STUDY ON ISOCHORIC SPECIFIC HEAT CAPACITY OF HFC-32 + HFO-1234ze(E) MIXTURE IN THE LIQUID PHASE

Kenichi, Yamaya, graduate student, National Defense Academy, Yokosuka, Kanagawa, Japan
Atsushi, Matsuguchi, Research associate, National Defense Academy, Yokosuka, Kanagawa, Japan
Noboru, Kagawa, Professor, National Defense Academy, Yokosuka, Kanagawa, Japan

Abstract: Recently, hydrofluoroolefins (HFOs) are considered as candidate groups of new refrigerants due to their mild impact on the environment. However, the accumulation of experimental measurements information about their thermodynamic properties is insufficient. Reliable equations of state for these working fluids are necessary to evaluate the cycle performance of refrigeration systems. In order to develop a reliable equation of state for a fluid, various thermodynamic property measurements of the fluid are required. Among them, isochoric specific heat capacity (c_v) measurements in the liquid phase provide a very useful check for calculations of the second derivative of the pressure with respect to temperature, which is essential information to develop a equation of state but is challenging to measure accurately. For liquid refrigerants, we have been reported several measurements with a twin-cell type adiabatic calorimeter. The adiabatic method is generally accepted in lots of techniques to give the most accurate results. In this work, isochoric specific heat capacity (c_v) measurements for a new refrigerant mixture of HFC-32 + HFO-1234ze(E) are measured at temperatures from 268 K to 457 K and at pressures up to 30 MPa. Behavior of the measured c_v data are compared with that of the component substances.

Key Words: Isochoric Specific Heat Capacity, HFC-32+HFO-1234ze(E), refrigerant, twin-cell type adiabatic calorimeter

1 INTRODUCTION

HFO-1234ze(E) is paid attention as a candidate of next generation refrigerant in place of Hydrofluorocarbons (HFCs) and Hydrochlorofluorocarbons (HCFCs). Compared with current fluorocarbon refrigerants, its effect to environment is very low. The ozone depletion potential (ODP) of HFO-1234ze(E) is 0, the global warming potential (GWP) is 6, the atmospheric life time is approximately two weeks, and flammability and toxicity risks are low. However, when used this as pure substance, the cycle performance of HFO-1234ze(E) is inferior to that of conventional refrigerants(e.g. R410A). Therefore, it is thought to use by mixing to HFC-32 whose cycle performance is high and GWP is relatively low among various HFC refrigerants (Koyama et al. 2010). Table 1 shows the fundamental constants of HFC-32 (Tillner-Roth and Yokozeki 1997) and HFO-1234ze(E) (Higashi et al. 2010). In this work, isochoric specific heat capacity (c_v) measurements for a new refrigerant mixture of *x*HFC-32+ (1-*x*) HFO-1234ze(E) with x=0.492 in the liquid phase were measured at temperatures from 268 K to 457 K and at pressures up to 30 MPa. The sample purity of HFC-32 and HFO-1234ze(E) was certified to have a minimum purity of 0.9997 mole fraction and 0.9996 mole fraction respectively by gas chromatographic analysis. A twin-cell type adiabatic calorimeter was used for these measurements. Temperatures were measured with a platinum resistance thermometer on the bottom of each cell and were reported based on the ITS-90. Sample pressures were measured with a quartz crystal transducer. Densities were calculated from the volume of the calorimeter cell and the sample mass.

2 MEASUREMENTS

2.1 Experimental Procedures

A twin-cell type adiabatic calorimeter was used for these measurements; it has been described previously in detail by Kuroki et al. (Kuroki et al. 2001) and Kitajima et al. (Kitajima et al. 2005). A spherical cell (approximately 33 cm^3) contains a sample, and a second identical cell serves as a reference. The calorimeter is capable of reaching 470 K. For the heat-capacity measurements, a precisely measured electrical energy (Q) is continuously applied and the resulting temperature rise ($\Delta T=T_2-T_1$) is measured. c_v is obtained from

$$c_V = \left(\frac{\partial U}{\partial T}\right)_V \cong \frac{\alpha\left(\Delta Q - \Delta Q_0\right) - W_{PV}}{m\Delta T} \tag{1}$$

