Determination of the Critical Temperature and Density of Hexafluoroethane

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Twenty-seven measurements of the temperature–density data on the coexistence curve for C_2F_6 were made by visual observation of "the disappearance of the meniscus" at the vapor–liquid interface in an optical cell. The measurements were conducted for the densities between 401.4 and 835.2 kg/m^3 and for the temperatures close to T_c, within 2.4 K. The critical opalescence was observed for 10 densities out of 27 measurements between 570.7 and 695.0 kg/m^3. The error of density and temperature measurements was estimated ±0.1% and ±10 mK, respectively. The critical temperature was determined as $T_c = 293.035 \pm 0.010$ K and the critical density 622 ± 10 kg/m^3. The critical pressure was calculated $P_c = 3.042 \pm 0.008$ MPa by using the published vapor-pressure data with the present value of T_c.

Although hexafluoroethane (C_2F_6) is as good an insulating material as sulfur hexafluoride (SF_6), its thermodynamic properties have not been known with high accuracy. A measurement of saturated liquid and vapor density (*9*) and some of the calorimetric measurements (*2*, *3*, *6*, *8*) have been reported, and some tabulated data for thermophysical properties (*1*) are available. A thermodynamic investigation on this substance in the range of temperatures between 188 and 363 K to a maximum pressure of 8.2 MPa was carried out by the authors; a part of the experimental results on *PVT* properties and vapor-pressure data was presented (*5*). This paper reports experimental temperature–density data on the coexistence curve by careful visual observation of "the disappearance of the meniscus". Based on these data the critical temperature (T_c) and density (ρ_c) of C_2F_6 are also reported.

Experimental Section

In a previous publication (*5*) an experimental apparatus for observation of "the disappearance of the meniscus" at the vapor–liquid interface and an optical cell with two sapphire windows was described. The optical cell made of 304 stainless steel was a cylinder (50 mm long and 19 mm i.d., 15.894 ± 0.006 cm^3 in inner volume) and was installed in a water bath. The bath temperature was controlled by adding chilled water drop by drop. After evacuation and flushing the cell several times, 99.987 wt % pure sample was supplied into the cell. Gas chromatographic analysis showed that the remaining impurities were trifluorochloromethane ($CClF_3$) (≤0.006 wt%), tetrafluoromethane (CF_4) (≤0.001 wt %), air (≤0.004 wt %), and water (≤0.002 wt %). The sample mass confined in the cell was determined by weighing the mass of the cell on a chemical balance with a sensitivity of 1 mg before and after charging the sample. Then the cell was placed in the water bath. On the two side walls of the bath, the glass windows were mounted through which the reflected rays of 10-W white fluorescent light were transmitted for observing "the disappearance of the meniscus".

Densities of the sample in the cell were determined by dividing the sample mass confined by the inner volume of the cell. Temperatures were measured with a precision of 5 mK on IPTS-68 by use of a 25-Ω platinum resistance thermometer which was mounted in the vicinity of the cell at the same height in the water bath. The thermometer had been calibrated at the National Research Laboratory of Metrology, Japan, and the periodic observations of the ice-point resistance of the thermometer showed no significant change. The resistance of the thermometer was measured by a Mueller-type bridge.

