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Vapor Pressure of Chlorine Trifluoride from 300 K to 317 K

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Vapor pressure of chlorine trifluoride was measured by a static-type apparatus from 300 K to 317 K with corresponding pressures from 0.1848 MPa to 0.3349 MPa. The uncertainty of the measurement was less than ±0.03 K in temperature and ±0.3 kPa in pressure. The purity of the sample was more than 99.9999 mass %. The vapor pressure at 313.15 K was 0.2947 MPa. The experimental data were correlated by the Antoine and Frost−Kalkwarf equations. The correlated deviations of both equations were less than ±0.05%.

Introduction

Chlorine trifluoride (ClF_3) is widely used as a nonplasma etching or cleaning gas, especially in the semiconductor manufacture. It offers most of the qualities of liquid fluorine in terms of performance with fewer problems of storage and handling owing to its higher critical temperature and boiling point. As ClF_3 is generally heated below 313 K in order to be supplied at higher pressure, a knowledge of the vapor pressure around room temperature is necessary for industrial applications. Grisard et al. (1951) measured the vapor pressure in the temperature range from 226 K to 303 K.

In Japan, it is very important whether the vapor pressure of a substance is higher or lower than 0.2975 MPa at 313.15 K because the High Pressure Gas Control Law is applied to gases with the vapor pressure above 0.2975 MPa at 313.15 K. In the present study, we measured the vapor pressure of ClF_3 in the temperature range from 300 K to 317 K and determined the vapor pressure at 313.15 K.

Experimental Section

Figure 1 shows an experimental apparatus used for the measurement of vapor pressures. It is a static-type apparatus and mainly consists of an equilibrium vessel placed in a thermostated water bath, precise temperature and pressure measuring devices, and a sample gas supplying unit. All vessels and tubes are made of 316 stainless steel which is a corrosion-resistant alloy for ClF_3. The sample with a high purity was introduced from a gas cylinder to the evacuated equilibrium vessel. The mass of the sample charged into the vessel was determined from the loss in the mass of the gas cylinder put on an electronic balance. The volume of the liquefied sample supplied into the vessel of 25 cm^3 was about 20 cm^3.

The temperature of the thermostated water bath was kept constant within ±0.02 K by the PID controller. The equilibrium temperature and pressure are measured after the sample was kept at a constant temperature at least 3 h. The fluctuation of the pressure was found to be less than 0.3 kPa for 1 h.

The vapor pressure of the sample was measured by a pressure gauge (P1: Baratron model 690A). It is based on the principle that a deformation of the diaphragm caused by the pressure varies the electric capacity between the electrode and the diaphragm. As instrument error caused by a fluoride film on the diaphragm of the pressure gauge made of Inconel was not clear, we provided another standard pressure gauge (P2) to check the reliability of P1. P2 was the same type as P1 and was exposed to only helium gas during the experiment. P1 and P2 were calibrated first, and the readings of these two gauges were compared after the experiment by putting the same pressure of helium gas.

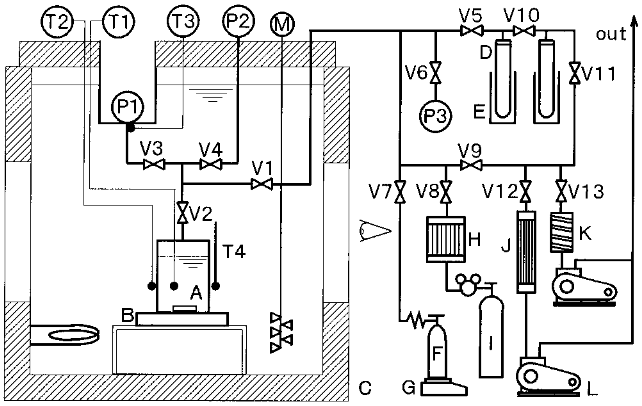

Figure 1. Experimental apparatus: (A) equilibrium vessel, (B) magnetic stirrer, (C) thermostated water bath, (D) distillation vessel, (E) dewar vessel, (F) sample gas cylinder, (G) electronic balance, (H) molecular sieve dryer, (I) helium gas cylinder, (J) halogen filter, (K) oil diffusion pump, (L) oil rotary pump, (P1−P3) pressure gauges, (T1−T3) platinum resistance thermometers, (T4) mercury standard thermometer, (V1−V13) diaphragm stop valves.