Where U is the internal energy, ΔQ_0 is the energy difference between the sample cell and reference cell when both cells are empty, ΔQ refers to the energy added during an experiment with a sample in the cell and a blank (vacuum) in the reference cell, W_{pv} is the change-of-volume work due to the slight dilation of the cell, α (determined to be 0.940) is the available electrical energy supplied to the heater wire, and m is the mass of sample in the sample cell. To calculate the c_v, the value of temperature rise ΔT was used as ΔT =1 K.
To prepare for measurements, the sample cell was cooled to about 263 K and completely evacuated. The sample was charged into the calorimeter by a cryopump method. Then, measurements were performed by raising the temperature until either the upper temperature or the pressure (30 MPa) was reached on the quasi-isochore. At the completion of the run, a portion of the sample in the cell was filled into a light cylinder so as to obtain the next filling density. Then it was weighed with an electronic balance. At 30 MPa which is sufficiently higher than the critical pressure, the composition of the mixture should be always liquid in the cells and the connecting tubes. The next run was started with a lower density. After all these runs are completed, the remaining sample in the cell was filled and weighed. The measurement were carried out by heating the sample cell whose temperature will follow the temperature of the reference cell heated with a constant current.

2.2 Materials

High-purity samples of HFO-1234ze(E) were used for this measurement. The HFO-1234ze(E) was certified to have a minimum purity of 0.9996 mole fraction that was obtained by gas chromatographic analysis carried out by a sample manufacturer, and the minimum purity of HFC-32 was 0.9997 claimed by it's manufacturer. The mixture of this study was prepared inside the calorimeter cell. A quantity of each pure component was filled into its own lightweight cylinder (75 cm^3) and was weighed with a digital balance. Then the mixture composition was determined. After both components of the mixture were introduced into the cell from its cylinder, the cell was cooled below 278 K by a mini-cooler. The remaining mass in each cylinder was weighed, and the composition of the sample in the cell was calculated from the mass charged to the cell. The sample composition of the mixture consists of xHFC-32+ (1-x) HFO-1234ze(E) with x=0.492. To ensure complete homogenization prior to measurements, the sample temperature was rapidly increased until the sample pressure reached 20 MPa, then it was cooled, and this process was repeated twice or three times.

2.3 Assessment of Uncertainty

The experimental expanded uncertainty (with a coverage factor k=2) of the absolute temperature measurement is 13 mK, by considering the calibration report of the PRTs (±2 mK), temperature gradients in the cell, and the accuracy of each instrument. The value for

the pressure measurement for k=2 is 8 kPa, based on the pressure transducer specifications and the accuracy of the instruments. The standard uncertainty of the inner volume of the cell is 0.025 cm^3, estimated by calibration with distilled water, and that of the mass measurement is 0.15 mg, based on balance specifications and the standard uncertainty of the air buoyancy effect. The estimated expanded uncertainty of the density is 0.16 %, as derived from the standard uncertainties of the inner volume of the cell and the mass measurement. The expanded uncertainty of c_v is estimated from a combination of the standard uncertainty of the elapsed time required for a 1 K temperature rise (0.65 %), that of the change-of-volume work (20 %) which contributes 0.3 % to the uncertainty of c_v, the experimental standard deviation of α of 0.6 %, the uncertainty of the density, and the temperature fluctuation of adiabatic shields which contributes an amount of $0.4/(m\ c_v)$ $J \cdot g^{-1} \cdot K^{-1}$ to the uncertainty of c_v. The resulting expanded uncertainty (k=2) of c_v is from 1.75 % to 4.25 % in the liquid phase.

3 RESULTS

Isochoric specific heat capacity (c_v) of xHFC-32+ (1-x) HFO-1234ze(E) with x=0.492 mixture has been measured in the liquid phase along four isochores of the temperature range from 270 K to 450 K at pressures up to 30 MPa. Table 2 shows the experimental c_v results for xHFC-32+ (1-x) HFO-1234ze(E) with x=0.492 mixture in the liquid phase at interval of 5 K at temperature.

Figure 1 shows the pressure and temperature distributions of the experimental measurements obtained by this work. The data are plotted at interval of 2 K. c_v of HFO-1234ze(E) have been measured with same calorimeter previously. The solid line and the broken line show the saturated vapor pressure for HFC-32 (Tillner-Roth and Yokozeki 1997) and HFO-1234ze(E) (Higashi et al. 2010) respectively.

Figure 2 shows the density and temperature distributions of the experimental measurements obtained by this work. The solid line and the broken line show the saturated liquid density for HFC-32 (Tillner-Roth and Yokozeki 1997) and HFO-1234ze(E) (Higashi et al. 2010) respectively.