The vapor–liquid interface in the optical cell, in which the measured mass of sample was confined, was observed through a window of the water bath by unaided eyes. Observation was started at a temperature where the meniscus existed undoubtedly. The behavior of the meniscus was observed at least for 2 h, while the temperature of the bath was held constant within a fluctuation of ±2 mK. Then the bath temperature was raised by 2 to 3 mK, and the observation was continued. This procedure was repeated until the meniscus disappeared completely. This temperature when the vapor–liquid interface disappeared was determined as the saturation temperature. When a nominal density was less than ρ_c, the meniscus went downward with increasing temperature and disappeared at the bottom of the cell. When a nominal density was greater than ρ_c, the meniscus went upward with increasing temperature and disappeared at the top of the cell. When a nominal density was close to ρ_c, the drift of the meniscus, which was positioned at the middle of the cell, became less sensitive with increasing temperature variation, and finally the meniscus did not change its position any more even with increasing temperature. Under these condtions the critical opalescence was clearly observed. Therefore the observation was carried out carefully and the bath temperature was kept constant longer than 6 h. However, it was so hard to confirm "the disappearance of the meniscus", and hence the following criterion was introduced. When one looks down into the vapor–liquid interface at nearly grazing angle, an inner wall of the cell is observed as illustrated in Figure 1. If the meniscus does not exist, a fringe of the cylindrical wall is observed as a circle without any distortion because of its uniform density profile in the cell. If the meniscus does exist, the fringe is observed as two circles overlapping each other as illustrated in Figure 1. The lower circle (ACB in Figure 1) is a real one but the upper one (A′C′C″B′ in Figure 1) is an image refracted by the meniscus. For densities close to ρ_c, the density profile in the cell becomes continuous but it has a very sharp stratification, even after the meniscus has disappeared. This phenomenon is observed partly because of the density fluctuations, which cause the critical opalescence, and partly because of the vertical density variation due to the gravity. Therefore the fringe is observed to be a single continuous shape as illustrated in Figure 2, although it is very much distorted.

Results

The unsmoothed experimental temperature–density data on the coexistence curve of C_2F_6 are given in Table I. Twenty-seven measurements were made for the densities between 401.4 and 835.2 kg/m^3 with an uncertainty of ±0.1%. The uncertainty quoted here is composed of errors with respect to the volume and mass measurements and an uncertainty resulting from neglect of the cell deformation due to temperature and pressure variations. The deformation at a condition of the critical temperature and pressure would amount to no greater than 2

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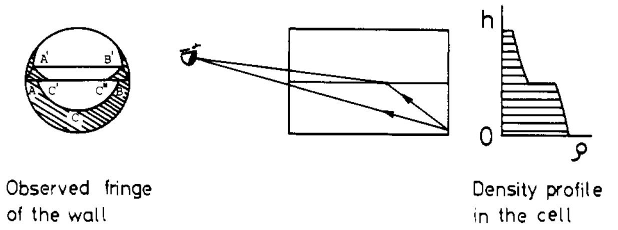

Figure 1. Schematic diagram of the meniscus observation in the case of the existence of the meniscus.

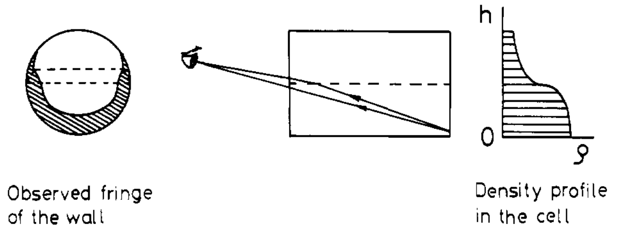

Figure 2. Schematic diagram of the meniscus observation just after the disappearance of the meniscus.

Table I. Experimental Temperature-Density Data on the Coexistence Curve[a]

T, K	ρ, kg m^{-3}	T, K	ρ, kg m^{-3}	T, K	ρ, kg m^{-3}
290.654	401.4	292.944	545.1*	292.975	691.2
291.431	421.8	292.995	570.7*	292.976	695.0*
291.857	445.6	293.018	579.5	292.905	713.7
292.292	470.9	293.032	595.1	292.764	735.8
292.491	491.7	293.035	613.9	292.662	746.1
292.606	496.2	293.028	620.9	292.449	760.7
292.809	522.7	293.029	640.8	292.160	785.3
292.799	524.4*	293.020	654.7	291.745	811.3
292.922	542.2*	293.006	674.0*	291.203	835.2

[a] Values with an asterisk were measured with an uncertainty of ±0.2%.

mm^3 corresponding to 0.01% of the total inner volume, even if the optical cell was assumed to be constructed only by 304 stainless steel. The density values marked with an asterisk in Table I were measured with an uncertainty of ±0.2%, because those mass measurements were made less accurately than others. Critical opalescence was observed for ten densities between 570.7 and 695.0 kg/m^3. The meniscus disappeared at the middle of the cell for four densities from 595.1 to 640.8 kg/m^3, where the critical opalescence was observed most strikingly. In this region the critical opalescence started at a temperature lower than that of "the disappearance of the meniscus" by 10–20 mK and ceased at a temperature higher than that by 20–30 mK. The disappearance temperature of the meniscus was observed higher than the reappearance temperature by 2 to 3 mK. The uncertainty of temperature measurements was estimated to be ±10 mK which is composed of the precision of thermometer used, the fluctuation of temperature controlled, and an individual difference of the observed temperature, i.e., 2 to 3 mK.

