matching, it was necessary to calibrate each gain setting of the amplifier separately.

Examination of a number of triethylamine solutions revealed that at concentrations above about 0.2 m the relationship between output voltage and molality deviates from linearity. Appropriate corrections were made for this effect in computing the values of N in Table II.

Nuclear Magnetic Resonance Spectra.—The proton magnetic resonance spectra were obtained on a Varian Associates Model A-60 instrument. The ethyllithium chemical shift measurements were made with respect to the center of the solvent meth-

ylene absorption in triethylamine and ether and converted to τ-values by separate measurement of the τ-values of the solvent absorptions. In toluene solutions the ring proton absorption was employed as intermediate reference.

The ^{7}Li spectra were obtained in the manner described previously.[3]

Hydrolysis of Xenon Hexafluoride and the Aqueous Solution Chemistry of Xenon[1,2]

BY E. H. APPELMAN AND J. G. MALM
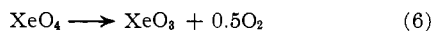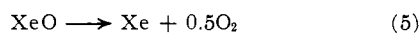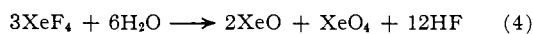
Both XeF_4 and XeF_6 hydrolyze in water to produce aqueous solutions of nonvolatile XeO_3 molecules. These solutions are stable, but they are strongly oxidizing. rapidly liberating chlorine from strong HCl. The Xe–Xe(VI) potential is estimated to be 1.8 v. in acid and 0.9 v. in base. The XeO_3 molecule is a weak acid, forming $HXeO_4^-$ above pH 10.5. In strongly basic solution Xe(VI) disproportionates to give xenon gas and octavalent xenon, while in such solutions ozone oxidizes Xe(VI) nearly quantitatively to Xe(VIII). Sodium and barium salts of Xe(VIII), perxenates, have been characterized, with typical compositions $Na_4XeO_6 \cdot 2.2H_2O$ and $Ba_2XeO_6 \cdot 1.5H_2O$. A salt of mixed oxidation state, $K_4XeO_6 \cdot 2XeO_3$, has also been observed. Aqueous solutions of sodium perxenate evolve oxygen slowly to give Xe(VI). The reaction becomes almost instantaneous below pH 7. Octavalent xenon is an extremely powerful oxidizing agent, rapidly oxidizing iodate to periodate and Mn^{+2} to permanganate. The Xe(VI)–Xe(VIII) potential is estimated at 3.0 v. in acid and 0.9 v. in base. In basic solution Xe(VIII) is present as the ion $HXeO_6^{-3}$. Below pH 10 the principal species becomes $H_2XeO_6^{-2}$. Both Xe(VI) and Xe(VIII) have characteristic. pH-dependent. ultraviolet absorption spectra which can be attributed to the several species present.

Introduction

The three well-characterized xenon fluorides have been shown to react with water according to the following equations[3-5]

$$XeF_2 + H_2O \longrightarrow Xe + 0.5O_2 + 2HF \qquad (1)$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF \qquad (2)$$

$$3XeF_4 + 6H_2O \longrightarrow XeO_3 + 2Xe + 1.5O_2 + 12HF \qquad (3)$$
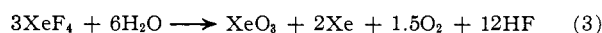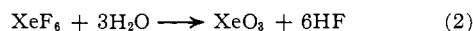
Thus when XeF_6 is hydrolyzed, the xenon is quantitatively retained in solution as aqueous hexavalent xenon, while when XeF_4 is hydrolyzed, one third of the xenon is so retained. The stoichiometry of reaction 3 can be explained by a mechanism such as[5]

$$3XeF_4 + 6H_2O \longrightarrow 2XeO + XeO_4 + 12HF \qquad (4)$$

$$XeO \longrightarrow Xe + 0.5O_2 \qquad (5)$$

$$XeO_4 \longrightarrow XeO_3 + 0.5O_2 \qquad (6)$$

Divalent xenon has never been identified in aqueous solution, but reaction 6 is consistent with our knowledge of aqueous Xe(VIII).[5,6]

In addition to these reactions, XeF_6 reacts with strong base to precipitate solid compounds containing

octavalent xenon.[5] The nature of this reaction will be discussed in our paper. We will also discuss in detail the properties of aqueous Xe(VI) and Xe(VIII).

Experimental

Preparation and Hydrolysis of Xenon Hexafluoride.—The XeF_6 was prepared as described elsewhere.[7] It was distilled *in vacuo* and condensed on the bottom of a glass bulb. For the preparation of pure aqueous XeO_3 the bulb also contained magnesium oxide. The bulb was sealed off from the vacuum line and opened by means of a break-seal. The solution used for the hydrolysis was then added carefully to the frozen fluoride.

Preparation of Pure XeO_3.—Approximately 5 g. of xenon hexafluoride was hydrolyzed in about 100 ml. of water in the presence of at least 1.5 g. of MgO per gram of XeF_6. At least this much MgO was needed to neutralize rapidly all the HF produced. The resulting slurry was agitated until it was slightly alkaline and was then filtered through a sintered glass filter of medium porosity. To remove magnesium the solution was passed through a column of hydrous zirconium phosphate[8] which had been washed with 2 M HNO_3 or $HClO_4$. Residual fluoride was then removed by passage through a column of hydrous zirconium oxide[8] which had been converted to the nitrate form by exhaustive washing with 0.1 M HNO_3. The final product was a solution *ca*. 0.1 M in xenon(VI) and *ca*. 0.005 M in acid.

Other Materials.—Sodium perchlorate was prepared by neutralization of sodium carbonate followed by recrystallization. Mallinckrodt primary standard grade potassium iodate served as an iodometric standard, and N.B.S. potassium acid phthalate served as an acidimetric standard. Ozone was prepared from commercial oxygen by the usual silent discharge method.[9] Commercial "pre-purified" nitrogen was used and all other chemicals were commercial products of reagent grade. Distilled water was redistilled first from alkaline permanganate, then from dilute sulfuric acid, and finally once more without additive before being used in these studies.

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(3) F. B. Dudley, G. Gard, and G. H. Cady, *Inorg. Chem.*, **2**, 228 (1963).

(4) S. M. Williamson and C. W. Koch, *Science*, **139**. 1046 (1963).

