

consequently shows only a slight inductive stabilization of osmium(III), the 4-CH₃ substituent may enter into ligand π - d_{π} delocalization and distribute more effectively the positive charge. This will be better for osmium(III) and will therefore stabilize this ion. Alternatively, the effect may be considered in terms of a reduction in metal-to-ligand π bonding. This metal-to-ligand π bonding will be more effective for osmium(II) than for osmium(III) and for the unsubstituted pyridine than for the 4-CH₃ derivative, resulting in a stabilization of osmium(III) in the latter couple. On replacing the 4-CH₃ by a 4-C₂H₅ group the stabilization of osmium(III) will now be somewhat

reduced owing to a reduction in hyperconjugation of the substituent and a consequent reduction in π -electron density in the pyridine ring. $\Delta(\Delta H^{\circ}_{\text{LF}})$ and $\Delta(\Delta H^{\circ}_{\text{LF}})$ will be reduced and the osmium(II) ion stabilized. A similar explanation can be given for the further stabilization of osmium(II) found in the R = *i*-C₃H₇ couple.

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Heteropoly Blues. I. Reduction Stoichiometries and Reduction Potentials of Some 12-Tungstates

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The reduction of five isostructural polytungstates, the heteropolyanions, [PW₁₂O₄₀]³⁻, [SiW₁₂O₄₀]⁴⁻, [Fe^{III}W₁₂O₄₀]⁵⁻, [Co^{II}W₁₂O₄₀]⁶⁻, and the isopolymetatungstate anion, [H₂W₁₂O₄₀]⁶⁻, has been studied by polarographic and potentiometric methods. Each anion can accept two electrons without decomposition. Further electrons can be added in acidic solutions where protonation can accompany reduction and keep the over-all ionic charge low. In neutral solutions, reduction proceeds until the charge on the reduced species is -8. Formal reduction potentials for the initial one-electron reductions vary with the ionic charge in a manner consistent with a simple electrostatic model for the electron affinities of these approximately spherical polyanions.

Introduction

Heteropoly blues, the reduction products of certain heteropoly molybdates and -tungstates, particularly those 1:12 anions with the Keggin structure,¹ have received little fundamental study, although empirical analytical applications of such compounds are well-known.² Polarographic³⁻⁶ and potentiometric⁷ studies have indicated, with some conflicting results, that Keggin-structure anions can accept a limited number of electrons (*e.g.*, four) without decomposition, and in some cases the reduced compounds have been isolated.⁸⁻¹² It seems probable that the formation of

heteropoly blues may be formally compared with the reduction of polynuclear aromatic hydrocarbons to the corresponding anions.

The formation, properties, and structural features of various heteropoly blues are currently being studied in this laboratory with a view to elucidating further the stabilities and bonding of nonreduced polyanions. This paper reports the reduction stoichiometries and potentials of five Keggin-structure polytungstate anions whose over-all charges range from -3 to -6. Chemical, spectral, and magnetic properties of the heteropoly blues derived from these anions will be discussed in subsequent papers.

Experimental Section

Preparation and Analysis of Compounds.—Sodium 12-tungstophosphate was precipitated with sodium chloride from a concentrated solution of the free acid, which was prepared according to Wu.⁵ The salt was recrystallized from dilute (~0.5 M) sulfuric acid. *Anal.* Calcd for Na₃[PW₁₂O₄₀]·10H₂O: P, 0.99; W, 70.57. Found: P, 0.98; W, 70.42.

Potassium 12-tungstosilicate was prepared similarly from 12-

(1) The general formula for such anions is [AⁿX₁₂O₄₀]⁽⁸⁻ⁿ⁾⁻ where A can be one of several representative or transition elements and X is either Mo(VI) or W(VI). The main features of this structure were first elucidated in Keggin's X-ray study of H₃PW₁₂O₄₀·5H₂O [*Proc. Roy. Soc. (London)*, **A144**, 75 (1934)].

(2) See, for example, F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, 3rd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1949, pp 196, 233, 660, 695.

(3) P. Souchay, *Ann. Chim. (Paris)*, [11] **18**, 73, 169 (1943).

(4) J. H. Kennedy, *J. Am. Chem. Soc.*, **82**, 2701 (1960).

(5) R. Massart and P. Souchay, *Compt. Rend.*, **257**, 1297 (1963).

(6) K. Grasshoff and H. Hahn, *Z. Anal. Chem.*, **168**, 243 (1959); **180**, 18 (1961); **187**, 328 (1962).

(7) J. D. H. Strickland, *J. Am. Chem. Soc.*, **74**, 862, 868 (1952).

(8) H. Wu, *J. Biol. Chem.*, **43**, 189 (1920).

(9) I. P. Alimarin, Z. F. Shakhova, and R. K. Motorkina, *Dokl. Akad. Nauk SSSR*, **106**, 61 (1956).

(10) E. Bamann, K. Schriever, A. Freytag, and R. Toussaint, *Ann. Chem.*, **605**, 65 (1957).

