

Measurement of the Specific Enthalpy of Vaporization on 1,1,1,2-Tetrafluoroethane in the Temperature Range from 180 to 240 K¹

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An apparatus is described which is capable of measuring the enthalpy of vaporization in the temperature range from 100 to 250 K. The sample (R134a; purity, at least 99.999%) is located in the measuring cell at the saturated vapor pressure, $p = p_s$. A control circuit allows p to be kept constant by opening a motor-operated valve to a weighing cylinder after having switched on the electrical measuring cell heater. During the experiment, the temperature is kept constant within a 10 mK. In the range 180 to 230 K, the data for R134a are compared with calculated values from the fundamental equation given by Tillner-Roth and Baehr, which is recommended by Annex 18 of the International Energy Agency (IEA) as an international standard. Good agreement within a standard uncertainty of 1.6×10^{-3} is obtained. At temperatures of only 10 K above the triple-point temperature, the enthalpy of vaporization calculated from the Clausius–Clapeyron equation shows considerable uncertainty due to the determination of the small vapor pressure. It is chiefly in this range that it is advantageous to have the new apparatus.

KEY WORDS: Clausius–Clapeyron equation; enthalpy of vaporization; R134a; 1,1,1,2-tetrafluoroethane.

1. INTRODUCTION

High-precision measurements of the enthalpy of vaporization on alternative refrigerants have not yet been performed. With the new apparatus developed at PTB, it is possible to measure this quantity at pressures up

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to 0.1 MPa with a relative measurement uncertainty of less than 1.6×10^{-3} at a confidence level of 68%. The first measurements have been carried out on 1,1,1,2-tetrafluoroethane (R134a), a well-known substance with a fundamental equation established in 1994 by Tillner-Roth and Baehr [1]. This equation was recommended as an international standard by Annex 18 (Thermophysical Properties of Environmentally Acceptable Refrigerants) of the International Energy Agency (IEA). It is of considerable interest to compare the measured data with the fundamental equation, since no measured data of the enthalpy of vaporization were used when the fundamental equation was formulated.

2. EXPERIMENTAL

2.1. Description of the Apparatus

The apparatus consists of the following main parts (Fig. 1):

- The measuring cell (designated 1 in Fig. 1) located in an evaporation cryostat operated with liquid nitrogen.
- A Paroscientific pressure sensor (3) Model 223 AT for the 0.1-MPa range, operated with a Hewlett-Packard 5384A frequency counter. The pressure sensor is calibrated with a deadweight tester; the relative measurement uncertainty is 1×10^{-4} .

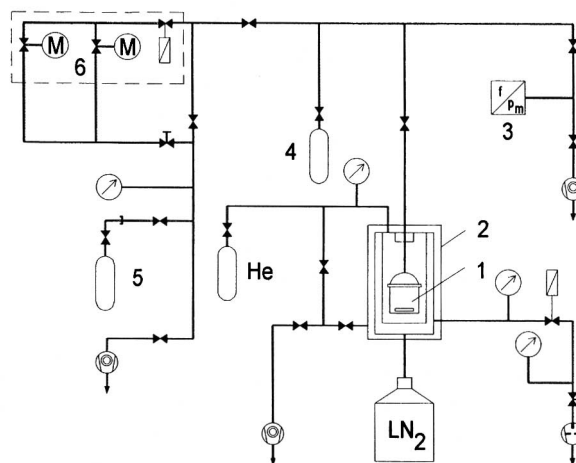


Fig. 1. Diagram of heat of vaporization apparatus: (1) measuring cell; (2) cryostat; (3) Paroscientific pressure transducer; (4) gas supply; (5) weighing cylinder; (6) computer operated valves.

- Two motor-driven computer-operated fine metering valves (6), which, together with the pressure sensor, form a PI control circuit to keep the pressure constant. The reason for two valves is as follows: in the case of R134a, the vapor pressure at 240 K is about 26 times the vapor pressure at 190 K, and assuming a constant valve metering, the mass flow to the weighing cylinder at 240 K is about 420 times the mass flow at 190 K.

Therefore, at least, two valves for the temperature ranges above and below 210 K are necessary.

- A Hewlett-Packard 6633A DC power supply and two 3457A multimeters to measure the voltage and the electric current of the heater located in the measuring cell, using four-wire techniques.
- Two 25- Ω platinum resistance thermometers located in the measuring cell, an ASL switching unit, and an ASL F17 measuring bridge. The 25- Ω Pt thermometers are calibrated according to the International Temperature Scale of 1990 (ITS 90) at PTB Berlin.
- A PC giving the time necessary for the calculation of the electric energy and for the documentation of the measured data.
- A weighing cylinder (5) kept at the temperature of liquid nitrogen.