(5) J. G. Malm, B. D. Holt, and R. W. Bane, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 167 ff.

(6) E. H. Appelman, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 185 ff.

(7) J. G. Malm, I. Sheft, and C. L. Chernick, *J. Am. Chem. Soc.*, **85**, 110 (1963).

(8) Manufactured by Bio-Rad Laboratories, Richmond, Calif.

(9) See, for example, D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944. p. 262.

Analytical Procedures.—The xenon present in solutions and salts was determined by decomposing the material either thermally or by the addition of excess acid iodide, measuring the amount of gas evolved, and determining the composition with a mass spectrometer. The carbon dioxide content of salts was determined similarly after addition of acid or acid iodide. The oxygen evolved when perxenates were treated with acid was also determined in a similar fashion. The water content of salts was determined by ignition to 820° in an aluminum boat and absorption of the water in magnesium perchlorate.

Fluoride was determined on a macroscale by titration with $Th(NO_3)_4$, using sodium alizarin sulfonate as an indicator, and on a microscale by the colorimetric method of Frere[10] using "Amadec F" from Burdick and Jackson Laboratories.[11] Samples for fluoride analysis were first treated with excess hydrogen peroxide to destroy xenon compounds. The excess of peroxide was then destroyed by making the solution slightly alkaline and boiling it in contact with platinized platinum.

Magnesium was determined by emission spectrography, and alkali metals by flame photometry. The metal ion content of xenon salts could be most accurately determined by dissolving the salt in a measured amount of acid exceeding the quantity necessary to neutralize it and back-titrating the excess. In the absence of nonbasic anionic impurities, the metal content determined in this way always agreed with that determined directly.

The oxidizing power of salts and solutions was determined by adding an excess of sodium iodide, making the solution acid, and titrating the triiodide formed with standard thiosulfate to an amylose end point. We found that if the solution was made acid *before* the iodide was added, we always found 6 equiv. of oxidizing power per mole of xenon, any octavalent xenon having decomposed to Xe(VI) and oxygen. If, however, the iodide was added first, all the initial oxidizing power was captured as triiodide. Thus the titer determined by adding first acid, then iodide was six times the xenon molarity and provided a convenient method for routine xenon determination.[12] If the titer obtained by adding first iodide, then acid was different, the ratio of the two, multiplied by six, gave the mean oxidation state of the xenon and allowed us to determine the fraction present as Xe(VIII).

The acid or base content of xenon solutions was determined by potentiometric titration with standardized acid or base (*vide infra*).

All titrations were made with 1.0- and 10.0-ml. displacement burets manufactured by the Emil Greiner Co.

Periodate species and elemental halogens were semiquantitatively determined by their characteristic ultraviolet absorption spectra under appropriate conditions.

Tracer Studies.—In some experiments radioactive xenon tracer was used to permit rapid relative determination of xenon concentrations. A mixture of radioactive xenon isotopes was obtained from Oak Ridge National Laboratory and was used to synthesize XeF_6, which was then hydrolyzed to give aqueous Xe(VI). Aliquots of radioactive solutions were placed in glass vials and were counted in a well-type thallium-activated sodium iodide scintillation crystal, using a single-channel pulse analyzer set to count the 81 kev. peak of Xe^{133}. Unbound xenon was removed from the solutions by bubbling in pure nitrogen.

Conductance and Freezing Point Measurements.—Specific conductances were measured with an ordinary a.c. bridge. After the conductance of a solution had been measured, the xenon compounds were destroyed by the addition of hydrogen peroxide and the conductance was again measured to determine the "blank" due to the acid present. Freezing points were measured with a conventional apparatus,[13] using a thermometer with 0.1° subdivisions.

Spectrophotometric Measurements.—A Cary Model 14 recording spectrophotometer was used. Measurements were made at 25° in silica cells of 1.0- or 0.10-cm. light path. Blanks were run using solutions identical except for the absence of the

xenon compounds. Phosphate buffers were used to make up solutions of pH 7.5 and 11, borate buffers for solutions of pH 8–10.5. Sodium perchlorate was added to make the ionic strength close to 0.1. Except in the case of the pH 11 solution, the predominant electrolyte was 1:1. Spectra of Xe(VIII) were corrected for slight decomposition when necessary.

pH Measurements and Potentiometric Titrations.—A Beckman Model G pH meter with a regular or E-2 (low sodium error) glass electrode and a calomel reference electrode was used for pH measurements. Commercial buffer solutions were used as pH standards. Since xenon compounds oxidized pH indicators, it was necessary to determine the end point of analytical acid-base titrations potentiometrically. Such titrations were carried out with a Beckman Model H pH meter using a regular glass electrode and a calomel reference electrode. This system was also used for the rapid titration of Xe(VIII) shown in Fig. 5. In that case, the nomograph prepared by Beckman Instruments, Inc., was used to correct for sodium error.

Precise acid-base titrations of Xe(VI) and Xe(VIII) were made with a Cary Model 30 vibrating reed electrometer as a null detector. A Rubicon Type B potentiometer was in series with the electrometer on the low impedance side of the circuit and an Eppley unsaturated Weston cell was used for standardization. An E-2 glass electrode was used as an indicator of hydroxide ion concentration, being standardized by a titration of strong acid with strong base in a medium nearly identical with the experimental one. The reference electrode was a silver-silver chloride electrode of the thermal-electrolytic type[14] dipping into a solution about 0.04 M in HCl and with $NaClO_4$ added to make the total salt concentration comparable to that in the experimental solution. The experimental and reference compartments were connected by a salt bridge consisting of a sodium perchlorate solution equal in concentration to the sum of HCl plus $NaClO_4$ in the reference compartment. The bridge itself was constructed as an "H" of glass tubing. The two legs were open at the top and ended at the bottom in two female standard-taper joints. Male plugs were carefully lapped into these joints to make them leaktight. Thin glass rods were sealed to the narrow ends of the plugs. These rods were run up through the legs of the "H" to permit the plugs to be pulled into the joints from above. This was done while the joints were immersed in the sodium perchlorate solution with which they were to be filled. Then the "H" was filled with the solution to a level above the cross tube. The outside of the "H" was wiped dry and one leg was placed in each of the two cell compartments. Both reference and experimental solutions were saturated with nitrogen and during the titration a vigorous stream of water-saturated nitrogen was used to stir the experimental solution. Sodium perchlorate was added to the experimental solution or to the titrant as was necessary to maintain nearly constant total salt concentration. The entire cell was immersed in a water bath held at 25.0°.

