Table III. Enthalpy of Solution of H_2O in 9.93 *m* HCl at 40 °C

Sample wt, g	Cor temp rise, °C	−Enthalpy of soln, cal/sample	$-\Delta H_4$,[a] cal/mol
10.020 05	0.3551	254.4	457
11.010 88	0.3873	277.8	455
12.054 48	0.4242	305.7	456
13.021 93	0.4572	329.0	455
15.028 65	0.5268	380.1	456

[a] $\Delta H_4 = -458 + 0.20w$, $w = 13.144\ 93$, std dev = 1, $\Delta H_4 = -455$.

Table IV. Enthalpy of Solution of $NH_4H_2PO_4$ in 9.93 *m* HCl + Stoichiometric H_2O at 40 °C

Sample wt, g	Cor temp rise, °C	Enthalpy of soln, cal/sample	ΔH_5,[a] cal/mol
12.915 02	−0.8600	624.8	5565
13.310 58	−0.8879	646.3	5585
13.695 95	−0.9125	663.5	5572
14.119 04	−0.9392	684,3	5575
14.514 73	−0.9650	703.6	5576

[a] $\Delta H_5 = 5534 + 2.95w$, $w = 13.316\ 08$, std dev = 7, $\Delta H_5 = 5573$.

equations of the enthalpies of solution as a function of sample weight, *w*, were fitted to the observed values by the "least-squares" method. These equations were solved where *w* was the average weight of $(NH_4)_5P_3O_{10}\cdot H_2O$ or the stoichiometric amount of $H_3PO_4\cdot 16.26H_2O$, $NH_4H_2PO_4$, or H_2O corresponding to that weight. The equations along with the standard deviations and the values of ΔH_2, ΔH_3, ΔH_4, and ΔH_5 for the specified values of *w* also are listed in Tables I–IV. Substitution of these calculated values of the enthalpies of solution in eq 6 gives −31 592 ± 66 cal (standard deviation) for the enthalpy of reaction 1 at 40 °C. This value was adjusted by 242 cal to give −31 350 ± 66 cal for the enthalpy of reaction 1 at 25 °C according to the equation

$$\Delta H_1(25\ ^\circ C) = \Delta H_1(40\ ^\circ C) + \int_{40\ ^\circ C}^{25\ ^\circ C} \Delta C_P\ dT \qquad (7)$$

through use of polynomial equations for determining differences between the heat capacities of the products and the reactants. The heat capacity equations were derived from the data of Osborne et al. for water (*8*), of Stephenson and Zettlemoyer for $NH_4H_2PO_4$ (*9*), of Egan et al. for phosphoric acid solutions (*2*), and of Luff and Williard for $(NH_4)_5P_3O_{10}\cdot H_2O$ (*6*).

The data of Egan and Luff (*1*) were used to determine ΔH_8 and ΔH_9, the enthalpies of reactions 8 and 9 at 25 °C, as −436

$$H_3PO_4\cdot 16.26H_2O + 84.24H_2O = H_3PO_4\cdot 100.5H_2O \qquad (8)$$

$$H_3PO_4\cdot 100H_2O + 0.5H_2O = H_3PO_4\cdot 100.5H_2O \qquad (9)$$

and −1 cal, respectively. Subtracting twice the difference between ΔH_8 and ΔH_9 from ΔH_1 at 25 °C gives ΔH_{10}, the enthalpy of reaction 10 at 25 °C, as −30 480 cal.

$$(NH_4)_5P_3O_{10}\cdot H_2O + 2(H_3PO_4 \text{ in } 100H_2O) + H_2O = 5NH_4H_2PO_4 \qquad (10)$$

The standard enthalpies of formation of $NH_4H_2PO_4$(c), H_2O(l), and H_3PO_4 in $100H_2O$ are −345.38, −68.315, and −308.176 kcal/mol, respectively (*7*). Substituting these enthalpies of formation and the enthalpy of reaction 10 in the equation

$$\Delta H_f^\circ((NH_4)_5P_3O_{10}\cdot H_2O) = 5(\Delta H_f^\circ(NH_4H_2PO_4)) - 2(\Delta H_f^\circ(H_3PO_4 \text{ in } 100H_2O)) - \Delta H_f^\circ(H_2O) - \Delta H_{10} \qquad (11)$$

gives −1011.8 kcal/mol as the standard enthalpy of formation of $(NH_4)_5P_3O_{10}\cdot H_2O$.

