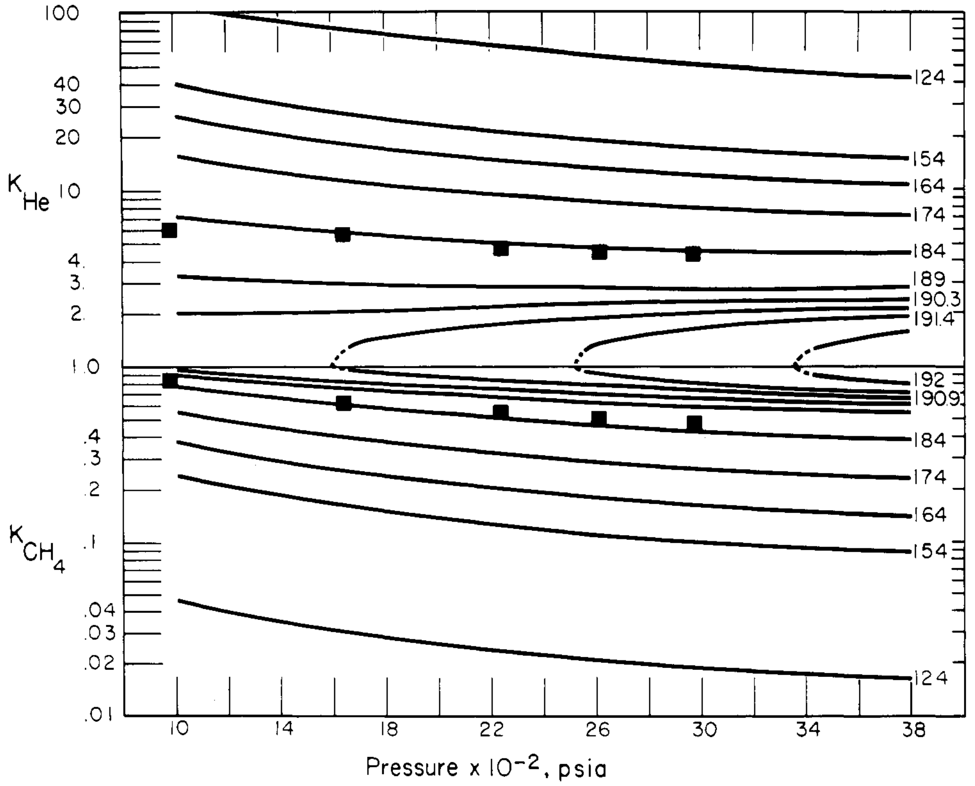

Figure 4. Equilibrium vaporization ratios (K-values)
■ Heck and Hiza (3)
— This work

