Density, Vapor Pressure, Critical Properties, Dielectric Constant, and Specific Conductivity of Chlorine Pentafluoride

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Selected phase and electrical properties of chlorine pentafluoride (ClF_5) have been experimentally determined over useful liquidus temperature ranges. The liquid density and vapor pressure of ClF_5 were measured over a temperature range of −80° to 143° C. The normal boiling point and the heat of vaporization at the normal boiling point were calculated from the resulting vapor pressure equation. *PVT* measurements established the critical density, critical temperature, and critical pressure. The dielectric constant and specific conductivity of liquid ClF_5 were determined from −80° to −17° C. in an FEP-Teflon conductivity cell, and the dielectric constant for gaseous ClF_5 was measured at 10 mHz., 23.9° C., and 746.5 mm. of Hg using a custom built instrument.

THE synthesis of chlorine pentafluoride has recently been achieved, but only a few of its physical and chemical properties have been determined (*3, 4, 8, 14*). The study reported herein was concerned with more extensively determining some of these properties. The ClF_5 used in this investigation was prepared by the fluorination of alkali metal chlorotetrafluorides (*8*). A typical chemical analysis of the ClF_5 gave the following composition: 98 wt. % ClF_5, 1 wt. % ClF_3, 0.1 wt. % ClF, 0.1 wt. % F_2, and 0.3 wt. % HF.

EXPERIMENTAL TECHNIQUE

Density. The liquid density of ClF_5 was measured over a temperature range of −23° to 146° C. using a variable-volume apparatus described by Poole and Nyberg (*9*). The densimeter was constructed entirely of 300 series stainless steel and is capable of withstanding pressures up to 1500 p.s.i., well in excess of the critical pressure of ClF_5. The instrument was provided with a stainless-steel bellows which permitted variation of its internal volume. Density measurements over a range of temperatures were thus possible without reloading.

The densimeter operated on the principle that a sudden rise in pressure would be sensed by a transducer upon the disappearance of all vapor as the volume of the cavity containing the liquid ClF_5, in equilibrium with its vapor, was reduced by mechanical adjustment of the bellows. The volume of the contained liquid at this point was indicated by micrometer attached to the bellows. Since the weight of contained liquid was known and the volume was known (by prior calibration of the micrometer with degassed conductivity water), the density could be calculated.

After condensing a known amount of ClF_5 into the evacuated sample cavity, the densimeter was placed in a constant-temperature environment and allowed to reach thermal equilibrium at selected, regulated temperatures. The constant temperature environment of the apparatus was maintained either by placing it in a Dewar flask with a circulating coolant or in a Fisher Isotemp oven, depending on the temperature desired. The equilibrium temperature of the sample was measured to ±0.05° C. by a Chromel-Alumel thermocouple taped to the outside of the densimeter.

At thermal equilibrium, a slight pressure was applied to the back of the bellows with gaseous nitrogen. The sample cavity volume was decreased by turning the micrometer knob until a rapid rise in pressure was observed by the pressure-transducer readout system. This indicated that all ClF_5 vapor had been condensed, and that the volume of the sample cavity at that point represented the volume occupied by liquid ClF_5. The bellows was contracted and the procedure repeated several times at each temperature at which a data point was obtained. The volume of the sample cavity was ascertained by relating the micrometer setting to the calibration graph. All apparatus manipulations above ambient temperature were made remotely without opening the oven.

The temperature and pressure readout equipment, which was also used for vapor pressure and critical temperature measurements, was a Leeds and Northrup Student potentiometer, Model No. 7645, and a Model No. 2430-C galvanometer. Line operated power supplies were designed as convenient permanent replacements for the standard cell and working cell normally used with this potentiometer. Two separate power supplies were built because of the potentiometer requirement for complete isolation between the supplies.

The reference voltage supply, which replaced the standard cell, besides being compensated against line voltage variation, was temperature compensated by inclusion of a Type 1N2623, 9.3 volt reference diode specified to drift no more than 0.001% per ° C. in output voltage. Hence, the reference voltage was stabilized against both changes in ambient temperature and in line voltage. A voltage divider was used to bring the voltage level near 1 volt, which was within the range of measurement of the Leeds and Northrup potentiometer.

The constant current power supply, used to replace the working cells, supplied the 2.2 ma. required by the potentiometer. This supply was also stabilized against changes in line voltage and in temperature and was provided with both coarse and fine adjustments for the output current.

