The positive group adjacent to the phosphate would tend to decrease the electron releasing effect of the dinegatively charged acyl phosphate. It should, therefore, serve to catalyze the reaction by causing a favorable shift of electrons as well as by attracting the substrate to the enzyme surface. The effect of the positively charged group near the carboxyl ion portion of the amino acid is more complicated. In neutral solution, glycine ethyl ester reacts more rapidly than glycine, but a comparison on the basis of both reactants being present in the form of the free amino compound indicates that the glycine reacts more rapidly, presumably because of its greater electron releasing tendency. A positive site should, therefore, attract the substrate to the enzyme surface, but cause an unfavorable shift of electrons at the amino nitrogen. In future publications, the nature and mode of action of the catalytic groups will be discussed in more detail.

Acknowledgment.—The author wishes to express his appreciation to Dr. Paul D. Bartlett for his stimulating discussions during the course of this work. He also wishes to thank the Atomic Energy Commission for the fellowship grant.

CAMBRIDGE 38, MASS. RECEIVED JANUARY 29, 1951

[CONTRIBUTION NO. 90 FROM THE INSTITUTE OF ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Composition and Stability of the Beryllium-sulfosalicylate Complex Ion[1]

BY H. V. MEEK[2] AND CHARLES V. BANKS

The composition and stability of the "colorless" beryllium-sulfosalicylate complex ion was studied by means of its ultraviolet absorption spectra. The Vosburgh and Cooper extension of Job's method of continuous variations was used to show that in the optimum *p*H range (9 to 11) only one complex ion is present in appreciable quantity and that the mole ratio of sulfosalicylate to beryllium in this complex ion is 2 to 1. Evidence is presented that the phenolic hydrogen of the participating sulfosalicylate ions is removed in the process of forming the beryllium-sulfosalicylate complex ion. The true equilibrium constant for the dissociation of $Be(O_3SC_6H_3(O)COO)_2^{-4}$ into $O_3SC_6H_3(OH)COO^{-2}$ and an unknown beryllium species, Be_x, was found to be approximately 2.1×10^{-9} at $25 \pm 1°$.

Introduction

Recently a new spectrophotometric method for determining beryllium was reported by Meek and Banks[3] which is based on the fact that the absorption maximum characteristic of $O_3SC_6H_3(OH)COO^{-2}$ is displaced appreciably toward the longer wave lengths by the presence of beryllium (Fig. 1). This displacement is not sufficient to give a "color" but is sufficient to make it possible to establish the composition of the beryllium-sulfosalicylate complex ion and to estimate its instability constant.

Experimental

Materials.—Only reagent-grade materials or materials carefully purified or synthesized by the authors were used in this study. Extreme care was taken to select only those lots of materials in which the iron content was negligible since its presence would be particularly undesirable.[4]

The source and purification of the beryllium basic acetate and the N,N,N',N'-tetrakis-(carboxymethyl)-ethylenediamine are described elsewhere.[3]

Sulfosalicylic acid from two commercial sources was recrystallized several times from water and then compared with 5-sulfosalicylic acid, prepared according to the method of Meldrum and Shah,[5] by potentiometric titration and by checking the ultraviolet absorption spectra of equal molar solutions of these acids at the same *p*H with and without beryllium being present (Fig. 1). All of these experiments indicated that the behavior of the commercial acids is, at least for the purpose of this study, identical with 5-sulfosalicylic acid. Stock solutions of sulfosalicylic acid were standardized by titration with standard alkali.

Apparatus.—Silica cells (1.000 cm.) and a Cary recording spectrophotometer (Model 12) were employed in the spectrophotometric studies. Beckman glass electrode *p*H meters (Models H-2, M and G) were used for the *p*H measurements. Appropriate sodium ion corrections were made where accurate knowledge was considered necessary.

