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Experimental Study of P-V-T Properties of Fluorocarbon Refrigerant R 13 (CClF_3)[#]

(First Report : Experimental Method and Experimental Results)

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The P-V-T properties of fluorocarbon refrigerant R 13, i.e. trifluorochloromethane, were experimentally determined using a constant volume apparatus of 270 cm^3 approximately in its inner volume, which is useful in the ranges of temperatures from -120°C to 100°C and pressures up to 100 kgf/cm^2 , as described in the present paper in detail. The present measurements for this substance were made with special attention to the neighbourhood of the saturation line in the range of temperatures from 0°C to 100°C with accuracies of $\pm 0.010^\circ\text{C}$ above 20°C and $\pm 0.015^\circ\text{C}$ below 20°C , in the range of pressures up to 100 kgf/cm^2 with accuracy of 0.014 kgf/cm^2 maximum and in the range of specific volumes from $0.95 \text{ cm}^3/\text{g}$ to $10 \text{ cm}^3/\text{g}$ with accuracy of 0.01% . The present results show good agreement with those by Michels et al. and could be useful as the reference data for correlating the equation of state.

1. Introduction

The experimental studies of thermodynamic properties of fluorocarbon refrigerant R 13, namely trifluorochloromethane (CClF_3), have not been conducted so often. As for the pressure-volume-temperature relation, i.e. P-V-T relation, of this substance, the representative experimental studies are tabulated in Table 1 and are illustrated on a P-T diagram of Fig. 1 including the present study. The experimental results by Michels et al. seem to be better in the purity of the sample and also in the accuracies of P-V-T property values even in such a wide region in comparison with the results shown in Table 1, but are lacking in the measurements near the saturation pressure curve.

In the present study, the experimental equipment for P-V-T property measurement of fluorocarbon refrigerants was installed for

the precise measurements in the ranges of pressures up to 100 kgf/cm^2 , the accuracy being better than 0.014 kgf/cm^2 , and temperatures from -120°C to 100°C , the accuracy being 0.010°C or 0.015°C . Furthermore, the P-V-T property values of fluorocarbon refrigerant R 13 were experimentally determined with this equipment in the range of temperatures above 0°C including the critical point with special attention to the behaviour near the saturation pressure curve. The accuracies of 204 points obtained experimentally in such a region and their reproducibilities were good as planned, and the observed results were found to be good for the absolute measurement after comparing them with the equations of state for fluorocarbon refrigerant R 13 reported previously. The experimental results and their comparisons with equations of state are described here with the details of the experimental equipment and method.

Table 1 Experimental studies of P-V-T properties for fluorocarbon refrigerant R 13

Investigators	Year	Temperature $^\circ\text{C}$		Pressure kgf/cm^2		Specific volume cm^3/g		Measured points	Purity of sample (wt %)
		Range	Uncertainty	Range	Uncertainty	Range	Uncertainty		
Riedel (1)	1941	-78.8-60.0	0.02	1.1-30.8	0.3-0.5%	5.3-222.7	—	66	—
Albright et al. (2)	1952	-57.5-129.4	0.01	2.9-143.1	0.3%	1.4-54.3	0.1%	87	99.7
Michels et al. (3)	1966	0.0-150.0	—	15.5-482.0	—	0.94-11.0	—	280	99.95

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which are usable also at low temperature and a tubing P connected to the diaphragm type pressure balance detector C. The pressure of nitrogen regulated to be equal to the pressure of the sample is transferred from the diaphragm type pressure balance detector to an oil-gas separator F. The oil-gas separator was made in a type of the mercury U-tube to protect it from the contact of spindle oil for a pressure gauge and nitrogen for pressure transmission. And two thick glass windows were mounted on one of the mercury vessels as the interface between mercury and nitrogen in order to observe about ten times as big as the mercury meniscus. The quantity of spindle oil or nitrogen was adjusted to keep the position of the mercury meniscus constant throughout the measurement. The pressure of the sample was obtained by measuring the pressure of spindle oil with a dead weight pressure gauge and by correcting the air buoyancy of the weights, the hydrostatic pressure difference between spindle oil and nitrogen and the district gravitational acceleration. Moreover, the piezometer and the diaphragm type pressure balance detector were immersed in a precisely thermostatted bath B and a platinum resistance thermometer D was set very near the main part of the piezometer. In this thermostatted bath of about 120 liter volume, water was contained in the range of temperatures above 5°C and fluorocarbon refrigerant R 11 in the range of temperatures below 5°C. And an electric heater H of 1 kw and a refrigerated coil were immersed also in it. The fluorocarbon refrigerant R 14 circulating in this coil was refrigerated by the method of three stage refrigeration using the refrigerators such as R 12, R 13 and R 14. The temperature of the thermostatted bath was controlled by adjusting the voltage of the electric heater by an automatic temperature controller or by a manual transformer, and was kept uniform and constant with a fluctuation less than 0.005°C in the range of temperatures above 20°C using only the electric heater and with a fluctuation less than 0.010°C below 20°C using it in working the refrigerated tubing. The platinum resistance thermometer had been calibrated by the National Research Laboratory of Metrology in Tokyo with an accuracy of 0.005°C based upon the International Practical Temperature Scale (1948) and was converted to the IPTS (1968). The mass of the sample in the piezometer was measured using a 2 kg precision chemical balance with a sensitivity better than 2 mg after pouring it in the main spherical piezometer.

