

Critical Constants of Xenon Hexafluoride

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The critical temperature of xenon hexafluoride, determined by the sealed-tube method, was found to be 502 ± 0.5 K. The critical pressure and critical density were estimated by the method of Hakuta and Hirata and are 4.70 ± 0.05 MPa and 1140 ± 10 kg/m³, respectively.

During the preparation of XeOF₄ by the reaction between liquid xenon hexafluoride and the walls of a quartz reaction vessel (1), it was found that the reaction rate depends very much upon the pretreatment conditions used during preparation of the reaction vessel. When the reaction vessel was thoroughly pretreated with XeF₆ before the reaction, the rate of formation of XeOF₄ was very slow, even at temperatures above 373 K.

These experimental observations led us to the idea that the critical temperature of XeF₆ could be determined in a sealed quartz tube by rapid heating, as has been done in the case of XeF₂ and XeF₄ (2). Critical temperature measurements add to our knowledge of the bulk properties of XeF₆ together with the possibility of estimating some of them by methods based on reduced quantities.

Experimental Section

Materials. Xenon hexafluoride was prepared in a nickel reaction vessel by the fluorination of a mixture of xenon fluorides with elemental fluorine under a pressure of 4 MPa at 574 K. The XeF₆ obtained, which still contained traces of XeF₄, was further treated with a large excess of KrF₂ at room temperature and then heated up to 323 K. Finally, the remaining krypton and fluorine were pumped off at 195 K.

The purity of XeF₆ so obtained was checked by infrared spectroscopy. Infrared spectra of the vapors showed only bands which could be attributed to XeF₆. The melting point of the sample was 322.4 K.

n-Hexane (Merck, Darmstadt, min 99%) was purified by distillation before transferring it on a vacuum line to the tube for critical temperature measurements.

Procedure. Prior to filling with XeF₆, the quartz tubes used for critical temperature measurements were thoroughly pretreated, first with pure elemental fluorine, then with XeF₆, and after XeF₆ was pumped off they were further baked at 873-973 K for at least 5 h. The tubes were sealed off while the lower parts of the tubes containing xenon hexafluoride were kept at 77 K. The filled tubes were stored at 77 K until measurement.

The critical temperature was determined by the method of disappearance of the meniscus. The sealed quartz tubes (i.d., 2 mm; o.d., 6 mm; 50 mm long) were heated rapidly by immersion in a liquid bath. The proper range of temperatures was determined by preliminary experiments. The temperature of the bath in the range between 501 and 503 K was examined in steps of 0.5 K.

The tube was immersed in the constant temperature bath and the behavior of the meniscus was observed. Prolonged heating was avoided in order to minimize the reaction of XeF₆ with the walls and thermal dissociation of XeF₆.

However, with some of the tubes the appearance and disappearance of the meniscus was also observed by varying the temperature of the bath. It was found that the critical tem-

Table I. Critical Constants of XeF₆

T_c , ^a K	no. of tubes	P_c , ^b MPa	ρ_c , ^b kg/m ³	V_c , ^b cm ³ /mol	Z_c , ^b
502 ± 0.5	5	4.70 ± 0.05	1140 ± 10	214.4 ± 2	0.241

^a Experimental values. ^b Calculated values.

perature so determined did not change over a period which was up to 3 times longer than the time required for the first reading. The temperature of the bath in an insulated vessel was measured by mercury-in-glass thermometer (1/10 K). The temperature was constant to ±0.1 K. The whole apparatus, including the thermometer and the procedure, was calibrated against the critical temperature of *n*-hexane at 507.4 K (3). For this purpose a quartz tube of the same dimensions as for the critical temperature measurements was filled with *n*-hexane.

The purity of some samples after critical temperature measurements was checked by recording Raman and infrared spectra and by melting point determinations.

Results and Discussion

Values of the critical constants of XeF₆ found or calculated are given in Table I. The critical temperature was determined as the average temperature of the bath where disappearance and appearance of the meniscus was observed twice while varying the temperature within the limits between 501.4 and 502.9 K with three tubes. The behavior of the meniscus was then explored with two tubes in a narrower range at 501.8 and 502.3 K and the same average temperature was found within the experimental uncertainty. Only those tubes were taken into consideration where the meniscus disappeared in the middle third of the tube. The critical temperature of the samples slowly increased on prolonging the time of measurement. The results obtained in the first 4 min of heating were used, since in this time interval, within experimental uncertainty, this effect was not observed.

The critical pressure and critical density of XeF₆ were estimated by the method of Hakuta and Hirata (4). In this estimation the experimentally obtained critical temperature and the density of liquid XeF₆ at the normal boiling point, calculated from ref 5, were used. The accuracies quoted were estimated on the basis of the accuracy with which the critical temperature was experimentally determined.

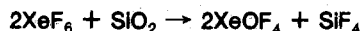
The value of the critical ratio Z_c was calculated from $Z_c = P_c V_c / RT_c$ by using the values of the critical constants given in Table I.

