# Thermodynamic Properties of Difluoromethane 

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#### Abstract

The pressure-volume-temperature (PVT) behavior of difluoromethane (R32) has been measured using a vibrating tube densimeter apparatus and a Burnett/isochoric apparatus. Liquid PVT data from the vibrating tube densimeter ranged in temperature from 242 to 348 K with a pressure range of $2000-6500 \mathrm{kPa}$. Data from the Burnett apparatus consisted of 11 isochores for the gas and supercritical fluid, along with vapor pressure measurements. The temperature ranged from 268 to 373 K . The gas-phase data are correlated with a virial equation of state. The compressed liquid data are fit with an abbreviated form of the modified Benedict-Webb-Rubin (mBWR) equation. A table of thermodynamic properties is presented for the saturated liquid and vapor states.


## Introduction

Chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) have been implicated as the cause of ozone depletion in the stratosphere (1). The Montreal Protocol prescribes a schedule for phasing out the production of CFCs and HCFCs around the world. The phasing out of environmentally harmful refrigerants forces us to consider alternatives that can perform as well or better than CFCs or HCFCs. Mixtures containing the alternative refrigerant difluoromethane (R32) are being considered as replacements for chlorodifluoromethane (R22), and for the azeotropic mixture (R502) of R22 and chloropentafluoroethane (R115). Calculation of the thermophysical properties of mixtures requires reliable data for the properties of the pure components. Difluoromethane is an especially interesting fluid because of its large dipole moment (1.98 D) (2). Therefore, it is important to know the thermophysical properties of pure R32 accurately in order that the properties of its mixtures can be accurately modeled. We have measured gas-phase and liquid-phase pressure-volume-temperature (PVT) data as well as vapor pressures for R32.

## Apparatus and Procedure

Difluoromethane (R32) was supplied by E. I. duPont deNemours, Inc. (3), with a stated purity of $99.99 \mathrm{wt} \%$. Gas chromatographic analysis of the sample was consistent with the manufacturer's analysis (4). No further analysis or purification of the sample was conducted.
A. Burnett Apparatus. The Burnett apparatus has been thoroughly documented in earlier publications (5-7), and is only briefly described here. The sample cell of the Burnett apparatus was composed of a heavy-walled nickel vessel with two gold-plated inner chambers. The ratio of the volumes of the inner chambers was $1.78206 \pm 0.00007(1 \sigma)$. The chambers were connected to a sensitive, diaphragm-type pressure transducer (5) through a small tube. The transducer separated the sample from an external, argon-filled manifold in which the argon pressure was balanced against the sample pressure using an automated, piston-type gas injector. The manifold pressure was measured with a Ruska quartz spiral bourdon pressure gauge and a Ruska dead weight gauge (3). Pressure could be measured with an uncertainty of $\pm 0.01$ kPa . The Burnett apparatus was mounted in a circulating thermostated oil bath. The temperature of the bath was

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measured with a platinum resistance thermometer (PRT) with an uncertainty of $\pm 0.002 \mathrm{~K}$. A feedback circuit using the thermometer, an ac bridge, a signal conditioner, and a programmable power supply controlled the temperature of the oil bath. A second PRT measured the temperature of the sample vessel. In the automatic mode, which was used for data acquisition on isochores, a microcomputer set the desired temperature, monitored equilibration, and measured temperature and pressure. The automatic mode was also used for measuring vapor pressures. For the Burnett expansion data on the isotherms at 373.124 K , the pressure was measured with a manually operated dead weight pressure balance. The uncertainty of the dead weight gauge pressure measurements was on the order of $\pm 0.01 \mathrm{kPa}$. The Burnett expansion mode was used to determine the density as a function of pressure on the isotherm 373.124 K . Thereafter, the pressure was measured as a function of temperature on isochores. All temperatures are given on the ITS-90 scale.
B. Densimeter. A stainless steel vibrating tube densimeter was used to measure compressed liquid densities. The apparatus has a liquid volume of $3.5 \mathrm{~cm}^{3}$; the vibrating tube is made of stainless steel with a wall thickness of 0.3 mm and an inside diameter of 2.4 mm . The densimeter apparatus is accurate to $\pm 0.0005 \mathrm{~g} / \mathrm{cm}^{3}$. The densimeter has been thoroughly discussed in an earlier publication (8); a brief description is given here. The temperature of the densimeter was regulated by a thermostated circulating bath. A water/ ethylene glycol solution was circulated through a heat exchanger surrounding the vibrating tube at temperatures above 273.15 K . At temperatures below 273.15 K , methanol was used in the circulating bath. The heat exchanger surrounding the vibrating tube was enclosed in a temperaturecontrolled air bath maintained at the same temperature. A platinum resistance thermometer monitored the temperature of the liquid exiting the heat exchanger. Temperatures (ITS90 ) are accurate to $\pm 0.01 \mathrm{~K}$.

A manifold located outside the air bath consisted of mercury reservoirs and a mercury manometer/separator. A glass capillary in the manometer/separator allowed us to locate the mercury level in the manometer, which separated the refrigerant sample from pressurizing argon gas. The pressure of the system was maintained above the vapor pressure of R32 in the vibrating tube at temperatures above ambient. When the vibrating tube was below room temperature, the lower pressure limit was determined by the vapor pressure of R32 at the temperature of the manometer. The pressure

Table 1. Burnett/Isotherm Data for $\mathbf{R 3 2}$ (Difluoromethane)

| $T / K$ | $\rho /\left(\mathrm{mol}^{\cdot} \cdot \mathrm{dm}^{-3}\right)$ | $P / \mathrm{kPa}$ | $T / K$ | $\rho /\left(\mathrm{mol}^{2} \cdot \mathrm{dm}^{-3}\right)$ | $P / \mathrm{kPa}$ |
| :---: | :---: | ---: | :---: | :---: | ---: |
| 373.130 | 2.55830 | 5258.13 | 373.128 | 0.07988 | 244.57 |
| 373.130 | 2.55830 | 5257.97 | 373.135 | 10.60310 | 9773.46 |
| 373.130 | 1.43561 | 3520.45 | 373.136 | 5.94990 | 7727.70 |
| 373.129 | 1.43561 | 3520.85 | 373.134 | 3.33880 | 6105.08 |
| 373.131 | 0.80559 | 2188.83 | 373.137 | 1.87350 | 4283.26 |
| 373.139 | 0.80559 | 2188.82 | 373.133 | 1.05133 | 2742.89 |
| 373.134 | 0.45206 | 1301.85 | 373.132 | 0.589 | 96 |
| 373.133 | 0.45206 | 1302.05 | 373.129 | 0.33106 | 972.58 |
| 373.133 | 0.25367 | 754.91 | 373.131 | 0.18577 | 559.05 |
| 373.132 | 0.25367 | 755.16 | 373.130 | 0.10425 | 317.92 |
| 373.130 | 0.14235 | 431.51 |  |  |  |

of the argon was monitored with a quartz pressure transducer. The pressures were accurate to $\pm 0.5 \mathrm{kPa}$. Before a sample was loaded, the apparatus was rinsed with ethanol and then acetone to remove any residue from previous experiments. Once the apparatus was filled, compressed liquid densities for R32 were measured. The resulting measurements were recorded by computer. The temperature and pressure of the densimeter were monitored by the computer and changed after each measurement was completed.

## Results

A. Burnett Measurements. Burnett expansion measurements were made at 373.124 K . Sixteen pressures were measured in two separate runs totaling 14 expansions ranging in density from 0.12 to $10.6 \mathrm{~mol} / \mathrm{dm}^{3}$. Results are given in Table 1. After the pressure-density relationship was established on the 373.124 K isotherm, data were collected on isochores. A total of 146 data were collected along 11 isochores between the temperatures of 268 and 373 K . The pressure measurement for each isochore at 373.124 K was used to determine the density. A temperature correction to the densities was made to compensate for the thermal expansion of the sample cell. The Burnett expansion data at 373.124 K with densities less than $1.05 \mathrm{~mol} / \mathrm{dm}^{3}(2.74 \mathrm{MPa})$ were analyzed with a two-term virial equation. The standard deviation of the fit was 0.19 kPa , and the virial coefficients had the values $B=-0.16436 \pm 0.00050 \mathrm{dm}^{3} / \mathrm{mol}$ and $C=$ $0.01239 \pm 0.00075 \mathrm{dm}^{6} / \mathrm{mol}^{2}$. The densities for higher pressure data were calculated using the cell constant, and then all of the data were fit with a polynomial so that they could be interpolated to calculate the densities where the isochores intersected the Burnett isotherm. Results of the isochoric measurements are given in Table 2 and are reported in the same order as the data were collected.

