shown in Fig. 2. Similar curves were obtained for Ce^{141}. The curves for Zr^{95} differ from those in Fig. 2 in two respects: (i) the summer minimum for northerly winds occurs late in September rather than late in July, and (ii) the spring maximum for southerly winds occurs in April rather than in January. It would appear from Fig. 2 that during the summer months, the gamma ray activity of fission products varies with wind direction in a way similar to that observed for ozone by Paneth and by Dobson. It would be interesting to determine whether, during the winter months, the ozone concentration in tropical air was greater than that in polar air. The data of Fig. 2 are also consistent with results obtained by Damon and Kuroda (*9*) who observed that during June and July, 1953, the fission product radioactivity of polar air was considerably greater than that of tropical air.

It would appear that the seasonal variation in fission product radioactivity, previously discussed (*2*), is due primarily to the marked seasonal variation in the activity of southerly winds; this variation could be accounted for if it could be shown that air from the south was washed by precipitation more thoroughly during summer months. A study of precipitation patterns along a trajectory extending 700 miles (roughly 1100 km) upwind from Carbondale, Illinois (lat. 38°N) at the time these samples were taken indicates that rainfall pecularities cannot account for the variations shown in Fig. 2. A more plausible explanation is to be found in the stratospheric circulation model of Brewer and Dobson, as presented by Machta (*10*), with two modifications: (i) the equatorial updraft, spanning perhaps 40° of latitude, is assumed to move north and south with the sun, and (ii) an appreciable portion of the downdraft is assumed to be just north and south of the updraft. According to this picture, during the winter, when the sun is south of the equator, stratospheric air would reach latitude 40°N most directly from the south. During the summer, however, the center of the updraft will be appreciably north of the equator, so that the associated downdraft will be north of latitude 40°N, and the most active air will reach Carbondale, Illinois, from the north.

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Permselective Membranes: Spectroscopic and Conductivity Effects

Abstract. *The absorption spectrum of permselective ion-exchange membranes containing positively charged groups shows specific effects which depend on the nature of the negative gegenion used. Such colored permselective membranes with positive or negative functional groups show increased conductivity after illumination with light flashes. The increased conductivity returns slowly to the original value.*

The nature of the anion influences the absorption spectrum of ion-pair complexes in homogeneous solution. There is a correlation for such complexes of one cation, between the properties of the anion—such as electron affinity or ionic radius—and the resulting spectrum in aqueous solution (*1*). Permselective ion-exchange membranes contain as their functional groups charged ions. There arises therefore the possibility to investigate through spectroscopic effects, the interaction between these charged functional groups located in the membrane, and gegenions adsorbed from solutions. We have chosen for our experiments permselective membranes (*2*) in which the active groups are positive quaternary ammonium groups produced by amination of polyvinyl chloride plastic membranes followed by quaternization. These membranes show deep reddish colors. We found that the absorption spectrum of these membranes in aqueous solutions is specifically affected by the nature of the anion used as the gegenion. For example, when the anion was changed in the series—fluoride, chloride, bromide, iodide—and, for comparison, perchlorate, the absorption edge in the red region of the spectrum changed with the change of halide in a regular manner. The membranes were permitted to come into equilibrium with saturated aqueous solutions of alkali halides, then rinsed thoroughly with distilled water, and the spectra were taken while the membranes were immersed in distilled water at *p*H 7. Thus only the halide gegenions bound to the membranes were retained. The wave length, $\lambda_{\frac{1}{2}}$, at which the transmittance of the membrane reaches 50 percent of its maximum, is 655, 648, 632, 622, and 640 mμ for the gegenions I^-, Br^-, Cl^-, F^-, and ClO_4^-, respectively. After equilibration in saturated aqueous NaCl, when the membranes were rinsed with distilled water and equilibrated with different solvents, a regular change in the absorption edge was observed, correlated with the polar and nonpolar nature of the solvent.

To examine the effect of illumination on the conductivity, we used membranes, in aqueous KCl, 0.1-mm thick with a surface area of approximately 0.5 by 3 cm. They were introduced into a quartz spectrophotometer cell and contact to either side of the membrane was through 0.02*M* KCl in capillary agar bridges. The bridges led to silver/silver chloride electrodes which were well protected against illumination. A bias of 0.5 volt (direct current) was applied to the circuit and the current was measured with a Metrohm Polarecord E 261 R instrument. As

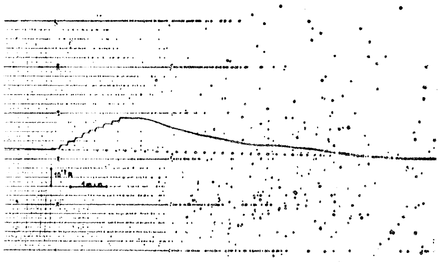

Fig. 1. Change in the current through the permselective membrane as a result of flash illumination.

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