Fig. 3 Main piezometer

3.1.2 Main Part of the Piezometer

The main part of the piezometer as shown in Fig. 3 is a spherical vessel of about 270 cm³ in its inner volume made of stainless steel SUS 304 which has been welded to the stainless steel tubings at both ends of the vessel. The spherical vessel was made by welding hemispheres to each other manufactured by machining and was annealed in an evacuated furnace after checking the welded portion with X-ray. The test pieces to measure the thermal expansion coefficient of the piezometer were also manufactured and annealed with the piezometer. The inner volume of this vessel was found by calculation of the specific volume of water multiplied by the mass of deaerated and distilled water filling it at atmospheric pressure, 14.0 kgf/cm², 42.0 kgf/cm², 67.8 kgf/cm², 94.4 kgf/cm² and 122.0 kgf/cm². The specific volume of water was calculated using the 1967 IFC formulation for industrial use⁽⁵⁾. As a result, assuming that this piezometer was a perfect spherical vessel with a thick wall except tubings, the inner radius r_{10} and outer radius r_{20} at 0°C and 0 kgf/cm² on both sides of the piezometer were determined as follows ;

$$r_{10} = 3.994 \text{ 21 cm} \dots\dots\dots (1)$$

$$\text{and } r_{20} = 4.493 \text{ 95 cm} \dots\dots\dots (2)$$

The inner volume of high pressure valves V_1 and V_2 and tubing was 1.7087 cm³ at 0°C, taking into consideration only the thermal expansion effects, because those walls were very thick and the volume change by the elastic deformation under pressure was negligibly small in comparison with the inner volume of the spherical piezometer. Therefore, the inner volume V cm³ of the whole piezometer was obtained at temperature t , pressure P and atmospheric pressure P_0 as follows ;

$$V = \frac{4}{3}\pi (r_1 + \xi)^3 + 1.7087(1 + \alpha t)^3, \dots\dots (3)$$

where

$$\xi = \frac{r_1}{E(1-a^3)} \{ (1-2\nu)(P a^3 - P_0) + \frac{(1+\nu)}{2}(P - P_0) \} \dots\dots (4)$$

$$r_1 = r_{10}(1 + \alpha t), \dots\dots\dots (5)$$

$$r_2 = r_{20}(1 + \alpha t) \dots\dots\dots (6)$$

and

$$a = \frac{r_1}{r_2} = \frac{r_{10}}{r_{20}} \dots\dots\dots (7)$$

The inner volume of the piezometer calculated by Eq. (3) agreed with deviations less than 0.001% with the experimental data for the radii r_{10} and r_{20} . The thermal expansion coefficient of stainless steel SUS 304 was measured in the range of temperatures from -150°C to 200°C and was correlated using the least squares method based upon those experimental results with a mean absolute deviation of not greater than 1.5% as follows ;

$$\alpha = 1.413 \times 10^{-5} + 1.582 \times 10^{-8} t - 3.3 \times 10^{-11} t^2 \dots\dots (8)$$

Young's modulus E ⁽⁶⁾,⁽⁷⁾ and Poisson's ratio ν ⁽⁶⁾ were also correlated as a function of temperature using the cited values, which include data at low temperature, as follows respectively ;

$$E = 1.994 \times 10^6 - 5.297 \times 10^2 t - 5.58 \times 10^{-1} t^2 + 2.402 \times 10^{-3} t^3 - 5.406 \times 10^{-6} t^4 \dots\dots (9)$$

and

$$V = 2.438 \times 10^{-1} + 2.162 \times 10^{-4}t + 1.345 \times 10^{-7}t^2 \quad (10)$$

Equation (9) could be effective in the range of temperatures from -250°C to 370°C and Eq. (10) from -100°C to 250°C .

