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New Thermodynamic Property Measurements of HFC-134A [1]

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ABSTRACT

Saturated vapor pressure, saturated liquid enthalpy, saturated vapor enthalpy, enthalpy and PVT data in the superheated region were measured for 1,1,1,2-tetrafluoroethane (HFC-134a). Saturated properties (21 experimental points for vapor pressure, 11 experimental points for saturated liquid enthalpy, and 12 experimental points for saturated vapor enthalpy) were measured over a temperature range from 250 to 340 K. Enthalpy and limited PVT measurements in the superheated region (48 experimental points for enthalpy and experimental 19 points for PVT) were made over a temperature range from 250 to 340 K and a pressure range from 140 to 1750 kPa. The technique for enthalpy measurements is based on adiabatic electrically heated calorimeter. The standard uncertainty of the enthalpy measurements is estimated to be less than 0.6%. A comparison of the obtained experimental results with available literature data is shown and discussed.

KEY WORDS: adiabatic calorimeter, density, enthalpy, saturated liquid, saturated vapor, superheated vapor, tetrafluoroethane, vapor pressure.

1. INTRODUCTION

HFC-134a has gained more and more importance in the last few years as a replacement for CFCs and HCFCs. A large amount of thermodynamic research have been done recently for this refrigerant. It was found that more than 4,000 experimental points including vapor pressure, saturated liquid and vapor densities, PVT, isochoric and isobaric heat capacity, speed of sound were obtained for HFC-134a. However, there is not sufficient enthalpy data, especially for the superheated vapors. At the same time, exact knowledge of the effect of pressure and temperature on enthalpy is of vital importance in the design of refrigeration equipment, particularly for medium and high capacity centrifugal chillers.

In this paper, we present new measurements of saturated vapor pressure, saturated liquid enthalpy, saturated vapor enthalpy, and also enthalpy and PVT data in the superheated region.

2. EXPERIMENTAL METHODS AND PROCEDURE

2.1. Enthalpy Measurements

Enthalpy was measured using electrically heated calorimeter. A schematic diagram of the enthalpy measuring device is given in Fig. 1.

Adiabatic measuring cell without head space made from stainless steel was placed to the vacuum chamber that was evacuated to reduce heat leakage. A set of perforated silver discs inside the cell provides for the isothermal conditions along the cell. Electric heater is located on the outer surface of the measuring cell. The temperature inside the cell was measured with a platinum resistance thermometer. This thermometer was previously checked with a reference thermometer that is traceable to international standards. Constant pressure inside the cell during the measurements in liquid phase or for saturated liquid was provided with the help of the special vessel installed in the additional temperature bath. During the experiments for the saturated liquid, the temperature of this bath was higher by approximately 0.3 K compared to the temperature of the main temperature bath.

Experimental procedure was as follows:

1. Measuring cell was filled with the fluid under investigation.
2. Required temperature was created by the main temperature bath.
3. Vacuum was created in the vacuum chamber and the adiabatic system was engaged.
4. Electric heater was switched on and appropriate heating rate (0.3 to 3 K/hour) was adjusted.
5. Heat flow by electric heater and the temperature of the fluid under investigation were measured automatically every 2 minutes.

Enthalpy increments were calculated from the measured temperature difference (T_1-T_2), current (I) and resistance (R) of electric heater, time of experiment (t), and amount of the fluid under investigation (m) as

$$\Delta h = \int_{T_1}^{T_2} \frac{I^2 R\tau}{m(T_1 - T_2)} dT \qquad (1)$$

The amount of the fluid under investigation was determined from the known cell volume and PVT data.

The accuracy of the enthalpy measurements is affected by the heat leakage and the accuracy of the instrumentation. All sources of uncertainty were evaluated in details in accordance with the guidelines given by the NIST.

Extensive experimental test runs and theoretical evaluation have been performed to find the heat leakage by radiation and conduction from the calorimeter. To get comparable numbers, all calculations have been performed at the worst case, i.e., conditions of maximum heat transfer.