Results

The Effect of *p*H.—The wave length of 317.0 mμ was chosen for the examination of the beryllium-sulfosalicylate complex ion because at this wave length the maximum change in absorbancy due to the presence of beryllium is observed. Solutions 6.00×10^{-4} *M* in sulfosalicylate, 0.1 *M* in sodium perchlorate (to maintain constant ionic strength), and having various *p*H values were scanned with the Cary instrument using distilled water as the reference solution. The absorbancies of these solutions are plotted in curve 2, Fig. 2. Solutions containing appreciably higher or lower sulfosalicylate concentrations show, respectively, shorter or longer *p*H intervals of constant absorbancy due to mass action.

Curve 1, Fig. 2, is a plot of similarly observed absorbancies for solutions 6.00×10^{-4} *M* in sulfosalicylate, 0.10 *M* in sodium perchlorate, 3.00×10^{-4} *M* in beryllium sulfate, and having various *p*H values. Again, the limits of the *p*H interval, through which the absorbancy remains constant, vary slightly with the concentration of the beryllium-sulfosalicylate complex ion.

Method of Continuous Variations.—The Vosburgh and Cooper[6] extension of Job's[7] method of continuous variations was used to study the number and composition of beryllium-sulfosalicylate complex ions present in the optimum *p*H range.

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[1] This document is based on work performed in the Ames Laboratory of the Atomic Energy Commission, Ames, Iowa.

[2] Abstracted from a dissertation submitted by Homer V. Meek to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1950. Procter and Gamble Company, Ivorydale, Cincinnati 17, Ohio.

[3] H. V. Meek and C. V. Banks, *Anal. Chem.*, **22**, 1512 (1950).

[4] R. T. Foley and R. C. Anderson, THIS JOURNAL, **70**, 1195 (1948).

[5] A. N. Meldrum and M. S. Shah, *J. Chem. Soc.*, **123**, 1986 (1923).

[6] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

[7] P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

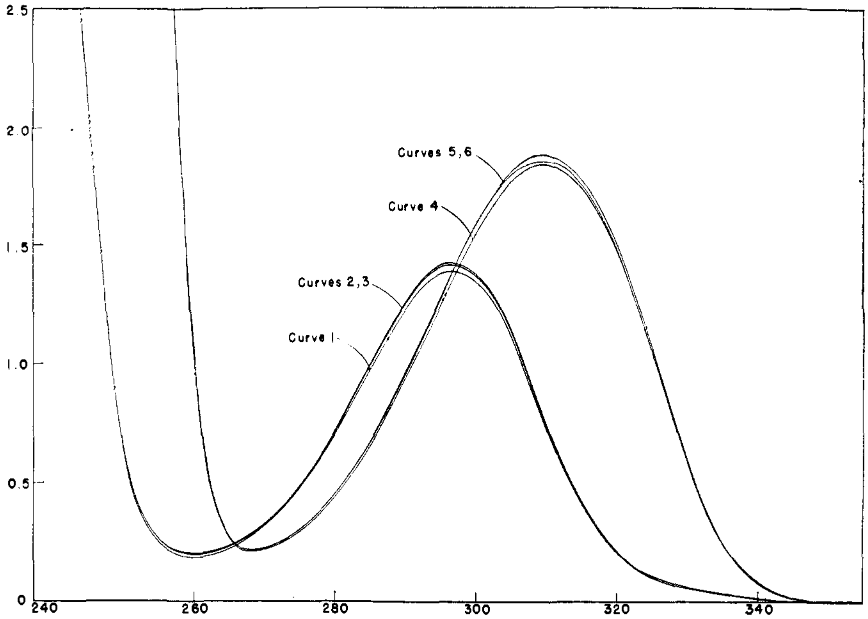

Fig. 1.—Absorption spectra of 5.00 × 10^{-4} *M* sulfosalicylic acids and of 5.00 × 10^{-4} *M* sulfosalicylic acids 2.50 × 10^{-4} *M* in $BeSO_4$ using the Cary instrument: curve 1, synthetic acid, *p*H 10.38; curve 2, commercial acid 1, *p*H 10.42; curve 3, commercial acid 2, *p*H 10.39; curve 4, synthetic acid plus beryllium, *p*H 10.30; curve 5, commercial acid 1 plus beryllium, *p*H 10.26; curve 6, commercial acid 2 plus beryllium, *p*H 10.28.