The evaporation cryostat shown in Fig. 2 was operated with liquid nitrogen. The coolant flows through a copper tube coil surrounding the measuring cell, which is also made of copper, and then evaporates. The cold gas then cools the radiation shield and flows through a control valve to the vacuum pump. Temperature control is provided by a proportional controller combined with a thermistor as a temperature probe, and an electrodynamic control valve is used as a control element to regulate the mass flowrate of the coolant. During the measurement, the space around the measuring cell is evacuated, and the sum of the heat transferred to the measuring cell and carried away from it is zero. During temperature changes, this space is filled with helium to guarantee temperature balance.

At 20° C and atmospheric pressure, the measuring cell (Fig. 3) has an inner volume of 80.8 cm³ (a mass of 437.5 g). The cell was tested at pressures up to 5 MPa. The outer surface is gold-plated to reduce radiation losses. The heater (wire-wound resistor; resistance, 68 Ω) with a maximum power consumption of 12 W and two 25- Ω Pt resistance thermometers are installed in the bottom of the measuring cell. The capillary connecting the cell with the tubing outside the cryostat has a wall thickness of 0.25 mm and an outer diameter of 4.5 mm. The capillary tubing is made of stainless steel.

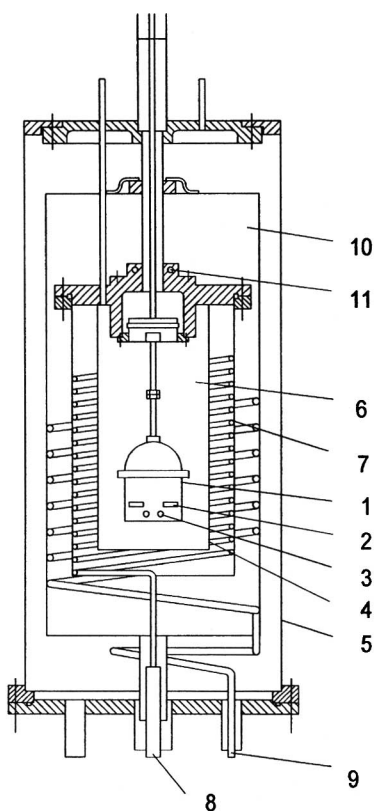


Fig. 2. Evaporation cryostat: (1) measuring cell; (2) cell heater; (3) 25- Ω Pt thermometer; (4) inner radiation shield; (5) outer radiation shield; (6) chamber for contact gas; (7) evaporation tube; (8) LN₂ inlet; (9) N₂ outlet; (10) vacuum; (11) thermometer.

2.2. Description of the Measurements

Before starting the measurement, it is necessary to determine the mass of the weighing cylinder. After this, the measuring cell, the cryostat, and the weighing cylinder are evacuated. When a vacuum of better than 0.1 Pa is reached, helium of a few kilopascals is introduced into the space between the measuring cell and the inner radiation shield, and the cryostat is cooled to the measuring temperature. The heater on the upper part of the radiation shield, where the capillary enters the cryostat (Fig. 3), is then switched on.

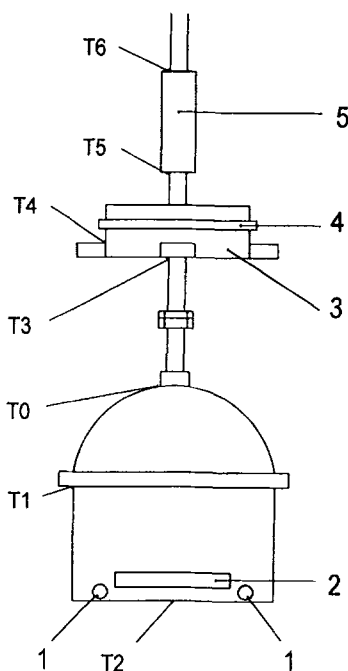


Fig. 3. Measuring cell with copper-constantan thermocouples T0...T6: (1) 25- Ω Pt thermometer; (2) measuring cell heater; (3) guard ring; (4) guard ring heater; (5) capillary tubing heater.

The substance to be investigated is condensed into the measuring cell. After thermal equilibrium is reached, the space between the measuring cell and the inner radiation shield is also evacuated, and the temperature is monitored. If the temperature stability is sufficient (better than $5 \text{ mK} \cdot \text{h}^{-1}$), the temperature of the cell is slightly below the temperature of the tubing and temperature gradients along the cell and tubing are small; then the vapor phase is removed from the probe to purge any air that still may be trapped in the measuring cell. The related temperature decrease is compensated by operating the cell heater. After thermal equilibrium is established, the vapor pressure is measured, and this value is taken as a reference. When the heater is switched on, the valve to the weighing cylinder (placed in liquid nitrogen) is operated in such a way that the pressure is kept equal to the reference pressure. When a sufficient amount of mass ($\approx 10 \text{ g}$) is condensed into the weighing cylinder, the cell heater is switched off. At the end of the

measurement, the vapor pressure is measured again. No significant differences in the vapor pressure and the cell temperature between the beginning and the end of the measurement were found. After changing the weighing cylinder, it is possible to repeat the measurement.