The principal sources of uncertainty are the cell heat capacity and the cell volume. Both of them were defined as a function of temperature and pressure by calibration experiments using the most reliable literature data for water and R-22. The uncertainty of the measured temperature difference is ±0.03 K, and for pressure it is less than ±0.04%. The

heat flow created by the electric heater is measured with the uncertainty of ±0.1%. The final uncertainty of enthalpy measurements can not be given as a fixed value for all test runs, because the measured enthalpy increments are a function of several parameters of varying importance in different temperature and pressure regions. Overall, the maximum value of the standard uncertainty of the enthalpy increments is estimated to be less than ±0.55% for the saturated liquid and less than ±0.48% for the saturated and superheated vapor.

2.2. PVT and Saturated Vapor Pressure Measurements

PVT measurements for the superheated vapors were performed using a constant-volume method. Stainless steel cylinder with volume of 180 cm^3 connected to the precision pressure transducer is installed in the temperature bath provided temperature control to within ±0.01 K. The temperature is measured with a platinum resistance thermometer. The uncertainty of the temperature is ±0.02 K, and for pressure it is less than ±0.04%. The amount of the mixture under investigation was determined by gravimetric method. Other details regarding the construction and operation of the measuring device are given elsewhere [1].

The principal source of uncertainty is the cell volume that has an estimated statistical uncertainty of ±0.005 % and estimated systematic uncertainty of ±0.025%. Overall, the uncertainty of the density values is estimated to be less than ±0.15%.

Saturated vapor pressures were determined by direct pressure measurements using stainless steel cell with volume of 50 cm^3 and precision pressure transducer. The uncertainty of the saturated vapor pressure measurements is estimated to be less than ±0.05%.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Saturated Properties

Experimental data of saturated vapor pressure, saturated liquid enthalpy, and saturated vapor enthalpy are given in Table 1.

Reliable saturated vapor pressure data are required for any thermodynamic experiments or calculations. A set of vapor pressure measurements is available by now. Vapor pressures are reported by Wilson and Basu [2], Weber [3], Kubota *et al.* [4], Piao *et al.* [5], Maezawa *et al.* [6], and Yamashita *et al.* [7]. The data [2, 3, 5] are consistent enough. Comparisons of our experimental results with the vapor pressures from [2, 3, 5] show that deviation does not exceed 0.14%.

3.2. Enthalpy and PVT Data in the Superheated Region

Enthalpy measurements in the superheated region were made over a temperature range from 250 to 340 K and a pressure range from 140 to 1750 kPa on 8 isobars. PVT data were obtained at the same isobars. Experimental enthalpy and PVT data in the superheated region are given in Tables 2 and 3, respectively.

In this work, density data of HFC-134a are required to determine the amount of the fluid under investigation for calculating enthalpy using Eq. (1). Our analysis shows that the obtained results are in good agreement with the most reliable PVT measurements reported in [2, 3, 5]. The absolute average deviation does not exceed 0.16%.

No experimental enthalpy data were found in current literature. Commonly, enthalpy is calculated using the appropriate equation of states (EOS) based on the available thermodynamic properties (vapor pressure, saturated liquid and vapor densities, PVT, heat capacity).

Availability of the experimental thermodynamic data for HFC-134a has been recently analyzed by Penoncello *et al.* [8]. It was found that more than 4.000 experimental points including vapor pressure, saturated liquid and vapor densities, PVT, isochoric and isobaric heat capacity, speed of sound were obtained for HFC-134a. However, the accuracy of the calculated enthalpy data strongly depends on the type of EOS and so called "baseline" (ideal gas heat capacity that is computed from spectroscopic data). For example, Huber and McLinden [9] selected a modified Benedict-Webb-Rubin (MBWR) EOS, and Tillner-Roth

and Baehr [10] used an equation for the dimensionless Helmholtz free energy. Both of them are based on the same set of experimental data, but the first gives the average deviation of 0.9% between experimental and calculated isobaric heat capacity, and the second gives the deviation of 0.6%.

Comparison of our experimental enthalpy data of HFC-134a in the superheated region on the isobar 343.10 kPa with those calculated by McLinden EOS [11] is shown in Fig. 2.