In precise titrations of Xe(VIII) corrections were applied for carbonate impurity and for decomposition.

Conventions

All oxidation potentials are given according to the IUPAC convention which makes the Li–Li$^+$ potential -3 v.

We have used two types of acid–base equilibrium constants. For a general equilibrium

$$HA \rightleftharpoons H^+ + A^- \tag{7}$$
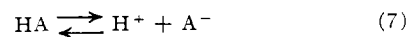
we define the quantity

$$K_B = \frac{[HA][OH^-]}{[A^-]} \tag{8}$$

and call it the base constant of A^-. We also define the quantity

$$pK_A = pH + \log [HA]/[A^-] \tag{9}$$

(10) F. J. Frere, *Anal. Chem.*, **33**, 644 (1961).

(11) The analytical procedures for fluoride were designed and carried out by Miss Irene Fox.

(12) Unbound elemental xenon was not detected in this way, of course, but it was generally the chemically bonded xenon in which we were interested.

(13) See, for example, F. Daniels, J. H. Mathews, and J. W. Williams, "Experimental Physical Chemistry," McGraw–Hill Book Co., New York, N. Y., 1941, p. 76.

(14) G. J. Janz, "Reference Electrodes," D. J. G. Ives and G. J. Janz, Ed., Academic Press, New York, N. Y., 1961, p. 179 ff.

where pH is measured with respect to standard buffers. Since both K_B and pK_A are expressed in terms of concentrations, both will be functions of the medium. Furthermore, in general, pK_A will be only very roughly equal to $14 + \log K_B$.

Results and Discussion

Properties of Aqueous Xe(VI).—Pure solutions of Xe(VI) in dilute aqueous acid are colorless, odorless, and stable. The slight decomposition sometimes observed over several months is most likely due to reduction of the xenon by accidentally introduced impurities. If the solutions are evaporated to dryness, however, the residue of xenon trioxide is highly explosive, as other workers have observed.[4,15] The Xe(VI) in these solutions shows no volatility. When the volume of a solution is reduced by a factor of ten by vacuum distillation at room temperature, less than 0.01% of the chemically bound xenon appears in the distillate.

These properties agree with those found by most other workers[3,4,16] but disagree sharply with the results of Kirschenbaum and Grosse,[17] who claim to have acid solutions of Xe(VI) which are unstable, have a pungent odor, and from which the bound xenon is readily distilled. We cannot explain this discrepancy.

The oxidation state of the xenon in our solutions was verified by measuring both the iodine liberated and the xenon evolved upon treatment with acid iodide. A typical sample had 6.09 mequiv. of oxidizing power per mmole of xenon. The difference from 6.00 lies within the experimental uncertainty of the gas analysis.

A 0.02 M Xe(VI) solution ca. 10^{-4} M in acid had a net molar conductance of less than 0.04 at 25°, indicating that the xenon(VI) species is probably a nonelectrolyte. A solution 0.78 M in Xe(VI) and 0.04 M in perchloric acid had a density of 1.112 and a freezing point of $-1.9 \pm 0.1°$. This corresponds to a net molal depression of 2.2° for the xenon(VI) species. However, measurement of the conductance of a diluted aliquot of this solution indicated that it contained, in addition to the acid, electrolytic impurity equivalent to 0.05 M NaCl, which had probably been introduced while the solution was being concentrated by evaporation. Allowance for this impurity reduces the molal freezing point depression of the Xe(VI) species to 1.95 $\pm$ 0.15°. We may thus conclude that the species contains only one xenon atom per molecule.

The solubility of xenon trioxide in water has not been determined, but it seems to be considerably greater than $2M$. Measurements made in this laboratory of the Raman spectra of these solutions strongly suggest that the solute is present principally in the form of XeO_3 molecules.[18]

Solutions of hexavalent xenon are powerfully oxidizing, the xenon being reduced to the elemental form. In agreement with the work of Williamson and Koch,[16] we find that iodide is oxidized to iodine very rapidly in acid solution, but fairly slowly above pH 7, while

(15) D. F. Smith, J. Am. Chem. Soc., **85**, 816 (1963).

(16) S. M. Williamson and C. W. Koch, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 158 ff.

(17) A. D. Kirschenbaum and A. V. Grosse, Science, **142**, 3592 (1963). and information presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(18) H. H. Claassen and G. N. Knapp, to be published.

bromide is oxidized rapidly to bromine in 1 M HBr but rather slowly at lower hydrogen and bromide ion concentrations. Chloride ion is oxidized to chlorine only slowly in 2 M HCl, at a moderate rate in 3 M HCl, and very rapidly in 6 M HCl. Acid manganous solutions are oxidized to MnO_2 over several hours and in the course of a day or two permanganate begins to form. In 2 M perchloric acid, iodine is very slowly oxidized to iodate. The rate is considerably greater in 6 M acid, and at this acid concentration the XeO_3 will also very slowly oxidize bromine to bromate. This means that the Xe–Xe(VI) potential probably exceeds 1.6 v.