All of the data having densities less than $2.56 \mathrm{~mol} / \mathrm{dm}^{3}$ were represented with a three-term virial surface:

$$
\begin{align*}
& \frac{P V}{R T}=1+\frac{B}{V}+\frac{C}{V^{2}}+\frac{D}{V^{3}}  \tag{1}\\
& B=B_{0}+B_{1} T_{\mathrm{r}}^{-1}+B_{2} T_{\mathrm{r}}^{-2}+B_{3} T_{\mathrm{r}}^{-3}+B_{4} T_{\mathrm{r}}^{-6}+B_{5} T_{\mathrm{r}}^{-8} \\
& C=C_{0} T_{\mathrm{r}}^{-5}+C_{1} T_{\mathrm{r}}^{-6}  \tag{2}\\
& D=D_{0}+D_{1} T_{\mathrm{r}} \\
& B_{0}=0.37371454 \\
& C_{0}=0.05386069 \\
& B_{1}=-0.92907548 \\
& C_{1}=-0.0359041 \\
& B_{2}=0.6031928428 \\
& D_{0}=-0.0026902 \\
& B_{3}=-0.22325804 \quad D_{1}=0.00198168 \\
& B_{4}=-0.02009819 \quad T_{c}=351.36 \mathrm{~K} \\
& B_{5}=0.001029230 \\
& T_{r}=T / T_{c} \\
& R=0.0831445 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}
\end{align*}
$$

$\mathrm{dm}^{3} / \mathrm{mol}$ and $0.0143 \mathrm{dm}^{6} / \mathrm{mol}^{2}$, respectively. To improve the reliability of the surface at low temperatures, we included in the fit, with a low weight, the values for the second virial coefficient estimated by Weber and Goodwin (9). A comparison of this surface with our own PVT data and with those of Qian et al. (10) in this density range is shown in Figure 1. The data of Qian et al. (10) deviate systematically from the surface by an average of $0.25 \%$. Most of our data are represented well by the surface; however, the two lowest density isochores also have rather large positive systematic deviations at low temperatures. The isochores having densities of 0.14 and $0.25 \mathrm{~mol} / \mathrm{dm}^{3}$ have average deviations of $0.28 \%$ and $0.12 \%$, respectively, at temperatures below 320 K . The remainder of our dataare fit with a standard deviation of $0.037 \%$.

The sign of the deviations of the lowest density isochores is such that they could be caused by physical adsorption of sample on the walls of the cell. Such behavior would not be surprising in view of the large dipole moment of the R32 molecules. No reasonable adjustment of the virial coefficients could reduce these deviations. For this reason, we believe that the surface given by eq 1 provides a better estimate of the vapor densities of R32 than either our own data or those from ref 10 .

The Burnett apparatus was also used to measure vapor pressures. Pressure measurements on isochores inside the two-phase region yielded vapor pressures. The 18 vapor pressure measurements given in Table 3 were collected in the range $268-348 \mathrm{~K}$. These data were measured on the isochores having nominal densities of 10.6 and $2.56 \mathrm{~mol} / \mathrm{dm}^{3}$. The good agreement between the data at two very different densities is consistent with the high purity of the sample. The present vapor pressure data were combined with the ebulliometric data of Weber and Goodwin (9) which range in temperature from 208 to 237 K and also with the unpublished results of Weber and Silva (11) between 235 and 265 K . The combined data set was correlated with the following equation:

$$
\begin{equation*}
\ln P=\ln P_{\mathrm{c}}+\left(T_{\mathrm{c}} / T\right)\left[x_{1} \tau+x_{2} \tau^{1.5}+x_{3} \tau^{2.5}+x_{\mathrm{r}} \tau^{5}\right] \tag{3}
\end{equation*}
$$

$$
\begin{array}{ll}
x_{1}=-7.4595986 & \tau=1-T / T_{\mathrm{c}} \\
x_{2}=1.7340320 & P_{\mathrm{c}}=5792.7 \mathrm{kPa} \\
x_{3}=-1.9941494 & T_{\mathrm{c}}=351.36 \mathrm{~K} \\
x_{4}=-2.5329263 &
\end{array}
$$

Equation 3 fits the data with a relative standard deviation of $0.028 \%$ in pressure. The critical temperature was fixed at the value measured by Schmidt and Moldover (12) (351.36 K ). The critical pressure, which was an adjustable parameter in the correlation, was found to be 5792.7 kPa with an uncertainty of $\pm 2.4 \mathrm{kPa}$. Figure 2 shows the relative deviation of the data in Table 3 from eq 3 as well as the data of Weber and Goodwin (9), Malbrunot et al. (13), and Weber and Silva (11).

The saturated vapor densities were determined by substituting the equilibrium vapor pressure calculated from eq 3 and the temperature into the virial equation of state, eq 1 . The saturated vapor densities and pressures are listed in Table 4.
B. Densimeter Measurements. Compressed-liquiddensity measurements for R32 were made along 22 isotherms at pressures from 2000 to 6500 kPa . The densities, listed in Table 5 , span values from 12 to $22 \mathrm{~mol} / \mathrm{dm}^{3}$. Isotherms of the compressed liquid were extrapolated to the saturation boundary using the Tait (14) equation to determine the saturation densities. Coefficients for the Tait extrapolations can be furnished upon request. Above room temperature the measurements at the lowest pressure were close to the saturation boundary; however, at the lowest temperature,

Table 2. Burnett/Isochoric PVT Data for R32 (Difluoromethane)