In this work, enthalpy tables in the superheated region over a range of temperature and pressure (available upon request) were calculated on the basis of our experimental results using spline method. This software finds the continuous approximating function of two variables with continuous first and second derivatives.

REFERENCES

1. D. B. Bivens, A. Yokozeki, and V. Z. Geller, in *Proc. Int. Refriger. Conf.at Purdue*, 403 (1996).

2. D. P. Wilson and R. C.Basu, *ASHRAE Trans.* **94**: 122 (1988).

3. L. A. Weber, *Int. J. Thermophys.* **10**: 89 (1989).

4. H. Kubota, T. Yamashita, and Y. Tanaka, *Int. J. Thermophys.* **10**: 73 (1989).

5. C.-C. Piao, H. Sato, and K. Watanabe, *ASHRAE Trans.* **96**: 273 (1990).

6. Y. Maezama, H. Sato, and K. Watanabe, *J. Chem. Eng. Data*, **35**: 77 (1990).

7. T. Yamashita, H. Kubota, Y. Tanaka, and H. Kashiwagi, in *Proc. 10th Japan Sympos. Thermophys. Properties*, **2**: 75 (1989).

8. S. G. Penoncello, R. T. Jacobsen, K. M. de Reuck, A. E. Elhassan, R. C. Williams, and E. W. Lemmon, *Int. J. Thermophys.* **16**: 3 (1995).

9. M. L. Huber and M. O. McLinden, in *Proc. Int. Refriger. Conf.at Purdue*, 112, (1992).

10. R. Tillner-Roth and H. D. Baehr, *J. Phys. Chem. Rev. Data,* **23**: 76 (1994).

11. M. O. McLinden, *ASHRAE Trans.* **95**: 116 (1989).

Table 1. Saturated properties of HFC-134a

Temperature (K)	Saturated vapor pressure (kPa)	Temperature (K)	Saturated liquid enthalpy (kJ/kg)	Temperature (K)	Saturated vapor enthalpy (kJ/kg)
253.14	132.6	253.78	174.6	252.04	385.9
257.10	157.0	264.48	188.5	262.28	392.1
261.66	189.1	273.77	200.7	269.42	396.4
265.70	221.6	284.28	215.1	277.61	401.2
286.35	245.3	293.18	227.6	283.48	404.5
269.56	255.3	303.59	242.5	288.72	407.4
274.79	310.7	305.97	246.0	299.84	413.2
277.48	341.6	309.98	251.9	310.95	418.4
282.31	403.5	319.57	266.3	317.87	421.4
286.19	458.7	329.67	281.9	326.61	424.6
292.75	565.3	334.75	290.1	330.73	425.9
297.39	650.8			336.2	427.4
301.65	738.4				
305.37	821.4				
308.39	893.5				
313.35	1022.0				
318.07	1158.4				
325.36	1393.3				
330.78	1591.5				
335.46	1777.2				
337.48	1837.4				

Table 2. Experimental enthalpy data of HFC-134a in the superheated region

Temperature (K)	Enthalpy (kJ/kg)	Temperature (K)	Enthalpy (kJ/kg)	Temperature (K)	Enthalpy (kJ/kg)
P = 138.6 kPa		**P = 699.6 kPa**		**P = 1526.6 kPa**	
254.14	387.2	299.82	413.2	329.05	425.4
254.65	387.5	300.55	414.1	329.63	426.3
258.71	391.0	303.31	416.9	332.42	429.8
264.81	395.9	309.60	423.1	335.68	434.0
273.73	403.4	313.44	427.3	341.73	441.2
279.51	409.1	319.12	432.7	346.15	446.0
288.30	415.6	323.57	437.3	354.30	456.0
		330.48	444.8	361.74	464.5
P = 343.1 kPa		338.00	453.3		
277.60	401.2			**P = 1723.5 kPa**	
278.20	401.7	**P = 957.9 kPa**		334.19	426.9
280.25	403.7	310.95	418.4	334.60	427.7
283.47	406.6	311.58	419.2	336.30	429.8
287.58	410.2	314.65	422.6	339.25	434.1
290.88	413.2	317.56	425.9	345.85	441.0
295.44	417.4	322.67	431.4	349.04	446.2
301.42	422.8	328.51	437.4	354.76	452.9
		332.68	441.9	363.44	463.3
P = 497.5 kPa		341.85	451.3		
288.71	407.4				
289.19	408.0	**P = 1237.8 kPa**			
292.00	410.7	320.67	422.5		
295.23	413.8	321.41	423.6		
302.20	420.4	326.06	429.1		
309.21	426.9	332.27	436.1		
320.05	437.3	340.65	445.5		
		350.26	456.1		
		356.93	463.2		

