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# THERMODYNAMIC PROPERTIES OF NEW REFRIGERANTS

-- HFC-32 AND HFC-125 --

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## ABSTRACT

Among the proposed candidates to replace HCFC-22 and an azeotropic refrigerant R-502, two essential alternative refrigerants, HFC-32 and HFC-125, are considered being promising by applying them as a component of refrigerant mixtures. It is also reviewed, however, that availability of reliable thermodynamic properties of these new refrigerants is so much limited up to the present. The scarcity of reliable thermophysical property data is currently retarding the engineering challenge to apply these refrigerants in various applications.

The present paper summarizes a series of experimental measurements of thermodynamic properties including vapor pressures, PVT properties, compressibility factors and virial coefficients in extensive range of temperatures and pressures for these important alternatives.

## INTRODUCTION

Several proposals for accelerating the phasedown of CFC chemicals and stopping their production and consumption, except for certain essential uses and servicing existing equipments, have been issued recently. In conjunction with such a recent movement to speed up complete phaseout of CFCs, the desire to establish phaseout dates for HCFCs which are under non-mandatory controls in the existing Montreal Protocol becomes significant.

The phaseout dates, especially for HCFC-22, should be reassessed in detail in future reviews of the protocol but it seems to the present authors fair to mention that the future international regulation to ban use of HCFC-22 in new equipments would be agreed for the year of 2010 or so. Unfortunately, however, satisfactory and environmentally-safe alternatives to replace most HCFC-22 applications are not identified and proven at the present stage. The phaseout dates for HCFC-22 must be examined carefully through permitting full evaluation and testing of alternatives for toxicity, chemical and material compatibility, performance, global warming potential and many other essential factors.

Besides these factors to be considered, it is needless to stress an importance of revealing thermophysical properties of alternatives rather extensively in order to support various engineering R & D with environmentally-acceptable refrigerants. Long advance notice of phase-out regulations would become feasible by accumulating reliable sets of information about thermophysical properties of candidates in earlier stage.

HFC-32 and HFC-125 have been proposed as promising candidates to substitute HCFC-22 and R-502 by applying them as a component of refrigerant mixtures rather than by applying them as single refrigerants. To the best knowledge of the present authors, however, only a very limited number of thermodynamic property data both for HFC-32 and HFC-125 are available in restricted range of physical conditions at the present stage. The present paper reports some essential thermodynamic property data on vapor pressures, PVT properties or compressibility factors and

some detailed comparison of the present results with available correlations for HFC-32 and HFC-125.

## EXPERIMENTAL APPARATUS

### Burnett Apparatus

The compressibility factors and vapor pressures of HFC-32 have been measured by a Burnett apparatus which is shown schematically in Fig. 1. It consists of cell system, temperature control and measuring systems, and pressure measuring system.

The cell system consists of two cells and an expansion valve. A sample cell (A) and an expansion cell (B) are thick-walled spherical vessels made of SUS 304 with about 500 cm<sup>3</sup> and 250 cm<sup>3</sup> in their respective inner volumes, whereas the expansion valve (V1) is a constant-volume valve.

The temperature was measured by a platinum resistance thermometer (D) installed near the cells in a thermostated bath (I). For establishing a uniform temperature field around the sample cell, the expansion cell and a differential pressure detector (C), all coupled together, are immersed in the thermostated bath. Silicone oil was used as the heat transfer medium in the bath and was circulated by a stirrer (E). The temperature of bath was regulated by adjusting the current through an electric heater (F). The uncertainty of temperature measurements was estimated being better than  $\pm 10$  mK.

The sample pressure was transmitted to an external pressure measuring system through the diaphragm-type differential pressure detector (C) by balancing the sample gas pressure with pressure of nitrogen gas in the pressure measuring system. Then the nitrogen gas pressure was directly measured by an air-piston pressure gauges (M or N). The uncertainty of pressure measurements was not worse than  $\pm 0.8$  kPa.

Accurate determination of the cell constant defined as a ratio of volumes of two different cells (A and B) at zero pressure is one of the essential factors in the Burnett method. Helium gas was used not only for the determination of cell constant but also for the confirmation of reliability of the present experimental procedure. Measurements were conducted twice at 370 K and once at 320 K by using the helium with 99.9999 mol% purity. The cell constant thus determined with high accuracy was  $1.50368 \pm 0.00029$ .