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Pressure–Volume–Temperature Relationships of Several Polar Liquids

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The specific volumes of liquid CCl_2F_2, $CHClF_2$, CH_3Cl, CH_3I, CH_3Br, C_2H_5Br, and CH_3COOCH_3 have been measured at several temperatures from −20 to +40 °C and at pressures from the saturated vapor pressures to near 1600 atm with an accuracy better than 0.13%. The data were fitted to the Tait equation of state at each temperature with a maximum deviation of 0.2%.

An accurate knowledge of the specific volumes of polar liquids under high pressures is important in the interpretation of the polarity effect on the compressibility in connection with the elucidation of the internal structure problems of polar liquids. Most studies of *P–V–T* relationships have been made on nonpolar liquids, and very few measurements are available on polar liquids. The purpose of the present work is, therefore, to obtain the specific volumes of polar liquids. The measurements were made at temperatures from −20 to +40 °C, and at pressures up to near 1600 atm.

Experimental Section

Materials. The origin and purity of samples are recorded as follows: CCl_2F_2 and $CHClF_2$, Daikin Kogyo Co., Ltd., Japan, 99.9%; CH_3Cl, Matheson Gas Products, a Division of Will Ross, Inc., 99.5%; CH_3I, Kokusan Kagaku Co., Ltd., Japan, 98.2%;

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Table I. Experimental Specific Volumes

Compound	Pressure, atm	Specific volume, cm^3/g				Ref of vol data
		−20.00 °C	0.00 °C	20.00 °C	40.00 °C	
CCl_2F_2	(P_0)	0.685 46 (1.5)[a]	0.715 92 (3.0)[a]	0.752 44 (5.6)[a]	0.798 02 (9.5)[a]	3
	95.3			0.728 37	0.761 82	
	283.1	0.652 73	0.671 72	0.694 67	0.718 19	
	469.5	0.639 15	0.654 94	0.673 12	0.692 97	
	654.9	0.625 81	0.640 73	0.656 61	0.674 10	
	841.4	0.616 40	0.629 08	0.643 10	0.658 06	
	1027.9	0.607 75	0.619 66	0.632 67	0.645 40	
	1214.1	0.600 08	0.610 26	0.622 60	0.634 66	
	1400.5	0.592 90	0.603 50	0.614 27	0.626 08	
	1587.2	0.586 81	0.597 87	0.607 83	0.617 87	
$CHClF_2$	(P_0)	0.742 74 (2.4)[a]	0.780 35 (4.9)[a]	0.826 46 (8.0)[a]	0.886 06 (15.1)[a]	8
	95.4			0.800 36	0.847 02	
	283.1	0.709 79	0.735 19	0.762 02	0.794 50	
	468.6	0.693 73	0.712 86	0.736 69	0.763 25	
	651.2	0.679 16	0.698 09	0.716 83	0.740 39	
	836.9	0.669 00	0.686 79	0.702 69	0.722 34	
	1022.4	0.658 75	0.675 96	0.690 51	0.706 68	
	1206.5	0.652 13	0.664 38	0.679 53	0.695 00	
	1390.7	0.643 33	0.656 13	0.669 55	0.684 24	
	1574.7	0.636 38	0.649 07	0.659 98	0.673 90	
CH_3Cl	(P_0)	0.99 72 (1.2)[a]	1.03 43 (2.5)[a]	1.07 75 (4.8)[a]	1.12 62 (8.3)[a]	
	283.1	0.966 55	0.995 96	1.029 6	1.064 4	
	468.6	0.950 16	0.976 24	1.004 3	1.035 2	
	651.2	0.936 60	0.959 74	0.985 01	1.011 9	
	836.9	0.924 42	0.945 16	0.968 27	0.992 89	
	1022.4	0.913 16	0.932 97	0.954 21	0.976 60	
	1206.5	0.904 79	0.922 12	0.942 26	0.962 66	
	1390.7	0.894 28	0.912 06	0.931 25	0.950 14	
	1574.2	0.886 42	0.903 01	0.920 64	0.939 62	
CH_3I	(P_0)	0.417 73 (0.1)[a]	0.427 92 (0.2)[a]	0.438 44 (0.4)[a]	0.449 90 (0.9)[a]	
	283.1	0.409 55	0.418 31	0.427 60	0.436 64	
	468.6	0.405 26	0.413 30	0.421 36	0.429 96	
	651.2	0.401 36	0.408 84	0.416 19	0.424 25	
	836.9	0.397 78	0.404 50	0.411 92	0.418 97	
	1022.4	0.394 33	0.400 91	0.407 72	0.414 17	
	1206.5	0.391 27	0.397 59	0.403 77	0.410 07	
	1390.7	0.388 33	0.394 22	0.400 44	0.406 40	
	1574.2	0.385 69	0.391 28	0.397 24	0.402 86	
CH_3Br	(P_0)	0.560 60 (0.4)[a]	0.577 47 (0.9)[a]	0.595 92 (1.8)[a]	0.616 28 (3.3)[a]	
	283.1	0.547 66	0.560 73	0.575 40	0.590 70	
	468.6	0.540 28	0.552 70	0.565 61	0.579 49	
	651.2	0.534 07	0.545 53	0.557 63	0.570 35	
	836.9	0.528 48	0.538 89	0.550 01	0.561 48	
	1022.4	0.523 25	0.533 01	0.543 66	0.554 01	
	1206.5	0.519 00	0.527 71	0.537 77	0.547 34	
	1390.7	0.514 51	0.522 74	0.532 16	0.541 33	
	1574.2	0.510 57	0.518 28	0.526 49	0.535 36	
C_2H_5Br	(P_0)	0.648 45 (0.1)[a]	0.666 43 (0.2)[a]	0.685 23 (0.5)[a]	0.705 41 (1.1)[a]	
	194	0.638 14	0.653 73	0.669 71	0.685 95	
	388	0.629 67	0.643 82	0.657 38	0.672 95	
	581	0.622 34	0.634 79	0.647 26	0.661 83	
	774	0.615 88	0.627 13	0.638 50	0.651 28	
	968	0.609 25	0.620 10	0.630 46	0.642 49	
	1161	0.604 19	0.613 79	0.623 53	0.634 47	
	1354	0.598 74	0.608 29	0.616 80	0.627 49	
	1547	0.594 42	0.603 00	0.611 34	0.621 69	
CH_3COOCH_3	(P_0)	1.017 5 (0.0_3)[a]	1.043 0 (0.1)[a]	1.072 7 (0.2)[a]	1.105 6 (0.5)[a]	
	194	1.002 8	1.025 9	1.052 1	1.079 5	
	388	0.990 1	1.011 5	1.035 0	1.060 0	
	581	0.978 5	0.998 5	1.020 4	1.043 2	
	774	0.968 5	0.988 0	1.008 1	1.028 2	
	968	0.959 7	0.979 1	0.997 1	1.015 1	
	1161	0.952 0	0.969 6	0.987 0	1.004 6	
	1354	0.944 6	0.961 2	0.978 1	0.994 9	
	1547	0.937 7	0.954 4	0.970 3	0.986 1	