Solutions were prepared which were 5.00 × 10^{-4} *M* in total beryllium plus total sulfosalicylate, 1.00 × 10^{-2} *M* in N,N,N′,N′-tetrakis-(carboxymethyl)-ethylenediamine (to buffer the solutions and to maintain constant ionic strength), and had *p*H values ranging from 10.37 to 10.49 as adjusted with sodium hydroxide. These solutions were scanned on the Cary instrument and, for various wave lengths, the difference *Y* between the measured absorbancy and the absorbancy which would have been observed had no reaction taken place was plotted against the volumes of equimolar solutions of beryllium and sulfosalicylate used in preparing the solutions (Fig. 3). From Fig. 3 it is evident that only one beryllium-sulfosalicylate complex ion is present in appreciable quantity in this *p*H range and that the mole ratio of sulfosalicylate to beryllium in this complex ion is 2 to 1. Identical results were obtained in another experiment in which sodium perchlorate was substituted for the N,N,-N′,N′ - tetrakis - (carboxymethyl)-ethylenediamine.

Stoichiometry.—It was of interest to determine whether the phenolic hydrogen of the participating sulfosalicylate ions remains intact (Eq. 1) or is displaced (Eq. 2) in the process of forming the beryllium-sulfosalicylate complex ion in the optimum *p*H range.

$$Be_4O(OAc)_6 + 8O_3SC_6H_3(OH)COO^{-2} + 2H^+ \longrightarrow 4Be(O_3SC_6H_3(OH)COO)_2^{-2} + 6OAc^- + H_2O \quad (1)$$

$$Be_4O(OAc)_6 + 8O_3SC_6H_3(OH)COO^{-2} + 6OH^- \longrightarrow 4Be(O_3SC_6H_3(O)COO)_2^{-4} + 6OAc^- + 7H_2O \quad (2)$$

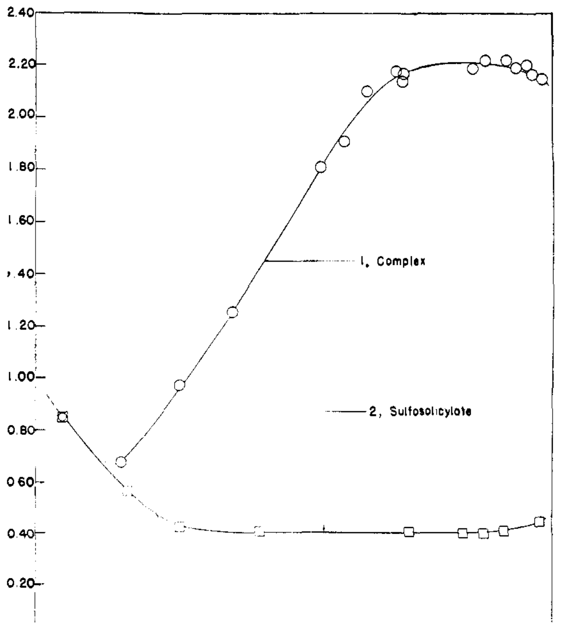

Fig. 2.—Effect of *p*H on absorbancy at 317 mμ: curve 1, 6.00 × 10^{-4} *M* in sulfosalicylate, 3.00 × 10^{-4} *M* in beryllium sulfate, 0.10 *M* in sodium perchlorate; curve 2, 6.00 × 10^{-4} *M* in sulfosalicylate, 0.10 *M* in sodium perchlorate.