3.1.3 Diaphragm Type Pressure Balance Detector^{(8),(9)}

It is quite necessary to immerse the pressure transmission apparatus in the same temperature field in which the piezometer is installed in order to take out accurately the pressure of the sample. In the present study, a sensitive and precise diaphragm type pressure balance detector was used to detect the pressure difference between the sample and nitrogen of pressure transmission so that the inner volume of the piezometer might not be changed. This pressure balance detector as shown in Fig. 4 was designed and manufactured originally, in which a teflon O-ring seal was mounted in order to obtain better sensitivity especially in the range of temperatures above 0°C . Although this O-ring seal was used not to overload the diaphragm under pressure, it could not be used in the range of temperatures below 0°C because of the difference of the thermal expansion coefficients between teflon and stainless steel. Bakelite and teflon were used as the electric insulating materials. On the other hand, a nickel foil of 50μ thickness was used as the diaphragm, to one side of which the sample was introduced and to the other side of which nitrogen was introduced. And a dough-nut shaped nickel foil of 50μ thickness, 21 mm inner diameter and 49 mm outer diameter was mounted at both sides of the diaphragm to keep a uniform distance between the electrode and the diaphragm. The stainless steel electrode of 16 mm diameter had a hole of 0.3 mm diameter at its center, through which nitrogen was introduced, and was covered with bakelite for the electric insulation and the installation. The properties of the sample were not influenced by the electric effects because the diaphragm and the piezometer were connected to the ground and the electrode was installed in nitrogen. At the piezometer side of the diaphragm, there was a flange made of stainless steel with a hole of 0.3 mm dia-

Fig. 4 Diaphragm type pressure balance detector

meter for introducing the sample. The pressure difference between nitrogen and the sample was measured by the transformer bridge to detect the unbalance from the equilibrium state between the ratio of the capacitances and the value of the ratioformer. The value of the ratioformer had been calibrated at the balanced state of pressures concerning the ratio of the capacitance of the clearance between the electrode and the diaphragm to the capacitance of 10 pF condenser situated at about 20°C . The pressure of nitrogen was automatically controlled by the indication of the meter-relay originated from the unbalance of the transformer bridge due to the displacement of the clearance between the electrode and the diaphragm. The two electromagnetic valves, one of which was installed near the nitrogen bottle as the high pressure source and the other of which was set up to drive nitrogen into the atmosphere, were automatically controlled to open or to close by the signal of the meter-relay. The pressure change was easily detected within 2 mmHg which could be decided as the sensitivity of this bridge system. The relationship between the pressure difference $\Delta P_d \text{ mmHg}$ and the indication of the meter-relay is described in Fig. 5. The final sensitive control of the pressure was conducted manually and the pressure of the sample was determined by measuring the pressure of nitrogen controlled to be equal to it. Then the pressure measurement was made without any change in the purity of the sample.

3.1.4 System of the Pressure Measurement

The pressure was measured using a dead weight pressure gauge⁽¹⁰⁾. The effective ram area of the pressure gauge had been precisely calibrated by the results of the saturation pressure measurement of carbon dioxide, purity of which was $99.995 \text{ wt\%}$, because its saturation pressure of 34.847 bar at 0°C was utilized as one of the pressure fixed points. Moreover, this pressure gauge was compared to

Fig. 5 Relation between P_d and indication of meter-relay of pressure balance detector

the mercury column at about 2 kgf/cm^2 and also compared to the standard pressure gauge⁽¹¹⁾ of the National Research Laboratory of Metrologia in Tokyo which was reported to be available for the precise pressure measurement below 100 bar within 0.01 %. Every calculated or calibrated effective ram area of this pressure gauge agreed within 0.01% after making those comparisons. The minimum weight used for this pressure measurement was 1 g weight of the chemical balance, which corresponded to 0.004 kgf/cm^2 , and was detected very easily and sensitively.