The critical temperature can be determined to be the highest temperature along the vapor-liquid coexistence curve. The top of this curve, however, is so flat that temperatures for four densities between 595.1 and 640.8 kg/m^3 agreed within a difference of 7 mK, which is much smaller than the uncertainty of the temperature measurements. Here the critical temperature was determined as 293.035 ± 0.010 K by a graphical analysis using a temperature–density diagram.

Plotting the reduced density, $\Delta\rho = (\rho - \rho_c)/\rho_c$, against the reduced temperature, $\Delta t = (T - T_c)/T_c$, for the whole measurements along the coexistence curve in a logarithmic scale, we ascertained that the reduced density was proportional to the reduced temperature by about 1/3. But particular considerations of the experimental data for a reduced temperature above 10^{-4} corresponding to about 30 mK below T_c showed that the power for the liquid densities was slightly smaller than that for the vapor densities. This means that the coexistence curve is not symmetrical even in the present interest region. Therefore the critical density was found by fitting the experimental results to the equation

$$\rho = \rho_c(A\cdot\Delta t + 1) \pm \rho_c B\,|\Delta t|^{\beta} \quad (1)$$

which was used by Moldover (*7*) to find the critical density of CO_2. Here ρ_c, A, B, and β are adjustable parameters. The "+" sign is used for liquid densities and "−" sign for vapor densities. By use of the trial and error method, β was fixed to 0.345, for which A, B, and ρ_c were determined as given in Table II with a standard deviation of 4.7 kg/m^3 by fitting 27 measurements. A result of error analysis shows that the error in the critical density due to the gravity effect, which amounts to about 10 kg/m^3, estimated by using *PVT* data for SF_6 by Wentorf (*10*), is twice as large as the standard deviation of the fit and much larger than the uncertainty of the density measurements, i.e., 0.6 kg/m^3. Therefore the critical density of C_2F_6 was determined as 622 ± 10 kg/m^3.

Table II. Numerical Constants of Coefficients in Eq 1

$A = -1.150$	$\rho_c = 622$ kg m^{-3}
$B = 1.934$	$T_c = 293.035$ K
$\beta = 0.345$	

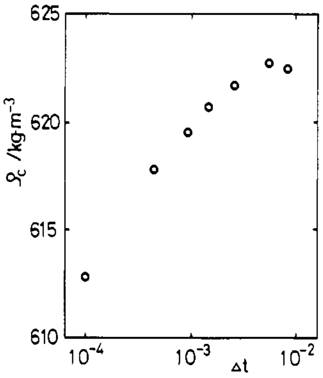

Figure 3. Dependence of calculated ρ_c values due to eq 1 on the reduced temperature.

To find the critical pressure using the present value of T_c, the published vapor-pressure data of Kijima et al. (*5*) were used. The result was P_c = 3.042 ± 0.008 MPa, the quoted uncertainty of which was composed of that of pressure measurements, 1 kPa, and the uncertainty resulting from the uncertainty in the present determination of T_c, 7 kPa.

Discussion

The value of ρ_c calculated with eq 1 by a procedure of least squares was dependent on the temperature range of the input data as shown in Figure 3. For example, for the data corresponding to the reduced temperature lower than T_c by 7×10^{-3}, the calculated ρ_c value was smaller than the present value. The calculated ρ_c value decreased with reducing the temperature range and thus it might be concluded that the rectilinear diameter is not definitely straight but slightly bend to the smaller densities in the vicinity of the critical point. This similar asymmetric trend of the rectilinear diameter has been described for SF_6 by Ivanov et al. (*4*).