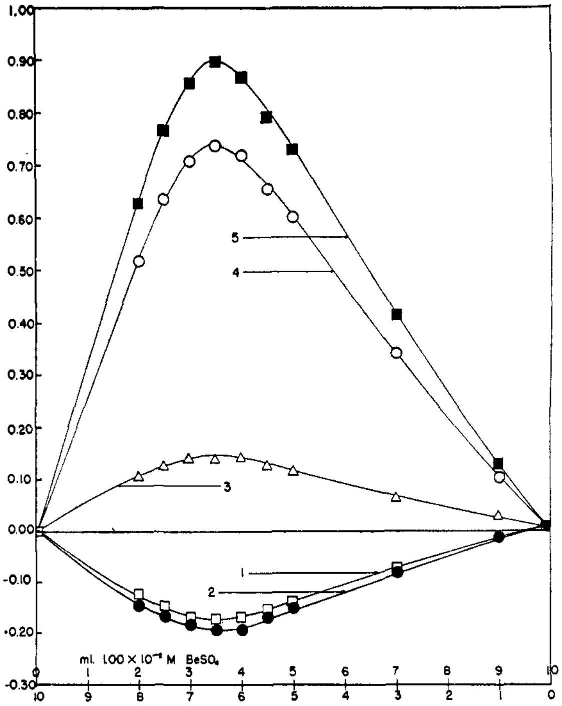

Fig. 3.—Method of continuous variations: curve 1, 280.0 mμ; curve 2, 290.0 mμ; curve 3, 300.0 mμ; curve 4, 310.0 mμ; curve 5, 317 mμ.

Two accurately weighed samples (about 0.35 g.) of pure anhydrous beryllium basic acetate were dissolved in separate mixtures of 50.0 ml. of 0.5 M disodium sulfosalicylate solution (pH 10.6) and 40.0 ml. of 0.1049 N alkali solution. After complete dissolution these solutions were titrated potentiometrically with 0.1032 N hydrochloric acid solution. A blank solution containing the same amounts of disodium sulfosalicylate and alkali was also titrated. Table I shows the apparent purity of the beryllium basic acetate as calculated at various pH values using the equivalent weight of beryllium basic acetate indicated by the stoichiometry of Eq. 2.

TABLE I

TITRATION OF BERYLLIUM BASIC ACETATE IN EXCESS DISODIUM SULFOSALICYLATE

Final pH	Apparent percentage purity of $Be_4O(OAc)_6$ Sample 1	Sample 2
10.0	98.42	97.80
9.5	99.23	98.35
9.0	99.27	98.02
8.5	99.07	97.76

It is apparent, therefore, that Eq. 2 accurately describes the over-all process of forming the beryllium-sulfosalicylate complex ion and that the phenolic hydrogen of the participating sulfosalicylate ions is removed in this process.

Molar Dissociation Constant.—At constant pH (within the optimum pH range) the dissociation of the beryllium-sulfosalicylate complex ion was considered to be best represented by Eq. 3

$$Be(O_3SC_6H_3(O)COO)_2^{-4} \overset{H^+}{\rightleftarrows} Be_x + 2O_3SC_6H_3(OH)COO^{-2} \quad (3)$$

where Be_x is an unknown species of beryllium ion. Since it was considered very unlikely that the absorption spectrum of the sulfosalicylate ion would be identical with that of any of the beryllium-sulfosalicylate complex ions that might be formed, the fact that the composition maximum (Fig. 3) does not vary with wave length[6] was considered justification for assuming that only one beryllium-sulfosalicylate complex ion was present under the experimental conditions. The molar dissociation constant, K', may then be written as

$$K' = \frac{[Be_x][O_3SC_6H_3(OH)COO^{-2}]^2}{[Be(O_3SC_6H_3(O)COO)_2^{-4}]} \quad (4)$$