The purity of HFC-32 used was 99.98 wt%.

### Constant-volume Apparatus

The so-called pressure-volume-temperature relations (PVT properties) and vapor pressures of HFC-125 have been measured by a constant-volume apparatus which is shown schematically in Fig. 2. It consists of constant-volume cell system, temperature control and measuring systems, and pressure measuring system.

A constant-volume cell (A) in which sample fluid of HFC-125 is confined is thick-walled spherical vessel made of SUS 304 with about 139 cm<sup>3</sup> in its inner volume. The inner volume of the constant-volume cell was carefully calibrated with the known density of pure water and compensated its volume change due to the difference in temperature and pressure condition by using the thermal expansivity and Young's modulus of the stainless steel. The density of the sample was determined from the inner volume of the cell and the mass of the sample confined in the cell, which was measured by a precision chemical balance. The uncertainty of the cell volume was about 0.02 to 0.12 % depending on temperature and pressure, while that of sample mass measurements was  $\pm 3$  mg.

The temperature of silicone oil filled in the thermostated bath(C) was controlled within  $\pm 2$  mK by the PID temperature controller. At the thermal equilibrium which was confirmed by the pressure of the sample fluid in the cell being stable, the pressure and the temperature of the sample were measured.

The pressure of the sample was measured by the pressure gauges(O1, O2 and O3). The sample cell is connected with a differential pressure detector(B), which transfers the pressure of the sample to pressure-transfer medium, nitrogen gas. The mechanical behavior of the differential pressure detector was carefully calibrated before and after each series of measurements. The temperature was measured by using a standard platinum resistance thermometer(D), which was installed nearby the sample cell. The platinum resistance thermometer was calibrated according to the IPTS-68 at the National Laboratory of Metrology, Tsukuba, Japan.

The experimental uncertainty of the present measurements on HFC-125 was estimated being within  $\pm 10$  mK in temperature and  $\pm 2$  kPa in pressure, respectively. By considering to the uncertainties of volume of the sample cell and sample mass confined, the uncertainty of density was estimated being within  $\pm 0.1\%$ . The purity of the sample analyzed by the supplier was 99.9 wt%, although we could not find any significant difference in results by our preliminary measurements using the sample with 99.5 wt% purity supplied by other manufacturer.

## EXPERIMENTAL RESULTS AND DISCUSSION

### Thermodynamic Properties of HFC-32

A set of 9 vapor pressure data for temperatures 280-350 K and 95 compressibility factors for the range of temperatures 290-370 K and pressures up to 6.6 MPa have been measured for HFC-32. The uncertainty of the present compressibility factor measurements was estimated being within  $\pm 0.5\%$  and we have also determined the second and third virial coefficients for temperatures 290-370 K[1]. It should be also noted that we have reported similar sets of data including vapor pressures, compressibility factors and virial coefficients for HFC-134a[2] and for HCFC-123[3] by the same Burnett apparatus.

Figure 3 illustrates the present measurements together with the data reported by Malbrunot et al.[4] on a pressure vs. temperature diagram. A comparison of the vapor pressure data is shown in Fig. 4 where the correlation proposed by Malbrunot et al.[4] was chosen as a reference of comparison and the vapor-pressure correlation by McLinden[5] is also included. An agreement between the present results and the data by Malbrunot et al. is acceptable for the temperatures overlapped, though the scatter of the present data is far less than that of Malbrunot et al. McLinden[5] proposed his correlation on the basis of the vapor pressure data by Malbrunot et al. exclusively and therefore we found it is necessary to reestablish the vapor-pressure correlation for HFC-32.

From our measurements of compressibility factors, we have calculated the density values or PVT properties of HFC-32. At the present stage, a Martin-Hou type equation of state by Malbrunot et al.[4] is a single representation to cover the range of temperatures 273-373 K, of pressures up to 20.3 MPa and of specific volumes up to 0.045 m<sup>3</sup>/kg. Hence we have used this equation of state just for the comparison of the present PVT data with those by Malbrunot et al. by extrapolating this representation even beyond the claimed range of validity as shown in Fig. 5 where the deviation in pressure from the equation is plotted against the specific volume values. The PVT data by Malbrunot et al. start to deviate from the equation at larger specific volume values they measured but the present PVT data show an excellent agreement with the equation even at much higher specific volumes as clearly seen in Fig. 5. Since the Martin-Hou representation reproduces the ideal-gas behavior at lower densities, such an agreement between the present data and the equation confirms the reliability of the present measurements.