| T/K | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{-3}\right)$ | $\mathrm{P} / \mathrm{kPa}$ | T/K | $\rho /\left(\right.$ mol $\cdot$ dm ${ }^{-8}$ ) | $\mathrm{P} / \mathrm{kPa}$ | T/K | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{-3}\right)$ | $\mathrm{P} / \mathrm{kPa}$ | T/K | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{-3}\right)$ | $\mathrm{P} / \mathrm{kPa}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 338.104 | 2.56101 | 4090.31 | 363.120 | 0.45225 | 1259.9 | 283.164 | 0.25463 | 547.224 | 353.111 | 5.95490 | 5930.64 |
| 343.118 | 2.56047 | 4265.14 | 358.128 | 0.45234 | 1238.99 | 278.129 | 0.25468 | 534.892 | 358.095 | 5.95366 | 6387.23 |
| 348.125 | 2.55994 | 4436.54 | 353.130 | 0.45244 | 1217.88 | 273.143 | 0.25474 | 522.559 | 363.135 | 5.95240 | 6840.92 |
| 353.095 | 2.55940 | 4603.931 | 348.152 | 0.45253 | 1196.78 | 268.916 | 0.25478 | 512.057 | 368.142 | 5.95115 | 7286.73 |
| 358.084 | 2.55887 | 4769.34 | 343.144 | 0.45262 | 1175.37 | 268.834 | 0.25478 | 511.840 | 373.145 | 5.94989 | 7728.75 |
| 363.143 | 2.55832 | 4934.86 | 338.128 | 0.45272 | 1154.47 | 368.109 | 0.14238 | 425.416 | 343.151 | 3.34300 | 4724.23 |
| 368.129 | 2.55779 | 5096.09 | 333.118 | 0.45282 | 1132.15 | 363.120 | 0.14241 | 419.294 | 348.130 | 3.34231 | 4964.34 |
| 373.143 | 2.55725 | 5256.39 | 328.073 | 0.45291 | 1110.44 | 358.130 | 0.14244 | 413.125 | 353.117 | 3.34061 | 5199.12 |
| 363.119 | 2.55832 | 4934.19 | 323.186 | 0.45300 | 1089.37 | 358.130 | 0.14244 | 413.125 | 353.117 | 3.34161 | 5199.12 |
| 363.129 | 2.55832 | 4934.42 | 318.156 | 0.45310 | 1067.23 | 353.126 | 0.14250 | 400.884 | 363.135 | 3.34020 | 5658.67 |
| 368.103 | 1.43591 | 3441.3 | 313.101 | 0.45320 | 1044.79 | 348.126 | 0.14250 | 400.884 | 363.135 | 3.34020 | 5658.67 |
| 363.121 | 1.43621 | 3361.93 | 308.158 | 0.45329 | 1022.66 | 343.157 | 0.14253 | 394.770 | 368.142 | 3.33950 | 5883.66 |
| 358.124 | 1.43651 | 3281.77 | 303.140 | 0.45338 | 999.969 | 338.080 | 0.14256 | 388.492 | 373.086 | 3.33881 | 6103.12 |
| 353.128 | 1.43682 | 3200.72 | 298.125 | 0.45348 | 977.073 | 333.070 | 0.14259 | 382.250 | 328.222 | 1.87703 | 3255.45 |
| 348.159 | 1.43712 | 3119.25 | 293.172 | 0.45357 | 954.2209 | 323.130 | 0.14262 | 376.086 | 333.082 | 1.87665 | 3373.69 |
| 343.139 | 1.43742 | 3036.07 | 288.132 | 0.45367 | 930.6519 | 323.130 | 0.14265 | 369.874 | 338.103 | 1.87626 | 3493.40 |
| 338.132 | 1.43772 | 2952.06 | 283.166 | 0.45376 | 907.07 | 323.175 | 0.14265 | 369.837 | 343.124 | 1.87586 | 3611.04 |
| 333.119 | 1.43802 | 2866.77 | 323.155 | 0.45300 | 1089.22 | 323.148 | 0.14265 | 369.777 | 348.141 | 1.87547 | 3726.92 |
| 323.130 | 1.43863 | 2692.81 | 278.145 | 0.45386 | 882.259 | 323.155 | 0.14265 | 369.793 | 353.120 | 1.87507 | 3840.35 |
| 318.099 | 1.43893 | 2602.63 | 281.187 | 0.45380 | 897.138 | 323.150 | 0.14265 | 369.831 | 358.145 | 1.87468 | 3953.46 |
| 372.446 | 1.43565 | 3509.56 | 368.110 | 0.25373 | 743.814 | 318.110 | 0.14268 | 363.448 | 363.133 | 1.87429 | 4064.42 |
| 372.442 | 1.43565 | 3509.64 | 363.170 | 0.25378 | 732.777 | 313.112 | 0.14271 | 357.156 | 368.140 | 1.87389 | 4174.68 |
| 368.109 | 0.80576 | 2149.14 | 358.133 | 0.25383 | 721.402 | 308.155 | 0.14274 | 350.916 | 373.142 | 1.87350 | 4283.79 |
| 363.115 | 0.80593 | 2108.95 | 353.133 | 0.25389 | 710.161 | 303.133 | 0.14277 | 344.557 | 308.164 | 1.05420 | 1994.00 |
| 358.120 | 0.80610 | 2068.62 | 348.155 | 0.25394 | 698.929 | 298.176 | 0.14280 | 338.316 | 313.138 | 1.05398 | 2055.91 |
| 353.127 | 0.80626 | 2027.99 | 343.140 | 0.25399 | 687.532 | 293.144 | 0.14283 | 331.853 | 318.131 | 1.05376 | 2116.95 |
| 348.163 | 0.80643 | 1987.31 | 338.129 | 0.25405 | 676.108 | 288.154 | 0.14286 | 325.478 | 323.145 | 1.05354 | 2177.34 |
| 343.100 | 0.80660 | 1945.35 | 333.121 | 0.25410 | 664.666 | 283.161 | 0.14289 | 319.180 | 328.145 | 1.05332 | 2236.59 |
| 338.134 | 0.80677 | 1904.01 | 328.063 | 0.25415 | 653.053 | 278.146 | 0.14292 | 312.783 | 333.148 | 1.05310 | 2295.19 |
| 333.165 | 0.80694 | 1862.22 | 322.930 | 0.25421 | 641.187 | 273.158 | 0.14295 | 306.300 | 338.150 | 1.05287 | 2353.09 |
| 328.057 | 0.80611 | 1818.84 | 318.138 | 0.25426 | 629.987 | 268.530 | 0.14297 | 300.240 | 343.109 | 1.05266 | 2409.88 |
| 323.135 | 0.80728 | 1776.45 | 313.161 | 0.25431 | 618.430 | 268.133 | 0.14298 | 299.730 | 348.136 | 1.05243 | 2466.83 |
| 318.143 | 0.80745 | 1733.15 | 308.156 | 0.25437 | 606.736 | 353.110 | 10.6083 | 6145.060 | 353.108 | 1.05221 | 2522.64 |
| 313.168 | 0.80762 | 1689.48 | 303.138 | 0.25442 | 594.911 | 358.089 | 10.6061 | 7014.010 | 358.138 | 1.05199 | 2578.58 |
| 308.177 | 0.80778 | 1645.0 | 298.122 | 0.25447 | 583.077 | 363.132 | 10.6038 | 7921.320 | 363.131 | 1.05177 | 2633.75 |
| 323.084 | 0.80728 | 1776.22 | 293.167 | 0.25453 | 571.318 | 368.149 | 10.6016 | 8842.059 | 368.139 | 1.05155 | 2688.66 |
| 368.106 | 0.45215 | 1280.8 | 288.191 | 0.25458 | 559.386 | 373.131 | 10.5994 | 9769.821 | 373.141 | 1.05133 | 2743.05 |



Figure 1. Density difference from eq 1 of this work ( $\bullet$ ) and the data of Qian et al. (10) (ם).

Table 3. Burnett Vapor Pressures for R32

| $T / \mathrm{K}$ | $P / \mathrm{kPa}$ | $T / \mathrm{K}$ | $P / \mathrm{kPa}$ |
| :---: | ---: | :---: | :---: |
| 268.154 | 690.56 | 313.122 | 2476.63 |
| 273.163 | 813.62 | 318.154 | 2794.65 |
| 278.137 | 951.22 | 318.169 | 2795.42 |
| 283.184 | 1108.22 | 323.161 | 3140.65 |
| 288.129 | 1280.21 | 328.202 | 3522.52 |
| 293.121 | 1473.50 | 333.105 | 3927.61 |
| 298.174 | 1690.81 | 338.150 | 4382.59 |
| 303.122 | 1926.26 | 343.110 | 4871.98 |
| 308.143 | 2189.50 | 348.081 | 5409.01 |

the extrapolation extends over 1000 kPa . However, nearly linear behavior of density with pressure at the lowest temperatures leaves the extrapolation relatively free of systematic errors. The saturation pressure for the extrapolation was calculated from eq 3. The saturated liquid


Figure 2. Pressure difference from eq 3 of this work ( ${ }^{( }$), the data of Weber and Goodwin (9) (土), the data of Malbrunot et al. (13) (ロ), the data of Weber and Silva (11) ( $\mathbf{\nabla}$ ), and the data of Qian et al. (10) ( + ).
densities are listed in Table 6. The saturated liquid densities were fit with the following function:

$$
\begin{align*}
\rho & /\left(\mathrm{mol} \cdot \mathrm{dm}^{-3}\right)=\rho_{\mathrm{c}}+\chi\left(\rho_{1}+\rho_{2} \chi+\rho_{3} \chi^{2}+\rho_{4} \chi^{3}\right)  \tag{4}\\
& \\
\rho_{\mathrm{c}} & =8.1247 \mathrm{~mol} / \mathrm{dm}^{3} \\
\rho_{1} & =2.2146649 \\
\rho_{2} & =0.13883522 \\
\rho_{3} & =-5.5374876 \times 10^{-3} \\
\rho_{4} & =1.7611411 \times 10^{-3}
\end{align*}
$$

The value of $\rho_{c}$ was taken from Niesen et al. (15). Equation 4 represents the measured saturated liquid densities within $\pm 0.002 \mathrm{~mol} / \mathrm{dm}^{3}$, well within the estimated uncertainty of these densities (see Figure 3.)


Figure 3. Difference of measured saturated liquid densities from eq 4 of this work ( $\bullet$ ) and the data of Malbrunot et al. (13) (口).