(11) (a) P. Souchay and R. Massart, *Compt. Rend.*, **253**, 1699 (1961); (b) R. Massart and P. Souchay, *ibid.*, **256**, 4071 (1963).

(12) (a) H. Hahn and F. Hahn, *Naturwissenschaften*, **49**, 539 (1962); (b) H. Hahn and G. Schmidt, *ibid.*, **49**, 539 (1962); (c) H. Hahn and W. Becker, *ibid.*, **49**, 513 (1962); (d) H. Hahn and W. Becker, *ibid.*, **50**, 402 (1963).

tungstosilicic acid.¹³ *Anal.* Calcd for $K_4[SiW_{12}O_{40}] \cdot 8H_2O$: K, 4.93; $WO_3 + SiO_2$, 89.53. Found: K, 4.93; $WO_3 + SiO_2$, 89.66.

Potassium monohydrogen 12-tungstocobaltate(II) was prepared by Simmons' method.¹⁴ *Anal.* Calcd for $K_8H[CoW_{12}O_{40}] \cdot 18H_2O$: K, 5.71; W, 64.41; equiv wt, 3426. Found: K, 6.26; W, 64.46; equiv wt, 3412.

Potassium 12-tungstoferrate(III) was prepared by a modification of Mair's method.¹⁵ A solution of 8.6 g of ferric nitrate in 100 ml of water, to which had been added 15 ml of a saturated solution of sodium acetate, was added dropwise to a hot (60–70°) solution of 56.0 g of sodium tungstate in 250 ml of 1 *M* nitric acid. The mixture was refluxed for 16 hr, and the heteropolyacid was isolated and purified as described by Mair.¹⁵ The acetate prevented precipitation of ferric hydroxide at any stage of the preparation and permitted the clean formation of the heteropolyanion during the reflux period. The very soluble potassium salt was precipitated from a concentrated solution of the acid by addition of potassium chloride and was recrystallized three times from acidified water. *Anal.* Calcd for $K_6[FeW_{12}O_{40}] \cdot 10H_2O$: K, 5.97; Fe, 1.70; W, 67.33. Found: K, 6.08; Fe, 1.69; W, 67.33. The absorption spectrum of an aqueous solution of this compound agreed with that reported by Brown.¹⁶

Sodium metatungstate was prepared by Freedman's method.¹⁷ *Anal.* Calcd for $Na_6[H_2W_{12}O_{40}] \cdot 22H_2O$: W, 65.23; H_2O , 11.71; equiv wt, 563.7. Found: W, 65.25; H_2O , 11.84; equiv wt, 563.6.

Tungsten was precipitated and weighed as the trioxide, phosphorus as magnesium pyrophosphate, and potassium as the tetraphenylborate. Water was determined by ignition. Iron was precipitated as the hydroxide (twice), dissolved in hydrochloric acid, and determined colorimetrically with *o*-phenanthroline.¹⁸ The equivalent weight of potassium 12-tungstocobaltate(II) was determined by a cerimetric titration to 12-tungstocobaltate(III).¹⁴ The equivalent weight of sodium metatungstate was determined by converting a sample to metatungstic acid by ion exchange on Dowex 50Wx8 resin and titrating the hexabasic acid with standard sodium hydroxide.

Hereafter, the heteropolyanions studied will be referred to simply as tungstophosphate, tungstosilicate, tungstoferrate, and tungstocobaltate.

Potentiometric Titrations.—Titrations were carried out at 30° in an atmosphere of purified nitrogen using a mercury indicator electrode and a saturated calomel electrode in conjunction with a Beckman Model 76 pH meter. All potentials reported in this paper are referred to the saturated calomel electrode. The calomel electrode was connected to the titration flask *via* a potassium chloride salt bridge. In titrations of the tungstophosphate

anion sodium chloride was used in the bridge to avoid precipitation of the very insoluble potassium 12-tungstophosphate.

Solutions 0.1 to 0.2 *N* in chromium(II) sulfate, vanadium(II) sulfate, and europium(II) chloride were prepared by reduction of chromium(III), vanadium(IV), and europium(III) solutions in 1 or 2 *M* acid, with amalgamated zinc. All three reducing agents could be stored over amalgamated zinc in the reservoirs of conventional automatic burets for several weeks without precipitation or loss of reducing power. The solutions were standardized periodically by potentiometric titration against ferric ion.¹⁹

Polarography.—Polarograms were recorded on a Sargent Model XV instrument using a dropping mercury electrode and a standard H cell with a saturated calomel electrode. As for the potentiometric titrations, it was necessary to avoid potassium ions with tungstophosphate, and so polarograms of this ion were determined in a cell made up with sodium chloride. The potential of the saturated sodium chloride calomel electrode was found to be about +0.010 v with respect to the saturated potassium chloride calomel electrode at 25°. The temperature of the cell was maintained within $\pm 0.02^\circ$ for all measurements, and the supporting electrolyte was 1.0 *M* sulfate (mixtures of sodium sulfate and sulfuric acid).²⁰ At 25° and -0.350 v, $t = 3.91$ sec/drop and $m = 1.79$ mg/sec in 0.9 *M* Na_2SO_4 , 0.1 *M* H_2SO_4 . The limiting currents of the polarographic waves varied with the square root of the height of the mercury reservoir and increased by about 1%/deg, indicating that the waves were diffusion controlled. The concentration of heteropolyanion was 5×10^{-4} *M* in most of the polarograms, although it was shown in separate experiments that the half-wave potentials did not vary over the concentration range 5×10^{-5} to 10^{-3} *M*. Potentials reported to three significant figures were reproducible within the accuracy of the instrument (± 3 mv); potentials given to two figures were estimated from waves with poorly-defined diffusion plateaus.

