shown in Fig. 1 a steady current (the value of which was determined as 7×10^{-6} Å) with a slow drift passed through the cell. One face of the membrane was now illuminated with light flashes from an Optatron xenon flash tube light source. Figure 1 shows a series of ten such consecutive illuminations, the time between flashes being of the order of 15 seconds. The current through the membrane rose after each illumination; the cumulative effect resulted in a total increase of current equal to 1.7×10^{-7} Å. After the last illumination the conductivity was allowed in the dark to return to its original value. The rapid rise in conductivity after the flash is followed by a rather slow return to the value before illumination (Fig. 1).

With colorless, opaque, polyethlene-polystyrene permselective membranes containing quaternary ammonium groups as the sites of permselectivity there was only minor light effect on conductivity. However, with polyethylene-polystyrene negatively charged permselective membranes which contained sulfonate groups (*3*) and had a deep color, illumination caused increased conductivity similar to that observed in the positively charged colored membranes.

Since the light flashes contain wavelengths upward of 3000 Å, light is absorbed by the colored membranes, where the color is apparently due to extended systems of conjugated double bonds.

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Thermochemical Properties of Xenon Difluoride and Xenon Tetrafluoride from Mass Spectra

Abstract. *The standard heats of formation for gaseous xenon tetrafluoride and xenon difluoride and the average strength of the bonds in these molecules have been determined from appearance-potential data obtained with a mass spectrometer. The experimental values are compatible with theoretical estimates of these quantities.*

The mass spectra of xenon difluoride, tetrafluoride, and hexafluoride, obtained in a time-of-flight instrument, have been reported by Studier and Sloth (*1*) and by Studier (*2*). Similar results for xenon difluoride and tetrafluoride have been obtained here in a 180° magnetic instrument equipped with a viscous leak and a variable constriction. In addition the appearance potentials of all fragments of ions from these two compounds have been measured. From these data, values for the heats of formation for these compounds and the average strength of the Xe-F bonds have been calculated.

Table 1. Ion abundances from XeF_4 and XeF_2

Ion	XeF_4	XeF_2
XeF_4^+	7	
XeF_3^+	100	
XeF_2^+	60	47
XeF^+	67	100
Xe^+	~800	

This work is an extension of the program here to use the mass spectrometer to determine thermodynamic properties of reactive inorganic gases (*3*). It should be possible to make similar studies on the fluorides of krypton and radon since calorimetric studies under precisely known conditions with these gases will be extremely difficult. The mass spectrometric method has the disadvantages that the ion source reaction stoichiometry is often difficult to assign and initial kinetic energy of fragment ions is difficult to measure. However, our experience with other similar reactive gases for which calorimetrically derived thermodynamic values are available, give us confidence in our assignments of reaction stoichiometry and kinetic energy values. Our initial results from a mass spectrometer which simultaneously collects positive and negative ions strengthens this confidence. The relative simplicity of the measurements and their insensitivity to impurities is of great advantage in studies of reactive or unstable materials.

For these experiments, xenon tetrafluoride was obtained from the Peninsular Chemical Research Corp. It contained a small amount of xenon difluoride—evidenced by the mass spectra—either as an impurity or a decomposition product due to reaction between the tetrafluoride and the materials of the sample system. The greater volatility of the difluoride made it possible to obtain the appearance potentials of ions from both the difluoride and the tetrafluoride by controlling the rate of flow of material into the mass spectrometer. Thus at very low flow rates the mass spectrum was only due to XeF_2 since no XeF_3^+ or XeF_4^+ ions were observed.

When the xenon fluorides were introduced into the mass spectrometer, extensive conditioning was required, similar to that when measurements are made on UF_6, WF_6, CrO_2F_2, VOF_3 and OsF_6. When conditioning is complete the ion currents for the various fragments reach a steady state and give consistent results. The abundance of ions from xenon difluoride and tetrafluoride for 70-v electrons are given in Table 1. The data are presented on the basis of a value of 100 for the principal fluoride-containing fragment. It was impossible to assign unequivocally a value of Xe^+ from XeF_2 since the presence of free Xe could not be excluded in this case and the appearance potentials of Xe^+ from XeF_2 and Xe do not allow for differentiation of the two sources of Xe^+.