3.2 Experimental Method

Special caution was taken not to cause any change in the purity of the sample in every filling of the piezometer. The sample considered to be one component substance was taken out in the liquid state from the bottom of the sample bottle in order to fill it in the state of as small specific volume as possible. After the main part of the piezometer with the valve V_1 and the vacuum pump were connected to the sample bottle, the flushing in the piezometer and tubings was continued three or four times for about three hours. Then a larger amount of the sample than expected was taken to fill the main piezometer after evacuating it thoroughly and adjusted to the expected amount of the sample by subtracting it to make it equivalent to the desired specific volume and weighing it with a precision chemical balance. The mass of the sample was calculated by subtracting the mass of an empty piezometer from the mass of the piezometer including the sample mentioned above and correcting the effect of the air buoyancy. When the piezometer was connected to the equipment as shown in Fig.2, the sample was filled up to the diaphragm type pressure balance detector by opening V_1 after V_2 was closed following evacuation of the tubing P up to 10^{-3} mmHg . The valve V_1 , the electromagnetic valve V_5 and V_6 were opened upon the sign of the meter-relay of the transformer bridge and the pressure of nitrogen was automatically controlled to equalize roughly to the pressure of the sample. Afterwards, the piezometer and the pressure balance detector were immersed in the thermostatted bath and the temperature of the bath fluid was controlled. Simultaneously, the pressure of nitrogen was automatically controlled as described above. After the uniform temperature field was established, the pressure of nitrogen was manually controlled exactly to the pressure of the sample. After all this, the P-V-T property values were determined by measuring the uniform temperature with a platinum resistance thermometer and the pressure with a dead weight pressure gauge and calculating the specific volume that is equal to the inner volume of the piezometer, i.e. Eq.(3), divided by the mass of the sample in it. Measurements in the expected range of temperatures were followed by another measurement with the similar experimental procedure, after weighing another mass filling the piezometer by the precision chemical balance.

As mentioned above, the present observed P-V-T property measurements were conducted along isochores in the superheated vapour

region and in the wet vapour region, with special attention paid to the states near the saturation boundary curve and the critical point.

4. Examination of the

Experimental Errors

4.1 Accuracy of Temperature Measurement

As mentioned in the section 3.1.1, the accuracies of temperature measurements were within 0.010°C above 20°C or within 0.015°C below 20°C , including the calibration accuracy of the platinum resistance thermometer, the fluctuations of the controlled temperature in the thermostatted bath and the accuracies of the instruments.

4.2 Error of Pressure Measurement

Since as mentioned in the section 3.1.4, the effective area of the ram of the dead weight pressure gauge was calibrated with an uncertainty of 0.01 %, the diaphragm type pressure balance detector could detect the pressure difference within 0.004 kgf/cm^2 and the correction of the air buoyancy to the weights and the corrections of the hydrostatic pressure of spindle oil and nitrogen were negligibly small in comparison with other errors of the pressure measurement. The total error of the pressure measurement was 0.014% at 100 kgf/cm^2 , 0.018% at 50 kgf/cm^2 or 0.03% at 20 kgf/cm^2 .

4.3 Error of the Inner Volume of the Piezometer

The error of the inner volume of the piezometer, δV , was obtained by the propagation law of errors using Eqs.(1) to (10). In obtaining the errors such as $\delta\alpha$, uncertainty of linear thermal expansion coefficient, δE , uncertainty of Young's modulus of stainless steel SUS 304, and $\delta\nu$, uncertainty of Poisson's ratio, the errors of measurements

Table 2 Experimental errors of specific volume

v cm ³ /g	m g	$ \delta v/v \times 100$ %	t °C	$ \Delta v/v \times 100$ %
1.0	270	0.011	20	0.026
			40	0.022
2.0	135	0.011	40	0.18
			100	0.039
5.0	54	0.011	20	0.081
			100	0.041
10.0	27	0.013	0	0.072
			100	0.046

Table 3 Purity of the sample (wt %)

R 13 (CClF ₃)	R 14 (CF ₄)	air
99.93	0.06	0.01

for α and the cited values for E and v were estimated to be 2%, 5% and 5% respectively and the errors of α , E and v due to the uncertainties of temperature measurements were calculated by the propagation law of errors using Eqs. (8) to (10). Therefore, the inner volume of the piezometer was obtained with an accuracy of $|\delta v/v| < 1.08 \times 10^{-4}$ namely within 0.0108%, taking into account the accuracies of temperature and pressure measurements and the deviation of about 0.01% in the specific volume of water between the experimental values and the 1967 IFC formulation for industrial use.

