Summary

The distribution of iodine cyanide between carbon tetrachloride and water and aqueous solutions of potassium iodide and cyanide has been determined. From the results the equilibrium constants, $1.17 = (I_2CN_2^-)/(ICN)(I^-)$ and $2.50 = (I(CN)_2^-)/(ICN)(CN^-)$, have been calculated. These values were used to correct the equilibrium constants given by Kovach for the reaction

$$ICN + H^+ + I^- = HCN + I_2$$

Measurements of the vapor pressure of solid iodine cyanide were made and the results were found to be well represented by

$$\log_{10} p_{\text{mm.}} = -\frac{13{,}940}{2.3026\,RT} + 10.225$$

By combining these values with those of others the standard free energy of formation of gaseous iodine cyanide was found to be $\Delta F^\circ_{298} = 45{,}940$ cal.

It was found that gaseous iodine and cyanogen do not react to form appreciable amounts of iodine cyanide. This fact led to the conclusion that the entropy of cyanogen is, in all probability, not negative as has previously appeared to be the case. Calculations based on the third law confirmed the experimentally found result.

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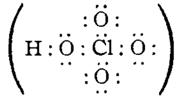
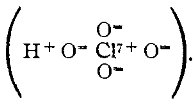
The Formulas of Antimonic Acid and the Antimonates

BY LINUS PAULING

The formula of a compound should not only express its chemical composition, but also give some information concerning the nature of the atomic aggregates present under the ordinary conditions for the substance. Thus the formula KH_2PO_4 indicates that the substance is an acid salt rather than a hydrated normal salt $KPO_3 \cdot H_2O$, etc. It is pointed out in the following pages that from this viewpoint the formulas of oxygen acids of elements in their highest valence states have been correctly assigned in most cases, the principal exception being antimonic acid, the correct formula of which has not previously been suggested; and it is shown that, when the existence of highly polymerized forms of the acids and their salts is recognized, a simple consideration of ionic sizes leads to the assignment of correct formulas on theoretical grounds.

Molecules of the oxygen acids can be represented as containing either covalent bonds  $\left(\begin{array}{c} :\ddot{O}: \\ H:\ddot{O}:\ddot{Cl}:\ddot{O}: \\ :\ddot{O}: \end{array}\right)$ or ionic bonds  $\left(H^+\,O^-\,\overset{O^-}{\underset{O^-}{Cl^{7+}}}\,O^-\right)$. Actually the bonds are intermediate in character,[1] and the properties of a molecule are best understood by considering both extreme electronic formulas. In the oxygen acids of elements in their highest valence states (other than the transition elements), however, the ionic extreme is more closely approached than the covalent extreme, and the properties of these acids can be discussed on this basis, as is done in this paper. In oxygen acids of elements in lower valence states, such as H_3PO_3, H_2SO_3, etc., and in those of the transition elements, such as H_2CrO_4, etc., the bonds have a much more pronounced covalent character, in the former case because of the influence of the unshared electrons of the central atom, and in the latter because of the unoccupied *d*-orbits of the shell next to the valence shell.

The strong central field of a small cation attracts oxygen ions, hydroxyl ions, and water molecules (with their large electric moments) to the cation, the configuration of maximum stability being reached when they are as close to it as possible. Ultimately the large ions will completely surround the cation, leaving no room for more. Considering the ions as rigid spheres, four anions at the corners of a tetrahedron are in contact with each other and with a cation at the center of the tetrahedron when the ratio ρ of cation radius to anion radius is $(\sqrt{3}/\sqrt{2}) - 1$ or 0.225. This is the lower limit of radius ratio leading to this arrangement, with coördination number four; for, if the radius ratio ρ be smaller, three anions in contact with the cation prevent a fourth from approaching to within the same distance of the cation, and the arrangement with coördination number four becomes less stable than that with coördination number three (triangular arrangement). Similarly the tetrahedron is stable only for $0.225 \leqslant \rho \leqslant \sqrt{2} - 1 = 0.414$, the octahedron (coördination number six) for $0.414 \leqslant \rho \leqslant \sqrt{3} - 1 = 0.713$, and the cube (coördination number eight) above this. The ionic radii to be used in these considera-