Studies at high ion source pressures, estimated to be between 10^{-3} and 10^{-2} torr, revealed the existence of $Xe_2F_5^+$, $Xe_2F_3^+$ and possibly $Xe_2F_2^+$. Positive identification of these di-xenon ions was made from the abundances of the xenon isotopes and measurement of the masses, with uranium hexafluoride as a reference. A pressure study on the more abundant $Xe_2F_5^+$ revealed that this ion is formed by a collision

Table 2. Appearance potentials of ions from XeF_4 and XeF_2.

Ion	XeF_4 (ev)	XeF_2 (ev)	Xe (ev)
$Xe_2F_5^+$	13.8 ± 0.2		
XeF_4^+	12.9 ± 0.1		
XeF_3^+	13.1 ± 0.1		
XeF_2^+	14.9 ± 0.1	12.6 ± 0.1	
XeF^+	13.3 ± 0.1	13.3 ± 0.1	
Xe^+	12.4 ± 0.1	12.0 ± 0.1	12.0 ± 0.1

Table 3. Standard heats of formation and Xe-F bond energies in XeF_4 and XeF_2 in kcal $mole^{-1}$.

Gunn and Wiliamson (*8*)	Gunn (*9*)	Stein and Plurien (*10*)	This work
$\Delta H_f(XeF_4)_{gas}$			
−50	−45	− 54.8*	− 53 ± 5 **
$\Delta H_f(XeF_2)_{gas}$			
			− 37 ± 10**
$D(Xe\text{-}F)_{XeF_4}$			
31	31	31.5	32 ± 2
$D(Xe\text{-}F)_{1,2 XeF_4}$			
			26 ± 3
$D(Xe\text{-}F)_{3,4 XeF_4}$			
			38 ± 7
$D(Xe\text{-}F)_{XeF_2}$			
			39 ± 10

* Temperature of 125°C reported (*10*).
** Ion source temperature estimated to be 150°C.

of an ion with a gas molecule in the ion source.

The appearance potentials shown in Table 2 were obtained by a method (*4*) which is applicable to conditions in which the sample pressure decreases continually with time as was the case in these measurements. Argon, running into the instrument simultaneously with the sample, was used to calibrate the electron-energy scale.

From these data it appears that $Xe_2F_5^+$ is formed by a condensation reaction according to the equation

$$XeF^+ + XeF_4 \rightarrow Xe_2F_5^+.$$

This type of reaction is similar to those discussed by Beynon *et al.* (*5*) and Lindholm (*6*) in hydrocarbon mass spectrometry.

The standard heats of formation and the bond strengths in xenon difluoride and xenon tetrafluoride have been calculated from these appearance-potential (AP) data. Ion-source reactions have been assigned on the basis of the uniqueness and reasonableness of the calculated values for the thermochemical quantities and our expectations of ion-pair production, based on experience with other volatile fluorides and oxyfluorides in a mass spectrometer which simultaneously detects positive and negative ions. The good agreement between the values derived for the heats of formation and bond strengths from the mass spectrometer and calorimetric values, where they exist, are a strong indication that correct stoichiometry has been assigned to the ion-source reactions in this study. Any other assignments give entirely unreasonable values.