Results

Potentiometric Titrations.—Acidic solutions of all five polyanions became dark blue on the addition of solutions of chromium(II), vanadium(II), or europium(II) ions. Satisfactory end points were observed in the titrations of tungstophosphate, tungstosilicate, and tungstocobaltate with these reducing agents; see Figures 1 and 2. The titrations were reproducible, and equilibrium potentials were established rapidly. Vanadium(II) titrations gave results which were superimposable upon those in Figures 1 and 2 with the exception of the second end point for tungstosilicate, which could not be reached with this reducing agent. Titrations with europium(II) confirmed the reduction stoichiometries but gave somewhat different potentials, as these measurements had to be made in chloride media due to the insolubility of the europium sulfates. Formal reduction potentials, for the anions which would be titrated, are given in Table I.

No end points could be reached in the titrations of tungstoferrate and metatungstate.

Polarography in 1.0 *M* Sulfuric Acid.—In this supporting electrolyte, polarograms of tungstophosphate, tungstosilicate, and tungstocobaltate showed well-defined waves corresponding to the titrimetric results. All three polarograms showed another wave at more

(13) (a) L. C. W. Baker and M. T. Pope, *J. Am. Chem. Soc.*, **82**, 4176 (1960). (b) 12-Tungstosilicates have been reported by several workers [see P. Souchay, *Bull. Soc. Chim. France*, 365 (1951), and references therein] to exist in two isomeric forms, "silicotungstates" and "tungstosilicates," differing in crystal form and solubility. Similar isomerism occurs with the α - and β -12-molybdosilicates.^{6,7,11} All X-ray crystallographic work has been carried out on the more easily prepared, stable isomers, "silicotungstate" and α -molybdosilicate, the free acids of which have been shown to be isomorphous with 12-tungstophosphoric acid [O. Kraus, *Z. Krist.*, **100**, 394 (1939)]. Under the conditions of preparation used in the present work, potassium "silicotungstate" (which, we propose, should now be called α -tungstosilicate) is formed almost exclusively [C. Marignac, *Ann. Chem.*, **125**, 362 (1863); H. Copaux, *Bull. Soc. Chim. France*, 101 (1908); P. Souchay, see above] and is purified from the more soluble "tungstosilicate" (β -tungstosilicate) by the sequence of recrystallizations. No isomerism has been reported for the other four 12-tungstates used in the present work, all of which have been shown to possess the Keggin structure found for α -tungstosilicate [R. W. G. Wyckoff, "Crystal Structures," 2nd ed, Interscience Publishers, New York, N. Y., 1965, Vol. 3, p 887 ff; L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, **78**, 4503 (1956); N. F. Yannoni, Doctoral Dissertation, Boston University, 1961].

(14) V. E. Simmons, Doctoral Dissertation, Boston University, 1963.

(15) J. A. Mair, *J. Chem. Soc.*, 2364 (1950). The compound is described as an 11-tungstate in this paper. A later publication [D. H. Brown and J. A. Mair, *ibid.*, 1512 (1962)] corrects the formulation.

(16) D. H. Brown, *Spectrochim. Acta*, **19**, 1683 (1963).

(17) M. L. Freedman, *J. Am. Chem. Soc.*, **81**, 3834 (1959).

(18) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 2nd ed, Longmans, Green and Co., London, 1951, p 647.

(19) Reference 18, p 326.

(20) Such mixtures have essentially no buffering capacity in neutral or mildly acidic solutions. However, polarograms run in an acetate buffer of pH 4.4 (tungstosilicate, tungstoferrate) and in a phosphate buffer of pH 6.63 (tungstoferrate, tungstocobaltate, and metatungstate) were identical, except for slight shifts in potentials, with those made in 1.0 *M* sulfate solutions of corresponding pH.

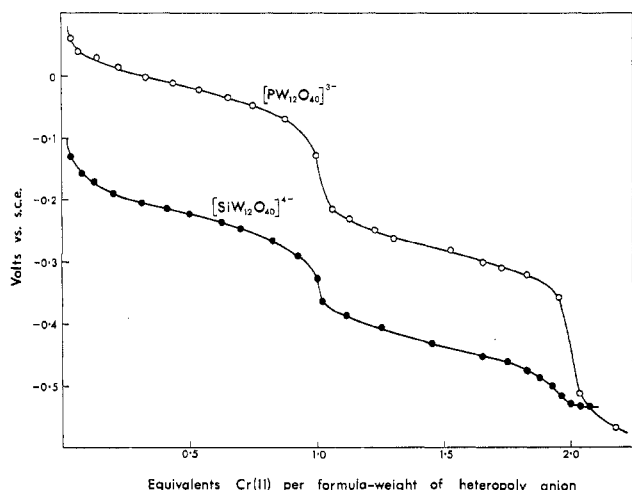


Figure 1.—Potentiometric titration of $Na_3[PW_{12}O_{40}]$ and $K_4[SiW_{12}O_{40}]$ with $0.1918 M CrSO_4$ in $1 M H_2SO_4$ at 30° . Concentration of heteropolyanion, $3 \times 10^{-3} M$.