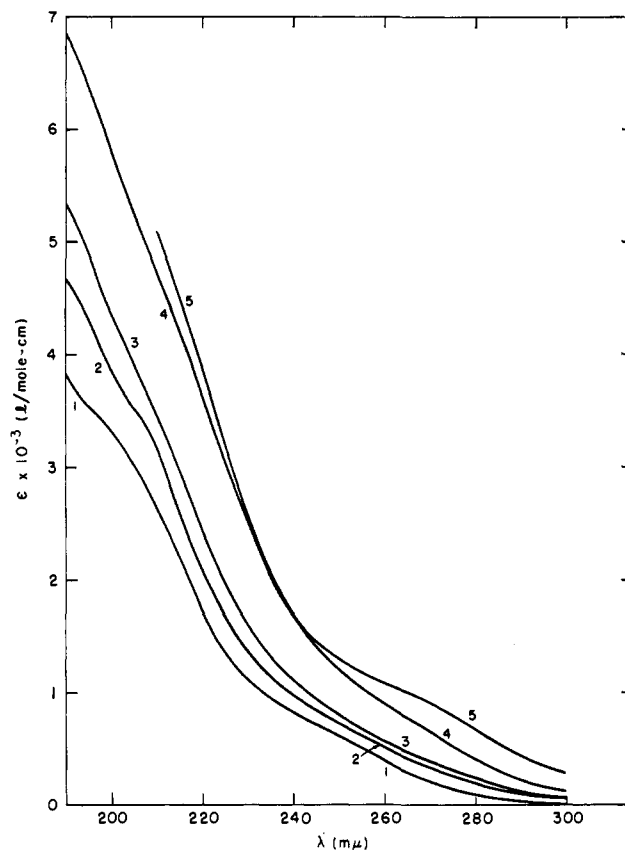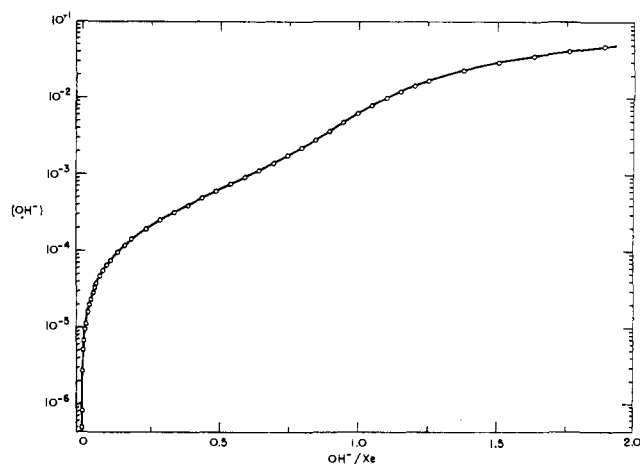Figure 1 shows the ultraviolet absorption spectrum of Xe(VI) as a function of pH. Measurements were

Fig. 1.—Ultraviolet absorption spectra of Xe(VI) at $\mu \sim 0.1$: 1, pH 2 and 8; 2, pH 10; 3, pH 10.5; 4, pH 11; and 5, pH 13.

made with $\sim$0.003 M solutions in cells of 1-mm. light path. We see that the spectrum is nearly constant below pH 10 and above pH 11 but changes rapidly in between. There are no real peaks, but in acid the spectrum has shoulders at 210 and 250 mμ, while in strong base it has a shoulder at 265 mμ. These spectra are quite different from those reported by Williamson and Koch,[16] who observed a definite peak which moved continuously to longer wave lengths as the pH rose, going from 198 mμ at pH 5.5 to 210 mμ in 0.006 M base. Our extinction coefficients are also considerably greater than those reported by Williamson and Koch.

We do not know the reason for this discrepancy. Our results, however, are what you would expect if XeO_3 underwent acid dissociation with a pK_A between

Fig. 2.—Titration of 0.07 M XeO$_3$ with 0.5 M NaOH at μ = 0.5

10.5 and 11. Then the spectrum at pH values below 10 is essentially that of XeO$_3$, while that at pH values above 11 is that of the deprotonated species.

To verify this conclusion we have titrated XeO$_3$ solutions with base. Solutions 0.07 and 0.007 M in Xe(VI) and 0.5 M in NaClO$_4$ were titrated with 0.5 M NaOH. The titration curve for the more concentrated solution appears in Fig. 2. The obvious break in the curve at OH$^-$/Xe = 1 indicates that we do indeed have a deprotonation reaction. The data were analyzed on the assumption that the principal equilibrium was

$$HXeO_4^- \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} XeO_3 + OH^- \qquad (10)$$
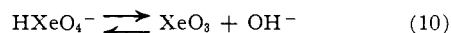
with equilibrium constant K_B. Figure 3 shows the values of K_B calculated at various values of (OH$^-$). Within the scatter K_B is constant at $6.7 \pm 0.5 \times 10^{-4}$ and we conclude that eq. 10 represents the principal equilibrium involved. The corresponding pK_A is about 10.5.[19] Analysis of the titration curves provides no evidence of any further deprotonation.

We have no knowledge of either the structure or the extent of hydration of the xenon(VI) anion. Thus a species such as H$_5$XeO$_6^-$ is quite possible. It is also possible that a hydroxide ion is loosely attached to an unaltered XeO$_3$ molecule to produce an anion which we may represent as XeO$_3$·OH$^-$.

If a 0.1 M HClO$_4$ solution is made 0.05 M in Xe(VI), the hydrogen ion activity changes less than 1%, signifying that the XeO$_3$ molecule is not appreciably basic.[20]

Hydrolysis of XeF$_6$ in Strong Base and Disproportionation of Xe(VI).—When XeF$_6$ is hydrolyzed in strong sodium hydroxide it is known that a fraction of the xenon is lost and the remainder precipitates as sodium perxenate, a salt of octavalent xenon.[5] The reaction was studied in detail in experiments in which about 30 ml. of 2.5 M NaOH was added to about 1.5 mmoles of XeF$_6$. The immediate product is a solution of Xe(VI) from which sodium perxenate slowly precipitates. The reaction proceeds at room temperature with initial half-times ranging from 2 to 20 hr.

(19) At ionic strength 0.1, pK_A rises to around 10.8, in agreement with the spectrophotometric results.

(20) In an early paper[6] we reported some evidence that Xe(VI) might have basic properties. We have subsequently found that the apparent basic behavior was due to a small amount of fluoride impurity that had escaped detecti
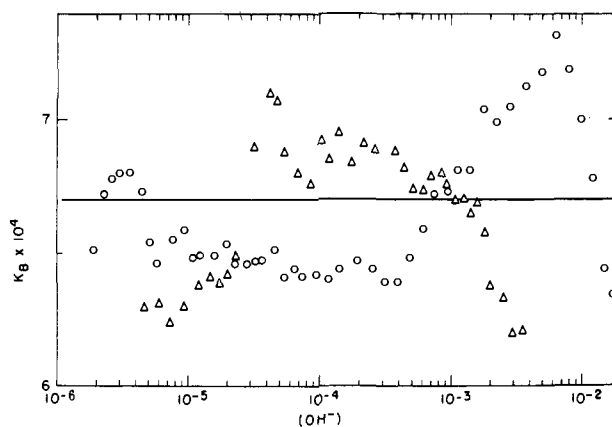

Fig. 3.—Base constant of HXeO$_4^-$ at μ = 0.5: O, 0.07 M Xe(VI); △, 0.007 M Xe(VI).