2.3. Viscous Flow Correction

Figure 4 is a simplified schematic diagram of the new apparatus. At the beginning of the measurement, before the cell heater is switched on, the measured pressure is $p_m = p_1 = p_{\text{sat}}$. Since p_m is kept constant during the evaporation of R134a, it was found that $p_m = p_{\text{sat}} < p_1$, due to a pressure gradient along the tubing from the measuring cell to the control metering valve. The pressure drop is estimated using the Hagen–Poiseuille law:

$$\Delta p = p_1 - p_{\text{sat}} = 8VL\eta/(PIR^4t) \quad (1)$$

$L = 1.1$ m is the length of the capillary tubing with an inner radius of $R = 2$ mm from the measuring cell to the Paroscientific transducer, η is the dynamic viscosity of the saturated vapor taken from REFPROP [2], t is the time of evaporation, and $V = m/\rho$ is the volume flow calculated from the evaporated mass m and the saturated vapor density. At 180 K, $\Delta p = 14.7$ Pa is calculated. This corresponds to a temperature increase in the measuring cell of 0.13 K during evaporation, and the specific enthalpy of vaporization is 3×10^{-3} too small. At 200 K, the correction may be neglected, e.g., $\Delta p = 1.8$ Pa, the temperature increases less than 0.01 K, and the enthalpy of vaporization is 2×10^{-5} too small.

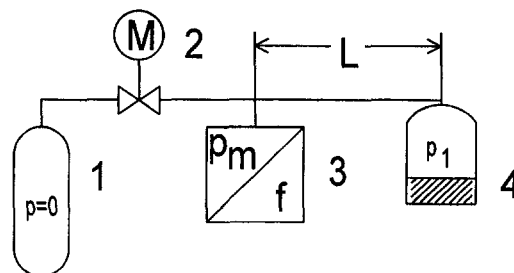


Fig. 4. Schematic diagram; (1) weighing cylinder kept at the temperature of liquid nitrogen; (2) control metering valve; (3) Paroscientific pressure transducer; (4) measuring cell.

2.4. Working Equation

From the first law of thermodynamics and the definition of the specific enthalpy of vaporization $\Delta_{\text{vap}}h$, it can be seen that

$$\Delta_{\text{vap}}h = Q[1 - (\rho''/\rho')]/m \quad (2)$$

where Q is the (electrical) energy dissipated in the cell heater, m is the resulting mass condensed into the weighing cylinder, and ρ' and ρ'' are the saturated liquid and vapor densities, respectively. During the experiment, the amount of evaporated liquid is replaced by saturated vapor in the measuring cell. This small amount of vapor is located in the measuring cell and not in the weighing cylinder, and for this reason, the correction term $1 - (\rho''/\rho')$ in Eq. (2) must be applied. For more details on the derivation of Eq. (2), the reader is referred to the paper by Ginnings and Stimson [3].

2.5. Estimate of the Measurement Uncertainty

The estimated standard deviation [4] of the specific heat of vaporization is given by

$$\begin{aligned} S_{\Delta_{\text{vap}}h} = \{ & [(\Delta_{\text{vap}}h)^2 s_Q^2/Q^2] + [(\Delta_{\text{vap}}h)^2 s_m^2/m^2] + [Q^2 \rho''^2 s_{\rho'}^2/(m^2 \rho'^4)] \\ & + [Q^2 s_{\rho''}^2/(m^2 \rho'^2)] + [(d\Delta_{\text{vap}}h/dT)^2 s_T^2] \\ & + [(d\Delta_{\text{vap}}h/d\Delta p)^2 s_{\Delta p}^2] \}^{1/2} \end{aligned} \quad (3)$$

where s_Q , s_m , $s_{\rho'}$, $s_{\rho''}$, s_T , and $s_{\Delta p}$, are the estimated standard deviations of the energy, the mass, the saturated liquid and vapor densities, the temperature, and the Δp correction term. The first term includes heat leaks of the adiabatic calorimeter, which, for the temperature range under consideration, are the largest contribution to the measurement uncertainty. To determine the amount of the heat leakage, the sealed cell, partly filled with R134a, was heated with 58.8 J. This resulted in a temperature increase of 0.256 K in the measuring cell. After 3 h, the time necessary for an evaporation experiment, this temperature difference decreased to 0.191 K. Since during the evaporation experiment, maximum temperature deviations of less than 0.2 K from the equilibrium value were observed, a maximum heat leakage of 10.75 J is estimated during the measuring period of 3 h. The determination of the mass of gas within the weighing cylinder (typically 10 g) is accurate to within ± 2 mg. The third and fourth terms on the right-hand side of Eq. (3) are also small. The densities of the saturated liquid and vapor are sufficiently well known from the fundamental equation to