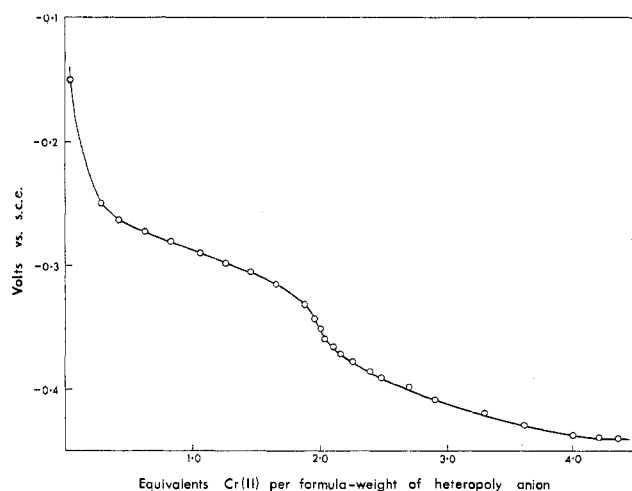


Figure 2.—Potentiometric titration of $K_5H[CoW_{12}O_{40}]$ with $0.1918 M CrSO_4$ in $1 M H_2SO_4$ at 30° . Concentration of heteropolyanion, $3 \times 10^{-3} M$.

TABLE I
FORMAL REDUCTION POTENTIALS IN $1 M$ SULFURIC ACID
AT 30°

Anion	E, v	No. of electrons
$[PW_{12}O_{40}]^{3-}$	-0.023	1
	-0.280	1
$[SiW_{12}O_{40}]^{4-}$	-0.228	1
	-0.433	1
$[CoW_{12}O_{40}]^{6-}$	-0.287	2

negative potentials, which, from its height, corresponded to a further two-electron reduction. Details of the three polarograms are given in Table II and a typical polarogram is shown in Figure 3.

The anodic half-wave potentials reported in Table II were determined from polarograms of solutions which had been reduced either by addition of chromium(II) sulfate solution or, for tungstocobaltate, by controlled-potential electrolysis at -0.350 and $-0.500 v$ vs. s.c.e.²¹

(21) The anodic waves of tungstophosphate and tungstosilicate showed evidence of adsorption of either the oxidized or reduced species on the dropping mercury electrode. The anodic waves of tungstophosphate had limiting currents which were much smaller than those of the cathodic waves.

TABLE II

POLAROGRAPHIC DATA IN $1 M$ SULFURIC ACID AT 30°

Anion	$E_{1/2}$ (cathodic), v	$E_{1/2}$ (anodic), v	No. of electrons
$[PW_{12}O_{40}]^{3-}$	-0.095	-0.035	1
	-0.343	-0.296	1
	~ 0.62		2
$[SiW_{12}O_{40}]^{4-}$	-0.245	-0.270	1
	-0.440	-0.440	1
	~ 0.63		2
$[CoW_{12}O_{40}]^{6-}$	-0.282	-0.275	2
	-0.395	-0.390	2

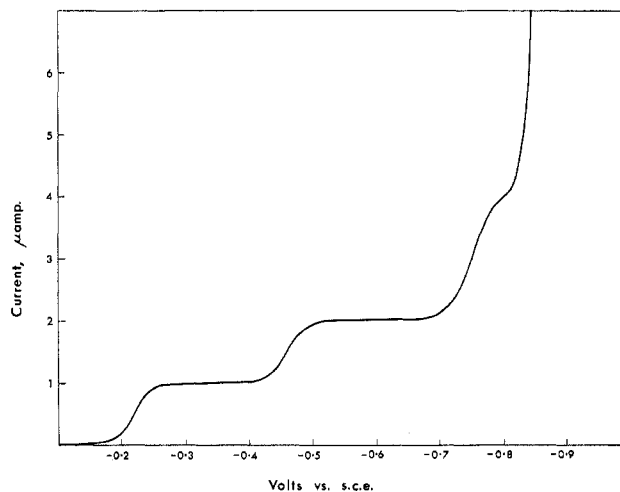


Figure 3.—Polarogram of $K_4[SiW_{12}O_{40}]$ in $1.0 M H_2SO_4$ at 30° . Concentration of heteropolyanion, $5 \times 10^{-4} M$.

Polarograms of metatungstate and tungstoferrate in $1.0 M$ sulfuric acid showed single multielectron waves which were only partially resolvable.