Table II. Experimental Data for Helium–Methane from 94° to 192° K

Vapor		Liquid		Equilibrium ratio	
Pressure, psia	Mole % He	Pressure, psia	Mole % He	Helium	Methane
Subcritical Temperature 94.00° K					
1009	99.62	1013	0.22	453	0.00381
1499	99.68	1501	0.28	356	0.00321
2023	99.78	2018	0.36	277	0.00221
124.00° K					
1005	95.44	1001	0.79	121	0.0460
1498	96.75	1498	1.12	86.2	0.0329
1997	97.44	1995	1.35	72.2	0.0261
2994	98.16	3002	1.96	50.1	0.0189
3795	98.49	3793	2.32	42.6	0.0155
154.00° K					
1002	76.18	999	1.92	39.7	0.2429
1500	83.14	1500	2.90	28.7	0.1736
2006	86.85	2000	3.76	23.1	0.1370
2997	90.48	2999	5.20	17.4	0.1004
3796	92.22	3798	6.18	14.9	0.0829
164.00° K					
999	63.00	999	2.38	26.4	0.3790
1253	69.24	1251	3.10	22.3	0.3174
1500	73.41	1501	3.78	19.4	0.2763
1995	79.00	2000	4.98	15.9	0.2210
2506	82.53	2505	6.09	13.5	0.1860
3004	84.99	3002	7.02	12.1	0.1614
3796	87.61	3801	8.36	10.5	0.1352
174.00° K					
999	45.80	997	2.91	15.7	0.5582
1248	53.86	1247	3.96	13.6	0.4804
1501	59.83	1495	4.93	12.1	0.4225
1997	67.68	1995	6.69	10.1	0.3464
2499	72.80	2496	8.20	8.87	0.2963
2999	76.42	2999	9.53	8.02	0.2606
3774	80.35	3768	11.26	7.136	0.2214
184.00° K					
999	25.18	1000	3.53	7.13	0.7756
1250	34.00	1251	5.25	6.47	0.6966
1499	40.81	1496	6.81	5.99	0.6351
1745	46.17	1743	8.20	5.63	0.5864
2007	50.82	2006	9.57	5.31	0.5438
2507	57.69	2504	11.87	4.860	0.4801
2996	62.71	2991	13.76	4.557	0.4324
3802	68.77	3800	16.21	4.242	0.3727
189.00° K					
999	13.99	1000	4.29	3.26	0.8987
1247	21.38	1245	6.80	3.14	0.8436
1500	27.69	1502	9.09	3.05	0.7954
1752	33.06	1746	11.12	2.973	0.7531
2000	37.60	2000	12.84	2.928	0.7159
2500	45.14	2502	15.85	2.848	0.6519
2750	48.34	2746	17.12	2.823	0.6234
3000	51.22	3006	18.18	2.817	0.5962
3798	58.61	3799	21.07	2.782	0.5244
Subcritical Temperature (*Continued*) 190.30° K					
1000	10.19	998	5.11	1.99	0.9465
1250	16.73	1245	8.19	2.04	0.9070
1500	22.36	1501	10.86	2.059	0.8710
1749	27.53	1748	13.16	2.093	0.8344
2001	32.11	1997	15.08	2.129	0.7995
2503	40.00	2499	18.06	2.215	0.7322
2999	46.51	2997	20.54	2.264	0.6732
3801	54.64	3801	23.27	2.348	0.5912
Supercritical Temperatures 190.60° K					
999	8.73	999	5.87	1.49	0.9696
1500	20.43	1499	11.82	1.728	0.9023
2000	30.29	1998	15.94	1.900	0.8293
2503	38.50	2496	18.99	2.027	0.7592
3000	45.03	3004	21.29	2.115	0.6984
3800	53.51	3798	23.95	2.234	0.6113
190.90° K					
1656	20.43	1656	15.62	1.309	0.9429
1723	22.10	1716	15.85	1.394	0.9257
1795	23.58	1792	16.20	1.456	0.9119
2002	27.87	2000	17.43	1.599	0.8736
2499	36.45	2498	20.12	1.812	0.7956
3003	43.61	2997	22.24	1.961	0.7252
3799	52.28	3798	24.72	2.115	0.6339
191.06° K					
1999	25.30	1993	19.36	1.307	0.9263
191.10° K					
3004	42.30	2999	23.06	1.834	0.7499
191.37° K					
2502	30.54	2501	24.78	1.232	0.9234
191.40° K					
2554	31.13	2552	25.26	1.232	0.9215
2599	32.63	2597	24.45	1.335	0.8917
2795	36.50	2799	24.39	1.497	0.8398
3001	39.91	2990	24.56	1.625	0.7965
3342	44.71	3342	25.32	1.766	0.7404
3802	49.87	3801	26.32	1.895	0.6804
191.68° K					
3003	35.89	2998	28.04	1.280	0.8909
192.00° K					
3428	38.49	3425	30.58	1.259	0.8861
3452	39.11	3450	30.80	1.270	0.8799
3602	42.27	3599	29.98	1.410	0.8245
3800	45.57	3802	29.44	1.548	0.7714
3797	45.48	3800	29.46	1.544	0.7728
192.20° K					
3801	42.88	3800	31.53	1.360	0.8342
192.29° K					
3800	40.71	3800	34.17	1.191	0.9007