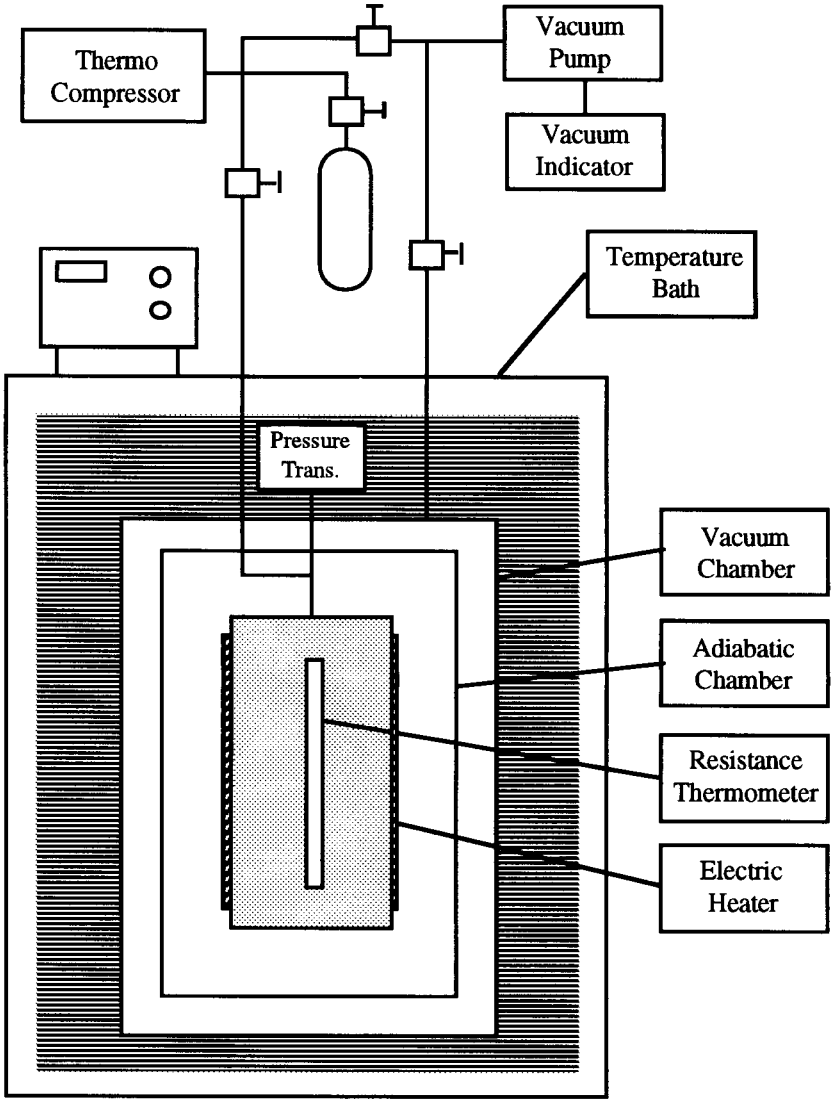
Table 3. Experimental density data of HFC-134a in the superheated region

Temperature (K)	Density (kg/m^3)	Temperature (K)	Density (kg/m^3)
P = 138.6 kPa		**P = 957.9 kPa**	
258.10	6.939	313.13	46.455
273.25	6.497	323.15	43.590
		333.10	41.251
P = 343.1 kPa			
283.18	16.344	**P = 1237.8 kPa**	
298.25	15.238	328.14	58.645
		343.7	53.354
P = 497.5 kPa			
293.21	23.614	**P = 1526.6 kPa**	
298.21	23.007	338.20	73.562
308.06	21.900	353.16	65.432
P = 699.6 kPa		**P = 1723.5 kPa**	
301.49	33.698	338.08	86.566
309.81	32.106	353.21	76.905
325.11	29.738		

FIGURE CAPTIONS

Fig. 1. Enthalpy measuring device.