## Thermodynamic Properties of HFC-125

Using the constant-volume apparatus which was applied for our previous measurements of vapor pressures and PVT properties of HFC-134a [6] and HCFC-123[7], we have measured the same thermodynamic properties of HFC-125 in the present study. Some of the preliminary results were reported recently[8].

A set of 29 vapor pressure data for temperatures 303-339 K and 54 PVT property data for the range of temperatures 310-423 K, of pressures up to 11.1 MPa and of densities 97-940 kg/m<sup>3</sup> were obtained.

Figure 6 shows the deviation of measured vapor pressure data for HFC-125 from our proposed correlation[8]. The reported data by Wilson et al.[9] and Defibaugh et al.[10] as well as available correlations by Defibaugh et al.[10], McLinden[5], Wilson et al.[9] and by Singh et al.[11] are also included in this Fig. 6. The data by Wilson et al.[9] show a considerable amount of scatter, whereas those by Defibaugh et al.[10] agree with the present results within about 0.5% in vapor pressure difference. Three different correlations[5,10,11] agree not only each other but also consistent with the present data and proposed correlation within about 0.5%, although the correlation by Wilson et al.[9] deviates considerably from the present correlation.

A distribution of the present PVT property data is shown in Fig. 7 which covers the entire fluid phase of HFC-125. Among the available equations of state[9,11], the representation developed by Wilson et al.[9] was chosen here for its comparison with the present PVT measurements as shown in Fig. 8. More extensive comparison of the reported PVT property data including the present results with this equation of state is also shown in Fig. 9. The data by Wilson et al.[9] scatter significantly and are less consistent with other sets of data, while the measurements obtained by a vibrating-tube densimeter[10] at NIST show some systematic deviations from the equation of state[9] both at lower densities and higher densities.

The present study of thermodynamic properties of HFC-125 is still in progress so as to accumulate additional information and we hope that more complete and comprehensive modeling will be developed on the basis of our own measurements.

### CONCLUDING REMARKS

The present paper summarized our recent progress in accurate measurements of various thermodynamic properties of CFC alternatives at our Thermodynamics Laboratory, Department of Mechanical Engineering, Keio University. Emphasis was given to report the thermodynamic properties both of HFC-32 and HFC-125 which are currently considered being promising substitutes to HCFC-22 and R-502.

Taking into consideration of a crucial situation to seek the best optimum substitute to replace HCFC-22, one of the most widely-used CFCs, it seems to the present authors essential to tackle with these two candidates especially for pursuing possible technical challenge in applying these new refrigerants as component of refrigerant mixtures.

In this connection, the availability of reliable information about thermodynamic properties of HFC-32 and HFC-125 is still so much limited and hence more extensive experimental assessment as well as analytical studies of modeling are definitely of urgent necessity.

### ACKNOWLEDGMENTS

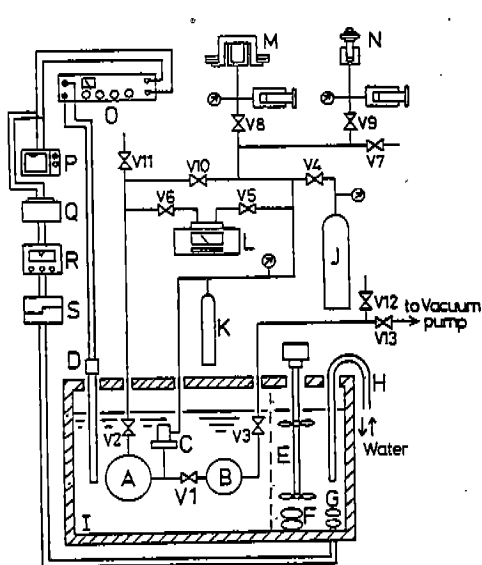
The present authors are indebted to Messrs. Yves Monluc, a former visiting researcher, and Takahiko Sagawa, a graduate student, especially for their assistance in measuring thermodynamic properties of HFC-125. Collaboration by Mr. Atsuo Nishimura, a visiting researcher, and