Vapor Pressure. The vapor pressure apparatus consisted of a 10-ml., 304 stainless-steel cylinder, with an immersion thermocouple, pressure transducer, and sample valve attached. The immersion thermocouple (Temptron No. 2092) had a Chromel-Alumel junction and 316 stainless-steel sheath. The thermocouple was sealed into the 10-ml. cylinder, permitting direct measurement of the temperature of the cylinder contents. The thermocouple was calibrated at the melting point and boiling point of water. Low temperature thermocouple calibration was carried out against a CO_2 vapor tension thermometer, which had been filled with resublimed Matheson "bone dry" CO_2. Temperatures employed for calibration were those of wet acetone slush and trichloroethylene–dry ice slush, which were −97.8 and −79.5° C., respectively, on the vapor pressure thermometer. Three Statham pressure transducers (0 to 25 p.s.i.a., 0 to 200 and 0 to 1000 p.s.i.g.) were connected in turn to the cylinder to measure vapor pressures over their respective ranges. The pressure transducers were calibrated with a Heise gage to corroborate the calibration factors reported by the manufacturer. The readout system described in the discussion of density was used to meet the readout requirements of the thermocouple and pressure transducers.

A sufficient amount of ClF_5 was loaded into the vapor pressure apparatus to ensure the presence of some liquid at all times over the range considered. The bomb and contents were allowed to reach thermal equilibrium at selected temperatures, and the equilibrium vapor pressures were recorded. Constant temperatures of 35° C. and below were maintained either by immersing the 10-ml. cylinder portion of the apparatus in a Dewar with a circulating coolant or in slushes of trichloroethylene–dry ice (−80° C.), chloroform (−65° C.), carbon tetrachloride (−24° C.), and water (0° C.). For temperatures above 35° C., the entire apparatus was placed in a Fisher Isotemp oven.

Critical Properties. The critical temperature of ClF_5 was measured in an apparatus of the type described by Ambrose and Grant (*1*). This method determined the critical temperature by the disappearance and reappearance of the liquid-vapor meniscus as the temperature of the ClF_5 sample contained in a sealed quartz capillary was raised and lowered through the critical point. *PVT* relationships generated in the vapor pressure measurements were used to substantiate the validity of these measurements as well as establish critical pressure and volume (density).

In the meniscus method, a quartz capillary, 5-cm. long, 2-mm. I.D., and 8-mm. O.D., was heated while under vacuum to ensure dryness. It was then passivated with small amounts of ClF_5 vapor (pressure about 200 mm. of Hg) in successive steps until the condensed ClF_5 remained colorless (indicating the absence of moisture). The capillary was then filled to one third of its volume with liquid ClF_5, which had first been passed over sodium fluoride to absorb any HF present. After heat sealing, the capillary was placed in a furnace preheated to 125° C. The furnace consisted of an electrically heated aluminum block, insulated with fire brick, and bored and slotted for reception and observation of the quartz capillaries. Temperatures were measured by a Chromel-Alumel thermocouple located near the meniscus. The temperature was increased at the rate of 0.2° C. per minute until the meniscus disappeared. The temperature was then decreased until the meniscus reappeared.

Electrical Conductivity and Dielectric Constant (Liquid). The specific conductivity and dielectric constant of liquid ClF_5 were measured in an FEP-Teflon conductivity cell equipped with nickel electrodes (Figure 1). An Electro Scientific Industries Model 250 DA Universal impedance bridge was used to measure (at 1 kHz.) the impedance and the a.c. resistance of the conductivity cell containing either liquid ClF_5 or calibration liquids. The cell constant was calculated from these measurements. The conductivity cell was maintained at constant temperatures ranging from −80° to −17° C. by immersion in a constant temperature bath.

The conductivity cell, with the impedance bridge connected to its external leads, was evacuated and loaded with enough liquid ClF_5 to extend 1 cm. above the top of the nickel electrodes. Capacitance measurements were taken from −80° to −17° C. After the run, the cell constant was determined by measuring the capacitance of spectrographic-grade carbon tetrachloride, heptane, and cyclohexane, and the a.c. resistance (at 1 kHz.) of 0.01 and 0.001*N* KCl solutions. The values of the cell parameters, calculated from the dimensions of the electrodes, were in good agreement with the values obtained experimentally.