Fig. 2. Comparison of experimental and calculated by McLinden [11] enthalpy data of HFC-134a at 343.10 kPa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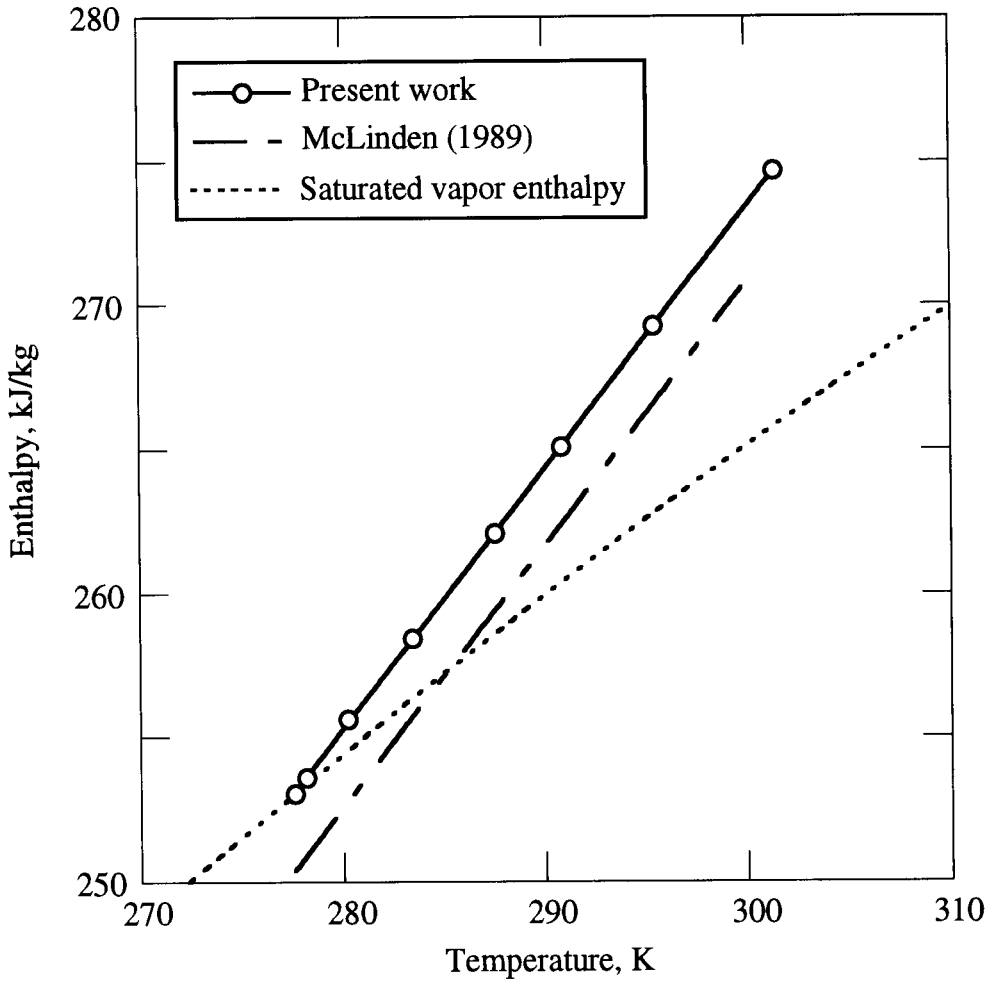
Present work
McLinden (1989)
Saturated vapor enthalpy
Enthalpy, kJ/kg
Temperature, K
280
270
260
250
270
280
290
300
310