Polarography in $1.0 M$ Sodium Sulfate-Sulfuric Acid.—The polarograms of metatungstate and tungstoferrate were better resolved in a supporting electrolyte of $0.9 M Na_2SO_4$, $0.1 M H_2SO_4$, and polarography of all the heteropolyanions was extended to solutions of higher pH. Since heteropolytungstates are decomposed by hydroxide ions, this investigation was limited to rather low pH values for the least stable ions.

The polarogram of tungstophosphate was observed up to pH 1.3, and that of tungstosilicate up to pH 5.0. Over these pH ranges the half-wave potentials of the first two waves were essentially unaltered.²² The third (two-electron) wave in the tungstophosphate polarogram was less reversible at pH 1.3, but its half-wave potential was still close to $-0.62 v$.²³ The corresponding wave in the tungstosilicate polarogram moved to more negative potentials by about $80 mv/pH$ unit. By pH 5 this wave had merged with the complex mixture of waves which probably corresponded to the general decomposition of the Keggin structure.²⁴

(22) Both waves for $[PW_{12}O_{40}]^{3-}$ became less reversible with increasing pH and even at pH 1.3 had both diminished in height due to partial decomposition. The first wave for $[SiW_{12}O_{40}]^{4-}$ was about $80 mv$ more negative in $1.0 M H_2SO_4$ than at any other pH studied.

(23) The polarograms of $[PW_{12}O_{40}]^{3-}$ were reproduced using two commercial preparations of 12-tungstophosphoric acid (from Merck and Mallinckrodt). We were unable to obtain the polarogram of this substance reported by Kennedy.⁴

(24) Large, obviously complex, waves which appeared in all the polarograms prior to the hydrogen evolution waves (see the metatungstate polarogram in Figure 4) were tentatively identified with processes involving the decomposition of the Keggin structure. With increasing pH these waves were considerably drawn out, but were never resolvable.

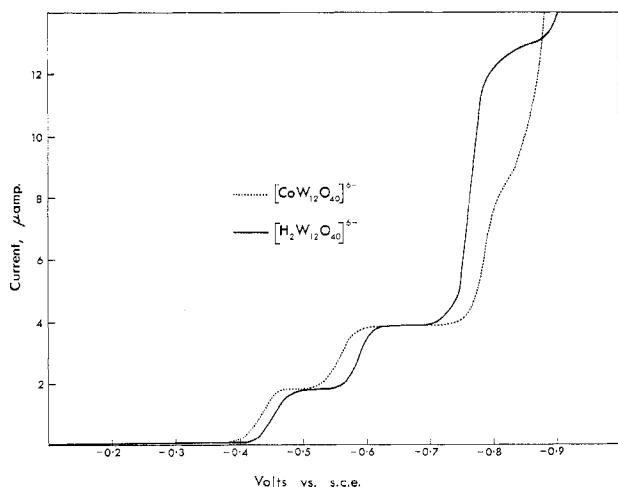


Figure 4.—Polarograms of $\text{K}_3\text{H}[\text{CoW}_{12}\text{O}_{40}]$ and $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$ in $0.1\text{ M H}_2\text{SO}_4$, $0.9\text{ M Na}_2\text{SO}_4$ at 25° . Concentration of heteropolyanion, $5 \times 10^{-4}\text{ M}$.

The polarogram of tungstoferrate was observed up to pH 6.95. At pH 1.67, three waves corresponding to one-, one-, and three-electron reductions at -0.349 , -0.464 , and -0.543 v were observed. From pH 1.67 to 4.00 the half-wave potential of the first wave did not change with pH, while the potentials of the second and third waves became more negative with increasing pH by 80 and 90 mv/pH unit. The second wave became independent of pH above pH 4 ($E_{1/2} = -0.580\text{ v}$). However from pH 4.00 to 5.88 the third wave gradually diminished to the height expected for a one-electron wave.²⁵ Within the pH range 3.0 to 4.0 a fourth (two-electron²⁶) wave was observed. The half-wave potential of this wave was -0.957 v at pH 3.00 and -1.031 v at pH 4.00.

In $0.9\text{ M Na}_2\text{SO}_4$, $0.1\text{ M H}_2\text{SO}_4$ the polarograms of metatungstate and tungstocobaltate were strikingly similar; see Figure 4. For both compounds, the two two-electron waves were pH-dependent up to pH 3. The half-wave potentials for metatungstate were $-0.313 - 0.090\text{pH}$ and $-0.448 - 0.100\text{pH}$, and for tungstocobaltate they were $-0.310 - 0.080\text{pH}$ and $-0.425 - 0.090\text{pH}$. Both waves in both polarograms became less reversible with increasing pH. Above pH 3, the first waves gradually split into two one-electron waves, the first of which became pH-independent at pH 4.9 and the second at pH 5.4. Half-wave potentials for these one-electron waves are given in Table III together with the potentials for the corresponding waves for the other heteropolyanions.

The second two-electron waves in the polarograms of metatungstate and tungstocobaltate began to diminish in height above pH 4.5, and the waves had completely disappeared by pH 5.5. A third two-electron wave ($E_{1/2} = -1.03\text{ v}$) was observed in the polarograms of metatungstate at pH 4.