Table 4. Burnett Saturated Vapor Densities for R32 (Difluoromethane)

| $T / \mathrm{K}$ | $P / \mathrm{kPa}$ | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{3}\right)$ | $T / \mathrm{K}$ | $P / \mathrm{kPa}$ | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{3}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 219 | 89.09 | 0.0509 | 289 | 1312.4 | 0.6941 |
| 224 | 114.93 | 0.0647 | 294 | 1509.7 | 0.8054 |
| 229 | 146.41 | 0.0813 | 299 | 1728.4 | 0.9326 |
| 234 | 184.35 | 0.1010 | 304 | 1970.2 | 1.0785 |
| 239 | 229.62 | 0.1244 | 309 | 2236.7 | 1.2466 |
| 244 | 283.15 | 0.1519 | 314 | 2529.6 | 1.4414 |
| 249 | 345.91 | 0.1840 | 319 | 2850.8 | 1.6690 |
| 254 | 418.93 | 0.2214 | 324 | 3202.3 | 1.9385 |
| 259 | 503.27 | 0.2645 | 329 | 3586.5 | 2.2631 |
| 264 | 600.05 | 0.3142 | 334 | 4005.9 | 2.6649 |
| 269 | 710.42 | 0.3713 | 336 | 4184.3 | 2.8552 |
| 274 | 835.58 | 0.4367 | 339 | 4463.9 | 3.1841 |
| 279 | 976.77 | 0.5114 | 340 | 4560.4 | 3.3084 |
| 284 | 1135.2 | 0.5967 | 343 | 4860.4 | 3.7403 |

The compressed liquid densities and saturated liquid densities were correlated with an abbreviated mBWR (16) equation of state, given by eq 5 . The temperature dependence

$$
\begin{equation*}
P=\sum_{n=1}^{3} a_{n}(T) \rho^{n}+\mathrm{e}^{-\left(\rho / \rho_{\mathrm{c}}\right)^{2}} \sum_{n=4}^{9} a_{n}(T) \rho^{2 n-5} \tag{5}
\end{equation*}
$$

of the coefficients is given by

$$
\begin{aligned}
& a_{1}= R T \\
& a_{2}=b_{1} T+b_{2} T^{0.5}+b_{3}+b_{4} / \\
& T+b_{5} T^{2} \\
& a_{3}=b_{6} T+b_{7}+b_{8} / T+b_{9} / T^{2} \\
& a_{4}=b_{10} / T^{2}+b_{11} / T^{8} \\
& a_{5}=b_{12} / T^{2}+b_{13} / T^{4} \\
& a_{6}=b_{14} / T^{2}+b_{16} / T^{3} \\
& a_{7}=b_{16} / T^{2}+b_{17} / T^{4} \\
& a_{8}=b_{18} / T^{2}+b_{19} / T^{8} \\
& a_{9}=b_{20} / T^{2}+b_{21} / T^{3}+b_{22} / T^{4}
\end{aligned}
$$

$$
T_{\mathrm{c}}=351.36 \mathrm{~K}
$$

$$
\rho_{\mathrm{c}}=8.1247 \mathrm{~mol} / \mathrm{L}
$$

$$
R=0.0831445 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}
$$

$\mathrm{MW}=52.023 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$

This equation was selected as a convenient means of correlating the liquid properties of this fluid and was used for comparison between 220 and 350 K and from the saturation pressure to 7000 kPa . Equation 5 is not an appropriate representation of R32 outside this temperature and pressure region. Equation (5) represents the data to $\pm 0.01 \%$ in density except near the critical point where the deviations rise to $\pm 0.15 \%$ at 348 K . Larger deviations occur as you approach the critical temperature point of the fluid. The larger deviation is attributed to the inadequacy of the mBWR equation to model highly curved isotherms in the critical region where the true equation of state has a nonanalytic character. Figure 4 shows the density deviation of the present data and of the data of Malbrunot (13) and Qian (10) from eq 5.
C. Thermodynamic Properties. In the previous sections of this paper we have discussed the experimental determination of the PVT properties of R32, both as a gas and as a compressed liquid, over a wide set of conditions. We have also described measurement of the vapor pressure from 268 to 348 K , which, when combined with the earlier measurements of Weber and Goodwin (9), and with those of Weber and Silva (11), allowed us to represent the vapor pressure of R32 from below the normal boiling point ( 221.49 K ) to the critical point ( 351.36 K ). The conditions spanned by these data are displayed in Figures 5 and 6.

These data combined with the ideal gas properties allow one to evaluate other thermodynamic properties, such as the heat capacities, enthalpies, and entropies.

The results of these calculations appear in Tables 7-10. The tables begin at 220 K , slightly below the normal boiling point and below the lowest temperature for which we made liquid or vapor PVT measurements. The entries arise from the virial equation of state and its extrapolation, the correlation of the saturated liquid densities and its extrapolation, and the derivatives $(\partial P / \partial T)_{v}$ and $(\partial V / \partial T)_{p}$, for the saturated liquid states. Values of these derivatives were determined from direct numerical differentiation of the data for the compressed liquid states without any reference to a correlation of the liquid PVT data. The values below 242 K were data obtained by extrapolation with a quadratic function of $T$.
Table 7 gives the ideal gas properties from 200 to 400 K . The reference state for the entropy and the enthalpy in this table is the ideal gas at 101.325 kPa and 233.15 K . The ideal gas enthalpy is not a function of pressure or volume. The ideal gas entropy at the pressure or volume of the saturated vapor relative to the reference state described here can be evaluated by making the usual corrections, $R \ln (101.325 / P)$ for pressure and $R \ln (101.325 V / R T)$ for volume. The pressure ( kPa ) and volume ( $\mathrm{dm}^{3} / \mathrm{mol}$ ) are the experimental values for the saturated vapor. The contribution of the vibrational modes to these properties was calculated from the normal mode frequencies measured by Suzuki and Shimanouchi (17). No corrections for anharmonicities were made because the least energetic of these modes has an equivalent temperature of 760 K and is substantially above the temperatures represented in the table and because the next least energetic mode has a temperature of 1568 K . An error of $0.5 \mathrm{~cm}^{-1}$ in each of the vibrational modes gives rise to an error of no more than $0.01 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ in the heat capacity, $0.002 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ in the entropy, and $0.5 \mathrm{~J} \mathrm{~mol}^{-1}$ in the enthalpy. The vibrational contribution to these properties at 233.15 K with respect to the ground-state properties at 0.0 K is noted at the end of the table. No contribution to the entropy due to the symmetry of the molecule has been included in the final entry.
Table 8 gives the properties of the saturated vapor from 220 to 340 K with a separate entry for the critical temperature. The reference state for this table is the saturated liquid at

Table 5. Densimeter PVT Data for R32 (Difluoromethane)

