wag of the associated species. This frequency is not as high as observed in H_2SO_4, indicating that they are more likely due to an impurity.

The last two bands are assigned to the PF_2 rocking and bending modes by analogy with the bands observed for POF_3, POF_2Cl, and $POBrF_2$.[26-28]

Figure 2 merits further discussion. It is justified in part by the assumption that the phosphoryl stretching frequency is free of mass and coupling effects;[30] in effect, this frequency is assumed to be factored out of the secular equation for the normal modes of vibration. The primary effect of the attached groups X in X_3PO may be considered, therefore, to be donation or withdrawal of electrons from the phosphoryl bond. In this approximation, gaseous phosphorus monoxide can be considered to have attached groups of the same electronegativity (2.2) as the P atom. This approximation is reasonable as shown by the square on Figure 2.

A theoretical explanation[31] of Figure 2 is that more electronegative substituents produce a net positive charge on the phosphorus. This in turn contracts the phosphorus 3d orbitals letting two of them accept electrons from the oxygen forming $p\pi$–$d\pi$ bonds. Vanadium, on the other hand, has d orbitals readily accessible, so that the corresponding shifts in the vanadyl stretching frequency are expected to be small. The data[28,32-34] are given in Table III. In agreement with the theory, the shifts are small.

Table III. M=O Frequencies (cm^{-1}) in X_3MO

X	P	V
F	1418[a]	1058[a]
Cl	1325[a]	1035[b]
Br	1261[a]	1025[b]
CH_3	1225[c]	
Monoxide	1231[d]	1012[e]

[a] See table given by Selig and Claassen[27] or ref 32. [b] Reference 32. [c] See caption to Figure 2, Goubeau and Berger. [d] Reference 33. [e] Reference 34.

In addition the monoxide frequencies[33] are shown. There is some question[34,35] about the assignment of the ground state for VO. By analogy with the phosphorus compounds, the vibration frequency 1012 cm^{-1} is reasonable.

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The H_0 Values of Aqueous Selenic Acid and Their Relationship with Aqueous Vapor Pressure[1]

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Abstract: The H_0 values of aqueous selenic acid have been obtained using a series of primary aniline indicators over the concentration range of 2.8 to 85.7 wt % acid. The H_0 values obtained fall on the curve of H_0 *vs.* water activity previously established for the sulfuric acid and perchloric acid systems.

During the past dozen years there has emerged a growing awareness of an interrelationship between the Hammett acidity function, H_0, and the water activity of aqueous solutions of mineral acids.[2-11]

A major breakthrough in this area was the observation by Wyatt[4] that for aqueous solutions of sulfuric, perchloric, hydrochloric, and nitric acids the H_0 values were identical at the same water activity. Independdently, the same observation was made by Braun,[12] who pointed out that a plot of H_0 *vs.* the logarithm of the partial pressure of water for these same acid solutiins is single valued and continuous. He noted that the region between $H_0 = -5.0$ and -8.4 was established by a single acid, sulfuric acid. In order to better establish the relationship in this area, he determined the H_0 values and aqueous vapor pressure of several particular acid solutions, including 85.4% selenic acid using anthraquinone as an indicator.

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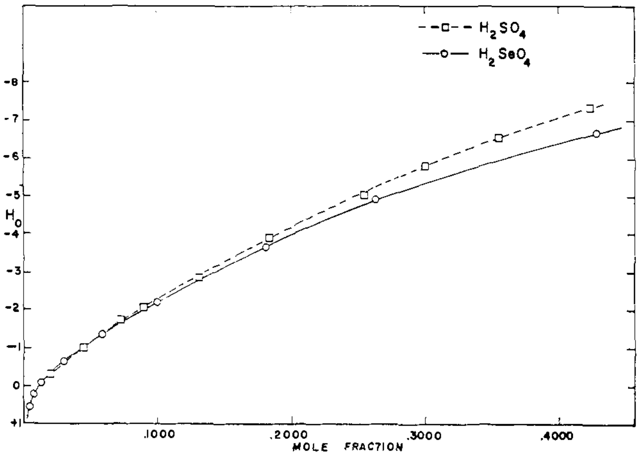

Figure 1. The H_0 values of sulfuric acid[15] and selenic acid *vs.* mole fraction of acid.