(25) Above pH 5 the third wave showed evidence of adsorption of the electroactive species on the mercury. The adsorption behavior could be avoided by the addition of a few drops of a 0.2% methyl red solution.

(26) Diffusion currents for a $5 \times 10^{-4}\text{ M}$ solution at 25° and pH 3.0 were 1.0, 1.1, 3.0, and $2.2\text{ }\mu\text{a}$ for the four waves.

TABLE III
HALF-WAVE POTENTIALS FOR ONE-ELECTRON REDUCTIONS
IN 1 M SULFATE AT 25°

Anion	$E_{1/2}$, v	pH Dependence
$[\text{PW}_{12}\text{O}_{40}]^{3-}$	-0.023	None
	-0.266	None
$[\text{SiW}_{12}\text{O}_{40}]^{4-}$	-0.187	None
	-0.445	None
$[\text{FeW}_{12}\text{O}_{40}]^{5-}$	-0.349	None
	-0.577	Below pH 4.0
$[\text{CoW}_{12}\text{O}_{40}]^{6-}$	-0.510	Below pH 4.9
	-0.714	Below pH 5.4
$[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$	-0.581	Below pH 4.9
	-0.730	Below pH 5.4

Discussion

Two- and four-electron reduction steps for tungstophosphate, tungstosilicate, and metatungstate have been identified by Souchay in his early polarographic studies of polytungstates.³ There was also some evidence for an initial one-electron step in Souchay's tungstosilicate polarograms and for a one-electron step in his electrolytic reduction of tungstophosphate, but no reduction potentials were reported.²⁷ More recent polarographic⁴ and preparative^{12d} investigations of these ions have reported only two- and four-electron reductions for tungstophosphate and tungstosilicate.²⁸

The polarographic and titrimetric data presented here clearly show that the first step in the reduction of tungstophosphate and tungstosilicate corresponds to the addition of one electron. Application of the Ilkovic equation to the first waves in these polarograms yields diffusion coefficients (D) of $3.36 \pm 0.15 \times 10^{-6}\text{ cm}^2\text{ sec}^{-1}$ for $[\text{PW}_{12}\text{O}_{40}]^{3-}$ in $1.0\text{ M H}_2\text{SO}_4$ at 25° and $2.56 \pm 0.15 \times 10^{-6}\text{ cm}^2\text{ sec}^{-1}$ for $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ in $0.9\text{ M Na}_2\text{SO}_4$, $0.1\text{ M H}_2\text{SO}_4$ at 25° . The difference in these values is due to the different viscosities (η) of the supporting electrolytes, 0.012 and 0.015 poise, respectively.²⁹ These values of η and D , when inserted in the Stokes-Einstein equation, $D = kT/6\pi\eta r$, yield identical hydrodynamic radii of 5.6 Å for these anions. Such a value of the hydrodynamic radius of a Keggin-structure anion has been previously found from sedimentation³⁰ and viscosity³¹ measurements and compares well with crystallographic results. The fact that the diffusion currents of all the one-electron polarographic waves are very similar suggests that the heteropoly blues retain the structure of the oxidized anions. However, the precision of the measurement of the limiting currents of most of the waves, combined with the theoretical inadequacies of the Ilkovic equation, precluded any investigation of possible effects of ionic charge upon diffusion coefficients.

(27) L. Malaprade has quoted some unpublished "orders of magnitude" for the reduction potentials of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ($+0.2\text{ v vs. nhe}$) and $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ ($+0.0\text{ v vs. nhe}$) in "Nouveau Traité de Chimie Minérale," Masson et Cie., Paris, 1959, Vol. 14, p 955.

(28) Souchay has very recently reinvestigated the reduction of tungstosilicate by polarography and obtained results in close agreement with those reported here. [P. Souchay and G. Herve, *Compt. Rend.*, **261**, 2486 (1965)].

(29) R. H. Stokes and R. Mills, "Viscosity of Electrolytes and Related Properties," Pergamon Press Inc., New York, N. Y., 1965, pp 123, 149.

(30) M. C. Baker, P. A. Lyons, and S. J. Singer, *J. Am. Chem. Soc.*, **77**, 2011 (1955).

(31) T. Kurusev, A. M. Sargeson, and B. O. West, *J. Phys. Chem.*, **61**, 1569 (1957).

The pH dependence of the polarograms of tungstoferrate, tungstocobaltate, and metatungstate can be interpreted in terms of protonation accompanying reduction. The slope of a plot of $E_{1/2}$ vs. pH for a reversible n -electron reduction involving the addition of m protons should equal $-0.059m/n$ v at 25° . Slopes for the pH-dependent waves ranged from -0.070 to -0.100 v. Such high values are due to the fact that the waves became less and less reversible, finally splitting into two one-electron waves, as the pH increased. At sufficiently high pH, under conditions where the reduced species were no longer protonated, the waves became independent of pH. Reference to Table III shows that the limiting potentials were reached at successively higher pH as the charge on the reduced species increased. When the reduction product had a charge of -6 or less, there was no pH dependence of reduction potential. This behavior is in accord with the results of pH titrations of $H_6[CoW_{12}O_{40}]^{14}$ and the heteropoly blue, $H_6[SiW_{12}O_{40}]^{12d}$ which show that the six protons in these acids are all equally strong. The trend of pH dependence shown in Table III indicates, not surprisingly, that the anions of highest charge are the strongest Brønsted bases.