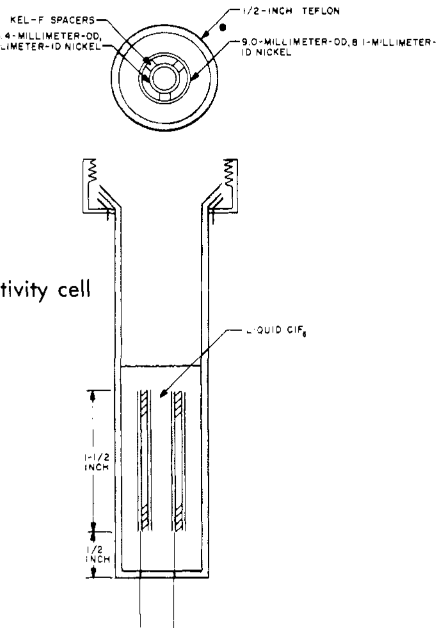

Figure 1. Conductivity cell

Dielectric Constant (Vapor Phase). The dielectric constant (ϵ) of gaseous ClF_5 was determined at 10 mHz., 23.9° C., and 746.5 mm. of Hg on a custom built instrument utilizing solid state components exclusively. The instrument used (Figure 2) consists of two symmetrical oscillator circuits, one operating at approximately 10 mHz. and the other at 1 mHz. away from the first. The frequency of the second was determined by the dielectric constant of the vapor contained between the plates of a 100 picofarad, flow-through cylindrical capacitor. The flow-through capacitor was constructed of nickel and Kel-F, and was as symmetrical as possible to minimize temperature induced drift. The signals from the two oscillating circuits were fed into a mixer circuit, the output of which was the sum and difference of their frequencies. The sum signal was again discarded, and the difference was fed into shaping and counting circuits which converted it to direct current, suitable for display on a meter or a recorder.

RESULTS

Density. With the variable volume capabilities of the densimeter, it was possible to cover the entire temperature range of −23° to 146° C. with four fillings of the apparatus (runs 2 through 5). However, measurements conducted with the Poole-Nyberg densimeter above 99° C. resulted in relatively large data spreads at each temperature. Therefore, density measurements from this point to the critical temperature were supplemented through the use of the constant volume vapor pressure apparatus (run 6). In the technique used with this apparatus, each density point represented a separate apparatus filling with various known quantities of ClF_5. The volume of the apparatus was calibrated with expanded CO_2 gas. Low temperature values were obtained by using a Kel-F pycnometer (run 1).

The experimental points obtained are given in Table I and Figure 3. The density data over the temperature range of −80° to 99° C. were curve fitted by a least squares computer program and resulted in the following equation:

$$\rho(\text{g./cc.}) = 3.553 - 1.396 \times 10^{-2} T_{(^\circ\text{K.})} + 4.565 \times 10^{-5} T^2_{(^\circ\text{K.})} - 6.311 \times 10^{-8} T^3_{(^\circ\text{K.})} \quad (1)$$

The standard error of estimate of this equation is 0.0059. Density values obtained from the densimeter between 107° and 146° C. resulted in data spreads up to 0.06 gram per