A typical "fast" experiment is detailed in Table I. We see that with every mole of xenon lost from the mixture 4 equiv. of oxidizing power is also lost, resulting finally in half the xenon being lost and the other
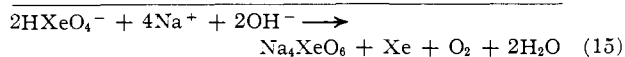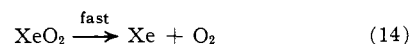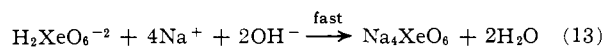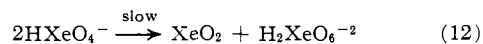
TABLE I

HYDROLYSIS AND DISPROPORTIONATION OF XeF$_6$ IN NaOH

Time, hr.	Xe(VI), mmoles	Xe(VIII), mmole	Lost oxidizing power / Lost Xe
0	1.392		
2	0.699	0.337	4.11
6	0.187	0.628	3.82
11	0.037	0.692	3.91
23		0.704	3.95

half being converted to Xe(VIII). This relation has been observed in all the hydrolysis experiments and implies the stoichiometry

$$2XeF_6 + 4Na^+ + 16OH^- \longrightarrow$$
$$Na_4XeO_6 + Xe + O_2 + 12F^- + 8H_2O \quad (11)$$
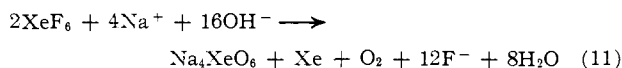
If NaOH is added to a pure XeO$_3$ solution of moderate concentration, sodium perxenate precipitates out very slowly and xenon is lost. Williamson and Koch[21] studied this reaction at elevated temperatures and found that Xe and O$_2$ were given off in a 1:1 mole ratio, indicating a stoichiometry analogous to eq. 11. They also found the rate of the reaction to be independent of hydroxide concentration over a considerable range. They postulated the formation of Xe(IV) as an intermediate in a reaction mechanism which we can formulate as

$$2HXeO_4^- \overset{slow}{\longrightarrow} XeO_2 + H_2XeO_6^{-2} \qquad (12)$$

$$H_2XeO_6^{-2} + 4Na^+ + 2OH^- \overset{fast}{\longrightarrow} Na_4XeO_6 + 2H_2O \quad (13)$$

$$XeO_2 \overset{fast}{\longrightarrow} Xe + O_2 \qquad (14)$$

$$2HXeO_4^- + 4Na^+ + 2OH^- \longrightarrow$$
$$Na_4XeO_6 + Xe + O_2 + 2H_2O \quad (15)$$

(21) S. M. Williamson and C. W. Koch, paper presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

We have observed that at room temperature a pure Xe(VI) solution in NaOH disproportionates much less rapidly than does the solution resulting from the hydrolysis of XeF_6 in NaOH. This is true even when fluoride is added to the former. For example, after a solution 0.07 M in Xe(VI), 0.5 M in NaF, and 1.8 M in NaOH has stood for 24 hr., 13.3% of the original xenon has precipitated as sodium perxenate and 70.7% remains in solution as Xe(VI). From these figures we can calculate that xenon and oxidizing power have been lost in the ratio 1:4.3, in agreement with eq. 15, and the extent to which the reaction has proceeded indicates a half-time of about 50 hr.

The enhanced and variable rate of the disproportionation reaction when XeF_6 is the starting material strongly suggests that the reaction is being catalyzed by an impurity. We have no real knowledge of the nature of this impurity, but oxyfluorides of xenon are possibilities.

We attempted to study the disproportionation of pure Xe(VI) under conditions such that the reaction was homogeneous. We used 1–4 M KOH which had been pretreated with ozone to destroy reducing impurities, and we kept the xenon concentration below 0.003 M. Under these conditions it seemed that anything could happen. In one experiment the Xe(VI) disproportionated quickly with no loss of oxidizing power, implying a reaction such as

$$4HXeO_4^- + 5OH^- \longrightarrow 3HXeO_6^{-3} + Xe + 3H_2O \quad (16)$$
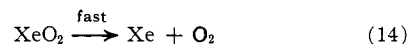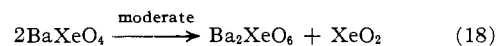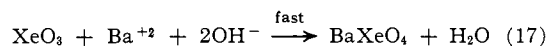
with no intermediate oxidation states of xenon produced. However, in other experiments under seemingly identical conditions, most of the xenon was lost rather rapidly and the small residue was entirely Xe(VIII). In still other nominally identical experiments, the Xe(VI) merely decomposed slowly over many hours or days, and no Xe(VIII) was formed at all. Again we must invoke catalysis by unknown impurities and admit that we really do not know what is going on at these low concentrations. It does appear, however, that quite aside from its disproportionation, Xe(VI) is less stable in strong base than in acid. Whether this would be true even in the complete absence of impurities is, of course, a moot point.

A most striking example of the disproportionation of Xe(VI) is its behavior in the presence of barium hydroxide. Kirschenbaum and Grosse[17] have reported the preparation of a barium salt of Xe(VI) by addition of excess barium hydroxide to an Xe(VI) solution at 0°. Attempting to repeat this work, we found that at least 95% of the xenon was instantly precipitated as a white, gelatinous solid. However, the precipitate continuously gave off gas bubbles, and when it was dried and analyzed it was found to be a salt of Xe(VIII).

We found that if the precipitate was redissolved in perchloric acid immediately after its formation, all the oxidizing power was returned to the solution. This suggested that the initial precipitate was a salt of Xe(VI), although it could conceivably have contained instead an equimolar mixture of Xe(IV) and Xe(VIII). If the precipitate was not immediately redissolved, however, it disproportionated rapidly. In a typical experiment 1 ml. of 0.2 M Ba(OH)$_2$ was added to 1.5 ml. of 0.007 M XeO$_3$ and the resulting slurry was stirred at room temperature. The reaction was com-

plete within 15 min. and the slurry then contained 49.6% of the original xenon and 65.7% of the original oxidizing power, indicating that the residue was entirely Xe(VIII).