TABLE I

RATIOS OF UNIVALENT RADII: CATION/OXYGEN

Be^{++}	B^{3+}	C^{4+}	N^{5+}		**RO_3 region**	
0.25	0.20	0.17	0.14			
Mg^{++}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}	**RO_4 region**
0.48	0.41	0.37	0.34	0.31	0.28	
Zn^{++}	Ga^{3+}	Ge^{4+}	As^{5+}	Se^{6+}	Br^{7+}	Kr^{8+}
0.50	0.46	0.43	0.40	0.37	0.35	0.33
Cd^{++}	In^{3+}	Sn^{4+}	Sb^{5+}	Te^{6+}	I^{7+}	Xe^{8+}
0.65	0.59	0.55	0.51	0.47	0.44	0.42
			RO_6 region			

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(1) Pauling, THIS JOURNAL, **54**, 988 (1932).

tions are the "univalent" radii,[2] which represent the relative extension in space of the outer electron shells of the ions.

Values for radius ratios of cations relative to oxygen are given in Table I. The coördination number three is indicated for B, C and N, whose acids should have the formulas H_3BO_3, H_2CO_3 and HNO_3, in agreement with observation, despite the fact that the bonds in these compounds have a more covalent character than those in the compounds discussed further on. Boron is not far below the transition point to coördination number four; actually the acid H_5BO_4 exists when stabilized by an outer $Mo_{12}O_{18}(OH)_{36}$ or $W_{12}O_{18}(OH)_{36}$ shell. The metaborates, usually written as salts of the acid HBO_2, are salts of a polymerized acid $(HBO_2)_x$ in which each boron ion is surrounded by three oxygen ions, as in H_3BO_3; this has been shown by the x-ray study of $Ca(BO_2)_2$.[3]

The normal acids H_4SiO_4, H_3PO_4, $HClO_4$, H_3AsO_4 and H_2SeO_4 and their salts are well known. Salts of acids with formulas usually written as H_2SiO_3, HPO_3, etc., are also known; these acids are, however, actually polymerized in such a way as to retain the tetrahedral arrangement of four oxygen ions about each cation. In Cl_2O_7, $H_2S_2O_7$, $H_4P_2O_7$, $H_6Si_2O_7$, two tetrahedra share one oxygen ion; in beryl, $Be_3Al_2Si_6O_{18}$, six silicon tetrahedra form a ring, the metasilicic acid being $H_{12}Si_6O_{18}$; the pyroxenes and amphiboles are derived from the acids $(H_2SiO_3)_\infty$ and $(H_6Si_4O_{11})_\infty$, respectively; and even silica itself, as quartz, cristobalite and tridymite, consists of SiO_4 tetrahedra with shared corners.

The coördination number of the beryllium ion is shown by its formation of the tetrahedral hydrate $[Be(H_2O)_4]^{++}$, as in $Be(H_2O)_4 \cdot SO_4$.[4] This hydrated ion loses protons only with difficulty, and so does not show acid properties.

Aluminum should have coördination numbers four and six. Its usual degree of hydration is six, the ion $[Al(H_2O)_6]^{+++}$ occurring in many crystals; and in crystals such as corundum, Al_2O_3, garnet, $Ca_3Al_2Si_3O_{12}$, etc., each aluminum ion is surrounded by an octahedron of six oxygen ions. The prediction[5] that it should also occur with coördination number four has since been verified by the examination of many crystals, including sodalite, mica, natrolite, etc.

The coördination number six should be the normal one for the remaining ions of Table I. The radius ratio for I^{7+} is not far above the tetrahedron–octahedron transition value, and, indeed, salts of periodic acid containing a tetrahedral IO_4^- ion, such as KIO_4 (whose crystal structure is known), exist. The usual state of periodic acid and its salts is, however, represented

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(2) Pauling, THIS JOURNAL, **49**, 765 (1927).

(3) Zachariasen, *Proc. Nat. Acad. Sci.*, **17**, 617 (1931). Dr. J. L. Hoard has pointed out to me that some metaborates might be salts of the acid $HB(OH)_4$, in which boron has the coördination number four.

(4) Beevers and Lipson, *ibid.*, **82**, 297 (1932).

(5) Pauling, THIS JOURNAL, **51**, 1010 (1929).

by the formulas H_5IO_6, Ag_5IO_6, $K_2H_3IO_6$, etc. The composition $M_2H_3IO_6$ of the acid salts is probably due to the formation of hydrogen bonds between pairs of oxygen ions, as in KH_2PO_4, though direct confirmation of this and of the octahedral configuration of the IO_6^{5-} ion through crystal structure investigations (under way in this Laboratory) is as yet lacking.