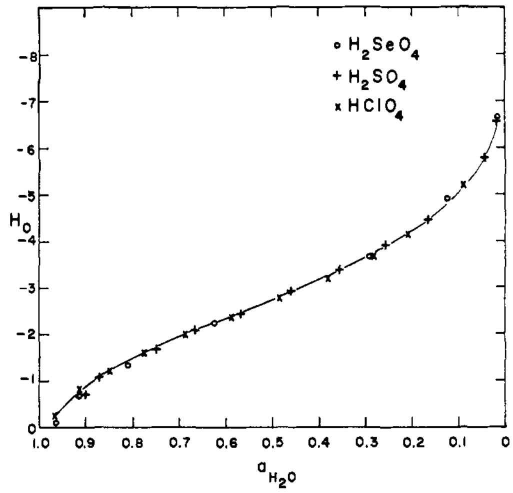

Figure 2. The H_0 values of selenic, sulfuric,[15] and perchloric[11] acids *vs.* water activity of the solutions.

It has recently been recognized that the H_0 values of an acid are not independent of the type of indicator used in establishing these values.[13] Accordingly, we thought that it might be desirable to repeat the selenic acid determinations using only primary anilines as indicators and studying a more complete concentration range.

Since the inception of our work, Yates and Wai[11] published the redetermination of the H_0 values of perchloric acid using only primary aniline indicators over a more extensive concentration region than previously reported. Their data give excellent support to the H_0-water activity relationship established by sulfuric acid. The results on selenic acid which we wish to report here offer further support for the relationship pointed out by Wyatt[4] and Braun.[12]

Experimental Section

Materials. Selenic acid either was purchased from Alfa Inorganic Chemicals as the crystalline acid or was synthesized in this laboratory following the procedure of Gilbertson and King.[14] In both cases the acid contained a small amount of seleneous acid impurity which could not be removed. Concentrations were determined by titrating weighed samples of the acid solutions with standardized sodium hydroxide.

All indicators used were purchased from the Aldrich Chemical Company as part of their Hammett indicator set. These were used without further purification. The indicators used in this study were: *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, 2,4-dichloro-6-nitroaniline, 2,4-dinitroaniline, and 6-bromo-2,4-dinitroaniline.

Procedure. All spectral measurements in this work were made on a Beckman Model DU spectrophotometer using 1-cm silica cells.

Selenic acid is a strong, though usually not kinetically fast, oxidizing agent. At the lower H_2SeO_4 concentrations, oxidation of the indicator was not a problem since the solutions could be prepared and the spectral measurements taken before significant oxidation occurred. At high acid concentrations, however, it was necessary to measure the absorbance of the test solution as a function of time and then extrapolate back to the time of mixing. The oxidation rate decreased with increasing nitration of the indicator. Due to the opposing effects of increasing acid concentration and an increased degree of nitration of the indicators used, the rate of oxidation was a maximum at about the 64% H_2SeO_4 where the absorbance increased approximately 500% in 5 min. Also, because of the side reaction of the indicators in concentrated selenic acid, the A_{BH^+} values were obtained by placing the indicators in sulfuric acid rather than in selenic acid. To obtain these A_{BH^+} values the indicator was placed in an acid solution whose H_0 was at least two H_0 units more negative than the pK_{BH^+} of the indicator.

Results and Discussion

H_0 values calculated from the experimental data by means of eq 1 are shown in Table I.

$$H_0 = \mathrm{p}K_{BH^+} - \log \frac{C_{BH^+}}{C_B} \qquad (1)$$

On a weight per cent basis selenic acid appears to be a much weaker acid than sulfuric acid. For example, 85% selenic acid has an H_0 value of −6.50 while the same weight per cent of sulfuric acid has an H_0 of −8.14.[15] A comparison on a mole fraction basis is shown in Figure 1. It can be seen from Figure 1 that in the dilute region the H_0 values for the two acids are essentially equal. However, at a mole fraction of about 0.037 the lines begin to gradually diverge, sulfuric acid being the more acidic, until at 0.400 mole fraction the difference in H_0 is about 0.50 H_0 unit.

Table I. H_0 Data for Selenic Acid

% acid	Log C_{BH^+}/C_B	pK_{BH^+}[a]	H_0	Estd error
2.79	0.42	0.99[b]	0.57	0.02
5.48	0.78	0.99	0.21	0.02
9.59	1.09	0.99	−0.10	0.04
20.10	0.39	−0.29[c]	−0.68	0.03
33.61	0.33	−1.03[d]	−1.36	0.05
47.23	1.18	−1.03	−2.21	0.10
63.85	0.33	−3.32[e]	−3.65	0.10
74.20	0.38	−4.53[f]	−4.91	0.05
85.73	−0.03	−6.68[g]	−6.65	0.05

[a] All pK_{BH^+} values are from Paul and Long[13] with the exception of the last value which is from Jorgenson and Hartter.[15] [b] *p*-Nitroaniline. [c] *o*-Nitroaniline. [d] 4-Chloro-2-nitroaniline. [e] 2,4-Dichloro-6-nitroaniline. [f] 2,4-Dinitroaniline. [g] 6-Bromo-2,4-dinitroaniline.