Thus, under conditions where no protonation accompanies reduction, it is possible to identify two one-electron reductions for each of the polyanions studied. The two-electron stoichiometry observed for some of the ions in acid solution is due to the coincidence of the second (pH-dependent) reduction potential with the first. The half-wave potentials for these one-electron reductions (Table III) show a linear dependence upon the ionic charge; see Figure 5. The line in Figure 5, drawn through the reduction potentials of tungstophosphate, tungstosilicate, tungstoferrate, and tungstocobaltate, has a slope of -0.16 v/unit charge. Reduction potentials for the heteropoly blues (second one-electron reduction potentials) and for metatungstate fall below this line. The linear dependence of reduction potential upon charge may to some extent be accounted for by the following argument.

The difference between the reduction potentials of two heteropolyanions depends upon differences in enthalpy, entropy, and electron affinity terms. In this series of isostructural ions of similar size, changes in the enthalpy and entropy terms will be very small, and the main cause of the variation of the reduction potentials will lie in the electron affinity variations. Diffusion,¹⁸ sedimentation,³⁰ and viscosity³¹ data indicate that Keggin-structure anions behave in solution as spheres with a radius of about 5.6 Å. The electron affinity of a sphere of charge $-ne$ in a medium of dielectric constant ϵ is the same as its electrostatic potential, $ne/\epsilon r$. The difference in electron affinity for two such spheres differing by unit charge will then be $e/\epsilon r$. Using 1.44×10^{-7} v for the electronic charge, 60.5 for the dielectric constant of 1.0 M sodium sulfate at 25° ,³² and 5.6×10^{-8} for r , $e/\epsilon r = 0.04$ v. Consider-

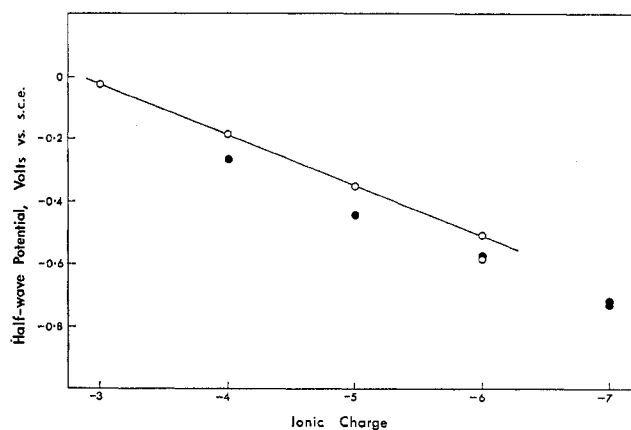
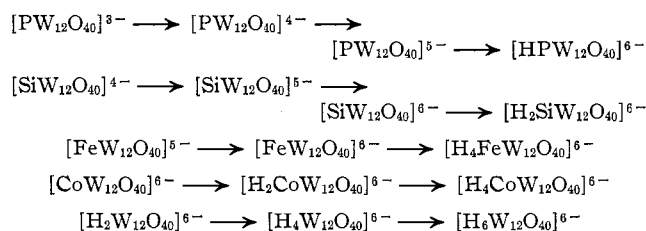


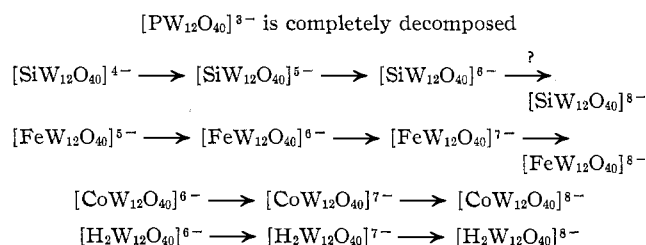
Figure 5.—Plot of half-wave potentials for one-electron reductions vs. charge of the electroactive species: ○, first one-electron reductions; ●, second one-electron reductions.

ing the assumptions which had to be made, this value is in satisfactory agreement with the slope of the line in Figure 5. It would appear, therefore, that the first electron to be added to a Keggin-structure anion enters an orbital whose energy is essentially independent of the nature of the central atom. This orbital is presumably composed of tungsten atomic orbitals.³³

The polarographic data can be summarized in the following reduction schemes. (a) In solutions of $pH \leq 1$



(b) In solutions of $pH \geq 5$



It is suggested, therefore, that the reduction of a Keggin-structure anion is limited by the over-all ionic charge and that the maximum number of electrons which can be added, without accompanying protonation, to an ion of charge $-n$ is $8 - n$. If the pH of the solution is such that protonation can accompany reduction, further electrons can be added.³⁴ In other words, a Keggin-structure anion can exhibit a maximum basicity of 8, and it is predicted that attempts to neutralize the protons in $[H_2CoW_{12}O_{40}]^{8-}$, for example, will result in

(33) The more negative potential of $[H_2W_{12}O_{40}]^{6-}$ (which has no central atom) compared with that of $[CoW_{12}O_{40}]^{6-}$ suggests that there is some contribution from the central atom, which effectively lowers the energy of the electron-accepting orbital in $[CoW_{12}O_{40}]^{6-}$.

