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Vapor Pressure and $P-V-T$ Measurements for 1,1,1,2,3,3-Hexafluoropropane (R-236ea)

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A constant-volume cell was used to measure saturated vapor pressure and $P-V-T$ properties for 1,1,2,3,3,3-hexafluoropropane (R-236ea). A temperature range from 255 K to 363 K and a corresponding pressure range from 35 kPa to 1269 kPa were covered in the saturated pressure region. The results were fitted to the modified Riedel equation. The $P-V-T$ measurements in the superheated vapor region were taken along four isochores from 313 K up to 367 K and from 275 kPa up to 914 kPa. For the gas-phase region, the second virial coefficients were calculated using the Tsonopoulos and Weber correlating methods. Using the Orbey and Vera, and the Weber correlating methods, the contribution of the third virial coefficients was also considered. In the results of our measurements, 80 data points were collected, 43 and 37 of which were obtained, respectively, for the saturated pressure and superheated regions. The $P-V-T$ measurements were compared with the few data available in the literature by means of a virial equation of state, revealing a good consistency.

Introduction

1,1,2,3,3,3-Hexafluoropropane (R-236ea) has a zero ozone depletion potential. In addition, because of its low global warming potential, this refrigerant is currently considered as the most promising substitute for chlorine-containing compounds in high-temperature heat pumps, centrifugal chillers, and chemical blowing agents (for use in the manufacture of polyurethane and phenolic resin foams) and as a component in cleaning fluids, fire suppressants, and propellants.

Its viscosity under saturated conditions[1] and its heat capacities and entropies[2] have recently been studied. Several publications have dealt with certain physical properties,[3] speed of sound measurements[4] and dipole moment.[5] Vapor−liquid coexistence curves in the critical region have also been studied.[6]

The vapor pressures for R-236ea have been measured: over a wide range of temperatures using a sample of 99.5% purity,[7] in a Burnett apparatus cell with a sample of 99.9% purity,[8] with four different types of ebulliometric apparatus, again using a sample of 99.9% purity,[9] and using a VLE apparatus.[10,11] Vapor pressure literature sources are summarized in Table 1.

To our knowledge, the only available measurements in the superheated region have been obtained using a Burnett apparatus over a temperature range of 330 K to 390 K.[12]

It is also worth noting that the data available on the thermodynamic properties of the fluid are rather heterogeneous, obtained by means of different experimental methods (e.g. ebulliometer, Burnett, isochoric, and VLE setup).

Experimental Section

Reagent. The sample was provided by Lancaster Synthesis, Inc. It was deaerated by immersion in liquid nitrogen and evacuation. Its purity was checked by gas chromatography (Carlo Erba Mega Series 5380) using a 2 m Porapack QS packed column and a hot wire detector with helium as the carrier gas; it was found to be better than 99.99%.

Table 1. Summary of the Available Literature Vapor Pressure Data for R-236ea

ref	T range K	sample purity %	uncertainty kPa	no. of exptl points
Beyerlein et al.[7]	283−414	99.5	±3	29
Zhang et al.[8]	300−410	99.9	±0.6	38
Defibaugh et al.[9]	248−370	99.93	±0.05	156
Bobbo et al.[10,11]	283−318	>98	±1	12
this work	255−363	99.99	±0.6	43

Apparatus. The experimental apparatus is schematically illustrated in Figure 1. A classical constant-volume apparatus with a volume of around 0.254 dm^3 was used. The apparatus has been described in detail elsewhere.[13,14] An AISI 304 stainless steel spherical cell contains the refrigerant sample and is connected to a differential diaphragm pressure transducer, coupled to an electronic null indicator. The spherical cell and pressure transducer are immersed in the main thermostatic bath containing a mixture of water and glycol and controlled by a proportional integrative derivative (PID) device. An auxiliary bath, also controlled by a PID device, helps the system to keep the temperature constant. A platinum resistance thermometer is immersed near the cell and is connected to a digital indicator. The instrument is calibrated according to ITS-90, and its uncertainty is certified as being within ±15 mK. The pressure measurement is obtained with a dead weight gauge, and the experimental uncertainty in the pressure measurements can be estimated to be within ±0.5 kPa.

