

Table 3. Standard heats of formation and Xe-F bond energies in XeF₄ and XeF₂ in kcal mole⁻¹.

Gunn and Williamson (8)	Gunn (9)	Stein and Plurien (10)	This work
	$\Delta H_f(\text{XeF}_4)_{\text{gas}}$		
-50	-45	-54.8*	-53 ± 5 **
	$\Delta H_f(\text{XeF}_2)_{\text{gas}}$		
			-37 ± 10**
	$D(\text{Xe-F})_{\text{XeF}_4}$		
31	31	31.5	32 ± 2
	$D(\text{Xe-F})_{1,2\text{XeF}_4}$		26 ± 3
	$D(\text{Xe-F})_{3,4\text{XeF}_4}$		38 ± 7
	$D(\text{Xe-F})_{\text{XeF}_2}$		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.

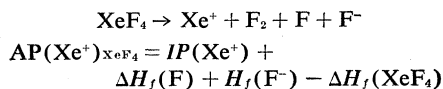
From these data it appears that Xe₂F₅⁺ is formed by a condensation reaction according to the equation



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.

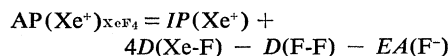
For the ion source reaction



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

$$\begin{aligned} 12.4 &= 12.1 + 0.8 - 2.8 - \Delta H_f(\text{XeF}_4) \\ \Delta H_f(\text{XeF}_4) &= -2.3 \text{ ev} = -53 \text{ kcal mole}^{-1} \end{aligned}$$

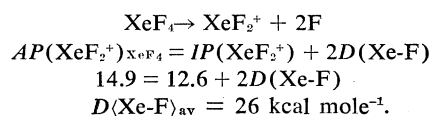
Similarly, the average bond energy in XeF₄ was obtained according to



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

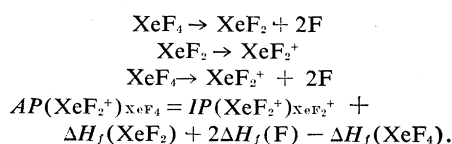
$$\begin{aligned} 12.4 &= 12.1 + 4D(\text{Xe-F}) - 1.6 - 3.6 \\ D(\text{Xe-F})_{\text{av}} &= 1.4 \text{ ev} = 32 \text{ kcal mole}^{-1} \end{aligned}$$

The average value for the strength of the first two Xe-F bonds in the dissociation of XeF₄ can be obtained from the equations



From the value for the average energy of the four Xe-F bonds in XeF₄, an average energy of 38 kcal mole⁻¹ is obtained for the last two Xe-F bonds to break during the dissociation of XeF₄.

The heat of formation of XeF₂ was calculated according to the equations



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

$$\begin{aligned} \Delta H_f(\text{XeF}_2) - \Delta H_f(\text{XeF}_4) &= 16 \text{ kcal mole}^{-1} \\ \text{or } \Delta H_f(\text{XeF}_2) &= -37 \text{ kcal mole}^{-1}. \end{aligned}$$

This yields 39 kcal mole⁻¹ as the average value for the strength of the Xe-F bonds in XeF₂. 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 XeF₄.

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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References and Notes

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- 12 September 1963

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:

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

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.

Table 1. Diffusion measurements on ethane, propane, and normal butane at 29.9°C.

Capillary length (cm)	Diffusion time (sec)	Concn. ratio, C_0/C_a	D (10^{-5} cm ² /sec)
<i>Ethane</i>			
2.412	81,000	2.10	1.56
2.413	79,620	2.07	1.54
2.407	82,380	2.20	1.64
2.475	83,100	2.11	1.60
Mean			1.59*
<i>Propane</i>			
2.475	123,960	2.36	1.30
2.405	127,020	2.37	1.24
2.405	101,220	2.19	1.33
2.475	102,420	2.09	1.29
2.407	86,580	1.94	1.24
Mean			1.28†
<i>Normal butane</i>			
2.475	162,000	2.38	0.96
2.475	178,980	2.49	0.99
2.407	177,420	2.70	1.04
2.475	116,220	2.06	1.05
2.407	116,720	2.07	1.10
Mean			1.03‡

* S.D. of mean, ± 0.01 . † S.D., ± 0.02 . ‡ S.D., ± 0.02 .