The temperature was measured with a platinum resistance thermometer (T1: Chino model NR) immersed in the sample directly. Its resistance was measured with a Mueller type bridge. The thermometer was calibrated by comparison with a mercury standard thermometer (T4: Shinnihon Keisoku model No. 1) which was calibrated according to ITS-90 at National Laboratory of Metrology, Ibaraki, Japan.

The experimental uncertainties are estimated to be within ±0.03 K in temperature and ±0.3 kPa in pressure. The purity of the samples are summarized in Table 1, where butane was used to examine the reliability of the vapor pressure measurement. The purity of ClF_3 analyzed after the measurement was more than 99.999 mass %.

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Table 1. Purity of Samples

sample	composition	concn
chlorine trifluoride	ClF_3	>99.999 mass %
	O_2	<2 mass ppm
	N_2	<2 mass ppm
	CO_2	<1 mass ppm
	HF	<4 mass ppm
	CF_4	<1 mass ppm
butane	butane	>99.960 mass %
	air	<50 mass ppm
	methane	0.5 mass ppm
	ethane	0.5 mass ppm
	propane	1.0 mass ppm
	2-methylpropane	162 mass ppm
	2,2-dimethylpropane	156 mass ppm

Table 2. Vapor Pressure of Butane

no.	T_{90}/K	p/MPa	p_{cal}/MPa[a]	$100(p - p_{cal})/p_{cal}$	samp[b]
1	300.80	0.2646	0.2645	+0.02	C
2	301.96	0.2739	0.2740	−0.03	B
3	302.75	0.2806	0.2806	−0.00	A
4	303.53	0.2872	0.2873	−0.02	B
5	303.59	0.2879	0.2878	+0.03	C
6	304.31	0.2940	0.2940	−0.00	A
7	305.04	0.3005	0.3005	+0.02	C
8	305.68	0.3062	0.3062	+0.00	A
9	306.40	0.3127	0.3128	−0.02	B
10	307.20	0.3202	0.3202	+0.01	C
11	308.04	0.3280	0.3280	−0.01	B
12	309.07	0.3381	0.3379	+0.04	C
13	310.06	0.3476	0.3477	−0.02	B
14	311.20	0.3591	0.3592	−0.02	C
15	311.65	0.3638	0.3638	+0.01	B
16	311.68	0.3640	0.3640	−0.01	A
17	312.96	0.3774	0.3774	+0.00	C
18	313.43	0.3822	0.3824	−0.05	A
19	313.67	0.3850	0.3850	+0.01	B
20	315.37	0.4035	0.4035	−0.00	A
21	315.38	0.4038	0.4036	+0.04	C
22	315.52	0.4052	0.4052	+0.00	B

[a] Vapor pressure calculated by eq 1. [b] A, B, and C mean the kinds of samples used for measurement.

Results and Discussion

Butane. The vapor pressure of butane was measured to check the reliability and accuracy of the whole measurement system. The reason for selecting butane is that reliable data are available in the literature and the values of vapor pressure are close to those of ClF_3. The sample of butane was recharged in the equilibrium vessel three times during the experiment. The experimental results are given in Table 2. The results were correlated by the Antoine equation (eq 1) with a deviation of ±0.05% in the temperature range from 301 K to 315 K and Frost−Kalkwarf equation (eq 2) with a deviation of ±0.05%.

$$\log_{10}(p/\mathrm{MPa}) = a - b/\{(T/\mathrm{K}) + c\} \qquad (1)$$

$$\ln(p/\mathrm{MPa}) = a + b/(T/\mathrm{K}) + c\ln(T/\mathrm{K}) + d(p/\mathrm{MPa})/(T/\mathrm{K})^2 \qquad (2)$$

The regressed parameters of both equations are presented in Table 3. The deviations were almost the same for both equations.