| T/K | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{-3}\right)$ | $\mathrm{P} / \mathrm{kPa}$ | T/K | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{-3}\right)$ | $P / \mathrm{kPa}$ | T/K | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{-3}\right)$ | $\mathrm{P} / \mathrm{kPa}$ | $T / \mathrm{K}$ | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{-3}\right)$ | $P / \mathrm{kPa}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 242.593 | 22.244 | 1999.2 | 264.505 | 21.078 | 4501.9 | 293.459 | 18.901 | 2000.4 | 323.110 | 16.626 | 5003.4 |
| 242.596 | 22.265 | 2499.3 | 264.520 | 21.105 | 5002.5 | 293.459 | 18.955 | 2500.3 | 323.109 | 16.734 | 5503.7 |
| 242.582 | 22.287 | 3001.3 | 264.518 | 21.132 | 5503.0 | 293.460 | 19.007 | 3001.4 | 323.111 | 16.835 | 6003.6 |
| 242.584 | 22.307 | 3501.1 | 264.511 | 21.160 | 6002.9 | 293.459 | 19.058 | 3501.5 | 323.111 | 16.931 | 6504.5 |
| 242.582 | 22.328 | 4001.0 | 264.524 | 21.186 | 6503.8 | 293.464 | 19.108 | 4001.2 | 327.960 | 15.689 | 3802.5 |
| 242.588 | 22.348 | 4502.0 | 269.378 | 20.622 | 2000.3 | 293.463 | 19.156 | 4502.2 | 327.962 | 15.757 | 4001.8 |
| 242.586 | 22.368 | 5002.3 | 269.382 | 20.654 | 2500.7 | 293.462 | 19.204 | 5003.0 | 327.962 | 15.917 | 4502.6 |
| 242.594 | 22.388 | 5502.2 | 269.381 | 20.685 | 3000.9 | 293.458 | 19.251 | 5503.4 | 327.964 | 16.062 | 5003.5 |
| 242.588 | 22.408 | 6002.1 | 269.387 | 20.716 | 3501.1 | 293.461 | 19.296 | 6003.3 | 327.963 | 16.195 | 5503.8 |
| 242.592 | 22.427 | 6503.0 | 269.397 | 20.747 | 4001.1 | 293.461 | 19.341 | 6504.2 | 327.968 | 16.319 | 6003.6 |
| 246.019 | 22.047 | 2000.8 | 269.398 | 20.777 | 4502.1 | 298.407 | 18.494 | 2000.4 | 327.964 | 16.434 | 6504.5 |
| 246.022 | 22.069 | 2499.9 | 269.397 | 20.807 | 5003.0 | 298.409 | 18.555 | 2500.4 | 332.789 | 15.089 | 4202.3 |
| 246.033 | 22.090 | 3000.9 | 269.400 | 20.837 | 5503.0 | 298.419 | 18.614 | 3001.4 | 332.795 | 15.219 | 4502.7 |
| 246.053 | 22.111 | 3501.2 | 269.393 | 20.867 | 6003.1 | 298.415 | 18.672 | 3501.4 | 332.800 | 5.415 | 5003.4 |
| 246.061 | 22.132 | 4000.8 | 269.396 | 20.896 | 6503.8 | 298.417 | 18.728 | 4001.3 | 332.799 | 15.588 | 5503.8 |
| 246.064 | 22.153 | 4502.1 | 273.999 | 20.315 | 2000.3 | 298.419 | 18.782 | 4502.3 | 332.799 | 15.745 | 6003.6 |
| 246.077 | 22.173 | 5002.9 | 274.003 | 20.350 | 2500.6 | 298.426 | 18.835 | 5003.1 | 332.800 | 15.888 | 6504.4 |
| 246.091 | 22.193 | 5503.2 | 274.003 | 20.384 | 3000.9 | 298.424 | 18.887 | 5503.3 | 337.788 | 14.291 | 4503.0 |
| 246.108 | 22.213 | 6003.1 | 274.004 | 20.418 | 3501.6 | 298.426 | 18.937 | 6003.2 | 337.792 | 14.597 | 5003.4 |
| 246.102 | 22.234 | 6503.9 | 274.008 | 20.452 | 4001.2 | 303.424 | 18.122 | 2501.3 | 337.793 | 14.847 | 5503.7 |
| 250.554 | 21.783 | 2000.6 | 274.007 | 20.485 | 4502.2 | 303.428 | 18.191 | 3001.4 | 337.790 | 15.060 | 6003.5 |
| 250.569 | 21.806 | 2500.7 | 274.010 | 20.518 | 5003.0 | 303.425 | 18.258 | 3501.6 | 337.792 | 15.248 | 6504.4 |
| 250.568 | 21.829 | 3000.8 | 274.005 | 20.550 | 5503.3 | 303.422 | 18.322 | 4001.5 | 347.638 | 13.564 | 6504.4 |
| 250.578 | 21.852 | 3501.1 | 274.008 | 20.581 | 6003.1 | 303.421 | 18.384 | 4502.4 | 347.675 | 12.540 | 5604.3 |
| 250.581 | 21.874 | 4001.2 | 274.011 | 20.613 | 6504.0 | 303.42 | 18.444 | 5003.1 | 347.701 | 12.827 | 5803.8 |
| 250.580 | 21.897 | 4501.9 | 278.812 | 19.988 | 2000.3 | 303.418 | 18.503 | 5503.5 | 347.682 | 13.073 | 6003.3 |
| 250.572 | 21.920 | 5002.9 | 278.813 | 20.026 | 2500.7 | 303.423 | 18.559 | 6003.2 | 347.659 | 13.285 | 6203.9 |
| 250.581 | 21.942 | 5503.2 | 278.816 | 20.064 | 3001.0 | 303.347 | 18.620 | 6504.2 | 347.603 | 13.473 | 6404.0 |
| 250.587 | 21.963 | 6003.0 | 278.827 | 20.101 | 3501.6 | 308.303 | 17.672 | 2501.1 | 347.562 | 13.564 | 6504.5 |
| 250.572 | 21.986 | 6503.9 | 278.827 | 20.137 | 4001.3 | 308.287 | 17.752 | 3001.3 | 348.530 | 11.646 | 5303.7 |
| 255.116 | 21.512 | 2000.4 | 278.833 | 20.173 | 4502.1 | 308.253 | 17.831 | 3501.5 | 348.537 | 11.733 | 5353.6 |
| 255.120 | 21.537 | 2500.8 | 278.835 | 20.208 | 5002.8 | 308.252 | 17.906 | 4001.4 | 348.568 | 11.673 | 5403.5 |
| 255.125 | 21.561 | 3001.1 | 278.828 | 20.244 | 5503.1 | 308.255 | 17.977 | 4502.3 | 348.569 | 11.808 | 5453.4 |
| 255.13 | 21.586 | 3501.2 | 278.822 | 20.278 | 6003.0 | 308.261 | 18.045 | 5003.2 | 348.592 | 11.924 | 5503.2 |
| 255.134 | 21.610 | 4000.8 | 278.815 | 20.313 | 6503.9 | 308.269 | 18.111 | 5503.4 | 348.608 | 12.032 | 5553.7 |
| 255.136 | 21.634 | 4501.9 | 283.647 | 19.646 | 2000.3 | 308.267 | 18.174 | 6003.3 | 348.601 | 12.142 | 5603.6 |
| 255.141 | 21.658 | 5002.7 | 283.647 | 19.688 | 2500.3 | 308.248 | 18.238 | 6504.2 | 348.599 | 12.244 | 5653.4 |
| 255.142 | 21.682 | 5503.1 | 283.647 | 19.730 | 3001.4 | 313.123 | 17.278 | 3001.7 | 348.600 | 12.340 | 5703.3 |
| 255.146 | 21.705 | 6003.2 | 283.647 | 19.771 | 3501.5 | 313.118 | 17.369 | 3501.6 | 348.605 | 12.429 | 5753.2 |
| 255.133 | 21.729 | 6503.9 | 283.647 | 19.811 | 4001.3 | 313.126 | 17.455 | 4001.3 | 348.622 | 12.511 | 5803.7 |
| 259.752 | 21.230 | 2000.6 | 283.642 | 19.851 | 4502.2 | 313.131 | 17.537 | 4502.3 | 348.629 | 12.583 | 5853.6 |
| 259.753 | 21.257 | 2500.7 | 283.641 | 19.890 | 5002.9 | 313.134 | 17.617 | 5003.1 | 348.567 | 12.672 | 5903.4 |
| 259.765 | 21.283 | 3000.9 | 283.643 | 19.928 | 5503.3 | 313.143 | 17.692 | 5503.5 | 348.578 | 12.747 | 5953.2 |
| 259.771 | 21.310 | 3501.3 | 283.643 | 19.966 | 6003.2 | 313.156 | 17.764 | 6003.3 | 348.567 | 12.817 | 6003.0 |
| 259.770 | 21.336 | 4001.0 | 283.643 | 20.003 | 6504.1 | 313.148 | 17.835 | 6504.2 | 348.568 | 12.880 | 6053.6 |
| 259.779 | 21.362 | 4502.2 | 288.527 | 19.285 | 2000.6 | 318.251 | 16.831 | 3502.3 | 348.577 | 12.938 | 6103.4 |
| 259.790 | 21.387 | 5002.8 | 288.530 | 19.332 | 2500.4 | 318.255 | 16.936 | 4001.7 | 348.584 | 12.994 | 6153.3 |
| 259.799 | 21.412 | 5503.2 | 288.533 | 19.378 | 3001.4 | 318.255 | 17.036 | 4502.6 | 348.601 | 13.044 | 6203.4 |
| 259.797 | 21.437 | 6003.0 | 288.526 | 19.424 | 3501.4 | 318.254 | 17.131 | 5003.5 | 348.611 | 13.093 | 6253.4 |
| 259.806 | 21.462 | 6503.9 | 288.529 | 19.469 | 4001.2 | 318.253 | 17.221 | 5503.8 | 348.609 | 13.145 | 6304.1 |
| 264.487 | 20.935 | 2000.5 | 288.529 | 19.512 | 4502.1 | 318.253 | 17.306 | 6003.7 | 348.607 | 13.193 | 6354.0 |
| 264.488 | 20.964 | 2500.5 | 288.531 | 19.555 | 5003.0 | 318.251 | 17.389 | 6504.5 | 348.595 | 13.244 | 6403.9 |
| 264.501 | 20.993 | 3000.9 | 288.529 | 19.597 | 5503.5 | 323.107 | 16.255 | 3502.4 | 348.604 | 13.289 | 6453.9 |
| 264.506 | 21.021 | 3501.5 | 288.532 | 19.638 | 5003.3 | 323.110 | 16.388 | 4001.7 | 348.595 | 13.335 | 6503.9 |
| 264.528 | 21.049 | 4001.1 | 288.531 | 19.679 | 6504.2 | 323.110 | 16.511 | 4502.7 |  |  |  |