4.4 Error of the Specific Volume

The specific volume v was determined as the inner volume V of the piezometer, i.e. Eq. (3), divided by the mass m of the sample filling it as follows ;

$$v = V/m \quad \text{..... (11)}$$

Taking into account the errors such as $\delta m = 0.002 \text{ g}$ and $|\delta v/v| < 1.08 \times 10^{-4}$, the error of the specific volume was calculated by the propagation law of errors, as follows ;

$$\left| \frac{\delta v}{v} \right| < 2 \times 10^{-3} \sqrt{2.916 \times 10^{-3} + \frac{1}{m^2}} \quad \text{... (12)}$$

Four examples of the errors of the specific volume, $|\delta v/v| \times 100 \%$, calculated by Eq. (12), are shown in Table 2. The specific volume of the sample could be within the errors shown in Table 2 in the process of measuring the P-V-T properties. The total experimental error of P-V-T property value was generally calculated by converting the errors of both pressure and temperature measurements to the error of the specific volume, as follows ;

$$\left| \frac{\Delta v}{v} \right| = \left| \frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \delta P \right| + \left| \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \delta T \right| + \left| \frac{\delta v}{v} \right| \quad \text{..... (13)}$$

As the partial differential values in Eq. (13) were the functions of temperature and pressure, the errors of the representative specific volume are shown in Table 2, using the equation of state formulated by Tanishita et al.⁽¹²⁾ Thus, the total experimental errors were finally determined concerning the specific volume within the accuracies of 0.03% in liquid state and of 0.05% in other state excluding near the saturation boundary and the critical point.

Table 4-1 Experimental results of P-V-T property values for fluorocarbon refrigerant R 13 (CClF₃) and their comparisons with equations of state

