The Critical Temperature of Xenon Difluoride

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In an attempt to determine critical constants of xenon fluorides we have measured the critical temperature of XeF_2. The disappearance and reappearance of the meniscus was observed on heating and cooling xenon difluoride in sealed quartz tubes. The experimental set-up was calibrated against the critical temperature of toluene, which was determined in the same way.

Xenon difluoride was prepared by photosynthesis at room temperature[1,2]. It was purified by pumping off the volatiles *in vacuo* at — 78⁰ C and stored in a nickel container. Infrared spectra of its vapour showed no other bands than those of xenon difluoride. Quartz tubes (i. d. 3 mm, o. d. 9 mm) to be used with xenon difluoride were thoroughly baked out in high vacuum in order to remove the last trace of moisture, filled with a proper amount of xenon difluoride by sublimation *in vacuo,* sealed off and stored in liquid nitrogen till the measurement. The overall density (gas + liquid) of loading was between 1.0 g./ml. and 0.6 g./ml. of XeF_2.

Molten xenon difluoride occupied at 130⁰ C approximately one third of the volume of the tube.

The sealed sample tube was fixed in an upright glass tube (35 mm i. d.), which was fitted with a double glass mantle. Hot air to heat the sample tube flowed from below into the center tube and then through the outer insulating mantle out of the set-up. Temperature differences between the bottom and the top of the sample tube amounted to about 3—4⁰. The EMFs of the thermocouples were recorded by a two-channel compensating recorder Linseis. The precision of the measurements was ± 1⁰ at 350⁰ C.

The surface temperatures of the sample tubes were measured by iron-constantan thermocouples (0.1 mm wire diameter). They were fixed on the lower, the middle and the upper part of the tubes. Only the temperature of the thermocouple nearest to the disappearing or appearing meniscus was used for the determination of the critical temperature. The rate of heating and cooling was varied between 1.7⁰ C/min and 0.02⁰ C/min.

When the employed rate of heating was low, the height of the meniscus was observed and measured with a cathetometer until the meniscus became flat, which happened about 4⁰ before the disappearance, and eventually disappeared (Fig. 1). As the meniscus disappeared a violent motion of the dense gas was observed. If the temperature was lowered slightly, the meniscus reappeared about the 30 mm above the bottom of the tube which was 40 mm high. Xenon difluoride vapour attacked quartz tubes at high temperatures in spite of the rigorous drying.
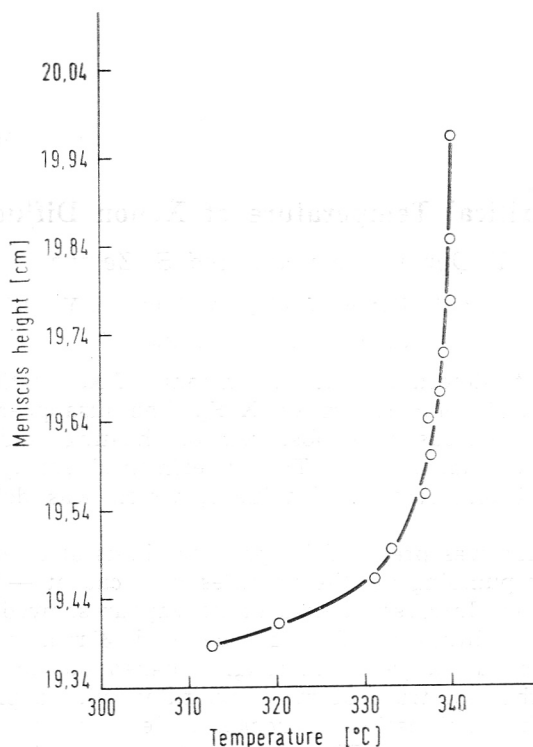
Fig. 1. Temperature dependence of the meniscus height for xenon difluoride close to its critical temperature.

The experimental set-up was calibrated against the critical temperature of toluene. The toluene (Fluka, over 99%, free of thiotolene) used for the calibration was dried with sodium metal[3], distilled over it and redistilled *in vacuo* into glass ampoules fitted with break-seals. From there it was then distilled again *in vacuo* into quartz tubes similar to the ones used with xenon difluoride. The critical temperature of toluene measured in our experimental conditions was found to be 323^0 C $\pm$ 1^0. The reported critical temperature for toluene is 318.8^0 C[4].

The results of the measurements are presented in Tables I and II.

TABLE I

The Critical Temperature of Toluene

Run	Meniscus, T (^{0}C)	
	Disappearance	Appearance
1	323.4	323.4
2	322.6	322.6
3	——	322.6
4	——	322.6

Average value: 323^0 C $\pm$ 1^0, the rate of heating and cooling 0.2^0 C/min.