[a] Saturated vapor pressure.

CH_3Br and C_2H_5Br, Tokyo Kasei Kogyo Co., Ltd., Japan, 99.8 and 99%, respectively; CH_3COOCH_3, Nakarai Chemicals, Ltd., Japan, 97.0%. These samples were subjected to further purification by distillation before use, and the reagent grade mercury was purified by a modified automatic mercury washer (*1*).

Apparatus and Method. The method used in this study was similar to one presented earlier (*10*), but the volume changes of liquids at high pressures were measured by a modified glass piezometer as shown in Figure 1. The glass piezometer used previously had the fault that air may be introduced into the piezometer during the removal of it from a vacuum line. The

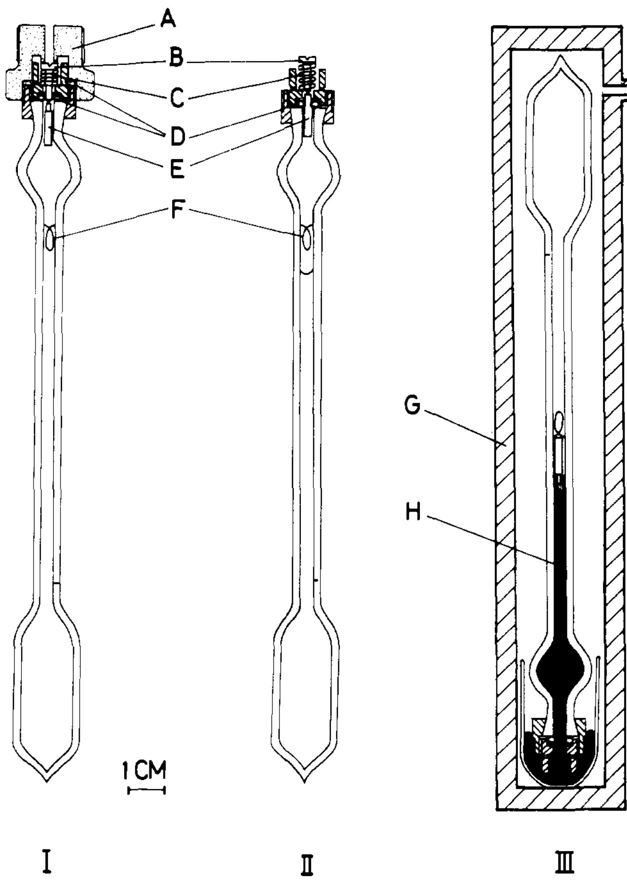

Figure 1. Glass piezometers: A, joint in vacuum line; B, screw; C, spring; D, O-ring; E, float; F, glass indicator; G, pressure vessel; H, mercury.