Since it can be logically assumed that under the experimental conditions (within optimum pH range and at 317.0 mμ) absorption is due only to $O_3SC_6H_3(OH)COO^{-2}$ and $Be(O_3SC_6H_3(O)COO)_2^{-4}$ the absorbancy, A_s, of a solution is

$$A_s = l(M_1a_{M_1} + M_2a_{M_2}) \quad (5)$$

where l is the path length of the cells (1.000 cm.), M_1 and M_2 are the molarities of $O_3SC_6H_3(OH)COO^{-2}$ and $Be(O_3SC_6H_3(O)COO)_2^{-4}$ respectively, and a_{M_1} and a_{M_2} are the corresponding molar absorbancy indexes. The molar absorbancy index, a_{M_1}, of the sulfosalicylate ion was calculated to be 691 at 317.0 mμ from the observed absorbancy and the known molarity of a solution containing only sulfosalicylate. The molar absorbancy index, a_{M_2}, of the beryllium-sulfosalicylate complex ion was approximated from the observed absorbancies of solutions at 317.0 mμ of known beryllium molarities and relatively large, known sulfosalicylate molarities. A more accurate value for a_{M_2} was determined in the following manner. Letting the total beryllium molarity be equal to M and the molarity of Be_x be equal to y, we may write

$$K' = \frac{(y)(2y)^2}{(M - y)} \quad (6)$$

and

$$A_s = (2y)(691) + (M - y)(a_{M_2}) \quad (7)$$

A stock solution of the beryllium-sulfosalicylate complex ion was prepared in which the mole ratio of sulfosalicylate to beryllium was adjusted as nearly as possible to 2 to 1. Six dilutions in the range of 3.00 × 10^{-4} to 5.00 × 10^{-5} M in total beryllium were prepared from this stock solution. The ionic strength of each solution was adjusted to 0.078 with sodium perchlorate and the pH of all solutions was adjusted with sodium hydroxide solution to be within the range 10.34 to 10.52.

From the absorbancies of these solutions at 317.0 mμ the value of a_{M_2} in Eq. 7 was adjusted by successive approximations to give values of y which when substituted into Eq. 6 gave nearly constant values for K'. For $a_{M_2} = 7.75 \times 10^3$ K' was found to be $2.63 \pm 0.24 \times 10^{-10}$ at 25° and ionic strength 0.078.

A similar study was made in which N,N,N′,N′-tetrakis-(carboxymethyl)-ethylenediamine was used to adjust the ionic strength to 0.078. In this study the value of K' was found to be $7.80 \pm 0.67 \times 10^{-10}$ for a_{M_1} equal to 680 and a_{M_2} equal to 7.70×10^3. Differences in the values for the constants were attributed to experimental error and, in the case of K', to the uncertainty in calculating the ionic strength from the ionization constants[8] for N,N,N′,N′-tetrakis-(carboxymethyl)-ethylenediamine.

The applicability of the constants a_{M_1}, a_{M_2} and K' found by studying the series of solutions in which the ionic strength was adjusted with sodium perchlorate was tested by preparing a similar series of solutions of the beryllium-sulfosalicylate complex ion and comparing the observed absorbancies of these solutions with those calculated from Eqs. 4 and 5. Table II shows the excellent agreement that was found between these absorbancy values.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED ABSORBANCY VALUES AT 317.0 mμ FOR SOLUTIONS OF THE BERYLLIUM-SULFOSALICYLATE COMPLEX ION

Total Be concentration, $M \times 10^4$	Absorbancy Obsd.	Calcd.
0.20	0.100	0.098
0.60	.372	.373
1.20	.806	.810
1.80	1.260	1.256
2.20	1.560	1.555
2.80	2.008	2.007
3.40	2.450	2.460

Another series of solutions of comparable ionic strength but in which the mole ratios of sulfosalicyl-

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[8] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

ate to beryllium were much greater than two to one were prepared. In no case did the observed and calculated absorbancies for these solutions differ by more than 0.005 absorbancy unit.

