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COHESION ENERGIES AND SOLUBILITY PARAMETERS FOR XENON
DIFLUORIDE AND XENON TETRAFLUORIDE

J. E. HOUSE, JR.

Department of Chemistry, Illinois State University, Normal,
IL 61761 (U.S.A.)

SUMMARY

Cohesion energies, molar volumes, and solubility parameters (δ) have been calculated for XeF_2 and XeF_4 . The values of δ at 300 K are calculated to be $16.3 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ and $15.1 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ for XeF_2 and XeF_4 , respectively. These high values are interpreted in terms of possible modes of intermolecular interaction.

INTRODUCTION

The cohesion energy of a liquid, E_c , is the heat of vaporization at constant volume and is related to the usual heat of vaporization, H , by

$$E_c = H - RT \quad (1)$$

where RT is the external work done [1-4]. Molecular interaction can be described by the cohesion energy density, E_c/\bar{V} , where \bar{V} is the molar volume [1]. The solubility parameter, δ , is given by

$$\delta = (E_c/\bar{V})^{1/2} \quad (2)$$

and its importance in predicting many molecular parameters as well as properties of liquids or solutions has been extensively reviewed [2,4]. Various attempts have been made to separate the molecular interaction into components and assign a solubility parameter for each type of interaction. Thus, considering the contribution from dispersion forces (δ_D), dipole-dipole forces (δ_P), and hydrogen bonding (δ_H), the total solubility parameter is

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (3)$$

However, little has been done to apply the methods to inorganic compounds and there appear to be no studies involving xenon fluorides. We report here the results of the analysis of data for xenon difluoride and xenon tetrafluoride.

METHODS

The computation of the cohesion energy is carried out by means of the equation

$$E_c = RT \left(\frac{2.303 BT}{(C + t)^2} - 1 \right) \quad (4)$$

where T and t are the temperature, K and °C, respectively, and R is the molar gas constant [5,6]. The constants B and C are constants in the Antoine equation relating vapor pressure and temperature,

$$\log p \text{ (mm)} = A - \frac{B}{C + t} \quad (5)$$

Thus, the Antoine constants are needed to compute E_c . Vapor pressures for XeF_2 and XeF_4 have been given by

$$\log p \text{ (mm)} = -3057.67/T - 1.23521 \log T + 13.96976 \quad (6)$$

for XeF_2 and

$$\log p \text{ (mm)} = -3226.21/T - 0.43434 \log T + 12.301738 \quad (7)$$

for XeF_4 [7]. In order to determine the values of the constants for the Antoine equation, vapor pressures were calculated at 10 °C intervals in the range 280-390 °C by means of Eqs. (6) and (7) and the data were fitted to the Antoine equation by the method of Thomson [8]. For XeF_2 , the constants are $A = 10.02048$, $B = 2684.748$, and $C = 261.736$. For XeF_4 , the values are $A = 10.90943$, $B = 3091.797$, and $C = 269.361$.

Molar volumes were calculated by making use of the density equations published by Ogrin, et al. [9]. Densities were calculated at the desired temperatures and these were fitted to an equation of the form

$$\rho = a + bT + cT^2 \quad (8)$$

The constants a, b, and c were included in the program for computing \bar{V} as a function of temperature for XeF_2 and XeF_4 .

RESULTS AND DISCUSSION

Having obtained the necessary values for the Antoine constants and the density function, the cohesion energy, molar volume, and solubility parameter were calculated in the range 280-390 K. As is customary in computing solubility parameters, a vaporizing solid phase is presumed to behave as a super-cooled liquid [2]. Table 1 shows these data for XeF_2 and XeF_4 .

TABLE 1
Computed parameters for XeF_2 and XeF_4

T (K)	XeF_2			XeF_4		
	E_c^*	$\bar{V}^\#$	δ^\dagger	E_c^*	$\bar{V}^\#$	δ^\dagger
280	12794	46.847	16.53	13981	59.702	15.30
290	12736	47.365	16.40	13947	60.406	15.20
300	12679	47.896	16.27	13915	61.128	15.09
310	12626	48.439	16.14	13883	61.867	14.98
320	12574	48.994	16.02	13852	62.624	14.87
330	12525	49.564	15.90	13822	63.399	14.77
340	12477	50.147	15.77	13792	64.194	14.66
350	12431	50.744	15.65	13763	65.010	14.55
360	12387	51.357	15.53	13734	65.846	14.44
370	12344	51.985	15.41	13706	66.704	14.33
380	12302	52.629	15.29	13679	67.585	14.23
390	12261	53.290	15.17	13651	68.489	14.12

* cal/mole; # cm^3/mole ; † $\text{cal}^{1/2} \text{cm}^{-3/2}$

For both XeF_2 and XeF_4 the value of δ is approximately a linear function of temperature. Further, for many purposes it would be possible to neglect the temperature dependence completely, as has been suggested for several other types of compounds [4].

For nonpolar molecules where London dispersion forces represent the only type of interaction, $E_c = -a/V$ where a is one of the constants in the van der Waals equation. Using the data at 300 K, converting E_c to l atm/mole and expressing \bar{V} in liters results in values of $a = 25.07 \text{ atm l}^2/\text{mole}^2$ for XeF_2 and $a = 35.12 \text{ atm l}^2/\text{mole}^2$ for XeF_4 . Further, if it is assumed that the molar volume at 300 K is

$$\bar{V} = 4\pi r^3 N_0 / 3 \quad (9)$$

where N_0 is Avogadro's number and r is an effective radius, it is found that radii of 2.66 Å and 2.89 Å are indicated for XeF_2 and XeF_4 , respectively. These values appear to be somewhat lower than those based on bond lengths, but this may be an indication of more efficient packing of the linear XeF_2 and planar XeF_4 molecules in the liquid state. It may be that the radii represent averages of nonisotropic values for an ellipsoid or oblate spheroid.

Typical values for δ range from about 6.0 to 36.1 $\text{cal}^{1/2} \text{cm}^{-3/2}$. The latter value is for H_2O where the bulk of the interaction is due to hydrogen bonding. The value for CH_3OH is 24.3 while that for benzene is 10.0 $\text{cal}^{1/2} \text{cm}^{-3/2}$. For other nonpolar inorganic halides, typical values are 7.6 for SiCl_4 , 8.8 for SiBr_4 , and 8.7 for SnCl_4 [3]. The higher values in the case of XeF_2 and XeF_4 (16.3 and 15.1, respectively, at 300 K) may reflect larger dispersion forces, but this seems unlikely. One factor in opposition to this is that the solubility parameter of XeF_2 is higher than that of XeF_4 . Also, the molecular weights are not that much different from those of the nonpolar SiCl_4 or SnCl_4 and, therefore, it seems unlikely that the polarizability of XeF_2 or XeF_4 would be large enough to cause δ values as high as those calculated. In view of the tendency of xenon to form a variety of complex bridged species, it may be that intermolecular interaction through extensive fluoride bridging causes the high values for δ in these cases. Another source of the interaction energy giving rise to high values of δ may be that while the XeF_2 and XeF_4 are nonpolar because of their symmetry, the Xe-F bonds may be sufficiently polar that considerable interaction of bond dipoles occurs. In accord with this, the linear XeF_2 could be expected to have

a greater extent of alignment of bond dipoles, and it does have the higher value of δ . In any event, the values of the cohesion energies and the solubility parameters are high enough to be an indication that dispersion forces alone may not account for intermolecular interaction.

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