As there is no EOS for the binary mixture of HFC-32 and HFO-1234ze(E), the deviations are only compared with their component substances.

Figure 3 shows the percentage deviations of the values calculated with equations of state proposed by McLinden et al. (McLinden et al. 2010), Akasaka (Akasaka 2010) and Tillner-Roth and Yokozeki (Tillner-Roth and Yokozeki 1997) from the experimental density for HFC-32 and HFO-1234ze(E) obtained by this work. The available range of the EOS reported by McLinden et al. (McLinden et al. 2010) is from 168 K to 420 K, below 20 MPa, and 1.5053 g/cm^3. As for the EOS by Akasaka (Akasaka 2010) is from 240 K to 400 K for temperature, below 20 MPa for pressure, and below 1.527 g/cm^3 for density. The deviations of the values are also presented outside of the available range of the equations by using the light-colored symbol. The calculated values from the EOS by McLinden et al. and Tillner-Roth and Yokozeki indicate good agreement with the measurements forward the critical temperature, but it increase from 1 % to 1.5 % near the critical temperature.

Figure 4 and Figure 5 show the experimental behavior of c_v data of xHFC-32+ (1-x) HFO-1234ze(E) with x=0.492 mixture, HFC-32 and HFO-1234ze(E). Particularly, Figure 5 shows a series of the experimental behavior of c_v data below 400 K and also represents the calculated values for HFC-32 and HFO-1234ze(E) from the EOS by Tillner-Roth and Yokozeki (Tillner-Roth and Yokozeki 1997), and McLinden et al. (McLinden et al. 2010). In the measurement range below 320 K, c_v of xHFC-32+ (1-x) HFO-1234ze(E) with x=0.492 mixture are on the average between HFC-32 and HFO-1234ze(E). On the other hand, the behavior of c_v is equivalent to HFC-32 above 320 K. Figure 6 shows the percentage deviations of the values calculated with the EOS by McLinden et al. (McLinden et al. 2010), Akasaka (Akasaka 2010) and Tillner-Roth and Yokozeki (Tillner-Roth and Yokozeki 1997) from the c_v data below 400 K. The deviations of c_v from the measurements below 380 K were within ± 5 % for the EOS by Akasaka (Akasaka 2010) and Tillner-Roth and Yokozeki (Tillner-Roth and Yokozeki 1997) at the available range of the equations. On the other hand, it

reaches around 8% for the EOS by McLinden et al. (McLinden et al. 2010). And the deviations increase rapidly above 380 K for all EOS.
Figure 7 shows the percentage deviations of the calculated values for *x*HFC-32+ (1-*x*) HFO-1234ze(E) with x=0.492 mixture which were estimated by using an ideal mixing rule(c_v=$xc_{v,HFC-32}$+(1-*x*)$c_{v,HFO-1234ze(E)}$) from the c_v measurements below 400 K. It is found that the deviations are almost less than 6 %. It is thought that the deviations could be smaller according to the development of the EOS for pure substance and mixing rule.

4 CONCLUSION

Isochoric specific heat capacity c_v of *x*HFC-32+ (1-*x*) HFO-1234ze(E) with *x*=0.492 mixture were reported in the temperature range from 268 K to 457 K with an uncertainty ranging from 1.75 % to 4.25 %. In order to clarify more detailed dependence of the composition for the binary mixture of HFC-32+HFO-1234ze(E), experimental c_v data with different mixing ratio are required.

ACKNOWLEDGEMENTS
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Table 1 The fundamental constants of HFC-32 and HFO-1234ze(E)

	HFC-32	HFO-1234ze(E)
Molecular Formula	CH_2F_2	$CF_3CH=CHF$
Critical Temperature (K)	351.255	382.51
Critical Pressure (MPa)	5.7826	3.632
Critical Density (g/cm^3)	2.358	0.486
Molar Mass (g/mol)	52.024	114.04

Table 2: Experimental c_v results for xHFC-32+ (1-x) HFO-1234ze(E) with x=0.492 mixture in the liquid phase.