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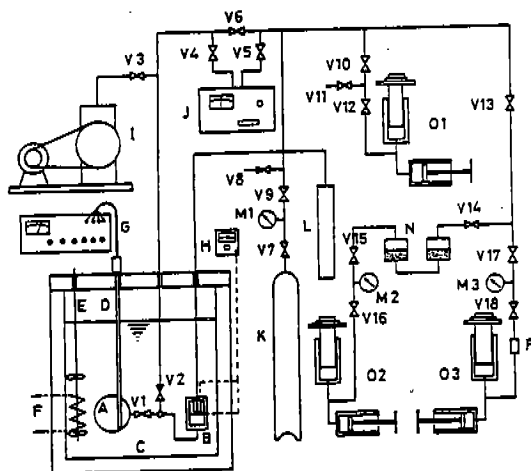
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- A: Sample cell
- B: Expansion cell
- C: Differential pressure detector
- D: Platinum resistance thermometer
- E: Stirrer
- F: Main heater
- G: Subheater
- H: Cooler
- I: Constant temperature bath
- J: N<sub>2</sub> bottle
- K: N<sub>2</sub> gas damper
- L: Precision Bourdon tube pressure gauge
- M: Air-piston type dead-weight pressure gauge(1.1-17.4 MPa)
- N: Air-piston type dead weight pressure gauge(0.1-1.1 MPa)
- O: Thermomter bridge
- P: Pen recorder
- Q: Voltage/Current converter
- R: P.I.D. controller
- S: DC power supply

- V1: Constant volume valve
- V2-V13: Valves

Fig. 1 Schematic diagram of the Burnett apparatus used for HFC-32



- (A) sample vessel, (B) differential pressure indicator, (C) thermostated bath, (D) platinum resistance thermometer, (E) stirrer, (F) heater, (G) bridge, (H) resistance meter, (I) vacuum pump, (J) precision Bourdon tube pressure gauge, (K) nitrogen bottle, (L) pressure damper, (M1-M3) pressure gauges, (N) oil-gas separator, (O1) air piston type pressure gauge (up to 0.4 MPa), (O2) oil piston type pressure gauge (up to 15.1 MPa), (O3) air piston type pressure gauge (1.1-15.1 MPa), (P) dust filter, (V1-V18) valves.