Figure 2 shows the correlated results by eq 1, as well as the difference from the literature data which were calculated by the vapor-pressure equation recommended by Haynes and Goodwin (1982) and Holldorff and Knapp (1988). Haynes and Goodwin determined optimized parameters of the Antoine equation using 150 data points. On the other hand, Holldorff and Knapp determined the optimal parameters from 20 experimental values. The results in this work agreed well with the previous measurements within ±0.03% over the temperature region studied.

Table 3. Vapor Pressure of Chlorine Trifluoride

no.	T_{90}/K	p/MPa	p_{cal}/MPa[a]	$100(p - p_{cal})/p_{cal}$	samp[b]
1	299.22	0.1795	0.1795	−0.00	C
2	300.60	0.1890	0.1890	+0.02	C
3	301.49	0.1953	0.1953	+0.01	C
4	302.18	0.2003	0.2003	−0.01	C
5	302.72	0.2043	0.2043	+0.00	C
6	303.13	0.2074	0.2074	−0.01	C
7	303.40	0.2095	0.2094	+0.03	A
8	303.42	0.2095	0.2096	−0.03	B
9	303.46	0.2099	0.2099	+0.02	C
10	304.98	0.2217	0.2218	−0.03	C
11	306.08	0.2306	0.2306	−0.01	C
12	307.01	0.2385	0.2384	+0.04	C
13	307.95	0.2463	0.2464	−0.04	C
14	308.65	0.2525	0.2525	+0.00	A
15	308.66	0.2526	0.2526	−0.01	C
16	308.72	0.2531	0.2532	−0.02	B
17	309.74	0.2623	0.2622	+0.02	C
18	310.60	0.2702	0.2702	+0.01	C
19	311.57	0.2792	0.2793	−0.03	C
20	312.21	0.2855	0.2855	+0.01	B
21	312.44	0.2876	0.2877	−0.02	A
22	312.48	0.2881	0.2881	−0.00	C
23	313.21	0.2953	0.2952	+0.03	B
24	313.33	0.2966	0.2965	+0.05	A
25	313.41	0.2971	0.2972	−0.04	D
26	313.43	0.2974	0.2975	−0.02	C
27	314.24	0.3057	0.3056	+0.03	B
28	314.29	0.3063	0.3062	+0.04	A
29	314.36	0.3068	0.3069	−0.03	C
30	315.38	0.3176	0.3175	+0.03	C
31	315.52	0.3189	0.3189	−0.01	D
32	316.29	0.3271	0.3272	−0.03	C
33	317.35	0.3388	0.3388	+0.00	D

[a] Vapor pressure calculated by eq 1. [b] A, B, C, and D mean the kinds of samples used for measurement.

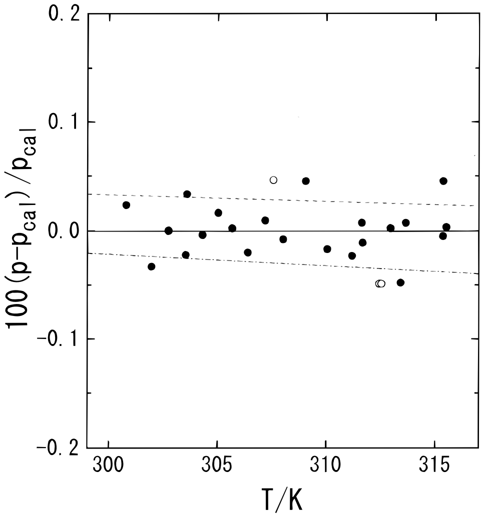

Figure 2. Comparison of experimental vapor pressure with literature and correlated results by the Antoine equation for butane: (●) this work; (- - -) Haynes and Goodwin (1982); (○, —•—) Holldorff and Knapp (1988). (The zero value at the y-axis is the correlated result by the Antoine equation.)