T (K)	P (MPa)	ρ (g·cm^{-3})	c_v (J·g^{-1}·K^{-1})	T (K)	P (MPa)	ρ (g·cm^{-3})	c_v (J·g^{-1}·K^{-1})
270.15	6.381	1.204	0.942	370.15	18.597	0.949	1.017
275.15	10.871	1.203	0.952	375.15	20.632	0.949	1.014
280.15	15.337	1.202	0.951	380.15	22.665	0.948	1.029
285.15	19.779	1.201	0.959	385.15	24.693	0.948	1.022
290.15	24.194	1.200	0.964	390.15	26.719	0.947	1.044
295.15	28.578	1.199	0.964	395.15	28.740	0.947	1.031
295.15	4.930	1.121	0.908	390.15	6.195	0.351	2.967
300.15	8.378	1.120	0.964	395.15	6.524	0.351	2.679
305.15	11.817	1.119	0.974	400.15	6.850	0.351	2.383
310.15	15.249	1.118	0.969	405.15	7.173	0.351	2.249
315.15	18.666	1.118	0.969	410.15	7.495	0.351	2.087
320.15	22.071	1.117	0.979	415.15	7.815	0.350	1.839
325.15	25.462	1.116	0.972	420.15	8.134	0.350	1.677
330.15	28.836	1.115	0.975	425.15	8.452	0.350	1.511
335.15	4.402	0.953	1.004	430.15	8.769	0.350	1.431
340.15	6.417	0.952	0.982	435.15	9.084	0.350	1.380
345.15	8.435	0.952	0.979	440.15	9.399	0.350	1.380
350.15	10.461	0.951	0.994	445.15	9.712	0.350	1.185
355.15	12.492	0.951	1.007	450.15	10.025	0.350	1.114
365.15	14.526	0.950	1.008	455.15	10.337	0.350	1.110

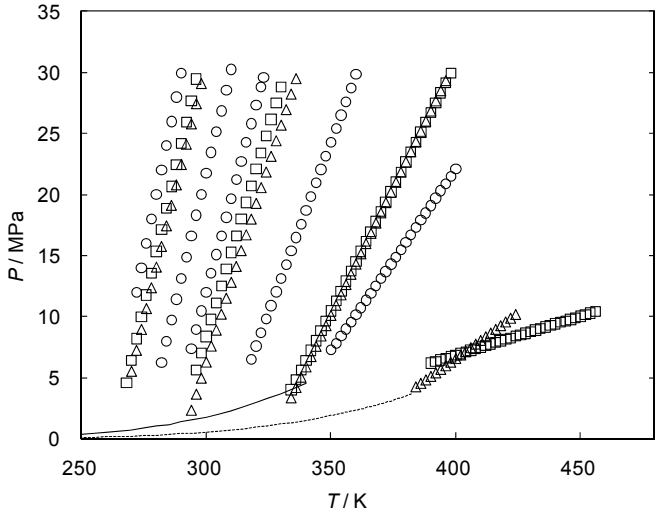


Figure 1: Pressure and temperature distributions of the experimental measurements obtained by this work. The symbol shows, □: *x*HFC-32+ (1-*x*) HFO-1234ze(E) with x=0.492 mixture, ○: HFC-32, Δ: HFO-1234ze(E), —: saturated vapour pressure for HFC-32, ---: saturated vapour pressure for HFO-1234ze(E).

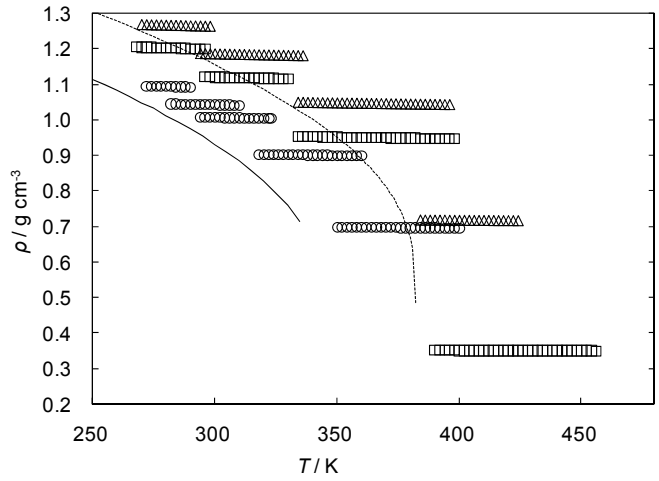


Figure 2: Density and temperature distributions of the experimental measurements obtained by this work. The symbol shows, □: *x*HFC-32+ (1-*x*) HFO-1234ze(E) with x=0.492 mixture, ○: HFC-32, Δ: HFO-1234ze(E), —: saturated liquid density for HFC-32, - - -: saturated liquid density for HFO-1234ze(E).