The charging procedure for a one-component system is as described elsewhere.[15] The overall uncertainty in the measurement of the mass inside the cell is estimated in the same way, amounting to ±10 mg for this sample. The volume of the cell, piping, and pressure transducer cavity is measured with an uncertainty of ±0.0003 dm^3. From the

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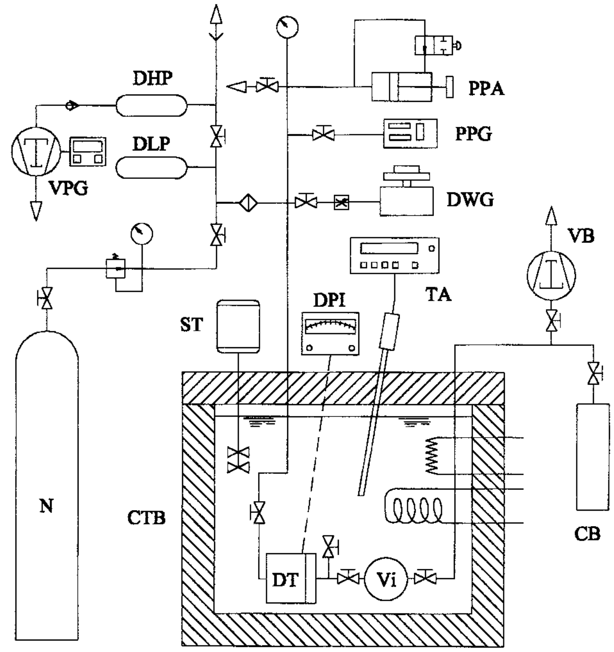

Figure 1. Schematic diagram of the apparatus: CTB, thermostatic bath; DHP, high-pressure expansion chamber; DLP, low-pressure expansion chamber; DPI, electronic null indicator (Ruska, mod. 2461); DT, pressure differential transducer (Ruska, mod. 2413); DWG, dead weight gauge (Ruska, mod. 2465); N, nitrogen reservoir; PPA, precision pressure controller (Ruska, mod. 3891); PPG, vibrating cylinder pressure gauge (Ruska, mod. 6220); ST, stirrer; TA, platinum resistance thermometer (Minco, mod. S7929, + Franco Corradi, mod. RP700); Vi, constant volume spherical cell; VP, vacuum pump (Vacuubrand, mod. RZ2); VPG, vacuum pump gauge (Galileo, mod. OG510); CB, charging bottle.

Table 2. Experimental Vapor Pressure Data of R-236ea

T_{90}/K	P/kPa	T_{90}/K	P/kPa	T_{90}/K	P/kPa	T_{90}/K	P/kPa
255.43	34.6	283.83	121.6	311.04	316.2	340.87	738.7
257.95	39.1	285.68	130.5	313.50	341.6	343.51	791.3
260.62	44.5	288.41	145.0	315.98	368.5	345.95	840.6
263.18	50.2	290.92	159.0	318.22	394.3	348.28	891.0
265.83	56.8	293.39	174.2	320.96	427.7	350.79	947.3
268.59	64.3	295.87	190.3	323.38	458.9	353.36	1006.8
270.79	70.9	298.41	208.1	325.77	491.3	355.80	1067.8
273.50	79.7	301.08	228.0	328.48	530.5	358.36	1133.4
275.77	87.7	303.56	248.0	331.00	568.5	360.90	1198.9
278.70	99.0	305.86	267.6	333.49	608.5	363.27	1265.9
281.50	110.9	308.54	292.1	338.38	692.8		

uncertainties in the mass measurements and in the cell volume measurements (also considering the correction for thermal expansion and pressure distortion, as reported elsewhere[14]), the uncertainty in the calculated molar volume was estimated to be always lower than ±0.07 $dm^3 \cdot mol^{-1}$.