Table 6. Densimeter Saturated Liquid Densities for R32 (Difluoromethane)

| $T / \mathrm{K}$ | $P / \mathrm{kPa}$ | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{-3}\right)$ | $T / \mathrm{K}$ | $P / \mathbf{k P a}$ | $\rho /\left(\mathrm{mol} \cdot \mathrm{dm}^{-3}\right)$ |
| :---: | ---: | :---: | :---: | :---: | :---: |
| 242.589 | 267.1 | 22.168 | 293.461 | 1487.4 | 18.845 |
| 246.063 | 307.9 | 21.974 | 298.418 | 1701.8 | 18.457 |
| 250.574 | 367.7 | 21.706 | 303.414 | 1940.7 | 18.044 |
| 255.132 | 437.0 | 21.433 | 308.266 | 2196.0 | 17.620 |
| 259.778 | 517.5 | 21.148 | 313.135 | 2477.0 | 17.178 |
| 264.509 | 610.6 | 20.853 | 318.253 | 2801.0 | 16.670 |
| 269.391 | 719.7 | 20.539 | 323.110 | 3137.4 | 16.147 |
| 274.006 | 835.7 | 20.231 | 327.963 | 3504.1 | 15.582 |
| 278.823 | 971.5 | 19.908 | 332.797 | 3901.7 | 14.955 |
| 283.645 | 1123.4 | 19.568 | 337.791 | 4349.4 | 14.175 |
| 288.530 | 1295.0 | 19.216 |  |  |  |

233.15 K . The accuracy of the saturated vapor states is determined by two quantities, the accuracy of the vapor pressure and the accuracy of the virial surface. The accuracy of the low-temperature vapor pressure measurements was limited by the variation of the temperature for the glass
comparative ebulliometer. During each measurement the variation was 0.003 K above 220 K . This propagates to a relative uncertainty of the vapor pressure of $0.01 \%$ from 220 to 230 K . The variation of the temperature for the steel ebulliometer that was used by Weber and Silva (11) was 0.006 K between 230 and 270 K . The uncertainty of the pressure measurement is $0.03 \%$. This resulted from the uncertainty of the vapor pressure of the reference fluid R123. The total uncertainty of the vapor pressures of R32 in this range is $0.05 \%$. In all cases, the accuracy was not limited by the accuracy of the thermometer. Above 270 K , the pressures were measured using a static method, where the uncertainty was $0.1 \mathrm{kPa}+0.0002 P$. The uncertainty was then $0.03 \%$ at 270 K and $0.02 \%$ at 340 K . The correlation of the vapor pressure measurements represents the data to $0.03 \%$ in pressure. We have chosen to assign an uncertainty of $0.04 \%$ in the vapor pressure over the entire range of measurement.


Figure 4. Density deviations from the mBWR correlation; this work, saturated liquid ( $\mathbf{A}$ ), compressed liquid ( $\boldsymbol{\bullet}$ ), and the data of Malbrunot et al. (13) (口).


Figure 5. Location in pressure and temperature of the data used to derive tables: liquid PVT ( $\quad$ ), vapor PVT ( $\left.{ }^{( }\right)$, extrapolated saturated liquid densities ( $\square$ ), and extrapolated saturated vapor densities ( $O$ ).


Figure 6. Location in density and pressure of the data used to derive tables: liquid PVT (■), vapor PVT ( $\bullet$ ), extrapolated saturated liquid densities (ם), and extrapolated saturated vapor densities ( $O$ ).

The uncertainty in the second virial coefficient dominates the accuracy of the virial surface. The uncertainty in $B$ is $0.0005 \mathrm{dm}^{3} / \mathrm{mol}$ at $340 \mathrm{~K}, 1.0 \%$ at 270 K , and $3 \%$ at 220 K . The uncertainty in the first derivative of $B$ is $2 \%$ at the highest temperature and increases to $8 \%$ at the lowest. For the second derivative of $B$ the uncertainty increases from $8 \%$ to $25 \%$ as the temperature is reduced. The uncertainties in $C$ are 10 times those for $B$, for $D, 100$ times those for $B$. The resultant uncertainty in the tabulated properties is noted below entries in the table at intervals of 20 K . As one would expect, the largest uncertainties are nearest the critical point where the virial expansion is least accurate. The enthalpy and entropy

Table 7. Properties of R32 Ideal Gas

| T/K | $\begin{gathered} C_{P}{ }^{0} / \\ \left(\mathrm{J} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}\right) \end{gathered}$ | $\begin{gathered} {\left[S^{\circ}(T)-\right.} \\ \left.S^{\circ}(233.15 \mathrm{~K})\right] / \\ \left(\mathrm{J} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}\right) \end{gathered}$ | $\begin{gathered} {\left[H^{\circ}(T)-\right.} \\ \left.H^{\circ}(233.15 \mathrm{~K})\right] / \\ \left(\mathrm{J} \cdot \mathrm{~mol}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: |
| 200.00 | 36.695 | -5.7554 | -1244.77 |
| 205.00 | 36.937 | -4.8464 | -1060.73 |
| 210.00 | 37.190 | -3.9531 | -875.36 |
| 215.00 | 37.448 | -3.0748 | -688.72 |
| 220.00 | 37.716 | -2.2110 | -500.85 |
| 225.00 | 37.992 | -1.3603 | -311.56 |
| 230.00 | 38.275 | -0.5221 | -120.90 |
| 233.15 | 38.465 | 0.0000 | 0.00 |
| 235.00 | 38.567 | 0.3043 | 71.22 |
| 240.00 | 38.868 | 1.1194 | 264.83 |
| 245.00 | 39.176 | 1.9241 | 459.95 |
| 250.00 | 39.492 | 2.7188 | 656.62 |
| 255.00 | 39.815 | 3.5041 | 854.91 |
| 260.00 | 40.145 | 4.2805 | 1054.83 |
| 265.00 | 40.482 | 5.0484 | 1256.40 |
| 270.00 | 40.826 | 5.8084 | 1459.68 |
| 275.00 | 41.178 | 6.5607 | 1664.69 |
| 280.00 | 41.535 | 7.3059 | 1871.46 |
| 285.00 | 41.897 | 8.0443 | 2080.07 |
| 290.00 | 42.267 | 8.7764 | 2290.55 |
| 295.00 | 42.640 | 9.5019 | 2502.76 |
| 300.00 | 43.020 | 10.2217 | 2716.89 |
| 305.00 | 43.403 | 10.9362 | 2933.03 |
| 310.00 | 43.791 | 11.6450 | 3150.98 |
| 315.00 | 44.182 | 12.3490 | 3370.96 |
| 320.00 | 44.578 | 13.0480 | 3592.90 |
| 325.00 | 44.975 | 13.7423 | 3816.79 |
| 330.00 | 45.377 | 14.4320 | 4042.68 |
| 335.00 | 45.782 | 15.1174 | 4270.57 |
| 340.00 | 46.185 | 15.7988 | 4500.52 |
| 345.00 | 46.594 | 16.4759 | 4732.43 |
| 350.00 | 47.005 | 17.1493 | 4966.45 |
| 355.00 | 47.415 | 17.8192 | 5202.57 |
| 360.00 | 47.827 | 18.4852 | 5440.67 |
| 365.00 | 48.240 | 19.1478 | 5680.85 |
| 370.00 | 48.655 | 19.8069 | 5923.06 |
| 375.00 | 49.068 | 20.4628 | 6167.37 |
| 380.00 | 49.482 | 21.1156 | 6413.81 |
| 385.00 | 49.895 | 21.7651 | 6662.26 |
| 390.00 | 50.308 | 22.4116 | 6912.75 |
| 395.00 | 50.721 | 23.0552 | 7165.38 |
| 400.00 | 51.132 | 23.6960 | 7420.09 |
| Vibrational Component with Respect to 0.0 K Ground State |  |  |  |
| 233.15 | 5.207 | 1.6498 | 286.18 |

for the critical point were evaluated by fitting the mean for each of these quantities at the vapor pressure $\left[\left(S_{1}+S_{g}\right) / 2\right.$ and $\left.\left(H_{1}+H_{g}\right) / 2\right]$ to quadratic functions of the temperature and extrapolating them to the critical temperature.