The following set of reactions can reasonably account for these observations

$$XeO_3 + Ba^{+2} + 2OH^- \xrightarrow{\text{fast}} BaXeO_4 + H_2O \quad (17)$$

$$2BaXeO_4 \xrightarrow{\text{moderate}} Ba_2XeO_6 + XeO_2 \quad (18)$$

$$XeO_2 \xrightarrow{\text{fast}} Xe + O_2 \quad (14)$$

We have never been able to isolate a barium salt of Xe(VI) and we do not know how Kirschenbaum and Grosse were able to prepare such a compound.

All in all, our knowledge of the disproportionation of Xe(VI) is in a very unsatisfactory state. We hope that work now in progress will lead to a better understanding of this reaction.

Compounds of Xenon (VIII), Perxenates.—Sodium perxenate was first discovered as the product of the hydrolysis of XeF_6 in strong NaOH.[5] We have found, however, that this material is more or less severely contaminated with sodium fluoride. A much purer product can be obtained by ozonizing a pure XeO_3 solution in 1 M NaOH. Sodium perxenate is insoluble in this medium and precipitates out nearly quantitatively. Its solubility in water is only about 0.025 M at room temperature and it may be washed moderately to remove excess base. The product is a white crystalline powder which may contain anywhere from 0.6 to 6 molecules of water per xenon, depending on the manner in which it is dried. The only contaminant is a small amount of sodium carbonate. A typical sample, dried in a stream of nitrogen, had the empirical composition $Na_4XeO_6 \cdot 2.2H_2O \cdot 0.02Na_2CO_3$. The analytical data (%) are: Na_2O, 34.6 (calcd., 34.7); XeO_4, 54.0 (calcd., 54.1); H_2O, 11.1 (calcd., 11.0); CO_2, 0.3 (calcd., 0.2); oxidizing equivalents per mole of Xe, 7.97 (calcd., 8.00).

The crystal structures of $Na_4XeO_6 \cdot 6H_2O$ and $Na_4XeO_6 \cdot 8H_2O$ have been determined by X-ray diffraction, and they show the presence of approximately octahedral XeO_6^{-4} ions.[22,23] Thus we are dealing here with true octavalent xenon and not with a peroxy compound.

Sodium perxenate is entirely stable at room temperature. It dehydrates to the anhydrous salt around 100° and decomposes abruptly at 360°.[24]

Barium perxenate was prepared in 50% yield as described in the preceding section. After drying in a nitrogen stream the gelatinous material decreased markedly in volume to leave a white, lumpy powder. The lumps were crushed in an agate mortar and were dried *in vacuo* over magnesium perchlorate to give a stable product with the empirical composition $Ba_2XeO_6 \cdot 1.5H_2O \cdot 0.05BaCO_3$. The analytical results (%) showed: BaO, 58.2 (calcd., 58.1); XeO_4, 36.2 (calcd., 36.1); H_2O, 5.1 (calcd., 5.2); CO_2, 0.6 (calcd., 0.6);

(22) W. C. Hamilton, J. A. Ibers, and D. R. MacKenzie, *Science*, **141**, 532 (1963).

(23) A. D. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, *ibid.*, **142**, 502 (1963).

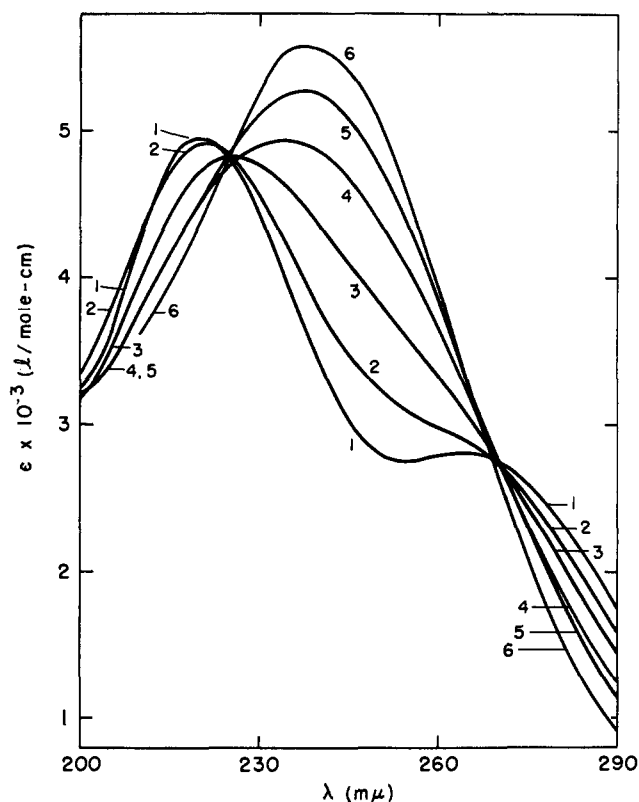(24) H. Selig and L. Kreider, unpublished thermogravimetric measurements.

Fig. 4.—Ultraviolet absorption spectra of Xe(VIII) at $\mu \sim$ 0.1: 1, pH 7.5; 2, pH 9.5; 3, pH 10; 4, pH 10.5; 5, pH 11; 6, pH 13.

oxidizing equivalents per mole of Xe, 7.95 (calcd., 8.00). Like the sodium salt this compound is quite stable, decomposing around $300°.^{24}$ It is nearly insoluble in water, a saturated solution at room temperature being only 2.3×10^{-5} M.

It has not been possible to prepare a pure potassium salt of Xe(VIII). Whether XeF_6 is hydrolyzed in KOH, aqueous Xe(VI) is allowed to disproportionate slowly in KOH, or an Xe(VI) solution in KOH is ozonized, the product is always a bright yellow solid which can be detonated by concussion even when wet and which cannot be dried without explosion. At room temperature this material dissolves in water to the extent of about 0.01 M xenon, two-thirds of which is present as Xe(VI) and one-third as Xe(VIII). The analytical data agree with the formula of a mixed salt $K_4XeO_6 \cdot 2XeO_3$. Typical results are: K^+/Xe, 1.336 (calcd., 1.333); oxidizing equivalents per mole of Xe, 6.69 (calcd., 6.67). It seems reasonable to conclude that the bright color of the solid arises from a charge-transfer spectrum of some sort.

More or less insoluble perxenates are formed by most of the other metallic ions, but none of these compounds has as yet been well-characterized. All of these salts decompose in acid to liberate oxygen and leave a solution of Xe(VI).

