

energy release ( $\Delta H_{\text{int}}$ ) over those for the bicyclic anions may be expected for the formation of the anions of 2-hydroxybenzaldehyde and 2-hydroxyacetophenone because the carbonyl group is free to rotate away from the negative oxygen (flip effect). Evidence from n.m.r. proton couplings for the flipped conformation in anions of salicylaldehydes has recently been reported.<sup>22</sup> Furthermore, the internal entropy change for the dissociation of a substituted phenol with an intramolecular hydrogen bond will probably be more positive than that for the parent to an extent which depends on the frequencies of motion of the hydroxyl and substituted groups in the intramolecularly bonded acid and in the species, HA and  $A_s^-$ .<sup>23,24</sup> The free energy effect of the substituent will be larger than the difference in the enthalpy changes for the substituent bond-

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(24) Free internal rotation of the hydroxyl, formyl, and acetyl groups seems unlikely in aqueous solution, but the entropy of torsions in the non-intramolecularly H-bonded species, which may be low in frequency relative to those in 2-hydroxybenzaldehyde and 2-hydroxyacetophenone, could account for much of the free energy effect.

ing. In the present study the increase in entropy cannot be distinguished from a negative increment in  $\Delta H_{\text{int}}$ ; either, however, operates to increase the substituent effect.

The influence of the freedom of the carbonyl substituent may be seen in Fig. 1; the  $pK$  values of 2-hydroxyacetophenone, 2-hydroxybenzaldehyde, and their nitro derivatives are much lower relative to those of the bicyclic acids than might be expected from the order of intramolecular H-bond strength. The magnitude of the flip effect is about one  $pK$  unit for 2-hydroxyacetophenone if one assumes the same H-bond strength as for 8-hydroxy-1-tetralone. The repulsive energy in the anion of 7-hydroxy-1-indanone must be somewhat less than that in the anion of 8-hydroxy-1-tetralone because of the greater distance between the oxygen atoms; but, if the energy could be released and the small contribution from the intramolecular H-bond removed, the  $pK$  of the acid would be smaller and comparable to that of the *para* isomer, 5-hydroxy-1-indanone. The data for the indanone acids thus indicate, as for the nitrophenols, that the stabilization by charge transfer is about the same for *o*- and *p*-substitution.

[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

## New Complexes of Guanidinium Ion with Tetraphosphate Ion

BY JAMES I. WATTERS AND SABURO MATSUMOTO

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New complexes of guanidinium ion with tetraphosphate ion have been identified and their complexity constants have been evaluated on the basis of the pH lowering due to complex formation during the titration of tetraphosphate ion with hydrogen ion. The stability of these complexes which is similar to that of alkali metal ions with polyphosphates is probably due to at least three hydrogen bonds between amine nitrogen and phosphate oxygen atoms. The complexes and their over-all complexity constants at 25° with the ionic strength adjusted to unity with tetramethylammonium chloride are  $C(NH_2)_3P_4O_{13}^{5-}$ ,  $\beta_{GP_4} = 10^{1.84}$ ;  $[C(NH_2)_3]_2P_4O_{13}^{4-}$ ,  $\beta_{G_2P_4} = 10^{2.76}$ ;  $C(NH_2)_3HP_4O_{13}^{4-}$ ,  $(GHP_4) = 10^{1.16}$ . A new method based on expressions for the mean number of bound hydrogen ions was used in evaluating these constants.

### Introduction

Guanidine, the analog of urea in the ammonia system, is a compound of considerable biological and physiological significance. Since its protonated ion is one of the few cations forming a crystalline precipitate with the tetraphosphate ion, reactions between these two ions in solution are of practical importance. Since both amines and polyphosphates play important roles in the life process, the interaction of the type detected in the present study may have physiological effects.

The guanidinium ion is unique in that it contains one carbon bonded to three equivalent  $NH_2$  groups. Resonance considerations indicate that a positive charge must be shared equally by the three equivalent  $NH_2$  groups in a planar structure and that the proton should be strongly bound. This structure has been confirmed by X-ray,<sup>1</sup> Raman,<sup>2</sup> infrared,<sup>3</sup> and n.m.r. studies.<sup>4</sup> The ion has been compared to the alkali metal ions since its salts with anions of strong acids are essentially neutral and the solution of guanidine in

water is a strong base. These properties are consistent with the exceedingly small acidic dissociation constant,  $10^{-13.65}$  of guanidinium ion, reported by Hall and Sprinkle.<sup>5</sup>