joint of this piezometer was modified for sampling in vacuo. I in Figure 1 indicates the piezometer under its connection with the vacuum line. As the piezometer filled with the liquid is removed from the line, the float (E) and the screw (B) are raised by the action of spring (C), and at last the float is tightly contacted with the O-ring (D) as shown in Figure 1, II. The specific volumes of liquids at high pressures are determined in a similar manner reported earlier after removing the screw and the spring from the float (see III in Figure 1). The saturated liquid volumes except for CCl_2F_2 and $CHClF_2$ were determined directly using the same piezometer placed in the thermostat by the usual method.

The volume data for H_2O at 25 °C and up to 1000 atm show agreement with the data of the literature (*9*) within the limits of accuracy of measurement (0.06%).

Result and Discussion

The specific volumes at four temperatures, −20, 0, 20, and 40 °C, were determined from the saturated vapor pressures to near 1600 atm. The specific volumes for seven liquids are presented in Table I. The maximum deviation from the smooth curves is 0.13% over the whole range of measurements. There are sources of *P–V–T* data for $CHClF_2$ (*13*), CH_3Cl (*7*), CH_3I (*5*), and C_2H_5Br (*2*, *4*, *12*), but the direct comparison of the present results with those is impossible because temperatures and pressures differ.

Many *P–V–T* data for liquids have been represented by the Tait equation (*6*), which may be written in the form

$$V_P = V_0(1 - C \ln [(B + P)/(B + P_0)])$$

The Tait parameters *B* and *C* were computed for each isotherm by a least-squares method fit to the *P–V–T* data and listed in Table II. The specific volume at the saturated vapor pressure, P_0, was chosen as V_0 in this evaluation. It has previously been reported (*11*) that the *C* value for NH_3 became constant in the lower temperatures and decreased in the neighborhood of the critical temperature. The *C* values for other liquids, as well as NH_3, were regarded as constant at experimental temperatures far from the critical temperature. Also, the average and the maximum deviation of the calculated values by the equation against the experimental data are indicated in Table II.

Table II. Tait Parameters, *B* and *C*

Compound	*T*, °C	*B*, atm	*C*	Av dev,[a] %	Max dev, %
CCl_2F_2	−20.00	394	0.0888	0.07	0.19
	0.00	285		0.07	0.17
	20.00	197		0.04	0.10
	40.00	125		0.08	−0.20
$CHClF_2$	−20.00	460	0.0963	0.10	0.17
	0.00	325		0.12	−0.21
	20.00	214		0.08	−0.19
	40.00	126		0.06	0.13
CH_3Cl	−20.00	791	0.1014	0.03	−0.13
	0.00	626		0.02	0.05
	20.00	485		0.05	−0.12
	40.00	368		0.04	−0.09
CH_3I	−20.00	1275	0.0953	0.02	0.05
	0.00	1085		0.03	−0.05
	20.00	936		0.03	±0.05
	40.00	786		0.02	−0.04
CH_3Br	−20.00	1020	0.0956	0.02	0.04
	0.00	822		0.03	−0.08
	20.00	670		0.05	−0.13
	40.00	536		0.07	−0.16
C_2H_5Br	−20.00	1085	0.0942	0.03	0.05
	0.00	887		0.01	−0.05
	20.00	722		0.02	−0.05
	40.00	610		0.06	−0.18
CH_3COOCH_3	−20.00	1063	0.0874	0.02	−0.04
	0.00	938		0.03	0.07
	20.00	779		0.02	±0.02
	40.00	631		0.03	±0.07

[a] Average deviation = $\Sigma_{n=1}{}^{n}(|(V_{calcd} - V_{exptl})/V_{exptl}| \times 100)/n$. n = number of data. V_{calcd}, V_{exptl} = specific volumes calculated by the Tait equation with parameters *B* and *C* in Table II and experimental values, respectively.

Glossary

B, *C*	Tait equation parameters
P	pressure, atm
P_0	saturated vapor pressure, atm
V_0, V_P	specific volumes at pressures, P_0 and *P* atm, respectively, cm^3/g

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