Properties of Aqueous Xe(VIII).—Although aqueous Xe(VIII) may be formed directly by passing ozone through very dilute solutions of Xe(VI) in base, it is more practical to prepare Xe(VIII) solutions by dissolving sodium perxenate in water. This results in a strongly basic solution, the pH corresponding approximately to the liberation of 1 mole of OH^- per

mole of the compound dissolved, according to the equation

$$Na_4XeO_6 + H_2O \longrightarrow HXeO_6^{-3} + OH^- + 4Na^+ \quad (19)$$

A 0.0036 M solution, for example, has a pH of 11.61 at 24°.

Aqueous perxenate solutions are unstable, slowly evolving oxygen and forming Xe(VI). The rate of decomposition is strongly pH dependent. At pH 11.5 a 0.003 M solution decomposes to the extent of about 1% per hour, while at pH 8 the decomposition rate exceeds 1% per minute. Below pH 7 the decomposition is almost instantaneous. In the vicinity of pH 7–9 the decomposition rate decreases with decreasing perxenate concentration, an effect which is not observed around pH 11–12. This suggests a complex mechanism for the decomposition which should be worth looking into.

Perxenate solutions are very powerful and rapid oxidizing agents, the Xe(VIII) being reduced to Xe(VI). These solutions oxidize iodide ion to iodine very rapidly even in 1 M base. They almost instantly oxidize bromide ion to bromine at pH 9 or less, and chloride ion to chlorine in dilute $acid.^{25}$ Also in dilute acid perxenate immediately converts Mn^{+2} to permanganate. Rapid oxidation of iodate to periodate and of Co(II) to Co(III) takes place in both acid and basic solution. The reactions that take place in acid must, of course, be fast enough to compete favorably with the rapid evolution of oxygen.

Our early measurements have shown Xe(VIII) solutions to have spectra that are markedly pH dependent.[6] We have repeated these measurements in a more systematic fashion and using purer solutions. The results appear in Fig. 4. The spectrum is independent of the particular buffer used to maintain the pH, and Beer's law is obeyed from 3×10^{-4} to 3×10^{-3} M perxenate over the entire pH range. Within the experimental error there are isosbestic points at 220 and 270 mμ, indicating that only two principal species are contributing to the spectra. Again it is reasonable to attribute the changing spectra to an acid–base equilibrium with a pK_A near 10, corresponding to the pH region in which most of the change occurs. The validity of Beer's law indicates that the equilibrium does not involve a change in aggregation over the concentration range studied.

Once more, we must turn to potentiometric titration to get a better view of what is happening, and again we improve on preliminary measurements reported earlier.[6] The solid curve in Fig. 5 represents a rapid titration of a sodium perxenate solution with acid. After 2 moles of acid has been added per mole of xenon, a slight further addition of acid causes the pH to drop sharply, then rise asymptotically toward its original value. This behavior continues until 4 moles of acid has been added. We can account for this phenomenon if we assume that after H^+/Xe reaches 2, a moderately rapid decomposition sets in which consumes another 2 moles of hydrogen ion per mole of xenon.

The long-dashed curve in Fig. 5 is a reference titration of NaOH. Its end point has been set to coincide with the break in the xenon curve, and for the sake of

(25) The iodine or bromine must be stabilized as I_3^- or Br_3^- by the presence of excess iodide or bromide. Otherwise hypohalites will be formed.
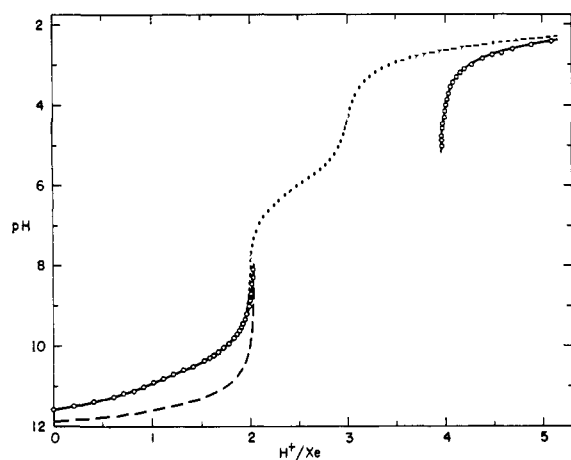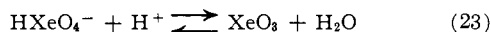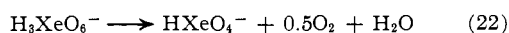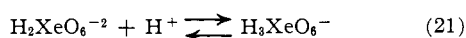
Fig. 5.—Titration curves: -O-O-O-, titration of 0.003 M perxenate with 0.1 M HClO$_4$ at 24° (corrected for carbonate impurity, but not for decomposition during the titration; no sodium perchlorate was added); ---------, calculated titration curve in the absence of decomposition; – – – –, reference titration of 0.006 M NaOH with 0.1 M HClO$_4$.

clarity only the portion to the left of the end point has been shown. When we compare the xenon curve with the reference we see definite evidence of buffering in the region of 1.5 moles of H$^+$ per mole of xenon, indicating that a weak base is being protonated by the second mole of acid added. The first mole of acid, of course, neutralizes the hydroxide ion liberated by reaction 19. The simplest set of reactions that can account for all these observations is the following

$$HXeO_6^{-3} + H^+ \rightleftarrows H_2XeO_6^{-2} \qquad (20)$$

$$H_2XeO_6^{-2} + H^+ \rightleftarrows H_3XeO_6^{-} \qquad (21)$$

$$H_3XeO_6^{-} \longrightarrow HXeO_4^{-} + 0.5O_2 + H_2O \qquad (22)$$

$$HXeO_4^{-} + H^+ \rightleftarrows XeO_3 + H_2O \qquad (23)$$

From the curve of Fig. 5 we estimate the pK_A for eq. 20 to be about 10.5 and by analogy with other acids we estimate eq. 21 to have a pK_A around 6. We may similarly estimate a pK_A of about 2 for the hypothetical reaction

$$H_3XeO_6^{-} + H^+ \rightleftarrows H_4XeO_6 \qquad (24)$$
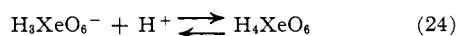
Equation 23, of course, is the conjugate of eq. 10 with a pK_A around 10.8, and the second part of the titration curve in Fig. 5 is merely the addition of acid to a XeO$_3$ solution.