The present study originated with the observation<sup>6</sup> that the pH was appreciably lowered during acidimetric titrations of tetraphosphate in the presence of the guanidinium ion introduced as the cation during the purification of the tetraphosphate by recrystallization.<sup>7</sup>

Applications of this effect in the evaluation of the complexity constants of polyphosphates have been made in this<sup>5</sup> and other laboratories.<sup>9,10</sup>

### Theoretical

The association of the tetraphosphate ion with the first and second proton occurred with a barely perceptible break which vanished in the presence of

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guanidinium ion. To eliminate any effect of overlap of the two equilibria a new mathematical procedure was developed which is related to Bjerrum's formation function. Briefly this procedure is based on the evaluation of the mean number of hydrogen ions,  $\bar{n}_H$ , bound to the ligand, L, in any form whether free or in the form of a complex with another species, M, thus

$$\bar{n}_H = \frac{\sum_{i=0}^N \sum_{j=1}^{N'} \sum_{k=1}^{N''} j[M_iH_jL_k] + \sum_{i=0}^N \sum_{j=0}^{N'} \sum_{k=1}^{N''} [M_iH_jL_k]}{\sum_{i=0}^N \sum_{j=0}^{N'} \sum_{k=1}^{N''} [M_iH_jL_k]} \quad (1)$$

Throughout this paper M and L indicate the guanidinium and tetraphosphate ions, respectively; ionic charges are omitted for convenience; brackets indicate concentrations, and parentheses indicate activities. The total concentration of an added species, independent of its equilibrium form, is indicated by the subscript t after the expression for its concentration. Since a relatively large excess of guanidinium ion was present, detectable concentrations of polynuclear species such as  $ML_2$  was highly improbable although such species may well exist in solutions containing an excess of the tetraphosphate ligand. Diprotonated complex ions can likewise be neglected since the titration curves obtained in the presence or absence of guanidinium ion become identical after adding two hydrogen ions per tetraphosphate ion. Hereafter, the symbol  $a$  will indicate the number of moles of hydrogen ion added per mole of tetraphosphate ion. If the postulated complex species are ML,  $M_2L$ , MHL, and  $M_2HL$ , eq. 1 can be rewritten as

$$\bar{n}_H = \frac{\{[HL] + 2[H_2L] + [MHL] + [M_2HL]\} + \{[L] + [HL] + [H_2L] + [ML] + [M_2L] + [MHL] + [M_2HL]\}}{\{[L] + [HL] + [H_2L] + [ML] + [M_2L] + [MHL] + [M_2HL]\}} \quad (2)$$

The mean number of bound hydrogen ions can be solved from the known added acid and ligand concentrations and the pH as

$$\bar{n}_H = \frac{\{[H^+]_t - [H^+]\}}{[L]_t} \quad (3)$$

Since the pH is in the range of 5 to 8, the  $[H^+]$  term is negligible. All equilibria including proton dissociation will be expressed in terms of over-all complexity constants in the following form during the mathematical treatment

$$\beta_{ijk} = [M_iH_jL_k] \div [M]^i(H^-)^j[L]^k \quad (4)$$

where  $i$ ,  $j$ , and  $k$  are the number including zero of bound M,  $H^+$ , and L ions. These constants are readily converted to conventional stepwise acidity or complexity constants. Rearranging eq. 1 yields

$$\bar{n}_H + (\bar{n}_H - 1)\beta_{011}(H^+) + (\bar{n}_H - 2)\beta_{021}(H^+)^2 + (\bar{n}_H - 1)\beta_{111}[M](H^+) + \beta_{211}[M]^2(H^+)^2 + \bar{n}_H\beta_{101}[M] + \bar{n}_H\beta_{201}[M]^2 = 0 \quad (5)$$

Since the acidity constants,  $\beta_{011}$  and  $\beta_{021}$ , are known, the simultaneous solution of four equations of this form for four solutions each favorable to relatively large concentrations of one of the complex species will yield consistent values for the constants of all species

actually present. In the region of  $a = 0.5$  the species which should be predominant are ML at low concentrations of M and  $M_2L$  at high concentrations. The region where  $a = 1.5$  is favorable to relatively large concentration of MHL and  $M_2HL$  at low and high M concentrations, respectively.