For the ion source reaction

$$XeF_4 \rightarrow Xe^+ + F_2 + F + F^-$$

$$\mathrm{AP}(Xe^+)_{XeF_4} = IP(Xe^+) + \Delta H_f(\mathrm{F}) + H_f(\mathrm{F}^-) - \Delta H_f(XeF_4)$$

where *AP* is the appearance potential, *IP* is the ionization potential, and ΔH_f is the standard heat of formation.

$$12.4 = 12.1 + 0.8 - 2.8 - \Delta H_f(XeF_4)$$
$$\Delta H_f(XeF_4) = -2.3 \text{ ev} = -53 \text{ kcal mole}^{-1}$$

Similarly, the average bond energy in XeF_4 was obtained according to

$$\mathrm{AP}(Xe^+)_{XeF_4} = IP(Xe^+) + 4D(\text{Xe-F}) - D(\text{F-F}) - EA(\mathrm{F}^-)$$

where *D* is the dissociation energy of the bond broken and *EA* is the electron affinity of the negative ion.

$$12.4 = 12.1 + 4D(\text{Xe-F}) - 1.6 - 3.6$$
$$D\langle \text{Xe-F}\rangle_{av} = 1.4 \text{ ev} = 32 \text{ kcal mole}^{-1}$$

The average value for the strength of the first two Xe-F bonds in the dissociation of XeF_4 can be obtained from the equations

$$XeF_4 \rightarrow XeF_2^+ + 2F$$
$$AP(XeF_2^+)_{XeF_4} = IP(XeF_2^+) + 2D(\text{Xe-F})$$
$$14.9 = 12.6 + 2D(\text{Xe-F})$$
$$D\langle \text{Xe-F}\rangle_{av} = 26 \text{ kcal mole}^{-1}.$$

From the value for the average energy of the four Xe-F bonds in XeF_4, an average energy of 38 kcal $mole^{-1}$ is obtained for the last two Xe-F bonds to break during the dissociation of XeF_4.

The heat of formation of XeF_2 was calculated according to the equations

$$XeF_4 \rightarrow XeF_2 + 2F$$
$$XeF_2 \rightarrow XeF_2^+$$
$$XeF_4 \rightarrow XeF_2^+ + 2F$$
$$AP(XeF_2^+)_{XeF_4} = IP(XeF_2^+)_{XeF_2^+} + \Delta H_f(XeF_2) + 2\Delta H_f(\mathrm{F}) - \Delta H_f(XeF_4).$$

From values in Table 2 and those in the equations above,

$$\Delta H_f(XeF_2) - \Delta H_f(XeF_4) = 16 \text{ kcal mole}^{-1}$$
$$\text{or} \quad \Delta H_f(XeF_2) = -37 \text{ kcal mole}^{-1}.$$

This yields 39 kcal $mole^{-1}$ as the average value for the strength of the Xe-F bonds in XeF_2. The value was expected and is in excellent agreement with the value 38 kcal $mole^{-1}$ for the strength of the last two Xe-F bonds in the dissociation of XeF_4.

Heats of formation derived from mass spectra are in excellent agreement with the current calorimetric values reported in Table 3 (*7*).

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Diffusion Coefficients of Hydrocarbons in Water: Method for Measuring

Abstract. *A modification of the capillary-cell method of measuring diffusion coefficients has been applied in studying the diffusion of paraffin hydrocarbons in water. Measurements on ethane, propane, and normal butane indicate that diffusion coefficients can be obtained with a precision of 1 to 2 percent.*

The capillary-cell method of measuring diffusion coefficients perfected by Wang (*1, 2*) has been successfully modified and simplified in studying the diffusion of paraffin hydrocarbons in water. In Wang's method a capillary is closed at one end and filled with a solution containing the solute under study. Diffusion takes place past the open end of the capillary while it is immersed in pure solvent, and the coefficient of diffusion (*D*) may be calculated from:

$$D = L^2/\pi^2 t \ln 8C_0/\pi^2 C_a \qquad (1)$$

where *L* is the length of the capillary (in centimeters); *t* is the time of diffusion (in seconds); C_0 is the concentration of solute in the capillary before diffusion (in any units); and C_a is the average concentration of solute in the capillary after diffusion (same units as C_0). Equation 1 applies as long as the ratio Dt/L^2 exceeds 0.2; otherwise a more complete expression given by Wang (*1*) must be used to avoid significant errors.