The overall experimental uncertainty in terms of pressure, calculated using the error propagation, was estimated to be less than ±0.6 kPa for measurements along the saturation line and less than ±1.1 kPa in the superheated vapor region.

Results and Discussion

Vapor Pressure. The experimental vapor pressures within a temperature range from 255 K to 363 K are given in Table 2. These data were fitted with the modified Riedel equation

$$\ln P = A + B/T + C \ln T + DT^2 + E/T^2 \qquad (1)$$

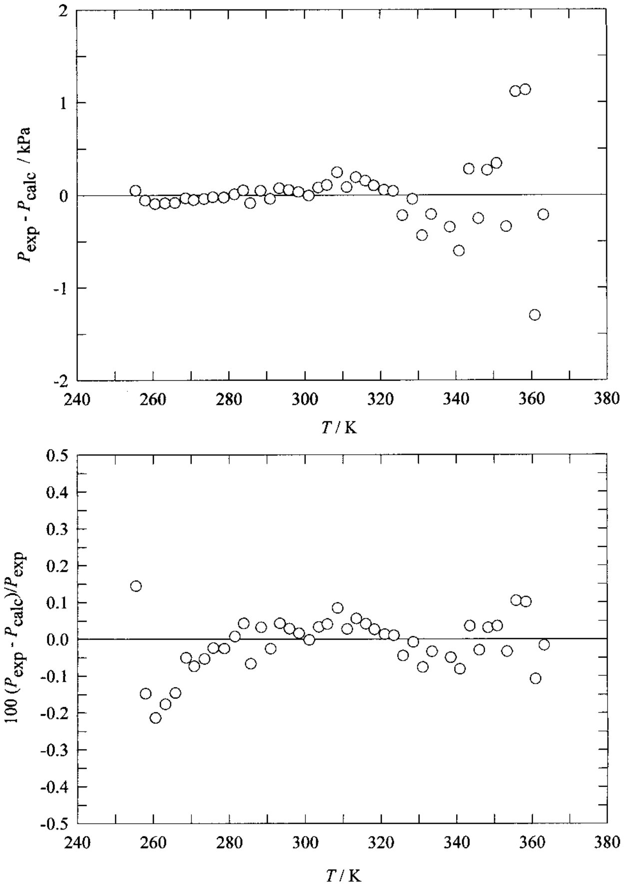

Figure 2. Scatter diagram of the saturated pressure deviations from the fit with the modified Riedel equation, eq 1.

where P is the pressure in kPa and T is the temperature in K. In the results of the data fit, the following values were found for the parameters: $A = 15.9302$, $B = -1725.4045$, $C = -0.4984$, $D = 3.2139 \times 10^{-6}$, and $E = -2.0096 \times 10^5$ with $dP = -0.01$ and $abs(dP) = 0.06$.

Deviations in pressure are defined as

$$dP = \frac{1}{n}\sum_{i=1}^{n}[(P_{exp} - P_{calc})/P_{exp} \times 100] \qquad (2)$$

$$abs(dP) = \frac{1}{n}\sum_{i=1}^{n}[abs(P_{exp} - P_{calc})/P_{exp} \times 100] \qquad (3)$$

where n is the number of experimental points. The error distribution is shown in Figure 2.

Figure 3 shows the deviation between eq 1 and high-precision results available in the literature.[8-11]

P−V−T. Thirty-seven experimental $P-V-T$ measurements in the superheated vapor region along four isochores are presented in Table 3. The measurements were taken in a density range from (0.11 to 0.36) $mol \cdot dm^{-3}$ [(17 to 54) $kg \cdot m^{-3}$], for temperatures from 313 K to 367 K and pressures from 275 kPa to 915 kPa.