Fig. 2 Schematic diagram of the constant-volume apparatus used for HFC-125

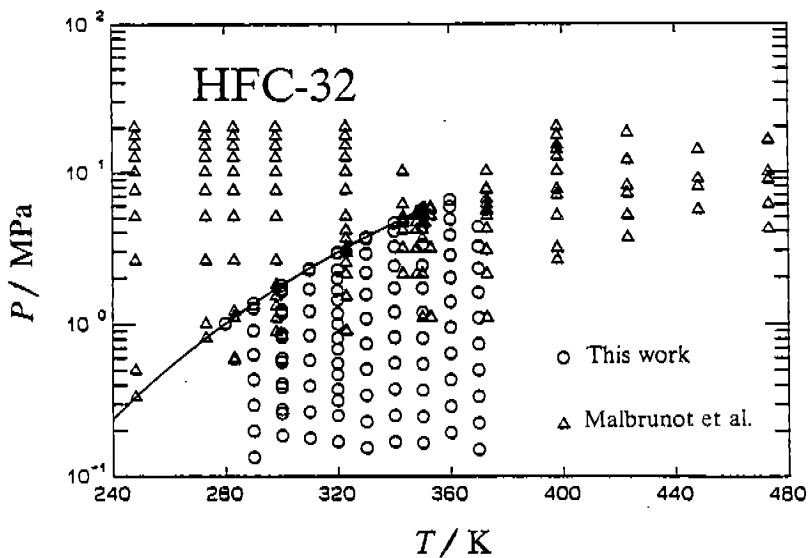


Fig. 3 Availability of the experimental thermodynamic property data for HFC-32

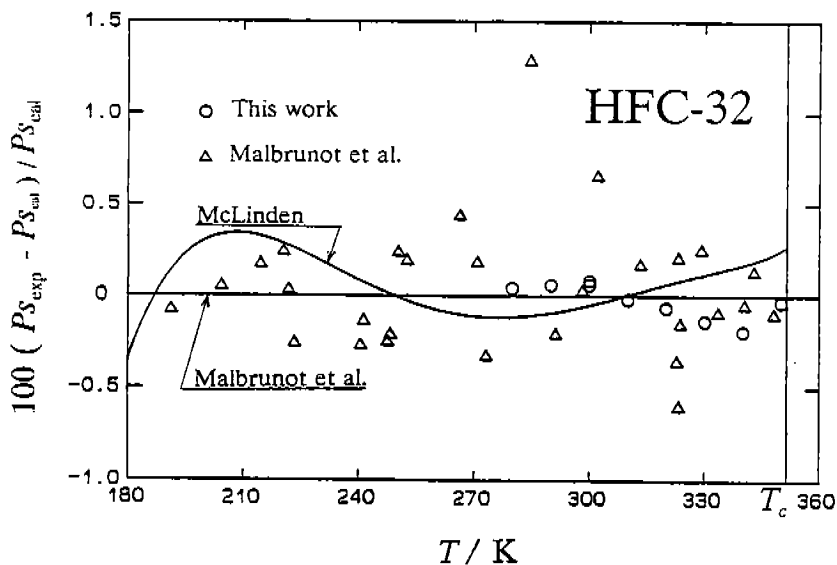


Fig. 4 Comparison of the measured data and correlations for vapor pressures of HFC-32



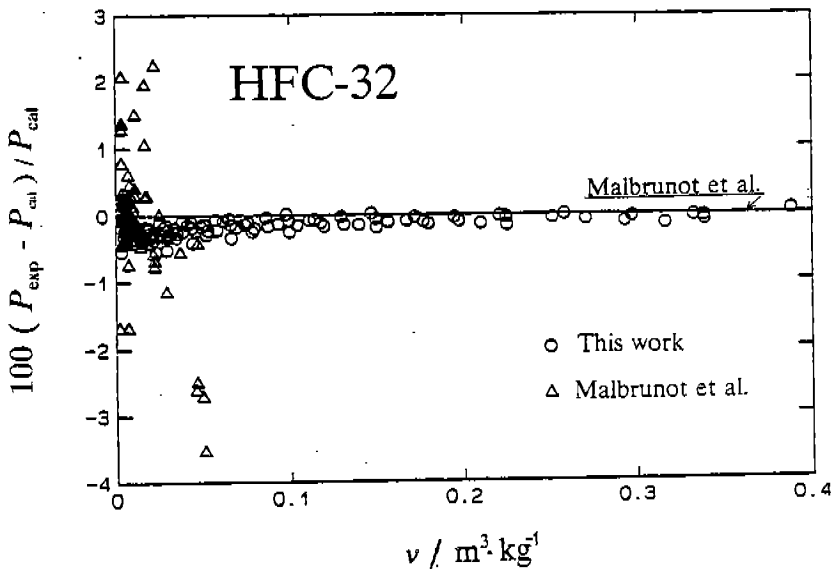


Fig. 5 Comparison of the experimental PVT property data with the extrapolated equation of state developed for HFC-32[4]

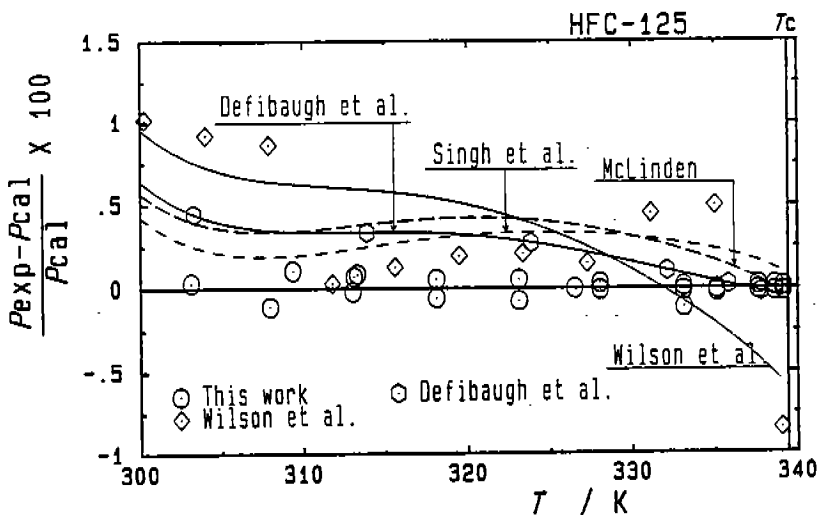


Fig. 6 Comparison of the measured data and correlations for vapor pressure of HFC-125