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This result is unexpected from the reported pK_2 values for the two acids, 1.7[16] for selenic acid and 1.98[17] for sulfuric acid.

Figure 2 is a plot of H_0 *vs.* water activity (determined from aqueous vapor pressure) for sulfuric,[15] perchloric,[11] and selenic acids.[18] All of these H_0 values have been obtained using primary aniline indicators. As can be seen the values for selenic acid fall on the curve described by the other two acids. Thus, all three acids at a particular water activity have the same proton donating ability. The values of Braun[12] for mixed acetic acid–sulfuric acid have not been included in Figure 2 yet they do fall on the curve described by the other acids. These data serve to validate the water activity–H_0 correlation at high acidities.

Perrin[9] has pointed out that it is even possible to determine the H_0 of a mixed perchloric acid–salt solution from the water activity of the solution and a plot such as Figure 2.

One note of caution must be stated here. Those acids which are commonly referred to as weak acids may not fit the H_0–water activity relationship. It has been pointed out that phosphoric[4,12] acid and hydrofluoric[4] acid solutions do not fit on the curve shown in Figure 2.

Acknowledgment. We wish to thank the National Science Foundation for financial support of this work.

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Structural Properties of Tetramethylammonium Tribromonickelate(II)[1]

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Abstract: The crystal structure of $(CH_3)_4NNiBr_3$ has been determined by three-dimensional, single-crystal, X-ray diffraction techniques. The structure consists of linear one-dimensional chains of nickel atoms bridged by three bromine atoms. The bromine atoms are not midway between the nickel atoms due to packing requirements of the $(CH_3)_4N^+$ ion, but are 2.45 and 2.67 A from the nickel atoms so that the site symmetry of the nickel atoms is C_{3v}. Lattice parameters and preliminary structural results are given for $CsNiBr_3$, $CsNiCl_3$, and $(CH_3)_4NNiCl_3$. The electronic absorption spectrum for $(CH_3)_4NNiBr_3$ is described and compared with that of $(CH_3)_4NNiCl_3$.

The different types of structures possible for octahedral complex halides of the type $R^IM^{II}X_3$, where R is an univalent cation, M a divalent metal, and X a halogen, have been discussed in detail by Wells.[2] The perovskite structure, in which octahedral edges are shared, is in general stable only for the more electronegative fluorides or oxides. The sharing of octahedral faces is rare, presumably because of the close approach of the metal atoms, and has been found almost always in complexes in which the metal atom has a formal oxidation number of three, *e.g.*, $Cr_2Cl_9^{3-}$, $V_2Cl_9^{3-}$, $Ti_2Cl_9^{3-}$,[3] $Tl_2Cl_9^{3-}$,[4] and $ZrCl_3$.[5,6] The disputed $BaNi^{IV}O_3$ structure[7] is presumably also of this type. If an increase in the atomic radius of the metal atom is not a determining factor, a linear chain of $M^{II}X_3^-$ groups with three bridging halogen atoms might be expected since the anion to cation formal charge ratio of 1.5 is the same as in $M^{III}_2X_9^{3-}$ anions. Since Wells' review,[2] when no structures with M^{II} were known, the only three-dimensional structural work has been with $CsCuCl_3$[8a,b] in which the Cu atoms form a nonlinear chain about a 6_1 axis with three copper–chlorine distances, 2.281, 2.355, and 2.776 A. This structure can be described as copper atoms sharing faces of their chlorine octahedra,[8a] or alternatively in view of the 0.5 A difference in copper–chlorine bond lengths as octahedra sharing edges.[8b] We wish to report here an X-ray study of a linear trihalogen bridged structure in which the metal atom has a formal oxidation number of two.

Experimental Section

$(CH_3)_4NNiBr_3$ was prepared by evaporating a 48.5% HBr solution containing 0.1 mole of $(CH_3)_4NBr$ and 0.1 mole of $NiBr_2 \cdot 6H_2O$. All compounds were reagent grade. The red-brown needle crystals had hexagonal cross sections and were assumed to be cylindrical for the absorption corrections described below. The crystals were somewhat hygroscopic and were sealed in thin-walled (0.01 mm) glass capillaries.

Anal. Calcd for $(CH_3)_4NNiBr_3$: Br, 64.3; Ni, 15.8; N, 3.8; C, 12.9; H, 3.2. Found: Br, 63.7; Ni, 15.1; N, 4.1; C, 14.3; H, 4.1.

A crystal with a diameter of approximately 0.10 mm and a length of 0.57 mm was used for collecting intensity data. Multiple-film equiinclination Weissenberg techniques were used to obtain

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