Second and Third Virial Coefficients. The virial equation of state in the Leiden form, expressed in terms of inverse molar volume and truncated after the third term, takes the following form:

$$P = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2}\right) \qquad (4)$$

where $R = 8.314\,51\ J \cdot mol^{-1} \cdot K^{-1}$ is the universal gas

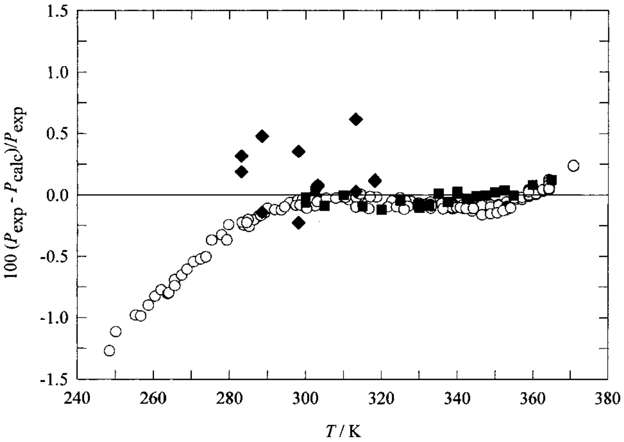

Figure 3. Vapor pressure deviations of 236ea from eq 1: Zhang et al.,[8] ■; Defibaugh et al.,[9] ○; Bobbo et al.,[10,11] ◆.

Table 3. Experimental *P*−*V*−*T* Data of R-236ea

T_{90}/K	*P*/kPa	*V*/dm^3·mol^{-1}	T_{90}/K	*P*/kPa	*V*/dm^3·mol^{-1}
313.64	275.3	8.708	363.27	395.6	7.144
318.50	280.5	8.709			
323.47	285.8	8.711	338.47	658.4	3.602
328.38	291.0	8.713	343.37	673.2	3.603
333.44	296.3	8.716	348.46	687.9	3.604
338.38	301.3	8.718	353.43	702.1	3.605
343.40	306.6	8.720	358.23	715.7	3.605
348.45	311.9	8.722	363.41	730.2	3.606
353.41	317.0	8.724			
358.29	322.1	8.726	348.28	841.3	2.806
			350.94	852.4	2.806
318.47	336.5	7.128	352.93	859.4	2.806
323.48	343.2	7.130	353.42	860.6	2.807
328.45	349.8	7.132	355.85	871.5	2.807
333.40	356.4	7.133	357.54	877.7	2.807
338.41	362.9	7.135	358.21	879.9	2.807
343.24	369.2	7.137	358.42	880.4	2.807
348.23	375.6	7.138	360.80	890.5	2.808
353.60	382.4	7.140	363.29	899.0	2.808
358.21	388.2	7.142	367.36	914.5	2.808

constant, *V* is the molar volume, *B* is the second virial coefficient, and *C* is the third virial coefficient.

Starting from the consideration that our experimental data cover a small pressure range and a low reduced temperature range ($0.76 < T_r < 0.89$), where $T_r = T/T_c$ and $T_c = 412.44$,[16] and also considering that our experimental method does not allow points to be retrieved along isotherms, we chose to compare them with general correlating methods instead of applying the fitting approach.

Most of these correlating methods are modifications of the corresponding state principle and describe virial coefficients as a universal function of temperature in terms of compound parameters (critical parameters, acentric factor, dipole moment, polarizability). In particular, to describe second virial coefficients, we chose the ones proposed by Tsonopoulos in two different versions[17,18] and by Weber.[19] In the first Tsonopoulos approach, the polar contribution is disregarded; in the second it is considered with a general expression of the polar term. Weber's approach is specifically addressed to fluoroderivatives of small molecular size, and it has slightly different expressions in terms of describing contributions from the acentric factor and dipole moment.