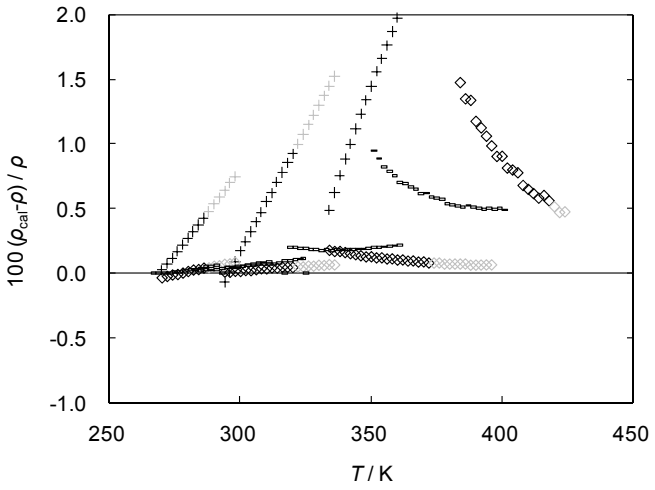


Figure 3: The percentage deviations of the values calculated with equations of state from the experimental density for HFC-32 and HFO-1234ze(E) obtained by this work. The symbol shows, -: the calculated values for HFC-32 from the EOS by Tillner-Roth and Yokozeki (Tillner-Roth and Yokozeki 1997), ◊: the calculated values for HF-1234ze(E) from the EOS by McLinden et al. (McLinden et al. 2010), +: the calculated values for HF-1234ze(E) from the EOS by Akasaka (Akasaka 2010). The light-colored symbol shows outside of the available range of the equations.

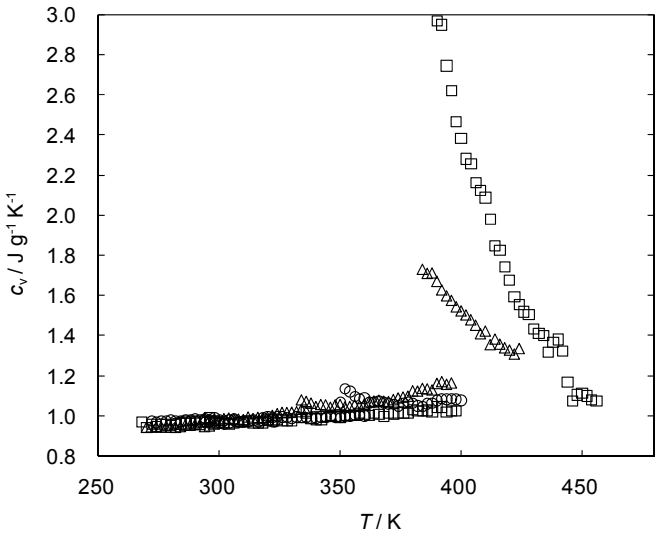


Figure 4: The experimental behavior of c_v data of *x*HFC-32+ (1-*x*) HFO-1234ze(E) with x=0.492 mixture, HFC-32 and HFO-1234ze(E). The symbol shows, □: *x*HFC-32+ (1-*x*) HFO-1234ze(E) with x=0.492 mixture, ○: HFC-32, Δ: HFO-1234ze(E).