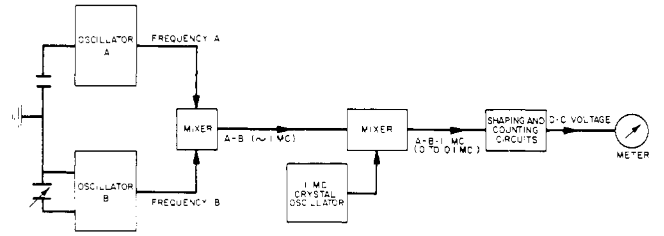

Figure 2. Block diagram of vapor phase dielectric constant measurement equipment

Table I. Experimental Density Data for Liquid ClF_5

Temp., °C.	Obsd. Density, G./Cc.	Calcd. Density, G./Cc.	$\Delta\rho \times 10^3$	Run No.
−80.00	2.100	2.104	−4	1
−57.00	2.036	2.030	6	1
−23.32	1.938	1.929	8	3
−23.00	1.922	1.928	−6	1
−3.05	1.872	1.869	3	3
0.00	1.863	1.859	4	3
8.52	1.834	1.832	2	3
8.75	1.832	1.831	1	3
12.33	1.818	1.819	−1	3
17.38	1.798	1.802	−4	3
23.28	1.778	1.781	−4	3
28.50	1.759	1.763	−4	2
34.08	1.733	1.742	−9	3
40.45	1.711	1.717	−7	2
48.82	1.677	1.683	−6	2
55.12	1.653	1.656	−3	2
61.50	1.629	1.627	2	2
66.02	1.615	1.606	9	3
67.18	1.606	1.601	5	2
70.75	1.595	1.583	12	2
78.25	1.548	1.545	3	2
83.98	1.509	1.514	−5	4
86.25	1.508	1.501	7	2
91.03	1.480	1.474	6	2
97.83	1.424	1.433	−10	5
98.90	1.421	1.427	−6	4
107.6	1.263	...	...	5
118.9	1.132	...	...	5
123.5	1.017	...	...	5
128.9	1.160	...	...	6
132.1	0.949	...	...	5
139.9	0.898	...	...	5
140.6	0.769	...	...	6
147.3	0.887	...	...	5

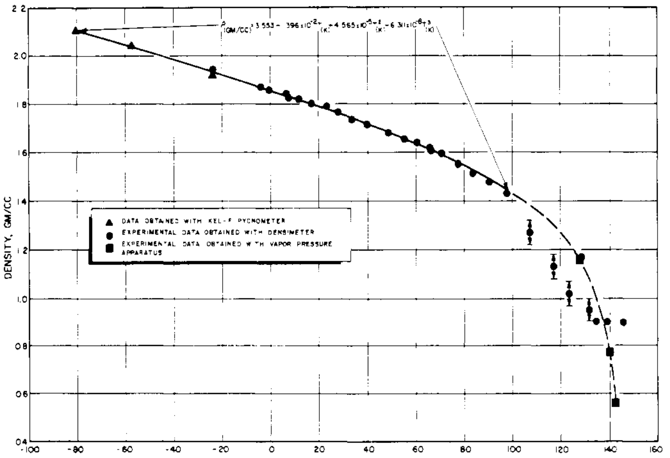

Figure 3. Saturated liquid density *vs.* temperature for ClF_5

cc. at each temperature, and were not used in the density curve fit. However, the fitted curve was extrapolated (as shown by the broken line, Figure 3) to the critical point using the data from the vapor pressure apparatus.

Vapor Pressure. The experimental vapor pressure data for ClF_5 are given in Table II. These data, fitted to equations of the Clapeyron form by a least squares computer program, resulted in the following equation:

$$\log P_{(\mathrm{Atm})} = 4.6029 - \frac{1197}{T_{(^\circ\mathrm{K.})}} \qquad (2)$$

The standard error of estimate in Equation 2 is 0.049. From the equation, a normal boiling point of −13.1° C. (Equation 2) was calculated.

Heat of Vaporization. The heat of vaporization at the normal boiling point was calculated from the Clapeyron equation resulting from vapor pressure measurements. A heat of vaporization value of 5.477 kcal. per mole was computed from Equation 2. The factor 0.97 was applied as an average correction factor for inorganic liquids to the above values to correct for the difference between the liquid and vapor compressibility (2), and a heat of vaporization of 5.313 kcal. per mole was obtained.

Critical Properties. Critical temperature determinations were made on two different samples of ClF_5 (sample assay >99 wt. % ClF_5) in two different capillaries. The temperatures resulting from observations of the ClF_5 liquid-vapor meniscus disappearance were in close agreement (within 1° C.). The average value for ClF_5 critical temperature by this method was established as 143.0 with a standard deviation based on 6 runs of 0.5° C.

During vapor pressure measurements, the constant volume apparatus was filled with various quantities of ClF_5, ranging in specific volume from 0.860 to 5.33 cc. per gram. Vapor pressure data were recorded on each of these samples from 90° to 150° C. A plot of log pressure *vs.* reciprocal absolute temperature (Figure 4) yielded temperatures at which changes in slope from the established vapor pressure curve were observed. These points of discontinuity mark the transition of the sample from a liquid-vapor system to a single phase system through complete vaporization or liquid expansion. The critical point was determined from these data by plotting the temperature of discontinuity for the various sample sizes *vs.* sample size, specific volume, or density.