We used a specially designed capillary of variable length having an internal diameter of about 0.1 cm. The capillary was made from a 50-ml syringe (3), with a flat barrel on one end. The close fitting stainless steel plunger that is a standard part of the syringe can be equipped with guide rods and a stopping device (Chaney adaptor) so that any desired length of capillary up to about seven centimeters may be used. By filling a known length of the capillary with an aqueous solution of a given hydrocarbon, the system is then ready for immersion in a temperature-controlled bath of pure water (Fig. 1).

The aqueous solutions were prepared by bubbling the hydrocarbon (4) gas through distilled water for about half

an hour to ensure saturation. The solution was then allowed to stand for a day in a constant temperature air bath in order to achieve equilibrium.

There are various sources of errors (5) in measuring diffusion coefficients such as mechanical sweeping of part of the solution out of the capillary as it is being immersed in the water bath. This error was eliminated by keeping an excess droplet of solution on the flat end of the capillary as it was carefully lowered into the bath. Gentle stirring in the water bath must be provided so that the concentration at the open end of the capillary remains effectively zero but this stirring must not cause appreciable convection currents. Wang (2) has discussed a procedure for checking this important experimental condition. The possibility of losing some of the hydrocarbons through the annular space between the plunger and the glass capillary was investigated and found to be negligible.

After an appropriate diffusion time had elapsed, the capillary was removed from the bath and equipped with a removable needle (Fig. 1) for injecting the contents directly into the analytical apparatus. This arrangement provides a distinct advantage over a capillary of fixed length. Tracer techniques were used by Wang in measuring solute concentrations, but in our method, hydrocarbon concentrations are measured with a hydrogen-flame ionization detector, thus eliminating the tracer apparatus. A short chromatographic column used with the detector consists of stainless steel tubing (0.3 cm by 1.5 m) packed with 60/80 mesh firebrick coated with 20 percent polymethylphenyl ether (six ring). By using a carrier gas that is approximately a 1:1 mixture of nitrogen and steam, the introduction of the liquid contents of the capillary simply produces additional steam and the detector reacts only to the hydrocarbons present. An analysis of 20- μ l samples can be made in less than 1 minute with a precision of about 0.5 percent.

An example of the results of diffusion measurements (6) on ethane, propane, and butane at 29.9°C is given in Table 1 (7).

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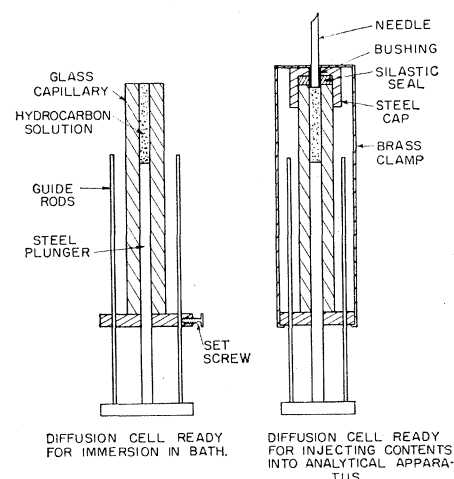


Fig. 1. Diagram of diffusion cell.

References and Notes

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7. We thank the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Symbiosis: On the Role of Algae Symbiotic with Hydra

Abstract. *Green algae living within gastrodermal cells of hydra photosynthetically incorporate $C^{14}O_2$. About 10 percent of the carbon fixed by the algae is released to the hydra where it is assimilated into animal cell components. The specific activity (counts per minute per microgram of protein nitrogen) of hydra animal tissue is 50 to 100 times greater than that of algae-free controls exposed to $C^{14}O_2$. Analyses were facilitated by a new method for rapid separation of hydra tissue layers.*

A variety of aquatic invertebrates contain unicellular algae as hereditary symbionts (1). The importance of these foreign, intracellular, self-reproducing "plasmids" (see 2) to the host animal is not known. There is radioautographic evidence that carbon-14 photosynthetically incorporated by the algae in some coelenterates appears in the host tissues (3). The metabolic fate of this material in the animal tissues has not been previously studied because of the difficulty of separating the animal tissues from the algae. Using green hydra and a new method for rapid separation of ectodermal (algae-free) and gastrodermal (algae-laden) tissues, we have shown that a portion of the carbon-14 photosynthetically assimilated by the algae is released and incorporated into the major chemical components of the animal.

All experiments were carried out with asexually reproducing *Chlorohydra viridissima* (Schulze, 1927) (4) at ambient laboratory temperatures (22° to 24°C) and in continuous light (2750 lu/m², Sylvania Cool White fluorescent). Most of the gastrodermal cells of this species contain 15 to 25