Table 9 lists the saturated liquid volume, entropy ( $S$ ), and enthalpy $(H)$ as well as the entropy and enthalpy of vaporization. The reference state for this table is the same as for Table 8, and the uncertainty of the respective properties is noted at 20 K intervals. The accuracy of the liquid volumes is $0.04 \%$ except near the critical temperature. Density accuracy is limited by the ability of the densimeter to reproduce the density of the calibrating fluid water (8), and near the critical point, by the errors in the extrapolation of highly curved isotherms to the saturation boundary. The uncertainties in the entropy and enthalpy of the phase transition are determined by the uncertainty of the vapor volume, the vapor pressure, and the derivative $\mathrm{d}(\ln P) / \mathrm{d}(1 /$ $T$ ). Over most of the temperature range the accuracy of the derived $\Delta S_{\text {vap }}$ and $\Delta H_{\text {vap }}$ is $0.2 \%$. Only near the critical point, where there is considerable uncertainty in the vapor volume, does the uncertainty rise to several percent. The accuracies of the liquid-state entropies and enthalpies are determined by the uncertainties in the saturated gas states and the phase transition properties.

Table 10 lists the values of the different heat capacities at saturated liquid conditions. The quantity $C_{\text {sat }}=\lim _{\Delta T \rightarrow 0}$

Table 8. Properties of R32 Saturated Vapor

| $T / \mathrm{K}$ | P/kPa | $\mathrm{V} /\left(\mathrm{dm}^{3} \cdot \mathrm{~mol}^{-1}\right)$ | S/(J. $\left.\mathrm{mol}^{-1} \cdot \mathrm{~K}^{-1}\right)$ | H/(J. $\mathrm{mol}^{-1}$ ) | $\mathrm{C}_{\mathrm{p}} /\left(\mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~K}^{-1}\right)$ | $C_{v} /\left(\mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~K}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 220.00 | 93.84 | 18.69 | 85.76 | 18831.1 | 45.1 | 33.9 |
|  | (0.04) | (0.01) | (0.03) | (5.8) | (0.8) | (0.3) |
| 225.00 | 120.75 | 14.744 | 84.33 | 18958.8 | 46.4 | 34.8 |
| 230.00 | 153.45 | 11.763 | 82.97 | 19081.0 | 47.9 | 35.7 |
| 233.15 | 177.41 | 10.259 | 82.16 | 19154.8 | 48.8 | 36.2 |
| 235.00 | 192.79 | 9.480 | 81.69 | 19197.4 | 49.4 | 36.6 |
| 240.00 | 239.63 | 7.713 | 80.47 | 19307.6 | 51.1 | 37.6 |
|  | (0.10) | (0.005) | (0.04) | (10.2) | (1.2) | (0.4) |
| 245.00 | 294.93 | 6.327 | 79.30 | 19411.1 | 52.9 | 38.6 |
| 250.00 | 359.66 | 5.231 | 78.19 | 19507.5 | 54.7 | 39.7 |
| 255.00 | 434.86 | 4.356 | 77.12 | 19596.2 | 56.8 | 40.7 |
| 260.00 | 521.60 | 3.650 | 76.08 | 19676.7 | 58.9 | 41.8 |
|  | (0.20) | (0.003) | (0.06) | (15.6) | (1.8) | (0.4) |
| 265.00 | 621.00 | 3.076 | 75.08 | 19748.2 | 61.3 | 42.9 |
| 270.00 | 734.23 | 2.606 | 74.12 | 19810.0 | 63.8 | 44.0 |
| 275.00 | 862.49 | 2.218 | 73.17 | 19861.1 | 66.6 | 45.1 |
| 280.00 | 1007.04 | 1.895 | 72.24 | 19900.5 | 69.7 | 46.3 |
|  | (0.40) | (0.001) | (0.08) | (20.1) | (2.4) | (1.2) |
| 285.00 | 1169.17 | 1.6253 | 71.32 | 19926.8 | 73.1 | 47.4 |
| 290.00 | 1350.24 | 1.3980 | 70.41 | 19938.8 | 76.9 | 48.6 |
| 295.00 | 1551.66 | 1.2053 | 69.50 | 19934.3 | 81.2 | 49.8 |
| 300.00 | 1774.89 | 1.0411 | 68.58 | 19911.5 | 86.2 | 51.0 |
|  | (0.70) | (0.0005) | (0.12) | (28.0) | (2.7) | (2.0) |
| 305.00 | 2021.49 | 0.9002 | 67.64 | 19867.6 | 92.1 | 52.3 |
| 310.00 | 2293.11 | 0.7787 | 66.67 | 19799.1 | 99.2 | 53.5 |
| 315.00 | 2591.51 | 0.6710 | 65.66 | 19701.7 | 108.0 | 54.9 |
| 320.00 | 2918.59 | 0.5809 | 64.59 | 19569.5 | 119.2 | 56.2 |
|  | (1.20) | (0.0007) | (0.15) | (34.0) | (5.2) | (3.0) |
| 325.00 | 3276.45 | 0.4996 | 63.44 | 19394.1 | 134.1 | 57.7 |
| 330.00 | 3667.45 | 0.4274 | 62.17 | 19163.4 | 155.1 | 59.2 |
| 335.00 | 4094.31 | 0.3622 | 60.74 | 18857.7 | 187.2 | 60.9 |
| 340.00 | 4560.31 | 0.3023 | 59.03 | 18440.4 | 243.5 | 62.8 |
|  | (1.8) | (0.013) | (0.30) | (54.1) | (78.6) | (5.6) |
| 351.36 | 5792.7 $(2.4)$ | 0.1231 $(0.0008)$ | $48.22$ | $14914$ | $\infty$ | $\infty$ |

Table 9. Properties of R32 Saturated Liquid

| T/K | $\mathrm{P} / \mathrm{kPa}$ | $\mathrm{V} /\left(\mathrm{dm}^{3} \cdot \mathrm{~mol}^{-1}\right)$ | S/(J.mol ${ }^{-1 .} \mathrm{K}^{-1}$ ) | $\Delta S /\left(\mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~K}^{-1}\right)$ | H/(M.mol ${ }^{-1}$ ) | $\Delta H_{\text {vap }} /\left(\mathrm{J} \cdot \mathrm{mol}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 220.00 | 93.84 | 0.04270 | -4.73 | 90.48 | -1076.4 | 19907.5 |
|  | (0.04) | (0.00 002) | (0.21) | (0.18) | (45.8) | (40.0) |
| 225.00 | 120.75 | 0.04319 | -2.91 | 87.24 | -669.1 | 19627.9 |
| 230.00 | 153.45 | 0.04371 | -1.12 | 84.09 | -259.3 | 19340.3 |
| 233.15 | 177.41 | 0.04404 | 0.00 | 82.16 | 0.0 | 19154.8 |
| 235.00 | 192.79 | 0.04424 | 0.65 | 81.04 | 153.4 | 19044.0 |
| 240.00 | 239.63 | 0.04480 | 2.39 | 78.08 | 569.5 | 18738.0 |
|  | (0.10) | (0.00 002) | (0.20) | (0.16) | (47.6) | (37.4) |
| 245.00 | 294.93 | 0.04539 | 4.11 | 75.19 | 989.5 | 18421.6 |
| 250.00 | 359.66 | 0.04600 | 5.81 | 72.37 | 1413.9 | 18093.6 |
| 255.00 | 434.86 | 0.04664 | 7.50 | 69.62 | 1843.1 | 17753.1 |
| 260.00 | 521.60 | 0.04732 | 9.17 | 66.92 | 2277.9 | 17398.9 |
|  | (0.20) | (0.00 002) | (0.19) | (0.13) | (51.4) | (35.8) |
| 265.00 | 621.00 | 0.04803 | 10.82 | 64.26 | 2718.5 | 17028.8 |
| 270.00 | 734.23 | 0.04878 | 12.47 | 61.65 | 3165.6 | 16644.4 |
| 275.00 | 862.49 | 0.04959 | 14.11 | 59.06 | 3619.7 | 16241.4 |
| 280.00 | 1007.04 | 0.05044 | 15.76 | 56.50 | 4081.6 | 15818.9 |
|  | (0.40) | (0.00 002) | (0.19) | (0.11) | (51.7) | (31.6) |
| 285.00 | 1169.17 | 0.05136 | 17.38 | 53.95 | 4551.8 | 15375.0 |
| 290.00 | 1350.24 | 0.05234 | 19.01 | 51.40 | 5031.4 | 14907.4 |
| 295.00 | 1551.66 | 0.05340 | 20.64 | 48.86 | 5521.0 | 14413.4 |
| 300.00 | 1774.89 | 0.05456 | 22.28 | 46.30 | 6022.0 | 13899.5 |
|  | (0.07) | (0.000 02) | (0.21) | (0.09) | (55.8) | (27.8) |
| 305.00 | 2021.49 | 0.05584 | 23.93 | 43.71 | 6536.1 | 13331.5 |
| 310.00 | 2293.11 | 0.05725 | 25.59 | 41.08 | 7064.9 | 12734.2 |
| 315.00 | 2591.51 | 0.05884 | 27.28 | 38.38 | 7611.3 | 12090.4 |
| 320.00 | 2918.59 | -060064 | 29.00 | 35.60 | 8178.8 | 11390.6 |
|  | (1.20) | (0.000 03) | (0.22) | (0.07) | (56.8) | (22.8) |
| 325.00 | 3276.45 | 0.06274 | 30.76 | 32.68 | 8773.0 | 10621.1 |
| 330.00 | 3667.45 | 0.06526 | 32.59 | 29.58 | 9402.0 | 9761.5 |
| 335.00 | 4094.31 | 0.06838 | 34.53 | 26.20 | 10079.9 | 8777.8 |
| 340.00 | 4560.31 | 0.07253 | 36.66 | 22.37 | 10834.6 | 7604.8 |
| 351.36 | 5792.7 | 0.1231 | 48.22 | 0.00 | 14914 | (21.00 |
|  | (2.4) | (0.000 8) | (0.66) |  | (165) |  |