Equilibrium 20 can account for the pH-dependent absorption spectra of Fig. 4. Curve 1 is then the spectrum of pure H$_2$XeO$_6^{-2}$, while curve 6 is the spectrum of pure HXeO$_6^{-3}$. Since the spectra were measured at ionic strength 0.1, the actual pK_A is shifted somewhat from that deduced from Fig. 5 (vide infra).

Using eq. 20, 21, and 24, we have calculated the titration curve of sodium perxenate as it would look if no decomposition took place. This appears as the short-dashed curve in Fig. 5.

Actually, of course, decomposition is taking place throughout the titration, but the rate increases greatly
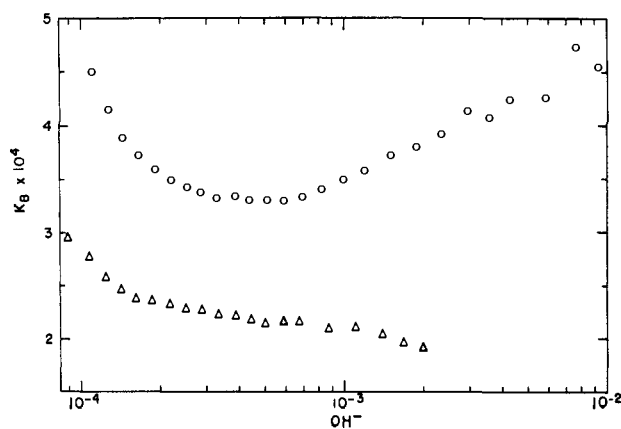

Fig. 6.—Base constants of HXeO$_6^{-3}$ at $\mu \sim 0.1$: O, 0.02 M perxenate titrated with 1.2 M HClO$_4$; △, 0.004 M perxenate titrated with 0.24 M HClO$_4$.

with the drop in pH that follows the addition of 2 moles of hydrogen ion per mole of xenon. No attempt has been made to correct the solid curve of Fig. 5 for this decomposition.

Because of the decomposition it is necessary to carry out the titration as rapidly as possible in order to get a clear-cut break at two hydrogens per xenon. Very concentrated solutions of perxenate decompose so rapidly at the lower pH values that the break cannot be well defined even when the titration is made quite speedily. A similar effect is observed at high concentrations of inert electrolyte, probably because equilibrium 20 is shifted to a lower pH region where decomposition is more rapid.

This decomposition, together with the severe medium effects associated with triply charged ions, makes precise measurements of the perxenate acidity constants extremely difficult. We have attempted to measure K_B for the conjugate reaction to eq. 20

$$HXeO_6^{-3} + H_2O \rightleftarrows H_2XeO_6^{-2} + OH^- \qquad (25)$$
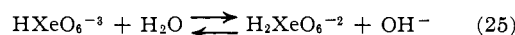
in a medium of approximate ionic strength 0.1. We have made the assumption that a 0.1 M sodium perchlorate solutions is an equivalent medium to a 0.02 M sodium perxenate solution. This assumption leaves something to be desired, for the apparent activity of hydroxide ion is some 20% greater in the latter medium than in the former, an effect which is presumably distributed between activity coefficients and liquid junction potentials.

Figure 6 shows the values of K_B obtained at two different perxenate concentrations. In calculating these values we have attempted to correct for the apparent variation in hydroxide ion activity. We see that K_B appears considerably greater in the more concentrated solution. While this could be taken to indicate the formation of a polymer such as Xe$_2$O$_{10}^{-4}$, we prefer to attribute the difference to medium effects. We will then consider the true value of K_B in 0.1 M NaClO$_4$ to be that obtained from the dilute perxenate solution, or 2.4 ± 0.5 × 10^{-4}. The corresponding pK_A of 10.1 agrees well with the spectrophotometric measurements.

Precise measurements showed a 0.00399 M sodium perxenate solution to be 0.00417 M in OH$^-$. If we correct for the small extent to which reaction 25 pro-
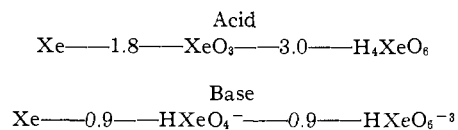
ceeds, we find 0.987 mole of OH^- in solution per mole of xenon, confirming the validity of eq. 19 and indicating that no appreciable amount of XeO_6^{-4} is present.

We may observe that if Pauling's empirical rules are valid, H_4XeO_6 should have pK_A values around -3, $+2$, 7, and 12, while the pK_A values we observe would be expected for the acid H_6XeO_7.[26] Rather than postulate species of such low symmetry, however, we are inclined to assume that Pauling's rules do not hold in this case.

Oxidation Potentials of Xenon in Aqueous Solution.—The data now available permit us to construct a rough potential scheme for xenon. Gunn measured the heat of formation of XeO_3 to be 96 kcal.[27] If we assume it to have a ΔS of 60 e.u., and note that its free energy of solution is probably around -1 kcal., we may set the Xe–Xe(VI) potential in acid at 1.8 v. We will then note that in base, since Xe(VI) does disproportionate, the Xe(VI)–Xe(VIII) potential cannot be much greater than the Xe–Xe(VI) potential. It must, however, be greater than 0.7 v., the iodate–periodate potential. These assumptions and observations, together with the data already presented, lead to the following potential schemes

(26) L. Pauling, "General Chemistry," W. H. Freeman and Co., San Francisco, Calif., 1947, pp. 394–396.

(27) S. R. Gunn, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 149 ff.

Acid

$$Xe \text{——} 1.8 \text{——} XeO_3 \text{——} 3.0 \text{——} H_4XeO_6$$

Base

$$Xe \text{——} 0.9 \text{——} HXeO_4^- \text{——} 0.9 \text{——} HXeO_6^{-3}$$

Thus we clearly see why perxenate is not stable in acid. These potentials suggest that extremely powerful oxidizing agents should be able to "fix" xenon in aqueous solutions, if only the formidable activation barrier can be surmounted. We have attempted unsuccessfully to oxidize xenon in acid solution with ozone and with persulfate, using silver ion as a catalyst, and in basic solution with uncatalyzed ozone, but the reactions may take place under more drastic conditions than those which we have employed. For the present, however, all the solution chemistry of xenon must derive from the hydrolysis of the xenon fluorides.