Experimental Results				Comparison	Experimental Results				Comparison		Experimental Results				Comparison	
P	v	t	ΔP _{Ta}		P	v	t	ΔP _{Al}	ΔP _{Ta}	P	v	t	ΔP _{Ri}	ΔP _{Al}	ΔP _{Ta}	
kgf/cm ²	cm ³ /g	°C	%		kgf/cm ²	cm ³ /g	°C	%	%	kgf/cm ²	cm ³ /g	°C	%	%	%	
25.874	0.95788	9.315	-6.62		36.960	1.2245	25.609		-0.60	40.710	1.7515	30.032		-0.58	-0.46	
27.435	0.95791	9.837	-6.16		37.571	1.2245	26.017		-0.52	45.109	1.7519	34.987		-0.46	-0.28	
33.520	0.95802	11.897	-4.51		39.114	1.2245	27.025		-0.40	49.602	1.7523	40.008		-0.40	-0.18	
42.733	0.95819	15.006	-2.93		40.632	1.2246	28.013		-0.30	54.064	1.7527	45.003		-0.31	-0.06	
57.779	0.95846	19.984	-1.88		42.149	1.2247	29.008		-0.16	58.549	1.7532	49.986		-0.28	-0.01	
73.062	0.95873	25.010	-1.30		43.618	1.2247	29.975		-0.01	63.099	1.7536	54.999		-0.30	-0.01	
79.077	0.95884	26.975	-1.17		51.578	1.2250	34.983		0.09	67.617	1.7540	59.994		-0.27	0.02	
82.179	0.95889	27.994	-1.08		59.744	1.2254	40.000		0.04	76.673	1.7549	69.994		-0.22	0.07	
85.153	0.95895	28.963	-1.04		67.961	1.2257	44.996		0.03	85.741	1.7558	79.999		-0.16	0.12	
88.391	0.95901	30.015	-1.00		76.320	1.2260	49.991		-0.05	94.766	1.7568	89.999		-0.06	0.19	
103.603	0.95928	34.988	-0.73		84.773	1.2263	55.000		-0.11	102.925	1.7576	98.995		-0.02	0.21	
103.637	0.95929	35.002	-0.73		93.243	1.2267	59.999		-0.13							
					101.760	1.2270	64.995		-0.14	39.762	1.9598	29.000		-0.17	-0.24	
28.127	0.99879	13.493	-8.21							40.564	1.9599	29.992		-0.23	-0.28	
29.480	0.99882	14.025	-7.53		38.535	1.3344	27.540	-16.94	-0.56	44.503	1.9603	34.995		-0.27	-0.24	
31.990	0.99887	14.993	-6.57		38.788	1.3344	27.708	-16.92	-0.64	48.393	1.9608	39.997		-0.22	-0.13	
45.095	0.99914	19.984	-3.58		39.137	1.3344	27.986	-16.75	-0.59	52.281	1.9613	45.000		-0.18	-0.06	
58.561	0.99942	25.018	-2.23		40.385	1.3345	28.992	-16.11	-0.38	56.169	1.9617	49.997		-0.16	-0.03	
66.583	0.99959	27.993	-1.75		41.655	1.3345	29.982	-15.60	-0.28	60.028	1.9622	54.997		-0.10	0.04	
69.297	0.99964	29.003	-1.59		48.256	1.3349	34.989	-13.61	-0.05	63.878	1.9627	59.999		-0.03	0.10	
71.978	0.99970	29.987	-1.50		55.075	1.3352	40.002	-12.27	-0.07	71.559	1.9637	69.995		0.08	0.17	
85.735	0.99998	35.021	-1.13		61.982	1.3355	45.008	-11.23	-0.10	79.199	1.9647	80.000		0.21	0.25	
99.348	1.00027	39.981	-0.89		68.975	1.3359	49.983	-10.47	-0.19	86.815	1.9657	90.003		0.33	0.32	
					76.106	1.3362	55.003	-9.84	-0.28	93.665	1.9666	99.018		0.42	0.36	
31.529	1.05149	18.054	-4.89		83.227	1.3366	59.988	-9.29	-0.32							
32.774	1.05152	18.604	-4.58		97.663	1.3373	70.005	-8.39	-0.38	38.859	2.2691	28.004	-0.28	0.02	0.04	
35.835	1.05160	19.985	-3.73		104.914	1.3376	74.995	-8.03	-0.40	39.218	2.2691	28.511	-0.29	-0.04	0.00	
47.225	1.05188	24.974	-2.11							39.351	2.2692	28.719	-0.27	-0.04	0.01	
51.902	1.05199	26.999	-1.71		39.614	1.4479	28.709	-6.50	-0.70	39.554	2.2692	29.011	-0.27	-0.06	-0.01	
54.277	1.05205	28.016	-1.57		39.944	1.4479	29.010	-6.42	-0.66	40.231	2.2693	30.006	-0.23	-0.12	-0.04	
56.559	1.05211	28.988	-1.47		41.022	1.4480	30.003	-6.13	-0.48	43.572	2.2698	34.977	-0.02	-0.30	-0.12	
58.880	1.05216	29.978	-1.36		46.707	1.4483	34.990	-5.34	-0.20	46.852	2.2704	40.008	0.29	-0.28	-0.04	
70.691	1.05245	34.992	-0.93		52.588	1.4487	40.001	-4.90	-0.14	50.042	2.2709	44.993	0.62	-0.18	0.09	
70.709	1.05245	34.994	-0.95		58.524	1.4490	44.990	-4.58	-0.12	53.217	2.2714	50.005	0.91	-0.05	0.22	
82.644	1.05274	40.000	-0.73		64.591	1.4494	49.999	-4.39	-0.18	56.369	2.2720	55.001	1.13	0.06	0.31	
94.522	1.05304	44.968	-0.56		70.705	1.4498	54.998	-4.25	-0.24	59.527	2.2725	60.033	1.31	0.16	0.40	
106.683	1.05334	50.013	-0.46		76.865	1.4501	60.004	-4.12	-0.28	65.723	2.2736	70.015	1.59	0.39	0.56	
					89.245	1.4509	69.998	-3.88	-0.31	71.857	2.2748	79.999	1.76	0.62	0.71	
34.031	1.12313	21.974	-1.96		101.714	1.4517	79.994	-3.66	-0.32	77.964	2.2759	90.013	1.83	0.82	0.83	
34.644	1.12315	22.303	-1.86							83.420	2.2770	99.028	1.84	0.99	0.94	
35.505	1.12318	22.779	-1.64		40.727	1.6563	30.002	-1.13	-0.52							
36.907	1.12322	23.517	-1.50		45.472	1.6566	34.996	-0.95	-0.32	37.445	2.7046	26.492	0.00	0.07	0.10	
39.679	1.12331	25.001	-1.10		50.293	1.6570	39.993	-0.88	-0.24	37.741	2.7046	27.005	-0.05	0.01	0.05	
45.453	1.12348	28.013	-0.69		55.153	1.6575	45.000	-0.84	-0.19	38.297	2.7047	28.009	-0.08	-0.04	0.03	
47.379	1.12354	29.000	-0.62		60.053	1.6579	49.998	-0.85	-0.18	38.860	2.7049	29.009	-0.13	-0.13	-0.03	
49.350	1.12360	29.991	-0.63		64.991	1.6583	55.006	-0.87	-0.19	39.416	2.7050	29.998	-0.19	-0.20	-0.08	
59.157	1.12389	34.971	-0.39		69.926	1.6587	59.998	-0.88	-0.20	42.098	2.7056	34.987	-0.19	-0.31	-0.09	
69.282	1.12420	40.019	-0.33		79.815	1.6595	69.998	-0.85	-0.17	44.742	2.7062	39.995	-0.13	-0.35	-0.07	
79.324	1.12450	45.001	-0.24		89.763	1.6604	80.004	-0.83	-0.16	47.303	2.7069	44.995	0.02	-0.26	0.04	
89.560	1.12481	50.003	-0.26		99.681	1.6613	90.011	-0.75	-0.11	49.863	2.7075	50.002	0.13	-0.21	0.10	
99.843	1.12512	55.004	-0.26		108.638	1.6621	99.065	-0.65	-0.04	52.414	2.7081	55.009	0.19	-0.18	0.12	
										54.912	2.7088	59.992	0.29	-0.11	0.17	
										59.861	2.7101	70.008	0.47	0.06	0.29	
										64.775	2.7114	80.001	0.53	0.17	0.33	
										69.647	2.7128	90.007	0.55	0.27	0.36	
										73.996	2.7140	99.008	0.54	0.35	0.38	