(34) The extra wave appearing at pH 3-4 in the metatungstate and tungstoferrate polarograms probably corresponds to a total addition of six electrons. According to Souhay,⁵ 12-molybdo-silicate is also capable of accepting six electrons.

decomposition of the anion. An analogous situation exists among the reduced species of the 2:18 heteropolyanions, where the maximum charge is -10 , and it has been shown by titration that the reduced acid, $H_{12}[P_2Mo_{18}O_{62}]$, has only ten replaceable protons.³⁵

Some ambiguity exists with the tungstoferrate blues concerning the oxidation state of the central atom. Simmons¹⁴ has studied the reduction of 12-tungstocobaltate(III) to 12-tungstocobaltate(II), and, using her value for the formal reduction potential, $+0.77$ v, she estimated³⁶ a reduction potential of -1.4 v for the corresponding Fe(III)-Fe(II) reduction. She predicted that the tungstate network of 12-tungstoferrate(III) would be reduced before the central atom,

(35) M. T. Pope and E. Papaconstantinou, in preparation.

(36) The difference in the potentials derives mainly from the difference in the third ionization potentials of Fe and Co, modified by the appropriate ligand field stabilization energies [see P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1959)].

as has been found in the present work. By analogy with the other anions studied, tungstoferrate should, in acidic solutions, be able to accept a total of four electrons. Since in fact it accepts five, it is reasonable to assume that the three-electron reduction (wave at -0.5 v, pH 1.67) involves reduction of the central atom to Fe(II) as well as addition of two electrons to the tungstate network. This may not be the case above pH 5, however, and further study of the reduced compounds is underway to establish the oxidation state of the iron.

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Redistribution Equilibria of Substituents between the Methyl- and Trimethylsilicon Moieties

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Scrambling equilibria resulting from the exchange of pairs of monofunctional substituents (halogen, methoxyl, methylthio, and dimethylamino) between the methyl- and trimethylsilicon moieties have been studied by proton nuclear magnetic resonance. Unexpectedly, these equilibria deviate greatly from the case corresponding to ideal random sorting of the substituents. The experimental data are evaluated in terms of three equilibrium constants—two for the scrambling of the two kinds of substituents on the methylsilicon moiety and an intersystem equilibrium constant describing the distribution of the substituents between the methyl- and trimethylsilicon moieties. The observed deviations from randomness are attributed to π -bonding effects.

Recent communications¹⁻³ from this laboratory have dealt with equilibria involving redistribution of two kinds of monofunctional substituents on two kinds of central atoms or moieties. In view of the observed unexpected preference of one kind of substituent for one of the central moieties in systems with silicon and germanium as the two kinds of central atoms, a study was undertaken to determine the equilibria between moieties of silicon of varying functionality. In a related paper⁴ equilibria in systems of the general type CH_3SiZ_3 vs. $(CH_3)_2SiT_2$ have been reported. In these studies, Z and T were monofunctional exchangeable substituents and the CH_3 groups remained fixed to silicon under the reported reaction condition. This

paper deals with the related equilibria in systems CH_3SiZ_3 vs. $(CH_3)_3SiT$.

Experimental Section

Materials.—Methyltrimethoxysilane and trimethylchlorosilane were purchased from Alfa Inorganics, Inc., Beverly, Mass., and distilled before use. Methyltribromosilane¹ and methyltris(dimethylamino)silane² were prepared according to methods described in the literature. Methyltris(methylthio)silane was prepared by refluxing methyltrichlorosilane with lead methylmercaptide in benzene, bp 105° (10 mm); yield, 47%. Trimethylbromosilane was obtained by passing dry hydrogen bromide into a methylene chloride solution of hexamethyldisilazane, bp $77-79^\circ$; yield, 69%.

Equilibrations.—The desired proportions of the starting materials (the methylsilicon compound and the trimethylsilicon compound) were sealed in three-quarters filled, 5-mm o.d. precision nuclear magnetic resonance (nmr) tubes and heated at 120° . The time required for reaching equilibrium at this temperature was determined in pilot runs. Equilibrium was considered to be attained when the nmr pattern did not change upon additional

(1) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **5**, 547 (1966).

(2) K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, in press.

(3) J. R. Van Wazer, K. Moedritzer, and L. C. D. Groenweghe, *J. Organometal. Chem.*, in press.

(4) K. Moedritzer and J. R. Van Wazer, *Z. Anorg. Allgem. Chem.*, in press.

(5) H. Breederveld and H. I. Waterman, *Research (London)*, **5**, 537 (1952).