For a graphic confirmation of the consistency of the data the equation can be rearranged to the following forms at  $\bar{n}_H = 0.5$  and 1.5, respectively.

$$F_{0.5} = \beta_{101} + \beta_{201}[M] = [M]^{-1}\{\beta_{011}(H^+) + 3\beta_{021}(H^+) + \beta_{111}[M](H^+) + \beta_{211}[M]^2(H^+)^2 - 1\} \quad (6)$$

$$F_{1.5} = \beta_{111} + \beta_{211}[M] = [M]^{-1}(H^+)^{-1}\{\beta_{021}(H^+)^2 - \beta_{111}(H^+) - 3\beta_{101}[M] - 3\beta_{201}[M]^2 - 3\} \quad (7)$$

The right side of the above equations can be solved to obtain  $F_{0.5}$  and  $F_{1.5}$  from the known acidity constants, iterated values for the complexity constants, the pH, and the concentration of free guanidinium ion. Since guanidinium ion is present in relatively large excess its concentration is readily solved by applying a small correction for that bound in the complex. Throughout most of the titration approximately one guanidinium ion is bound by each tetraphosphate ion present.

The values of  $F_{0.5}$  and  $F_{1.5}$  as a function of the free guanidinium ion concentrations can be used in the following graphic slope-intercept procedure to obtain the various complexity constants. First  $F_{1.5}$  is solved by the right side of eq. 7 from the data in Table I at  $a = \bar{n}_H = 1.5$ . The acid complexity constants which have been previously determined are defined in terms of conventional acidity constants by the following equations and their values are given for solutions with the ionic strength adjusted to unity with  $N(CH_3)_4Cl$  at 25°.

TABLE I  
EFFECT OF GUANIDINIUM ION ON THE ACIDIMETRIC pH  
TITRATION CURVE OF TETRAPHOSPHATE<sup>a,b</sup>

$a$	pH	$[P_4O_{13}^{6-}]_t, {}^c$ m.M	$[C(NH_2)_3^+]_t, {}^c$ m.M	log $F$
0.5	8.34	2.119	...	
	7.99	5.56	33.66	1.88
	8.02	5.56	33.66	1.84
	7.81	5.56	63.66	2.02
	7.80	5.56	63.66	2.01
	7.68	5.56	93.66	2.08
	7.69	5.56	93.66	2.07
	7.58	5.56	123.66	2.15
	7.59	5.56	123.66	2.13
	7.51	5.56	153.66	2.19
	7.49	5.56	153.66	2.21
	7.41	5.56	183.66	2.28
	7.26	2.119	242.7	2.41
	6.98	2.119	416.7	2.66
6.53	2.119	884.3		
1.5	6.61	2.119	0.00	
	6.27	1.014	72.1	9.52
	6.13	0.984	115.7	9.55
	6.21	19.29	115.8	9.49
	6.14	4.003	144.0	9.41
	5.99	3.853	231.5	9.42
	5.86	2.119	242.7	9.60
	5.76	19.29	347.2	9.58
	5.57	2.111	416.7	9.61

<sup>a</sup> The tetraphosphate concentration was held constant by its inclusion in both the acidic and acid-free solutions. The ionic strength maintained at 1.0 with tetramethylammonium chloride,  $T = 25^\circ$ . <sup>b</sup> In column 1 is given the number of moles of  $H^+$  added per mole  $P_4O_{13}^{6-}$  present in all forms (a). <sup>c</sup> The subscript t indicates total added millimolar concentration, m.M.

In first solving  $F_{1.5}$  the terms containing  $\beta_{101}$  and  $\beta_{201}$  can be neglected or they can be solved in terms of pre-

$$\beta_{011} = K_6^{-1} = \frac{[\text{HP}_4\text{O}_{13}^{3-}]/(\text{H}^+)[\text{P}_4\text{O}_{13}^{6-}]}{10^{8.34}} \quad (8)$$

$$\beta_{021} = K_5^{-1}K_6^{-1} = \frac{[\text{H}_2\text{P}_4\text{O}_{13}^{4-}]/(\text{H}^+)^2[\text{P}_4\text{O}_{13}^{6-}]}{10^{14.97}} \quad (9)$$

liminary values obtained by determinants since their contributions are relatively small. Plotting  $F_{1.5}$  vs.  $[\text{M}]$  should yield a straight line having an intercept equal to  $\beta_{111}$  and a slope equal to  $\beta_{211}$ . If the function is constant as in the present case the absence of the complex  $\text{M}_2\text{HL}$  is established.