The value for critical temperature (142.6° ± 1.0° C.), resulting from a plot of temperature of discontinuity *vs.* specific volume (Figure 5), was in good agreement with those observed by the meniscus method. This plot also gives the critical volume or density (0.565 ± 0.008 gram per cc.). The critical pressure corresponding to the critical temperature as taken from the vapor pressure equation is 51.9 ± 0.7 atm.

The critical compressibility factor (Z_c) was then calculated by substituting the measured critical constants into the expression:

$$Z_c = \frac{P_c V_c}{RT_c}$$

A value of 0.35 was obtained for Z_c. This number is rather large in comparison with the average value for normal liquid, namely 0.28. However, using Lyderson's correlation (5):

$$Z_c = \frac{1}{3.43 + 0.0067\,(\Delta H_v)^2} \qquad (4)$$

where ΔH_v = heat of vaporization at the normal boiling point, kcal. per mole. A value of 0.28 is obtained for ClF_5. This indicates that ClF_5 acts as a normal liquid under mild temperature and pressure conditions. But under

Table II. Experimental Vapor Pressure Data for ClF_5

Temp., °C.	Pressure, Atm.	Run No.	Temp., °C.	Pressure, Atm.	Run No.	Temp., °C.	Pressure, Atm.	Run No.	Temp., °C.	Pressure, Atm.	Run No.
−80.2	0.033	1	−38.6	0.316	7	−15.3	0.964	7	2.0	1.812	7
−79.2[a]	0.022	7	−36.8	0.344	7	−15.1	0.965	7	2.7	1.854	7
−65.3	0.085	1	−36.0	0.354	7	−14.9	0.951	7	3.8	1.905	7
−65.5	0.085	1	−35.0[a]	0.381	7	5.5	2.016	7	23.6	3.856	1
−63.2[a]	0.072	7	−34.6	0.367	7	7.5	2.169	7	24.8[a]	3.757	7
−58.8	0.095	7	−34.5	0.388	7	7.9	2.211	7	42.5	6.87	5
−54.8	0.122	7	−33.3	0.399	7	9.3	2.279	7	45.2	7.14	1
−51.7	0.150	7	−33.1	0.422	7	10.0	2.338	7	47.6	7.68	1
−50.0[a]	0.169	7	−32.7	0.426	7	10.8	2.406	7	61.1	10.88	5
−49.8	0.164	7	−32.6	0.415	7	11.7	2.485	7	61.2	11.02	1
−49.4	0.162	7	−31.8	0.441	7	12.3	2.510	7	61.3	10.88	5
−47.3	0.177	7	−30.8	0.464	7	12.6	2.568	7	61.6	10.74	1
−47.1	0.195	7	−30.7	0.436	7	13.5	2.630	7	62.0	11.02	1
−47.0	0.195	7	−29.3	0.488	7	14.2	2.704	7	65.1	12.24	1
−45.7	0.201	7	−29.2	0.483	7	14.3	2.876	1	65.8	12.44	1
−45.3[a]	0.218	7	−28.3	0.526	7	16.1	2.874	7	67.1	12.72	1
−45.1	0.218	7	−27.8	0.555	7	16.8	3.802	7	69.7	12.85	1
−43.6	0.241	7	−26.9	0.509	7	17.1	2.959	7	70.6	13.87	1
−43.4	0.245	7	−26.2[a]	0.581	7	17.4	2.961	7	73.1	14.21	1
−42.3	0.260	7	−26.2	0.596	7	17.8	3.020	7	73.2	14.28	1
−40.8	0.251	7	−25.8	0.570	7	17.8	3.027	7	76.2	15.44	5
−40.4	0.277	7	−25.1	0.627	7	18.6	3.095	7	83.1	17.27	4
−40.4	0.290	7	−24.7	0.626	7	21.1	3.344	7	84.9	18.43	1
−24.7	0.685	1	−14.6	0.965	7	21.3	3.360	7	85.9	19.38	3
−24.3	0.692	1	−14.6	0.970	7	22.8	3.788	1	94.5	22.24	5
−24.2	0.698	1	−14.5[a]	0.966	7	23.1	3.808	1	94.9	22.71	2
−23.7[a]	0.656	7	−13.7	0.989	7	95.0	21.90	6	119.6	35.6	1
−23.7	0.666	7	−12.5	1.055	7	95.1	22.78	2	119.7	35.7	1
−22.6	0.700	7	−10.4	1.148	7	95.1	22.98	2	120.1	35.9	1
−22.4	0.698	7	−9.2	1.200	7	95.2	22.85	2	120.2	36.0	1
−21.4	0.726	7	−8.2	1.242	7	96.0	22.92	1	121.8	36.0	4
−21.1	0.747	7	−6.8	1.311	7	96.1	22.98	1	122.3	37.3	2
−20.5	0.753	7	−3.7	1.463	7	96.2	22.92	1	126.2	40.2	1
−20.0	0.779	7	−3.1	1.480	7	100.5	24.48	4	126.7	39.6	6
−19.6	0.783	7	−2.7	1.548	7	101.9	26.18	3	126.9	40.0	5
−18.5	0.812	7	−2.4	1.531	7	106.8	28.02	5	128.9	40.5	4
−17.9[a]	0.834	7	−1.3	1.616	7	107.1	27.68	4	129.3	42.8	3
−17.8	0.845	7	−0.9	1.642	7	111.6	30.87	2	133.4	44.7	2
−17.2	0.865	7	−0.6	1.667	7	112.3	30.40	6	134.7	46.9	3
−17.0	0.874	7	−0.2[a]	1.701	7	113.3	31.96	1	135.0	46.9	3
−15.9	0.913	7	0.0	1.669	7	113.4	31.96	1	135.9	46.6	5
−15.4	0.930	7	0.0	1.752	1	117.8	34.48	3	140.1	49.0	4
−15.4	0.933	7	0.7	1.731	7	117.9	34.0	5			