Still further confirmatory evidence for the applicability of the estimated constants was obtained by solving Eqs. 4 and 5 for the molar concentration of the unknown beryllium species, Be_x, in solutions in which an insufficient but known amount of sulfosalicylate was present to prevent the precipitation of a solid hydrated beryllium oxide phase. Under these conditions it was expected that the molar concentration of Be_x would be constant. The calculated molarities for Be_x in three such solutions were 1.67×10^{-4}, 2.14×10^{-4} and 1.56×10^{-4}. This agreement was considered to be good substantiating evidence for the accuracy of the estimated values of the constants.

True Dissociation Constant.—The true dissociation constant, K, was estimated by studying K' as a function of the ionic strength as adjusted with sodium perchlorate. Two series of solutions of the beryllium-sulfosalicylate complex ion were examined at various ionic strengths. Series I was 3.00×10^{-4} M in total beryllium and series II was 1.50×10^{-4} M in total beryllium. Both series of solutions were scanned at 25 ± 1° and at 30 ± 1°. Corrections were not made for the changes in molarities brought about by warming the solutions from 25 to 30° because these changes were small compared to the changes in the absorbancies. Contributions by sulfate, hydroxyl, sodium, perchlorate, sulfosalicylate and beryllium-sulfosalicylate complex ions were included in the ionic strength calculations. The previously estimated values of a_{M_1} and a_{M_2} were used to calculate the values of K'. Table III indicates the square root of the ionic strength, observed absorbancies at 317.0 mμ, and the corresponding K' values for each series of solutions at the two temperatures. Figure 4 shows the plot of K' at the two temperatures *versus* the square root of the ionic strength. The values obtained for K were 2.1×10^{-9} and 2.6×10^{-9} at 25 and 30°, respectively.

TABLE III

VARIATION OF THE MOLAR DISSOCIATION CONSTANT WITH IONIC STRENGTH

	25 ± 1°		30 ± 1°	
$\sqrt{\mu}$	A_s	$K' \times 10^{10}$	A_s	$K' \times 10^{10}$
Series I. 3.00×10^{-4} M in total beryllium				
0.401	2.169	2.14	2.144	3.37
.313	2.144	3.37	2.138	3.76
.259	2.150	3.05	2.132	4.16
.189	2.125	4.61	2.123	4.76
.142	2.120	4.99	2.096	7.07
.066	2.043	13.60	2.018	17.79
Series II. 1.50×10^{-4} M in total beryllium				
0.398	1.030	2.74	1.005	4.75
.310	1.032	2.62	1.008	4.51
.254	1.032	2.62	1.001	5.20
.183	1.013	4.05	0.981	7.53
.133	0.992	6.18	0.960	10.77
.047	0.951	12.41	0.919	19.94

Discussion

Numerous attempts were made to account for the slope of curve 1, Fig. 2, in terms of the many equilibria and equilibrium constants reported in the literature for aqueous beryllium solutions. None was found suitable. However, in the *p*H range 3 to 8, the slope of the curve does have a very close dependence upon the first power of the hydrogen (or hydroxyl) ion concentration. It was concluded that the important beryllium species which is in equilibrium, at the optimum *p*H, with the beryllium-sulfosalicylate complex ion, should be referred to simply as an unknown beryllium species, Be_x. Above *p*H 10.8 the beryllium-sulfosalicylate complex ion is appreciably destroyed, presumably by the formation of other beryllium species (such as beryllate) and/or other beryllium-sulfosalicylate species. Many beryllium species could be postulated.

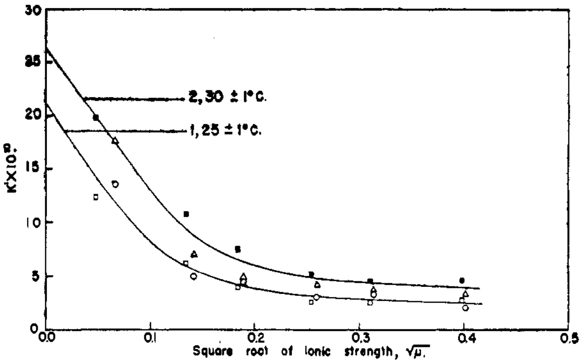

Fig. 4.—Variation of K' with the square root of the ionic strength: curve 1, 25°: ○ Series I, □ Series II; curve 2, 30°: △ Series I, ■ Series II.