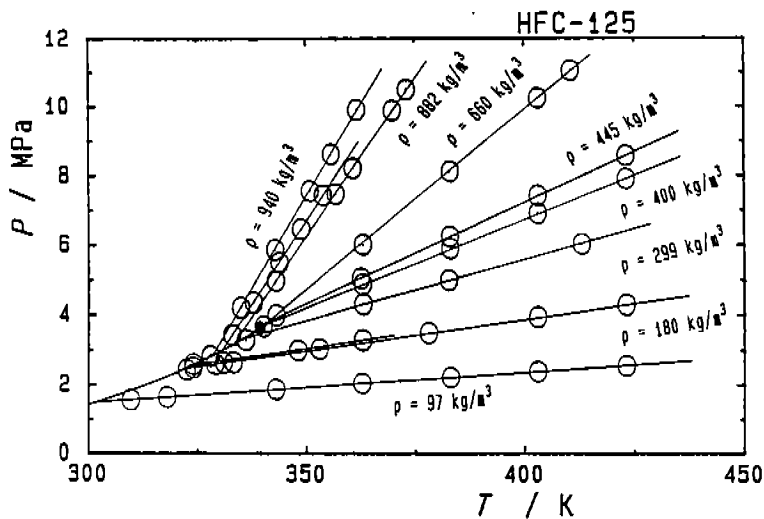


Fig. 7 Distribution of the present PVT property measurements for HFC-125

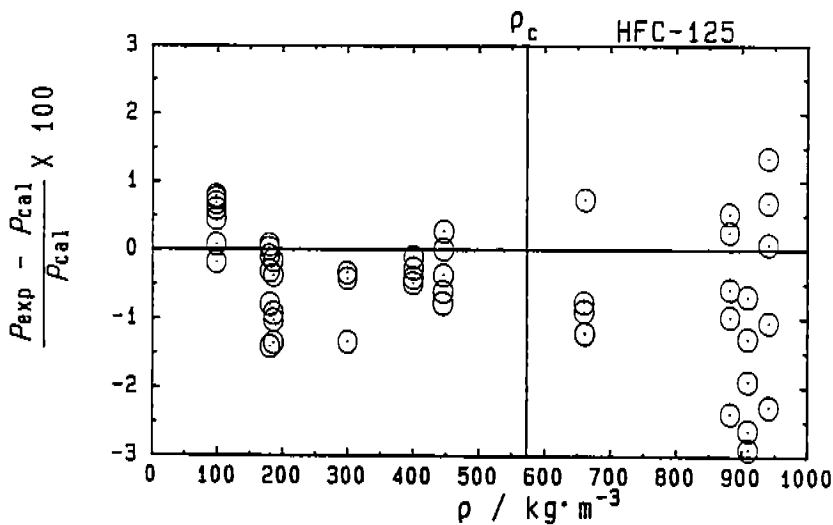


Fig. 8 Pressure deviation of the present PVT property data for HFC-125 from the available equation of state[9]

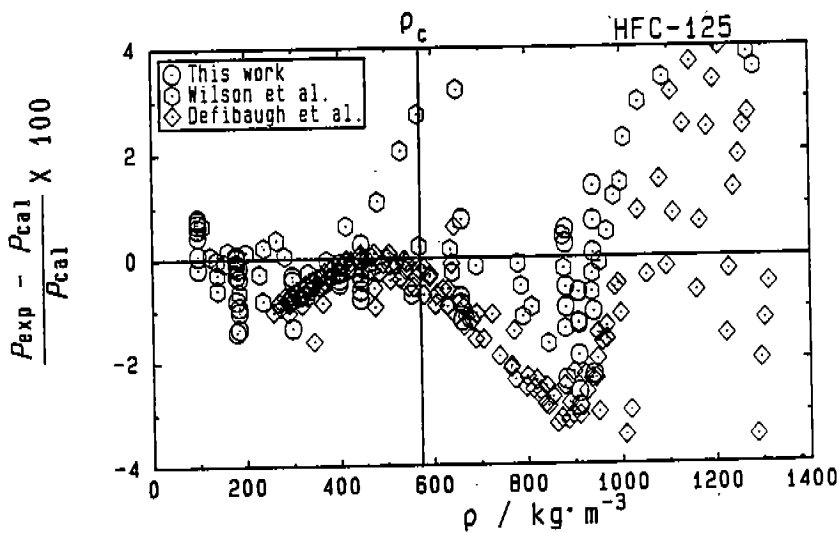


Fig. 9 Comparison of the available PVT property data for HFC-125 with the reported equation of state[9]