[a] Data of Pilipovich *et al.* (8).

Table III. Conductivity Cell Results for Liquid ClF_5

Temp., °C.	Measured Series Capacitance, Picofarads	Calcd. Parallel Capacitance, Picofarads	Calcd. a.c. Resistance, Megohms	Calcd. Dielectric Constant	Specific Conductivity, $Ohm^{-1} Cm.^{-1} \times 10^9$
−80.0	52.1	50.9	20.2	4.28	0.37
−70.5	54.2	49.1	10.1	4.11	0.74
−62.5	59.6	48.1	6.76	4.01	1.10
−57.5	62.2	47.6	6.03	3.96	1.24
−52.8	61.7	46.6	6.01	3.87	1.25
−48.8	60.4	45.9	6.17	3.80	1.22
−45.9	59.4	45.5	6.33	3.76	1.18
−42.9	57.8	44.9	6.62	3.70	1.13
−40.0	55.2	44.4	7.28	3.65	1.03
−37.0	53.1	44.0	7.95	3.62	0.94
−34.0	51.7	43.7	8.48	3.59	0.88
−31.0	49.2	43.1	9.80	3.53	0.77
−28.1	46.9	42.6	11.76	3.48	0.64
−25.1	46.3	42.3	12.23	3.45	0.61
−22.1	45.7	41.9	12.75	3.41	0.59
−19.0	44.1	41.5	15.36	3.38	0.49
−17.0	43.3	41.1	16.64	3.34	0.45