Telluric acid has been recognized as having the formula H_6TeO_6 (or $Te(OH)_6$) rather than $H_2TeO_4 \cdot 2H_2O$; x-ray data show definitely that the six oxygen atoms in the molecule are equivalently related to the tellurium atom. Representative salts are Ag_6TeO_6, Hg_3TeO_6, $Ag_3H_3TeO_6$, $K_2H_4TeO_6 \cdot 3H_2O$, etc. Many complex crystals such as $(NH_4)_4(HPO_4)_2 \cdot Te(OH)_6$, $2KIO_3 \cdot Te(OH)_6$, etc., contain telluric acid. Both the periodates and the tellurates combine with MoO_3 or WO_3 to form compounds such as $K_5I(MoO_4)_6$, $K_6Te(MoO_4)_6$, etc.

The important salts of stannic acid, such as $Na_2Sn(OH)_6$, $CaSn(OH)_6$, etc., have been recognized as derivatives of $H_2Sn(OH)_6$. Stannic acid and stannates also occur containing less water than is required by this formula. It is probable that these are polymerized, the tin atoms retaining the coördination number six; thus, $CaSnO_3$ is known to crystallize with the perovskite structure, each tin atom being surrounded by six oxygen atoms at the corners of a regular octahedron, and each oxygen atom being common to two octahedra, in such a way as to make the entire crystal one giant molecule, with the formula $(CaSnO_3)_\infty$. In colloidal stannic acid and stannates the polymerization process has gone only part way.

Despite the recognition of the correct formulas of periodic, telluric, and stannic acids, the interpolation to antimonic acid seems not to have been previously made, with the result that considerable confusion has existed regarding the chemistry of the antimonates. Thus Groth in his "Chemische Krystallographie" classed the antimonates with the pyrophosphates and pyroarsenates, despite the absence of isomorphism. Other textbooks and reference books in which potassium antimonate is given the formula $K_2H_2Sb_2O_7 \cdot xH_2O$ are H. Remy "Lehrbuch der anorganischen Chemie," Akad. Verlagsges. m. b. H., Leipzig, 1931; Roscoe and Schorlemmer, "Treatise on Chemistry," Macmillan, London, 1923; F. Ephraim, "Anorganische Chemie," Steinkopff, Dresden, 1929; Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," Macmillan, New York, 1929; W. Ostwald, "Grundlinien der anorganischen Chemie," Steinkopff, Dresden, 1919; etc. Mellor in his "Comprehensive Treatise on Inorganic and Theoretical Chemistry" (Vol. IX, p. 446) was led to a different formula. After writing "A review of the antimonates shows that our knowledge of these compounds is in an unsatisfactory state. The main difficulty encountered by previous workers turns on the constitutional water," he pointed out that the conductivity of potassium antimonate solutions shows the anion to be singly charged and that the solution has an acid reaction, so that the formula is neither $K_2H_2Sb_2O_7$ nor $KSbO_3$; and he concluded that the correct formula is KH_2SbO_4, the crystals containing $2H_2O$ in addition.

But the formula $KSb(OH)_6$ suggested by the radius ratio is also compatible with the evidence, and is, moreover, supported by the fact that the observed amounts of water in crystals in general correspond to the formula $HSb(OH)_6$ for antimonic acid. Representative salts in the new formulation are $NH_4Sb(OH)_6$, $LiSb(OH)_6$, $Ca[Sb(OH)_6]_2$, $Ba[Sb(OH)_6]_2$, $Be[Sb(OH)_6]_2$, $Mg(H_2O)_6[Sb(OH)_6]_2$, etc. The majority of crystallized antimonates reported in the literature contain just enough water to correspond to the formula $MSb(OH)_6$, though some contain additional water of crystallization. Some salts also are known containing less water than corresponds to this formulation, such as $KSbO_3$ and NH_4SbO_3. These are not to be considered salts of a meta acid $HSbO_3$, containing antimony with the coördination number three, but rather of a polymerized acid $(HSbO_3)_\infty$ in which a coördination number six is retained. It is probable that $KSbO_3$ and NH_4SbO_3 have the perovskite structure. The minerals romeite and schneebergite,[6] $(Ca,Mn,Fe,Na)_2Sb_2O_6(OH,F)$, also contain antimony with coördination number six.