TABLE II

The Critical Temperature of Xenon Difluoride

Run	Disappearance	Rate of heating (^{0}C/min)	Appearance	Rate of cooling (^{0}C/min)
1	339	0.1	——	——
2	336	0.02	334	1.7
3	335	0.7	——	——

The observed temperatures have been corrected for the error estimated by the determination of the critical temperature of toluene, that is for -4^0 C.

On the basis of these measurements we estimate the critical temperature of xenon difluoride to be 335^0 C $\pm 5^0$.

Further determinations of the critical constants of xenon fluorides are under way.

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IZVLEČEK

Kritična temperatura ksenonovega difluorida

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Izmerili smo kritično temperaturo XeF$_2$, ki je 335^0 C $\pm 5^0$. Uporabili smo metodo opazovanja meniska v zataljenih kremenovih kapilarah. Aparaturo smo umerili s toluenom.

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An Approximate Calculation of the Magnetic Shielding Constant

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In the recent years a number of different approaches have been used to calculate the magnetic shielding constant[1]. In this note we describe the perturbed Hartree-Fock theory using gauge-invariant atomic orbitals. The same approach has been used previously by Bley[2] who has calculated the magnetic susceptibility in diatomic molecules. With the use of the standard approximations[3] and the perturbation theory of the second order[1] we obtain for the energy the expression:

$$E^{(2)} = 2 \sum_i \sum_{pq} (c_{pi}^{(0)} H_{pq}^{(2)} c_{qi}^{(0)} - c_{pi}^{(1)} H_{pq}^{(1)} c_{qi}^{(0)}) \tag{1}$$

with $H_{pq}^{(1)}$ and $H_{pq}^{(2)}$ as in ref. 3. The coefficients $c_{pi}^{(1)}$ are obtained from

$$(\varepsilon_j^{(0)} - \varepsilon_i^{(0)}) \sum_p c_{pj}^{(0)} c_{pi}^{(1)} + \sum_{pq} c_{pj}^{(0)} G_{pq}^{(1)} c_{qi}^{(0)} = - \sum_{pq} c_{pj}^{(0)} H_{pq}^{(1)} c_{qi}^{(0)} \tag{2}$$

and from subsidiary conditions

$$\sum_p (c_{pi}^{(0)} c_{pj}^{(1)} - c_{pi}^{(1)} c_{jp}^{(0)}) = 0 \tag{3}$$

$$\sum_p c_{pi}^{(0)} c_{pi}^{(1)} = 0 \tag{4}$$

The final expression for the proton shielding constant is:

$$\sigma_{aa} = \sum_{pq} P_{pq} \frac{H_{pq}^{(2)}}{H_a \mu_a} + 2 \sum_i^{occ} \sum_{pq} (a_{pi} B_{pq} + b_{pi} A_{pq}) c_{qi}^{(0)} \tag{5}$$

where P_{pq} is the population matrix.

Pople's expression for $H_{pq}^{(1)}$ was separated into terms proportional to the magnetic field H_a and the magnetic dipol moment μ_a:

$$H_{pq}^{(1)} = i (A_{pq} H_a + B_{pq} \mu_a)$$

The coefficients $c_{pi}^{(1)}$ were separated in the same manner:

$$c_{pi}^{(1)} = i (a_{pi} H_a + b_{pi} \mu_a)$$

and the system of equations (2), (3), (4) are solved for a_{pi} and b_{pi}. The method has been tested by the calculation of the proton magnetic shielding constant in H_2O. The calculation was done in the INDO approximation with the parametrization from ref. 4. The results are collected in Table I (contributions from

TABLE I

Calculated Values of the Proton Shielding Constant (ppm) of H_2O
(x axis along O—H bond)

	σ^d	σ^p ($G_{pq} = 0$)	σ^p ($G_{pq} \neq 0$)
xx	— 7.8	15.6	29.0
yy	33.5	— 7.3	— 5.0
zz	33.2	— 8.5	0
average	19.6	— 0.1	8.0
		σ (total) 19.5	27.6

all atoms are summed into σ^p and σ^d) where the values in the second column were obtained with $G_{pq}^{(1)} = 0$ (standard approach[3]) Table I. As is seen from the calculated result the perturbed HF greatly improved the value of the unperturbed one [σ (experimental) = 30 ppm[6].] Some drawbacks of the method are: the complexity of the calculation, the necessity to use very accurate values for the coefficients $c_{pi}^{(1)}$. The last point means that some rounding errors can strongly influence the results. Such errors are of course quite common in the semiempirical approaches where the input parameters are not known to a high precision.

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IZVLEČEK

Aproksimativna metoda za račun kemičnega premika

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Opisana je metoda za račun kemičnega premika s uporabo perturbacij na Hartree-Fock teoriji in s uporabo »gauge-invariant« atomskih orbital. Metoda upošteva korelacijo med elektroni, ki pa ni vsebovana v Poplovi metodi[3]. Račun kemičnega premika vode, potrdi velik upliv korelacije med elektroni in rezultat se dobro ujema s eksperimentalno dobljenim.

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