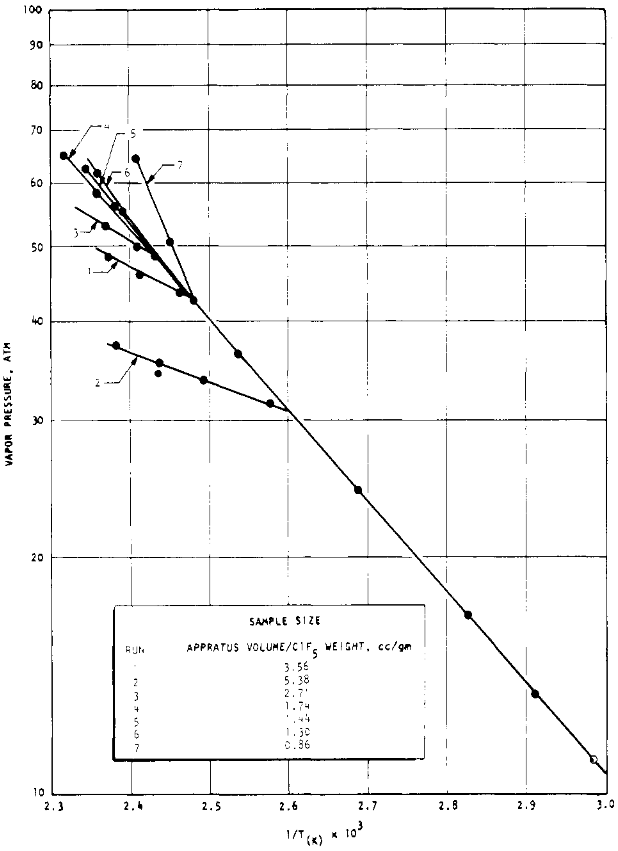

Figure 4. Temperature of discontinuity for various sizes of ClF_5 sample

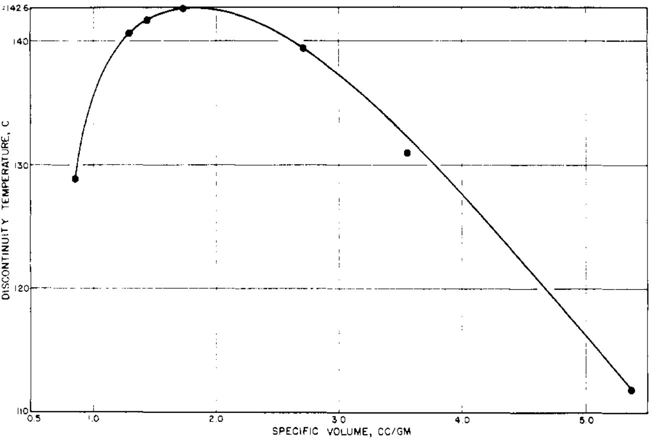

Figure 5. Temperature of discontinuity vs. specific volume

extreme conditions, near the critical region, it deviates from normal behavior. This is consistent with preliminary results of adiabatic compressibility measurements presently being performed in this laboratory. In particular, the fact that ClF_5 is more compressible than normal liquids is pertinent in evaluating the difference between Z_c values obtained by using Equations 3 and 4.

Electrical Conductivity and Dielectric Constant (Liquid). The dielectric constant and specific conductivity of liquid ClF_5 were calculated from the conductivity cell capacitance measurements (Table III). A plot of dielectric constant *vs.* temperature yielded a straight line ($\epsilon = -0.015t_{(°C.)} + 3.08$, standard error of estimate is 0.02) over the temperature range of −80° to −17° C. The specific conductivity of liquid ClF_5 is $<1.3 \times 10^{-9}$ ohm^{-1} cm.$^{-1}$ over the same temperature range. The variance in the values of specific conductivity listed in Table III was probably due to the impurities present in the ClF_5, as suggested in a similar study with ClF_3 (*4*). As expected, the values of dielectric constant and specific conductivity for ClF_5 are lower than those for ClF_3 at any given temperature (*10–12*).

Table IV. Calibration Values Used in Determining Gas Phase Dielectric Constant

Gas	$(\epsilon - 1) \times 10^{-6}$	References
He	65	(*7*)
N_2	548	(*7*)
ClF_3	3096	(*6, 10, 13*)

Dielectric Constant (Vapor Phase). For the determination of the dielectric constant of ClF_5, the sample side of the flow-through capacitor was passivated with ClF_3. Several alternate samples of ClF_5, ClF_3, N_2, and He were passed through the capacitor, and the respective difference frequencies were read on a calibrated frequency meter. A plot was then made of $(\epsilon - 1) \times 10^{-6}$ *vs.* difference frequency, and a curve was fitted to the known $(\epsilon - 1) \times 10^{-6}$ values for He, N_2, and ClF_3 (Table IV); these gases were used as calibration standards. An attempt to use CO_2 as an additional standard was abandoned since the CO_2 depassivated the surface of the capacitor. The dielectric constant of ClF_5 was determined by reading off the ϵ value which corresponded to its measured difference frequency. This value was 1.00279 ± 0.00007. The reported uncertainty in the value of ϵ is a best estimate rather than a sigma value because not enough points were taken to make a statistical analysis meaningful.