There are two possible ways for the purity of XeF₆ to deteriorate during the measurement: the reaction of XeF₆ with quartz which leads to XeOF₄ and SiF₄, and the thermal dissociation of XeF₆ which in the first step leads to XeF₄ and F₂.

Infrared spectra of the vapor phase and Raman spectra of solid XeF₆ after the measurement showed only the bands of XeOF₄ and SiF₄, besides XeF₆. No XeF₄ was detected. The lower limit of the detection of traces of XeF₄ in XeF₆ by infrared spectroscopy of the vapor is estimated to be about 2 mol %. The overall impurity content was determined by the lowering of the melting point. The maximum lowering was 0.8 K, which represents about 0.5 mol % of impurities, using 5743 J/mol for the enthalpy of fusion of XeF₆ (5).

The quantity of XeF_4 produced by thermal dissociation was estimated from the equilibrium data (6). At the critical temperature of 502 K and critical pressure of 4.70 MPa, the degree of dissociation is about 10%. Kinetically only about 6.5% of the final equilibrium value dissociates in the first 8 min at 566 K, as was determined by measurements of the thermal dissociation of XeF_6 (7). On the basis of all these data, it could be concluded that the degree of dissociation of XeF_6 at 502 K in the first 5 min of heating should be smaller than 0.5%.

Therefore it seems reasonable to consider XeOF_4 and SiF_4 as the main impurities in XeF_6 . Their origin is the reaction



The slow rise of critical temperature during prolonged heating (at least 3 times longer than the duration of the measurement) could be explained by the increasing influence of XeOF_4 . In view of the lack of reliable data concerning the value of the critical temperature of XeOF_4 , this was estimated from the vapor pressure at about room temperature (8) via the estimated boiling point at about 373 K to be somewhat higher than the critical temperature of XeF_6 . The influence of SiF_4 , with a

critical temperature of 259.0 K (9), is lower than that of XeOF_4 because of the relatively lower concentration.

On the basis of these evaluations the critical temperature of XeF_6 can be confidently given as 502 ± 0.5 K.

Registry No. XeF_6 , 13693-09-9.

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Excess Gibbs Energy for Binary Mixtures Containing Carboxylic Acids. 3. Excess Gibbs Energy for Isobutyric Acid and Trimethylacetic Acid + Cyclohexane and + *n*-Heptane

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Total vapor pressures for the binary mixtures containing isobutyric and trimethylacetic acids with cyclohexane and *n*-heptane at 298.15 and 318.15 K have been measured for the entire composition range by using the static manometric method. Positive deviations from Raoult's law for all the systems decrease with the increase of methylation of the acids and increase with the rise of temperature. Activity coefficients have been calculated by taking into consideration the dimerization of the acids in the vapor phase. Estimated TS^E values from experimental H^E values are negative and have about the same magnitude for all the systems. Negative TS^E values have been attributed to the increasing proportion of acid dimers with increasing proportion of the nonpolar component.

Introduction

In continuation of our studies (1, 2) on the excess Gibbs free energies of the binary mixtures containing carboxylic acids, in this paper we report such studies for two higher acids, i.e., isobutyric acid (IBA) and trimethylacetic acid (TMA), with either cyclohexane or *n*-heptane as the second component. Total vapor pressures of the mixtures over the entire composition range at 298.15 and 318.15 K have been measured by using a static manometer. Activity coefficients have been calculated by taking into consideration the dimerization of these acids in the vapor phase (1-3). Estimated TS^E values are compared with the already reported (1, 2) corresponding results for the

Table I. Physical Constants of Pure Compounds

compd	refractive index		density/g cm ⁻³	
	obsd	lit.	obsd	lit.
isobutyric acid	1.3933 ^a		0.94428 ^b	
trimethylacetic acid	1.3925 ^c		0.90396 ^c	0.90401 ^c
Dimerization Constants K_p , Torr ⁻¹				
<i>T</i> /K	AA	PA	IBA	TMA
298.15	1.982	2.301	7.755	842.9
318.15	0.379	0.388	1.208	15.58

^a At 293.15 K. ^b At 298.15 K. ^c At 313.15 K (from ref 4).

lower acids, i.e., acetic acid (AA) and propionic acid (PA). The magnitude and the sequence of the results have been interpreted in terms of both increasing dimerization constant and steric hindrance with the complexity of the acid molecule.

Experimental Section

Cyclohexane and *n*-heptane were the same as used in earlier reports (1, 2).

Isobutyric acid (L.R., SRL) was dried by refluxing it over phosphorus pentoxide and then fractionally distilled. The middle fraction was further refluxed over potassium permanganate and fractionally distilled. The fraction distilling at 427.5 K was collected. Trimethylacetic acid (G.R., Tokyo Kasei Kogyo Co. Ltd., Japan) was first fractionally crystallized and the liquid layer was discarded. The solid portion (mp 308.55 K) was then distilled under reduced pressure. The refractive index and