5. Experimental Results and Their Comparisons

5.1 Purity of the Sample

The used sample of the fluorocarbon refrigerant R 13 was extracted from the liquid phase of the bottle commercially manufactured by E.I. du Pont de Nemours Co. in the United State of America and was analyzed with a gas chromatograph as shown in Table 3. The averaged composition of five samplings of this refrigerant is listed in Table 3 as the result of using the column of 4 mm diameter and 4 m length at 70°C, the carrier gas of helium and one sampling amount of 2.03 cm³. Then, the molecular mass of the sample was determined to be 104.420.

5.2 Experimental Results

The P-V-T property measurements of 204 points were conducted along 15 isochores in the ranges of temperatures from 0°C to 99°C and pressures up to 100 kgf/cm² as shown in Table 4. Temperatures are shown based upon the International Practical Temperature Scale (1968). Pressures were obtained with corrections for the air buoyancy, the hydrostatic pressure of nitrogen and spindle oil and the gravitational acceleration.

5.3 Comparison of Experimental Results

In order to compare the experimental results shown in Table 4 with the results of studies by other investigators, the deviation of pressure between them was selected here instead of specific volume because the regions near the critical point and near the saturation boundary curve were included in the present study. Although it was desired to compare the observed results in Table 4 with those in Table 1 directly, it was impossible to compare them because the measured states were different from each other. Then they were compared, as shown in Table 4, with the equations of state formulated by Riedel, based upon his own results, by Albright et al., based upon their own results, and by Tanishita et al., based upon the results of Albright et al. and Michels et al. The significant region of each equation of state could be considered as corresponding to the experimental region used for its formulation, but each compared region was slightly extended from it as shown in Table 4 only for comparison. Moreover, other equations of state such as formulated by Rombusch, based upon the results of Riedel and Albright et al., and by Morsy, based upon the results of Michels et al., Riedel and Albright et al. are available, but they were not adopted in the present comparisons because the present purpose was comparison only with the experimental results shown in Table 1.

In comparison of the calculated pressure P_{Ri} from the equation of state by Riedel with the present observed pressure P , its deviation was defined as follows ;

$$\Delta P_{Ri} = \frac{P_{Ri} - P}{P} \times 100 \% \quad \text{..... (14)}$$

In the same way, ΔP_{Al} and ΔP_{Ta} were defined the same as for the equations of state correlated by Albright et al. and by Tanishita et al., respectively. In the compared re-

sults shown in Table 4, the present observed data show comparably good agreement with the equation of state correlated by Tanishita et al.⁽¹²⁾ excluding the region near the saturation boundary curve and a part of the liquid region, and the mean deviation between them is 0.25 % in the experimental region by Michels et al. Furthermore, any equation of state could not be well defined in the region near the saturation boundary curve and in the region from the critical point to the liquid state, which was revealed by the present study. The present results could be confirmed to be highly precise, because of their coincidence with the equations of state formulated by Albright et al. and by Tanishita et al. in the superheated vapour region. Especially allowing enough time before each measurement in order to keep the sample from condensing on the wall of the piezometer in this region and paying attention not to let it come too close to the saturation boundary curve, the present measurements were conducted along isochores in both superheated vapour region and wet vapour region. Such an experimental method was not adopted in the previous studies mentioned in Table 1.

Table 4-2 (Continued.)