The present value of T_c differs slightly from that reported in a previous paper (*5*), which was 293.010 ± 0.015 K, although the difference is in the same order of the quoted error. The previous work was carried out only by observing "the disappearance of the meniscus" near the critical density without any exact density measurements and additionally the temperature fluctuation was within ±5 mK. In the present study, however, the temperature control was improved within ±2 mK. This also brought higher resolution in the T_c determination with the aid of the exact density determination.

Hejmadi and Powers (*3*) presented their T_c value as 293.054 ± 0.03 K which was determined by using their calorimetric measurements near the critical point. This value of T_c is in good agreement with the present value with a difference of 19 mK, whereas the other previously reported values (*1*, *6*, *8*, *9*) are smaller than the present value by about 0.2 K.

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Glossary

A, B	coefficients in eq 1
P	pressure in MPa
T	temperature in K
Δt	reduced temperature, $\Delta t = (T - T_c)/T_c$
β	exponent describing the coexistence curve
ρ	density in kg/m^3
$\Delta\rho$	reduced density, $\Delta\rho = (\rho - \rho_c)/\rho_c$

Subscript

c	at the critical point

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Acid Strength of Molten Oxide Mixtures

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In order to evaluate the relative acid strength of molten oxides, a simple emf method was devised. In reference to the activity of Na_2O, an acid strength variation of $P_2O_5 > MoO_3 \approx WO_3 > B_2O_3 > GeO_2 \approx SiO_2$ was found. Variations in the relative basicity (in terms of Na_2O activity) of as much as 10^{15} were found among binary melts containing Na_2O, when combined with the data of concentration cells of the previous works.

1. Introduction

It is nearly 4 decades since the thermodynamic properties of the oxide mixtures were discussed in terms of the acid–base concept. Lux[1] introduced the relation

$$\text{base} = \text{acid} + O^{2-} \tag{1}$$

and employed an emf method as early as 1939. Flood and Førland[2] noted further that an acid oxide network reacts with the O^{2-} ion from the basic oxide to give

$$X{-}O{-}X + O^{2-} = 2X{-}O^- \tag{2}$$

if written in the present notation for the covalent bond. They and their co-workers have given a qualitative series of strength of acid and base oxides. Since then various definitions have been proposed and many experimental methods have been devised. Solubilities of acid gases, equilibrium measurement with metallic phases, use of indicators, and emf methods are the notable examples. Optical basicity,[3] currently under development, will be a promising alternative. These methods except for the emf one are applicable only to a limited range of compositions and are basically qualitative in general nature. In our laboratory,[4-8] concentration cells were devised in which the electrode reaction and the junction potential are well defined and the cells allow measurement for rather long durations of time. The thermodynamic activity of Na_2O in Na_2O + MO (MO; P_2O_5,[4] B_2O_3,[5] GeO_2,[6] SiO_2,[7] and MoO_3[8]) of over 10^8 range has been measured. The results were interpreted in terms of acid-to-base reaction upon mixing the component oxides.

In the present paper, the emf method is extended to cells consisting of two different binary melts where Na_2O is the common constituent and its activity determines the emf value. The experimental results give the relative strength of acid oxides. Quantitative evaluation of acid strengths of various oxides has not been carried out systematically in spite of its technological importance.

2. Experimental Section

The cell employed in the present work is of the type[6]

$$O_2(Pt)|Na_2O{-}MO_I(\text{reference})\|Na_2O{-}MO_{II}|O_2(Pt)$$

where $Na_2O{-}MO_I$ is the reference and $Na_2O{-}MO_{II}$ is the sample melt. The two melts were electrically connected with an alumina rod wetted with the melts. As in our previous works, it can be assumed that Na^+ is the sole conductor in the junction. Furthermore, the electrode reaction in an air atmosphere can be shown by

$${}^1/_2O_2 + 2e^- = O^{2-} \tag{3}$$

Therefore, a virtual current of 2 Faradays from the left to the right of the cell corresponds to a transfer of 1 mol of Na_2O from the left to right compartment. Thus the emf is given by

$$2EF = -RT \ln a_{Na_2O}/a^\circ_{Na_2O} \tag{4}$$

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