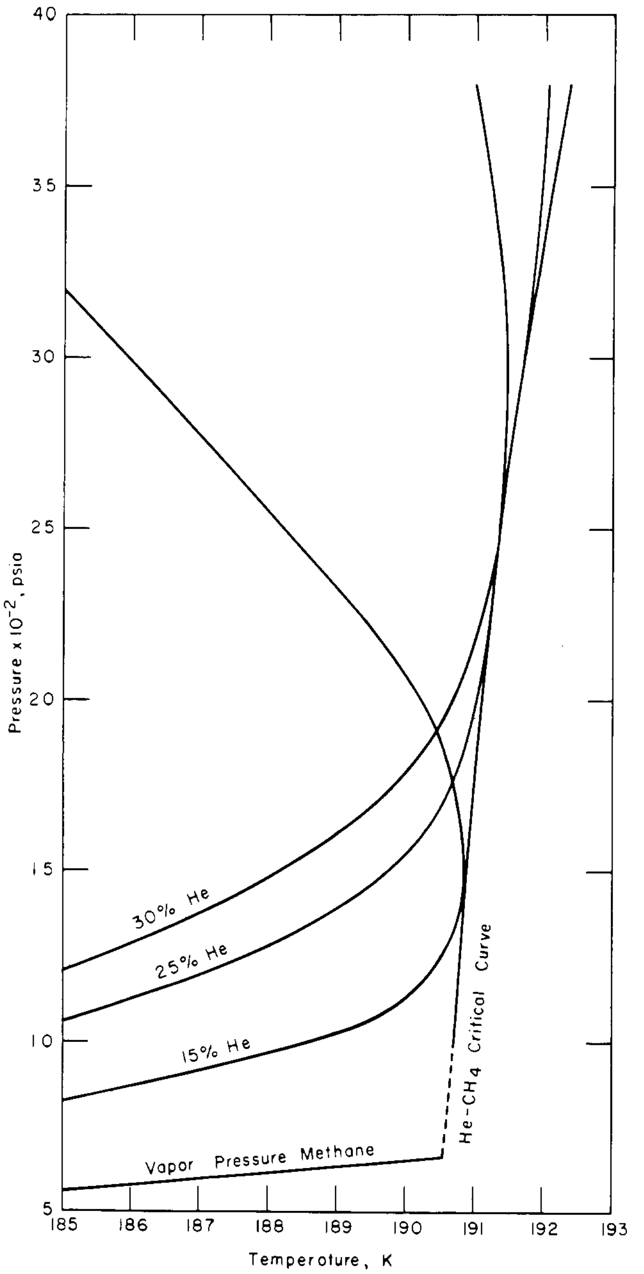

Figure 5. Critical curve

tion known to 0.005%. Replication of several data points gave conservative estimates of the uncertainties of 2 psi, 0.05% helium, and 0.01° K.

Feed mixtures of ultrapure helium containing less than 10 ppm of total impurities and the high quality methane mentioned above were prepared in compressed gas cylinders. Compositions were adjusted to ensure experimentation within the dewpoint-bubblepoint locus.

DISCUSSION

Isothermal experimental data are presented in Table II and graphically in Figure 1. Pressures for vapor and liquid samples differ by a few psi owing to manual interruption of regulator service before sampling the vapor phase. Below the critical temperature these differences are of little importance to vapor-liquid composition. However, near critical conditions compositions are extremely sensitive to small temperature or pressure changes.

Figure 1 (P-x diagram) shows extrapolated minimum pressures for two-phase coexistence at four supercritical temperatures. These pressures are believed to be within 10 psi of their true values, based on actual observations in the cell under circumstances where meaningful analyses were impossible.

At 94° K, a gas-solid phase was observed at 2160 psia. At this temperature, the freezing pressure of pure methane is calculated by the equation of Clusius and Wiegand (*1*) to be 1918 psia. No attempt was made to analyze either phase.

Selected data of Heck and Hiza (*3*), and Sinor *et al.* (*7*) are plotted on Figures 1, 2, and 3 for comparison with present results. Agreement is better with the former than with the latter, as discussed in detail below. Temperatures were converted to the 1968 IPTS.

Extrapolated isobaric critical temperatures are shown in Figure 2. These temperatures, based on observed phase behavior, are believed to be within 0.05° K of their true value. From the figure, it can be seen that our 2000 psia data agree with those of Heck and Hiza at 185° K, and disagree with those of Sinor *et al.*. We believe that they actually attained fluid-fluid equilibria at 190.99° K (1968 IPTS) where they reported an apparent vapor-liquid composition difference of 1% without further comment. Based on our data, both of their data points lie on the vapor locus. (T_c = 191.15° K at 2000 psia). As the densities of the coexisting phases approach each other, liquid entrainment becomes a problem, and phase compositions appear to be almost equal because of the suspension of liquid in the vapor. Therefore, in the vicinity of the critical, a windowed cell is essential to determine the physical state.

The complete 2000 psia isobar is shown in Figure 3. The discrepancies in the vapor analyses could be attributed to a nonequilibrium state, there not being enough methane there. The high helium content of the liquid is indicative of flashing.

The equilibrium vaporization ratios of K-values are shown in Figure 4. A smooth transition from subcritical to supercritical values is indicated. The loops of minimum pressure above the T_c of methane are characteristic of the fluid-fluid equilibria region.

Only Heck and Hiza's 184.86° K (highest) isothermal K-values have been plotted for comparison. These indicate good agreement with our 184° K data. Agreement is better at the lower temperatures. This is further indication that true equilibrium has been attained by both of us.

The critical curve for the system is shown in Figure 5. We have extrapolated the curve from 1000 psia down to the P_c of methane. A positive slope has been indicated throughout, although this has not been experimentally confirmed. We intend to complete our investigation in this low pressure region. If our assumption is true, the helium-methane system will be of van der Waals' type B of Kaplan's Type I fluid-fluid equilibria.

The helium-methane system does exhibit fluid-fluid equilibria, as predicted.

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Liquid and Vapor Densities of Aluminum Chloride

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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:

$$W_1 = V_1\mathrm{D} + (T_1 - V_1)\mathrm{d}$$

$$W_2 = V_2\mathrm{D} + (T_2 - V_2)\mathrm{d}$$

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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