The variation with *p*H of the absorption properties of solutions of sulfosalicyclic acid indicates that the ionization constants of this acid may be easily estimated by a method similar to that employed by Crouthamel, Meek, Martin and Banks.[9] The increased absorbancy found below *p*H 4, as shown in curve 2, Fig. 2, was attributed to the presence of $O_3SC_6H_3(OH)COOH^{-1}$ while the increased absorbancy above *p*H 10.8 was attributed to the presence of $O_3SC_6H_3(O)COO^{-3}$. Other methods of studying the ionization constants of sulfosalicylic acid have met with only qualitative success.[10]

That the composition maximum, as established by the method of continuous variations, occurs at a mole ratio of sulfosalicylate to beryllium of 2 to 1 was not surprising since beryllium is known to form similar compounds in which the sp^3 orbitals are involved.[11]

The titrimetric evidence for the applicability of Eq. 2 was considered indisputable, at least from the stoichiometric stand-point. All attempts to write other reasonable equations to account for the observed stoichiometry met with failure.

The equilibrium described by Eq. 3 was considered the simplest one consistent with all of the data. The complete accounting for the change in the ab-

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[9] C. E. Crouthamel, H. V. Meek, D. S. Martin and C. V. Banks, THIS JOURNAL, **71**, 3031 (1949).

[10] K. Okahara, *Science Repts. Tohôku Imp. Univ.*, [4] **6**, 593 (1931).

[11] W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.* (*London*), [A] **104**, 437 (1923); W. H. Mills and R. A. Gotts, *J. Chem. Soc.*, 3121 (1926); W. R. Angus and J. Farquharson, *Proc. Roy. Soc.* (*London*), [A] **136**, 579 (1932).

sorbancy of solutions of the beryllium-sulfosalicylate complex ion with dilution by means of this equation and the appropriate constants, and the accounting for observed absorbancies of solutions in which the mole ratios of sulfosalicylate to beryllium were greatly different than 2 to 1, were considered adequate reasons for the adoption of this equation.

The displacement of the phenolic hydrogens during complexation at this *p*H is, as indicated by Eq. 2, expected because of the increased acidity brought about by coördination of the phenolic oxygen atoms.

It is believed that considerable uncertainty is involved in the calculation of the lower ionic strengths used in the extrapolation to obtain K since in the very low ionic strength region the complex ions contribute the main portion of the ionic strength.

The fact that an increase in K is apparent for only a 5° increase in temperature indicates that by studying an appreciably larger temperature range $\mathrm{d}\ln K/\mathrm{d}T$ may be evaluated and an estimation of ΔH^0 be made.

AMES, IOWA RECEIVED FEBRUARY 22, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Kinetics of the Reaction of Germanium and Oxygen

BY RICHARD B. BERNSTEIN AND DANIEL CUBICCIOTTI

The rate of oxidation of germanium has been measured in the range 575 to 705°. The kinetics do not conform to any of the previously observed rate laws for metal oxidations but rather follow an equation of the form $Q = Q_\infty(1 - e^{-kt})$, where Q is the quantity of oxygen consumed by the metal in time t; Q_∞ and k are constants. Q_∞ varies approximately inversely to the oxygen pressure in the range 2 to 40 cm. and the rate constant, k, is temperature dependent. A mechanism is proposed in which the oxidation rate is controlled by the rate of evaporation of germanium monoxide. This rate of evaporation is in turn governed by the extent to which the surface is covered by impervious germanium dioxide.

Of the two oxides reported for germanium the monoxide is considerably more volatile than the dioxide.[1] This order of volatility may be contrasted with that of the majority of other metals which have volatile oxides, such as tungsten and molybdenum, where the higher oxide is the more volatile. The kinetics of the germanium oxidation have been found to be unusual because of this volatility.