As for the third virial coefficients, we used the correlation proposed by Orbey and Vera,[20] that is a function of reduced temperature and acentric factor, and the one by Weber,[21] that also includes the reduced dipole moment as a parameter.

Table 4. Overall Absolute Average Deviations (AAD) and *Bias* in Molar Volume Calculated According to Eqs 8 and 9[a]

	eq 6			eq 7		
	Ts1	Ts2	W	Ts1 + OV	Ts2 + OV	W + W
AAD/L·mol^{-1}	0.006	0.012	−0.005	−0.004	0.001	−0.012
bias/L·mol^{-1}	0.007	0.012	0.009	0.005	0.002	0.012

[a] Results under column Ts1 are obtained with the Tsonopoulos method disregarding polar contributions;[17] results under column Ts2 are obtained with the Tsonopoulos method considering polar contributions;[18] results under column W are obtained with the Weber method;[19] results under column Ts1 + OV are obtained with the Tsonopoulos method disregarding polar contributions[17] and the Orbey and Vera method for third virial coefficients;[20] results under column Ts2 + OV are obtained with the Tsonopoulos method considering polar contributions[18] and the Orbey and Vera method for third virial coefficients;[20] results under column W + W are obtained with the Weber method for the second[19] and the third virial coefficients.[21]

In the calculations an acentric factor of $\omega = 0.378\,42$ was derived from our vapor pressure data by means of eq 1, while the dipole moment was calculated both as a constant value of $\mu = 1.129$[16] and as a linear temperature-dependent parameter,[5] without appreciable differences in the results. In addition, considering that our range of temperature was rather limited, the constant value of the dipole moment was used in our calculations for the sake of simplicity. Thus, the calculated value for the reduced dipole moment was

$$\mu_R = (1 \times 10^5)\mu^2(P_c)/(T_c^{\,2}) = 79.8 \tag{5}$$

where P_c is the critical pressure expressed in atmospheres and μ is in Debyes.

For all the above-described options, the deviations in molar volumes were calculated, truncating eq 4 either after the second term (case a)

$$\mathrm{d}V = \left(\frac{PV}{RT} - 1\right)V - B \tag{6}$$

or after the third term (case b)

$$\mathrm{d}V = \left(\frac{PV}{RT} - 1\right)V - \left(B + \frac{C}{V}\right) \tag{7}$$

Deviations in molar volume in both cases were plotted versus reduced temperature in Figure 4a and b. In both parts of the figure, a small reduced temperature dependence can be identified and the third virial coefficients give their important contribution at high reduced temperatures.

Absolute average deviations (AAD) and *bias* in volume were calculated as

$$\mathrm{AAD} = \sum_{i=1}^{n} \mathrm{abs}(\mathrm{d}V_i)/n \tag{8}$$

and

$$\mathrm{bias} = \sum_{i=1}^{n} (\mathrm{d}V_i)/n \tag{9}$$

and they are shown in Table 4.

A first analysis shows that the dipole moment contribution is not very significant. In addition, on comparing the two cases, it is evident that in the region of our measurements the contribution of the third virial coefficient can