Chlorine Trifluoride. The sample of ClF_3 was recharged in the equilibrium vessel four times during the experiment. The experimental results of the vapor pressure of ClF_3 in the temperature range of 300 K to 317 K are given in Table 3. As the accurate vapor pressure at 313.15 K is required for Japanese law on high-pressure gases, many measurements were made around this tem-

Table 4. Parameters of Vapor Pressure Equations

substance	equation	*a*	*b*	*c*	*d*
butane	1	3.07198	1004.78	−25.4810	
	2	37.6216	−3990.58	−4.51131	20090.4
chlorine trifluoride	1	3.38984	1048.94	−45.5987	
	2	61.4209	−5574.54	−7.81482	22625.9

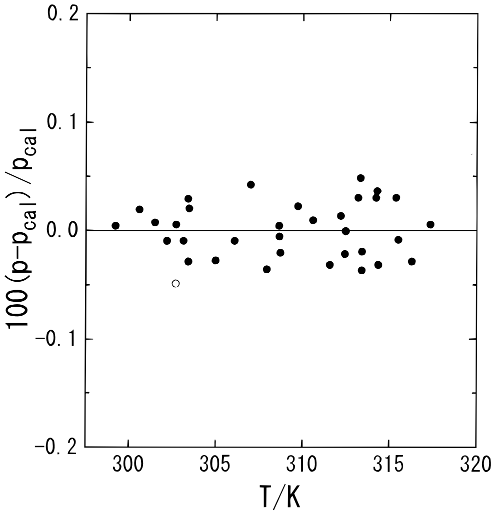

Figure 3. Deviation from correlated results by Frost-Kalkwarf equation and comparison with literature for chlorine trifluoride: (●) this work; (○) Grisard et al. (1951). (The zero value at the *y*-axis is the correlated results by the Frost−Kalwarf equation.)

perature. The results were correlated by the Antoine equation with a deviation of ±0.05% and Frost−Kalkwarf equation with a deviation of ±0.05%. The optimized parameters of both equations are presented in Table 4. To check the experimental error owing to the fluorine film coated on the diaphragm of the pressure gauge, the reading of the pressure gauge P1 was compared with that of pressure gauge P2 after each run. The variation of the reading of the P1 gauge was less than the uncertainty of the pressure gauge.

Figure 3 shows the correlated results by eq 2, as well as the difference from results reported by Grisard et al. (1951) in the temperature region of 226.2 K to 302.7 K. A datum point, which is in the temperature region in this measurement, was in good agreement with our experimental data. The vapor pressure of ClF_3 at 313.15 K was confirmed to be 0.2947 MPa for both eqs 1 and 2 which is less than 0.2975 MPa, as explained in the Introduction.

Conclusion

The vapor pressures of chlorine trifluoride was measured in the temperature range from 300 K to 317 K by the static-type apparatus. On the basis of the experimental data the pressure at 313.15 K was 0.2947 MPa.

Literature Cited

Grisard, J. W.; Bernhardt, H. A.; Oliver, G. D. Thermal Data, Vapor pressure and Entropy of Chlorine Trifluoride. *J. Am. Chem. Soc.* **1951**, *73*, 5725−5728.

Haynes, W. M.; Goodwin, R. D. Thermophysical Properties of Normal Butane from 135 to 700 K at Pressures to 70 MPa. NBS-MN-169 1982, No. PB82-249632.

Holldorff, H.; Knapp, H. Vapor Pressure of n-butane, dimethyl ether, methyl chloride, methanol and the vapor-liquid equilibrium of dimethyl ether-methanol: experimental apparatus, results and data reduction. *Fluid Phase Equilib.* **1988**, *40*, 113−125.

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