Experimental

The apparatus was similar to that used previously[2] for metal oxidations. The system was operated at essentially constant pressure and was capable of detecting changes of the order of a few micrograms of oxygen.

In a typical experiment, the sample was placed in the silica reaction tube, which was then evacuated to about one micron. A furnace, preheated and controlled to the appropriate temperature, was placed around the silica tube. After the sample was heated for 10 to 15 minutes *in vacuo*, oxygen was admitted to the desired pressure. The decrease of pressure in the reaction bulb, as observed with an oil manometer, gave a measure of the oxygen consumption. The change in pressure during a run was at most 2% of the total pressure. At the conclusion of each run the sensitivity of the system was determined by adding a measured amount of oxygen.

The germanium, obtained from the A. D. Mackay Company, was fused *in vacuo* and then polished with emery paper, finishing with number 4/0. The resulting rectangular parallelepiped was used for several runs; between runs it was repolished and weighed. The sample was generally found to have lost weight at the end of a run.

After oxidation the sample was coated with a thin blue film; the samples that were most extensively oxidized had a light-colored powdery film in addition. There was a deposit of white powder on the walls of the silica bulb near the sample and often a thin deposit of brown material at the cold end of the tube. When this brown film was heated in air, it seemed to evaporate and oxidize to a cloud of white powder which was unaffected by further heating.

X-Ray diffraction patterns were obtained from the edges of blocks of metal and oxidized specimens. The patterns of the germanium showed spots corresponding to all the interplanar spacings of germanium.[3] The patterns of oxidized samples also showed lines corresponding to germanium dioxide.[3] No extra lines were found in any of the patterns.

The brown substance was assumed[4] to be the germanium monoxide reported by Dennis and Hulse.[1] It was obviously more volatile than the white germanium dioxide since it was found in the cold part of the silica tube while the dioxide was found deposited in the hot zone of the tube. Apparently, the germanium monoxide evaporated from the metal surface during the oxidation. Most of it was then oxidized in the tube to the dioxide which deposited on the hot walls, while some of the monoxide diffused to the cold walls and deposited there as the brown material.

The fact that the weight losses of the samples were not due to evaporation of germanium itself was determined by evaporation experiments carried out with unoxidized samples in a 10^{-6} mm. vacuum at 800°. In a period of four hours the weight loss was less than 0.1 mg. per sq. cm.

Results

The reaction was studied from 575 to 705° at oxygen pressures from 2 to 40 cm. The data are shown in Figs. 1 to 4. In these figures the points show the experimentally observed data. These oxidation curves do not follow any of the usual theoretical oxidation equations, *i.e.*, the linear, parabolic or logarithmic laws.[5] Furthermore, the amount of oxidation is a function of the oxygen pressure, in contrast to the pressure independence of the usual metal oxidation.

It is possible to express the oxidation curves accurately by the equation

$$Q = Q_\infty(1 - e^{-kt})$$

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[1] L. Dennis and R. Hulse, THIS JOURNAL, **52**, 3553 (1930).

[2] D. Cubicciotti, *ibid.*, **72**, 2084, 4138 (1950).

[3] Am. Soc. Testing Met., "X-Ray Diffraction Patterns," 1942, Second Supplementary Set, 1950.

[4] A sample of this brown material, obtained as a sublimate on heating the metal in 0.1 mm. of oxygen, was found to have the composition $GeO_{1.04}$. The analysis was made by measuring the uptake of oxygen at 1 atm. and 1000°. A sample of germanium subjected to this method of analysis, as a check, took up 96% of the amount of oxygen calculated for the dioxide. Therefore, the brown material had the composition of GeO.

[5] For a discussion of the types of oxidation laws see: E. A. Gulbransen, *Trans. Electrochem. Soc.*, **91**, 573 (1947).