The ClF_3 data from Magnuson (*6*) covered the desired temperature range, but since it was taken at 9400 mHz., it could not be used directly. The data of Rogers, Pruett, and Speirs (*10*) were taken at 0.5 mHz. (close to the 10 mHz. of this work), but they did not cover the necessary temperature range. To obtain a value for the dielectric constant of ClF_3 at 10 mHz. and 23.9° C., it was necessary to extrapolate the 0.5-mHz. data to this temperature and then to weigh the ϵ's reported at 0.5 and 9400 mHz. by the inverse factor of their frequency ratios to 10 mHz. The 9400-mHz. determination was thus given a factor of 20 (10 mHz. per 0.5 mHz.) as compared with a factor of 940 (9400 mHz. per 10 mHz.) for the 0.5-mHz. value (this weighing method is of course not rigorously correct). The value of ϵ thus obtained was then corrected for the amount of dimer present from the interpolated monomer-dimer equilibrium constant at this temperature (*13*) by an equation derived by Magnuson (*6*).

Ideally, a plot of $(\epsilon - 1) \times 10^{-6}$ *vs.* difference frequency is a straight line. In an inductance-capacitance circuit with a fixed value of L and with the capacitance (C) proportional to ϵ,

$$DF = K\frac{1}{|\epsilon|^{1/2}} + F(\Delta C) \tag{5}$$

where DF = difference frequency, K = constant, ϵ = dielectric constant, and $F(\Delta C)$ = a function of the difference in capacitance of two oscillator circuits. Since $\epsilon \cong 1$ and $F(\Delta C)$ is small, DF may be approximated by:

$$DF = K\left[1 - \left(\frac{\epsilon - 1}{2}\right)\right] = K - \frac{K}{2}(\epsilon - 1) \tag{6}$$

K is effectively subtracted from the equation by the circuitry, and therefore:

$$DF = K'(\epsilon - 1) \tag{7}$$

Thus, a graph of DF *vs.* $(\epsilon - 1)$ should be a straight line passing through the origin. Experimentally, a slight curvature was noted owing to circuitry effects or the approximation that $F(\Delta C)$ was negligible. Since the value of ϵ for ClF$_5$ was determined by comparison with a curve, this deviation from ideality should not have affected its accuracy.

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Second Virial Coefficients of Binary Mixtures of Benzene with Methanol, Ethanol, Acetone, and Diethyl Ether

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Low pressure *PVT* data were obtained and second virial coefficients were derived for the benzene-methanol, benzene-ethanol, benzene-acetone, and benzene–diethyl ether at 40°, 60°, 80°, and 100° C. The standard deviation of the experimental second virial coefficients was 32 ml. per mole, and the standard deviation of the derived interaction coefficients was 52 ml. per mole. The Kihara potential represented the derived second virial coefficients of the pure materials within experimental error. The interaction second virial coefficients of benzene-methanol and benzene-ethanol were best represented by the Lennard-Jones potential when homomorph parameters were used as nonpolar estimates of the potential parameters, and the interaction coefficients of benzene-acetone and benzene-diethyl ether were best represented by the Kihara potential.

MODERN equations of state are based upon a microscopic view, which is dependent on intermolecular interactions. Through the statistical mechanical treatment of the forces between molecules in a gas, one can derive the virial equation of state. The second virial coefficient is dependent on only two body interactions. In formulating a potential energy function to describe the energy of interaction between molecules in a gas at low density, dispersion forces (due to definite electron configurations which cause instantaneous dipoles to be formed) and dipole forces (due to the interaction of the permanent dipoles of polar molecules) are the most important. In binary systems containing a polar and a nonpolar component, there is also an interaction energy arising from dipole-induced dipole forces.

These latter systems have not been thoroughly investigated. This study was undertaken to obtain experimental second virial coefficients for systems of this type and to examine the intermolecular potential energy functions which could be applied to them.

APPARATUS

A variable-volume piezometer was constructed of spherical glass bulbs connected with 2-mm. capillary tubing (*9*). The bulbs were sized such that, on each compression, the pressure would increase by approximately one half the initial pressure. The variable-volume piezometer is shown in Figure 1. The total volume of the piezometer was 318.77 ml. The pressure of the sample was measured by a constant leg mercury manometer. Mercury was also used to compress the sample in the piezometer bulbs. Air pressure or a secondary vacuum source was used to raise and lower the mercury in the piezometer and manometer.

The piezometer was placed in a constant temperature air bath (*10*). Two 140 cubic feet per minute blowers were used to circulate the air. Three 250-watt strip heaters and water cooling coils were used to heat and cool the bath. The heaters were controlled by a Fisher Model 44 thermistor probe temperature controller. The temperature was controlled within ±0.03° C. The bath had a double plate glass window in the front through which the mercury heights were measured using a cathetometer.

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