Salts of H_7SbO_6 seem not to have been prepared; though the mineral swedenborgite, $NaAl_2SbO_6$, probably can be classed in this group. Salts of the acid $H_7Sb(MoO_4)_6$, as yet unprepared, are probably stable.

The ions Mg^{++}, Zn^{++}, Cd^{++}, Ga^{+++}, and In^{+++} are known to form hydrates $[M(H_2O)_6]^{++}$ or $^{+++}$, as in the gallium and indium alums, for example. It is anticipated that these complexes can also lose protons, and that salts of the acids $H_3Ga(OH)_6$ and $H_3In(OH)_6$ can be prepared. Germanium shows both coördination numbers six and four, GeO_2 occurring with either the rutile or quartz structure. The octahedral configuration is probably shown in $BaGeO_3$, for which the perovskite structure is expected.

Xenic acid, H_4XeO_6, should form salts such as Ag_4XeO_6 and AgH_3XeO_6.

The univalent radii of $O^=$ and F^- have the ratio 1.29, so that radius ratios relative to F^- are to be obtained from the figures in Table I by multiplication by this factor. We are thus led to formulas such as KBF_4, $(NH_4)_3AlF_6$, $(NH_4)_2SiF_6$, KPF_6, SF_6, K_3HSnF_8, etc., in agreement with observation, and to the predicted formulas[7] KrF_6 and XeF_6, with XeF_8 as an unstable compound which might be capable of existence. The univalent radius of Cl^- is nearly the same as that of $O^=$, so that the accepted formulas H_3InCl_6, H_2SnCl_6, and $HSbCl_6$ are the expected ones.

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(6) Zedlitz, *Z. Krist.*, **81**, 253 (1932).

(7) The radius of a cation not showing its maximum valence (such as Xe^{6+}) is somewhat greater than that for maximum valence (Xe^{8+}).

Summary

With the aid of a table of ratios of ionic radii, formulas are assigned the oxygen acids of a number of elements in their highest valence states. In most cases these are the accepted ones; the formula $HSb(OH)_6$ for antimonic acid, supported by considerable evidence, has not, however, been suggested before, and its recognition clarifies the chemistry of the antimonates. It is pointed out that the change from an ortho to a meta acid (H_4SiO_4 to $(H_2SiO_3)_x$, H_3BO_3 to $(HBO_2)_x$, $H_2Sn(OH)_6$ to $(H_2SnO_3)_x$, etc.) in general involves polymerization rather than a change in coördination number.

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Some Properties of Electrolytes in the Solvent Sulfuric Acid[1]

BY LOUIS P. HAMMETT AND ALDEN J. DEYRUP[2]

Among the various evidences that water and organic oxygen compounds are bases in the same sense as are ammonia and its organic derivatives, there is none more convincing than Hantzsch's cryoscopic and conductivity work in the solvent sulfuric acid.[3] It is equally true that either freezing point or conductivity measurements in this solvent offer a most valuable method of investigating the ionic behavior of such weak bases under conditions of extremely high acidity. In the application of this method in the selection of a series of simple mono acid bases for use as indicators under such conditions,[4] we have, however, obtained quantitative results whose values, differing from those of previous workers, lead to a new and surprisingly simple interpretation of the physico-chemical nature of these solutions.

Apparatus, Method and Materials

We have used the familiar Beckmann freezing point method and apparatus with modifications necessary to prevent absorption of moisture. Those more accurate freezing point methods which depend upon the production of equilibrium between solid and liquid phases and the subsequent analysis of the liquid phase are here impossible because there is no method of sufficient precision for the determination of small amounts of water in sulfuric acid or for the recognition of pure sulfuric acid.

To prevent access of moisture from the air the hand operated stirring rod in the Beckmann apparatus passed through a sleeve of rubber tubing, lubricated with vaseline,

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(1) This article is based mainly upon part of a dissertation submitted by Alden J. Deyrup to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, March, 1932.

(2) Gottsberger Fellow, 1931–1932.

(3) Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); **62**, 626 (1907); **65**, 41 (1908); **68**, 204 (1909); *Ber.*, **55**, 953 (1922); **B63**, 1782 (1930).

(4) Hammett and Deyrup, THIS JOURNAL, **54**, 2721, 4239 (1932).