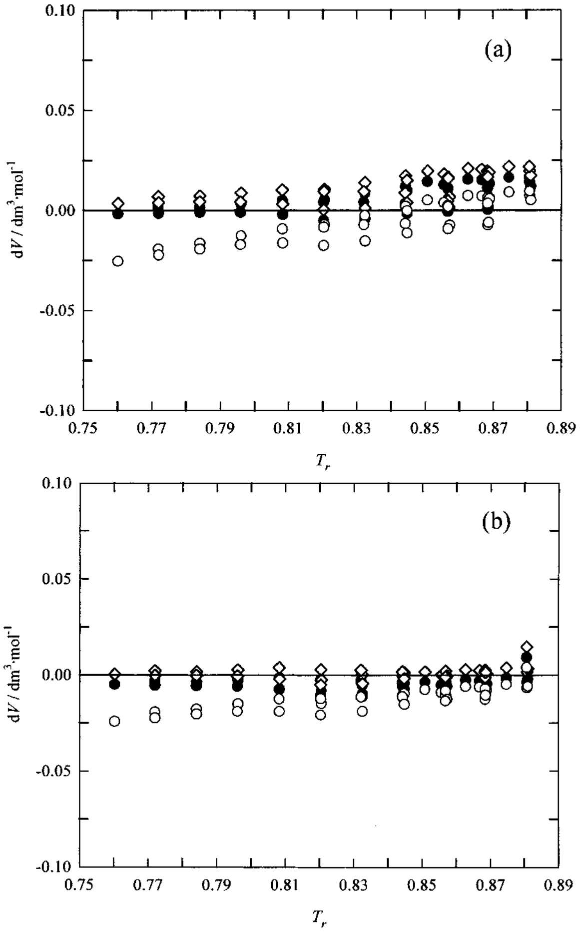

Figure 4. Deviations in molar volume for R-236ea as a function of reduced temperature T_r obtained by comparing experimental data with the Tsonopoulos method disregarding the polar contribution[17] (●), the Tsonopoulos method including the polar contribution[18] (◇), and the Weber method[19] (○).

be disregarded and that the second virial coefficients are able to describe our $P-V-T$ data adequately.

Until now, measurements in the superheated region have only been performed by Zhang et al.,[12] in whose paper virial coefficients are derived.

These derived virial coefficients were used in the present work to check the consistency of our experimental $P-V-T$ measurements with gas-phase points measured by ref 12. The results of this comparison are presented in Figure 5, which shows a good consistency [dP = 0.11 and abs(dP) = 0.12, with dP and abs(dP) defined as in eqs 2 and 3] between the two sets of data.

Conclusions

This work presents 80 experimental data points for saturated pressure and the superheated region of R-236ea, obtained using a constant-volume apparatus. Forty-three points describe the refrigerant's behavior in the saturated pressure region, and 37 points describe its $P-V-T$ behavior along four isochores in the superheated vapor region. The data collected for the saturated pressure were fitted to the modified Riedel equation and compared with reliable data available in the literature.

$P-V-T$ data in the superheated region were analyzed, calculating the second virial coefficients with the Tsonopoulos and the Weber correlating methods and the third virial coefficients with the Orbey and Vera, and the Weber correlating methods, and differences produced by the different methods were generally rather small. Moreover, the contribution of the third virial coefficients is not so appreciable, giving some results only at higher reduced temperatures. $P-V-T$ data were also compared with the gas-phase points reported by Zhang et al.[12] The consistency of both experimental saturated pressure and $P-V-T$ data with those published in the literature was very good.

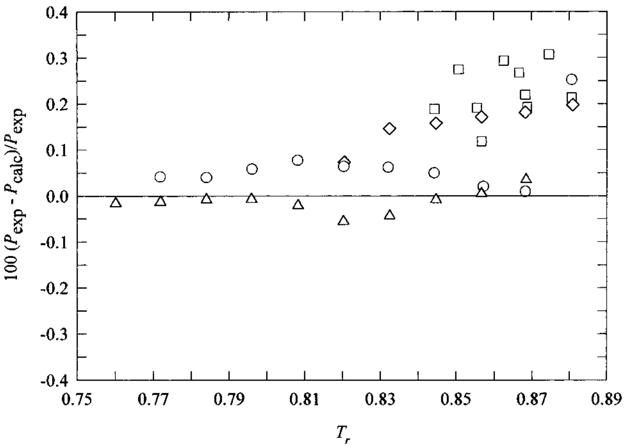

Figure 5. Scatter diagram of deviations as a function of reduced temperature T_r between experimental $P-V-T$ data and data from ref 12: □, 1st isochore; ◇, 2nd isochore; ○, 3rd isochore; △, 4th isochore.

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