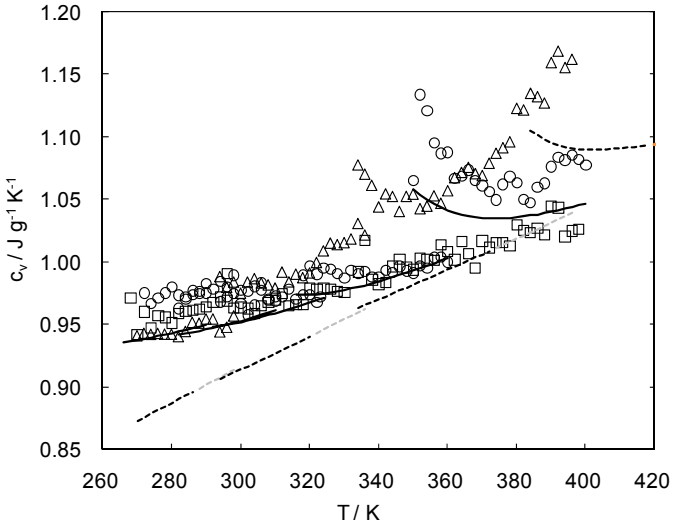


Figure 5: The experimental behavior of c_v data of *x*HFC-32+ (1-*x*) HFO-1234ze(E) with x=0.492 mixture, HFC-32 and HFO-1234ze(E) below 400 K. The symbol shows, □: *x*HFC-32+ (1-*x*) HFO-1234ze(E) with x=0.492 mixture, ○: HFC-32, Δ: HFO-1234ze(E), —: the calculated values from the EOS by Tillner-Roth and Yokozeki (Tillner-Roth and Yokozeki 1997), ---: the calculated values from the EOS by McLinden et al.(McLinden et at. 2010).

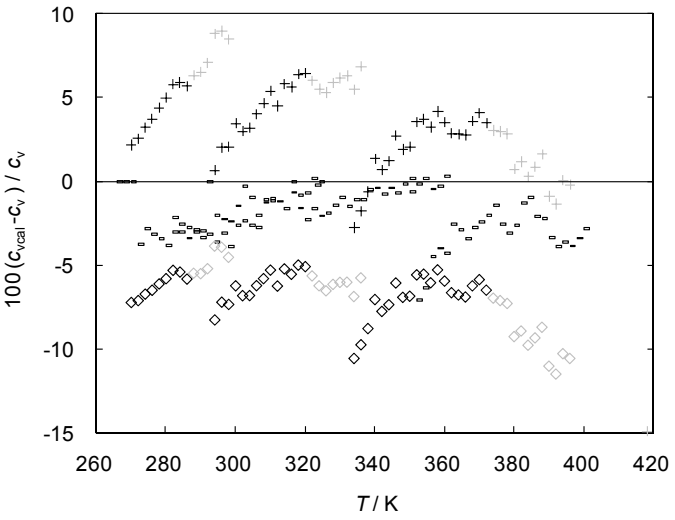


Figure 6: The percentage deviations of the calculated values from the c_v data below 400 K. The symbol shows, -: the calculated values for HFC-32 from the EOS by Tillner-Roth and Yokozeki (Tillner-Roth and Yokozeki 1997), ◊: the calculated values for HFO-1234ze(E) from the EOS by McLinden et al. (McLinden et at. 2010), +: the calculated values for HFO-1234ze(E) from the EOS by Akasaka (Akasaka 2010). The light-colored symbol shows outside of the available range of the equations.

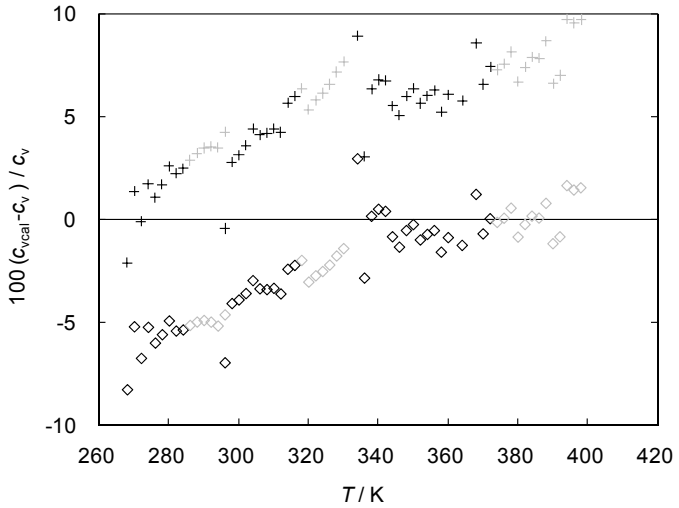


Figure 7: The percentage deviations of the calculated values for *x*HFC-32+ (1-*x*) HFO-1234ze(E) with *x*=0.492 mixture which were estimated by using an ideal mixing rule from the c_v measurements below 400 K. The symbol shows, ◊: the calculated values from the EOS by McLinden et al. (McLinden et at. 2010) and the EOS by Tillner-Roth and Yokozeki (Tillner-Roth and Yokozeki 1997), +: the calculated values from the EOS by Akasaka (Akasaka 2010) and the EOS by Tillner-Roth and Yokozeki (Tillner-Roth and Yokozeki 1997). The light-colored symbol shows outside of the available range of the equations.