calculate the correction factor in Eq. (2). At equilibrium, the temperature measurement is performed with a standard uncertainty of 2 mK. During the heating of the measuring cell, the temperature in the evaporating liquid layer is maintained by the pressure control already mentioned. At 200 K, pressure fluctuations are up to $1 \times 10^{-3} p_s$, corresponding to temperature fluctuations of up to 12 mK. Therefore, the fifth term in Eq. (3) is also small. The last term takes into account the viscous flow correction term. Since Hagen–Poiseuille’s law is not modified for gases, the temperature gradient along the tubing is neglected, and the inner diameter of the tubing is not measured, it is assumed that the correction term Δp lies within $\pm \Delta p$. Thus, the relative standard uncertainty of the enthalpy of vaporization of R134a in the temperature range from 180 to 230 K is estimated to be less than 1.6×10^{-3} at the 16 (68 % confidence) level.

3. RESULTS

The experimental results for R134a are given in Table I. The relative differences of these measured values from the specific enthalpy of vaporization of R134a calculated from the fundamental equation [1] are shown in Fig. 5. At 225 K, the data show a scatter of almost 3×10^{-3} . At 240 K, the

Table I. Experimental Results for the Enthalpy of Vaporization $\Delta_{\text{vap}}h$ of R134a

No.	T_{90} (K)	$\Delta_{\text{vap}}h$ (J · g ⁻¹)
1	180.295	258.47
2	180.292	258.36
3	180.204	258.67
4	184.862	255.06
5	190.287	251.03
6	199.868	245.49
7	199.908	245.32
8	210.296	239.48
9	210.263	239.75
10	215.310	236.72
11	219.951	233.77
12	219.985	233.66
13	225.083	230.90
14	225.154	230.87
15	225.196	230.14
16	228.699	228.93
17	239.900	222.35
18	239.867	222.52

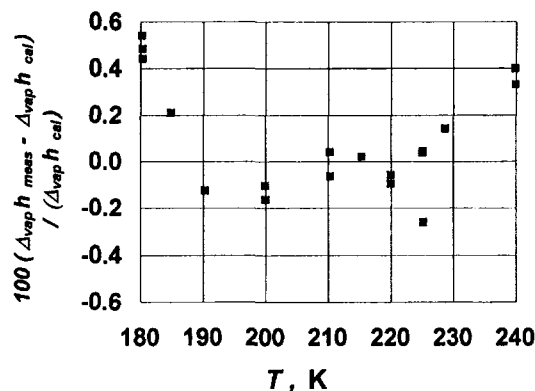


Fig. 5. Relative deviations $(\Delta_{\text{vap}}h_{\text{meas}} - \Delta_{\text{vap}}h_{\text{cal}})/\Delta_{\text{vap}}h_{\text{cal}}$ of measured enthalpies of vaporization from enthalpies of vaporization calculated with the fundamental equation of Tillner-Roth and Baehr [1].

pressure control is not sufficiently fast to maintain the pressure within (70 ± 1) kPa. From the Clausius–Clapeyron equation

$$\Delta_{\text{vap}}h = T(dp/dT)[(1/\rho'') - (1/\rho')] \quad (4)$$

Tillner-Roth [5] estimated a relative uncertainty of the specific enthalpy of vaporization of 3×10^{-3} (99% confidence level) at 200 K using the fundamental equation. This uncertainty increases with decreasing temperature, the pressure p decreases to very small values, and therefore, the uncertainty in dp/dT increases. No data for ρ'' are available in this temperature range. At temperatures from 190 to 230 K, good agreement between the experimental data and the calculated values within the combined standard uncertainty is achieved. At 180 K, all three measured data are about 5×10^{-3} larger than the calculated values.

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REFERENCES

1. R. Tillner-Roth and H. D. Baehr, *J. Phys. Chem. Ref. Data* **23**:657 (1994).
2. M. Huber, J. Gallagher, M. McLinden, and G. Morrison, *NIST Standard Reference Database 23 (REFPROP), Version 5.0* (U.S. Department on Commerce, Technology Administration, Gaithersburg, 1996).

3. D. C. Ginnings and H. Stimson, in *Experimental Thermodynamics, Vol. I*, J. P. McCullough and D. W. Scott, eds. (Butterworth, London, 1968), p. 395.
4. *Guide to the Expression of Uncertainty in Measurement* (ISO, Geneva, 1993).
5. R. Tillner-Roth, personal communication (Universität Hannover, Institut für Thermodynamik, Hannover, Germany, 1997).