$T\left[S_{\text {sat }}\left(T_{2}\right)-S_{\text {sat }}\left(T_{1}\right)\right] /\left[T_{2}-T_{1}\right]$ is calculated directly from the entropies in Table 9. To obtain $C_{p}$ and $C_{v}$, standard
thermodynamic expressions (18) were employed. These require the derivatives at saturated liquid conditions: (d $\rho /$

Table 10. Properties of R32 Saturated Liquid Heat Capacities

| $T / \mathrm{K}$ | $P / \mathrm{kPa}$ | $V /\left(\mathrm{dm}^{3} \cdot \mathrm{~mol}^{-1}\right)$ | $C_{\text {sat }}$ | $C_{p} /\left(\mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{~mol}^{-1}\right)$ | $C_{v}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 220.00 | 93.84 | 0.04270 | 80.9 | 81.0 | 46.0 |
|  | $(0.04)$ | $(0.00002)$ | $(1.5)$ | $(1.6)$ | $(3.2)$ |
| 225.00 | 120.75 | 0.04320 | 81.3 | 81.4 | 45.7 |
| 230.00 | 153.45 | 0.04371 | 82.1 | 82.2 | 46.0 |
| 233.15 | 177.41 | 0.04404 | 82.6 | 82.8 | 46.2 |
| 235.00 | 192.79 | 0.04424 | 83.0 | 83.2 | 46.3 |
| 240.00 | 239.63 | 0.04480 | 83.6 | 83.9 | 47.1 |
|  | $(0.10)$ | $(0.00002)$ | $(1.7)$ | $(1.8)$ | $(3.6)$ |
| 245.00 | 294.93 | 0.04539 | 84.2 | 84.6 | 46.3 |
| 250.00 | 359.66 | 0.04600 | 85.6 | 85.4 | 46.4 |
| 255.00 | 434.86 | 0.04664 | 85.9 | 86.5 | 46.7 |
| 260.00 | 521.60 | 0.04732 | 86.8 | 87.5 | 46.8 |
|  | $(0.20)$ | $(0.00002)$ | $(1.8)$ | $(1.9)$ | $(3.8)$ |
| 265.00 | 621.00 | 0.04803 | 87.9 | 88.7 | 47.2 |
| 270.00 | 734.23 | 0.04878 | 89.0 | 90.0 | 47.5 |
| 275.00 | 862.49 | 0.04959 | 90.2 | 91.4 | 48.0 |
| 280.00 | 1007.04 | 0.05044 | 91.5 | 92.9 | 48.6 |
|  | $(0.40)$ | $(0.00002)$ | $(2.0)$ | $(2.1)$ | $(4.0)$ |
| 285.00 | 1169.2 | 0.05136 | 93.0 | 94.9 | 49.1 |
| 290.00 | 1350.2 | 0.05234 | 94.6 | 96.9 | 49.6 |
| 295.00 | 1551.7 | 0.05340 | 96.3 | 99.1 | 49.9 |
| 300.00 | 1774.9 | 0.05456 | 98.3 | 101.7 | 50.1 |
|  | $(0.7)$ | $(0.00002)$ | $(2.1)$ | $(2.3)$ | $(4.5)$ |
| 305.00 | 2021.5 | 0.05584 | 100.6 | 104.8 | 50.1 |
| 310.00 | 2293.1 | 0.05725 | 103.1 | 108.4 | 50.3 |
| 315.00 | 2591.5 | 0.05884 | 106.2 | 113.4 | 50.5 |
| 320.00 | 2918.6 | 0.06064 | 110.0 | 118.7 | 51.0 |
|  | $(1.2)$ | $(0.00003)$ | $(2.2)$ | $12.9)$ | $(5.2)$ |
| 325.00 | 3276.5 | 0.06274 | 114.7 | 126.4 | 51.8 |
| 330.00 | 3667.5 | 0.06526 | 121.0 | 136.3 | 52.8 |
| 335.00 | 4094.3 | 0.06838 | 130.0 | 143.4 | 55.2 |
| 340.00 | 4560.3 | 0.07253 | 144.3 | 185.2 | 59.3 |
|  | $(1.8)$ | $(0.00005)$ | $(15.5)$ | $(20.0)$ | $(20.0)$ |
| 351.36 | 5792.7 | 0.1231 | $\infty$ | $\infty$ | $\infty$ |
|  | $(2.4)$ | $(0.0008)$ |  |  |  |
|  |  |  |  |  |  |

$\mathrm{d} T)_{\text {sat }}$ from eq $4, \mathrm{~d}(\ln P) / \mathrm{d}(1 / T)$ from eq 3 , and also $(\partial P / \partial T)_{\nu}$ and $P(\partial V / \partial T)_{p} / T$, which were obtained by differentiating the PVT data numerically. We assign an uncertainty of $5 \%$ to the numerical derivatives, and this accounts for the greater uncertainties in $C_{p}$ and $C_{\nu}$. As in Tables 8 and 9 , the estimated uncertainties are noted at 20 K intervals.

## Summary

The PVT surface for R32 (difluoromethane) is deduced from data collected by a vibrating tube densimeter apparatus and a Burnett/isochoric apparatus. A vapor pressure equation is presented which has a relative standard deviation of $0.028 \%$ in pressure. A three-term virial surface correlates the vapor data and represents the vapor densities to $0.06 \%$ except at the lowest temperature. An abbreviated mBWR equation is used to correlate the liquid surface for the compressed liquid and saturated liquid densities. The saturated liquid data are
correlated and represented to $0.2 \%$ in density. Tables of heat capacities, enthalpies, and entropies at saturation are presented which were derived by a direct analysis of the PVT data.

## Acknowledgment

We thank Mark Mclinden for providing software to evaluate the mBWR equation. We also thank Joe Magee for preliminary heat capacity data and L. A. Weber and A. M. Silva for vapor pressure data prior to their publication. This paper is dedicated in memory of Graham Morrison.

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Received for review July 29, 1993. Accepted November 15, 1993.* This research project is supported in part by U.S. Department of Energy Grant Number DE-FG02-91CE23810 (Materials Compatibility and Lubricants Research (MCLR) on CFC-Refrigerant Substitutes) and in-kind contributions from the air-conditioning and refrigeration industry.

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[^0]:    * Abstract published in Advance ACS Abstracts, January 15, 1994.