Experimental Results			Comparison		
P	v	t	ΔP_{Ri}	ΔP_{Al}	ΔP_{Ta}
kgf/cm ²	cm ³ /g	°C	%	%	%
34.217	3.3580	22.484	0.60	0.38	0.23
34.433	3.3581	22.988	0.56	0.34	0.21
35.301	3.3584	25.012	0.41	0.22	0.15
36.113	3.3687	26.999	0.36	0.20	0.18
36.532	3.3588	28.003	0.32	0.16	0.17
36.938	3.3590	29.000	0.29	0.15	0.18
37.345	3.3591	29.994	0.26	0.13	0.18
39.374	3.3599	34.982	0.13	0.03	0.16
41.360	3.3606	39.996	0.10	0.03	0.20
43.309	3.3614	45.013	0.12	0.07	0.26
45.215	3.3622	50.001	0.18	0.13	0.34
47.118	3.3630	54.997	0.20	0.18	0.38
49.003	3.3638	60.000	0.24	0.23	0.42
52.714	3.3654	70.006	0.34	0.36	0.52
56.351	3.3670	79.998	0.45	0.51	0.63
59.990	3.3687	90.015	0.48	0.59	0.67
63.217	3.3702	98.998	0.50	0.67	0.72
27.375	4.9998	12.991	0.50	0.21	-0.07
27.627	5.0000	13.998	0.46	0.21	-0.05
27.878	5.0002	15.003	0.42	0.21	-0.03
29.157	5.0013	19.998	0.12	0.06	-0.09
30.388	5.0023	25.007	-0.02	0.04	-0.06
30.875	5.0028	26.995	-0.07	0.02	-0.05
31.127	5.0030	27.984	-0.13	-0.02	-0.09
31.369	5.0032	29.003	-0.14	-0.01	-0.07
31.611	5.0034	29.992	-0.17	-0.02	-0.08
32.807	5.0045	34.987	-0.25	-0.03	-0.06
33.997	5.0056	40.008	-0.31	-0.04	-0.06
35.181	5.0068	45.000	-0.39	-0.09	-0.09
36.341	5.0079	49.999	-0.42	-0.08	-0.09
37.498	5.0090	55.001	-0.46	-0.10	-0.10
38.605	5.0102	59.998	-0.38	-0.01	-0.02
40.874	5.0126	69.997	-0.43	-0.03	-0.05
43.125	5.0150	80.007	-0.49	-0.07	-0.09
45.345	5.0174	90.027	-0.54	-0.09	-0.12
47.324	5.0197	99.025	-0.57	-0.10	-0.12
16.947	9.8079	0.000	-0.78	0.06	0.02
17.503	9.8098	4.995	-0.93	0.01	-0.01
18.030	9.8118	9.980	-0.93	0.08	0.06
18.566	9.8139	14.988	-0.99	0.07	0.06
19.094	9.8159	19.967	-1.03	0.07	0.05
19.625	9.8180	24.997	-1.07	0.05	0.03
19.828	9.8188	26.992	-1.05	0.07	0.05
19.937	9.8193	27.996	-1.08	0.04	0.02
20.039	9.8197	28.996	-1.07	0.05	0.03
20.139	9.8201	30.006	-1.05	0.08	0.05
20.642	9.8222	35.000	-1.00	0.13	0.09
21.155	9.8244	39.982	-1.02	0.11	0.06
21.659	9.8266	45.008	-0.98	0.14	0.08
22.161	9.8288	50.005	-0.96	0.14	0.08
22.667	9.8310	55.003	-0.97	0.12	0.05
23.165	9.8332	60.012	-0.95	0.12	0.05
24.164	9.8378	70.012	-0.95	0.08	0.00
25.149	9.8424	80.016	-0.93	0.07	-0.02
26.106	9.8471	90.008	-0.84	0.12	0.05

6. Conclusions

A lot of the experimental points of P-V-T property values, in comparison with the previously conducted studies, were obtained in the range of temperatures from 0°C to 100°C with satisfaction as shown in Table 4. Most of experimental results previously conducted showed good agreement with each other in the superheated vapour region, but near the critical point the present results showed best agreement with the data obtained by Michels et al. in the previously reported studies. After these comparisons, the expected experimental accuracies and the absolute measurements of P-V-T property values were confirmed to have been established as planned. The precisions of the previously conducted studies were not enough to represent the states in the region revealed first by the present study, including near the saturation boundary curve. And it may be necessary to formulate an equation of state to represent satisfactorily the thermodynamic properties also taking the present results into account. It can be said that the equation of state correlated by Albright et al., which is widely used recently, does not represent satisfactorily the states near the critical point and in the liquid region and that an equation of state defined in the wide region is not formulated yet.

The critical state parameters by Michels et al. are quite different from experimental data obtained by other investigators^{(1),(2)}, although the P-V-T property values by Michels et al. agreed comparably well with the present results. Thus, it is necessary to conduct the saturation pressure measurements. Therefore, in the second report, the results of such measurements will be shown in detail using the experimental equipment mentioned here.

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