The solved values of the complexity constants of the protonated complexes are then substituted into the right side of eq. 6 to obtain the remaining complexity constants by a similar graphic procedure. If the plot of  $F_{0.5}$  vs.  $[\text{M}]$  is a straight line the intercept is equal to  $\beta_{101}$  and the slope is equal to  $\beta_{201}$ .

### Experimental

The tetraphosphate was prepared by the hydrolysis of the commercial product "Cyclophos" manufactured by the Victor Chemical Works according to a procedure due to Thilo and Ratz<sup>11</sup> and the guanidinium salt,  $(\text{C}(\text{NH}_2)_3)_6\text{P}_4\text{O}_{13}\text{H}_2\text{O}$ , was recrystallized according to Quimby's procedure.<sup>7</sup> Experimental details are described in an earlier paper.<sup>6</sup> To eliminate the effect of hydrolysis, weighed portions of the salt were titrated to determine the equivalent weight of the salt which was found to be in close agreement with the above formula. Then weighed portions of the various salts and known amounts of nitric acid were mixed to obtain solutions having  $a = 0.5$  and  $1.5$ . The pH was measured immediately after bringing the temperature to  $25^\circ$  to obtain the data in Table I. Complete titration curves at constant tetraphosphate concentration were obtained by including the same tetraphosphate concentration in the acidic and acid-free solutions. The solutions were thermostatically kept at  $25 \pm 0.1^\circ$  under an atmosphere of nitrogen.

### Results and Discussion

From the curves in Fig. 1 it is observed that the presence of guanidinium ion lowered the pH throughout the range below  $a = 2$  but all of the curves blended for larger  $a$  values which indicated the presence of complexes between guanidinium and tetraphosphate ions containing not more than one hydrogen ion. Since a small activity coefficient effect can be observed in solutions containing relatively large guanidinium ion concentrations above  $0.15 M$ , only the data obtained in the presence of smaller concentrations were used in the final calculations.

The possibility of an effect due to protons liberated from the guanidinium ion on the pH at  $a = 0.5$  and  $1.5$  must be considered. The concentration of hydrogen ions originating from this source and equivalent to added acid is equal to the equilibrium concentration of guanidine. Substituting the highest pH of 8.02 and the highest guanidinium ion concentration of  $0.15 M$  used in these calculations into the expression for the acidity constant of guanidinium ion having Hall and Sprinkle's value of  $10^{-13.65}$  yields a concentration of guanidine less than  $10^{-6} M$ . This produces an effect equivalent to less than 0.1% of the added acid which is of the order of the experimental error. In all other solutions the effect was smaller. However, the absence of an appreciable decrease in pH at the beginning of the titration is probably due to this equilibrium.

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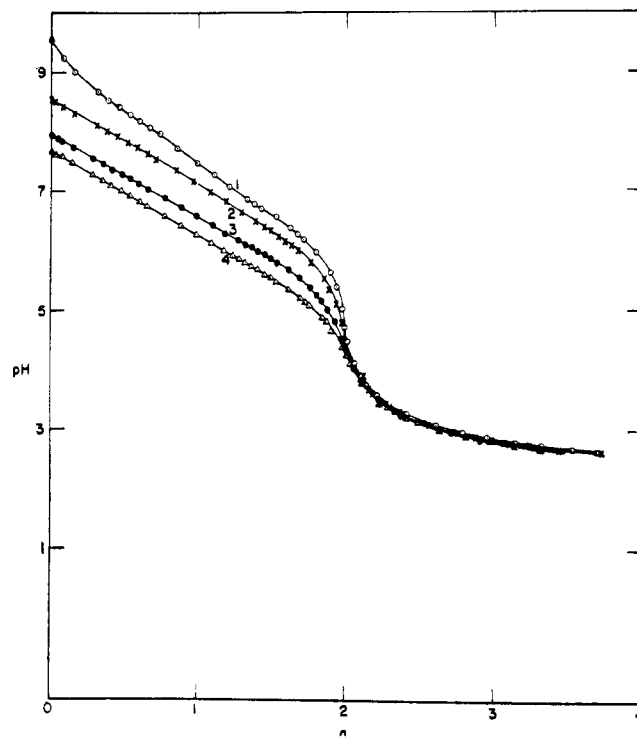


Fig. 1.—The effect of various concentrations of guanidinium ion on the titration of tetraphosphate ion with hydrochloric acid. Curve 1,  $0.001886 M ((\text{CH}_3)_4\text{N})_6\text{P}_4\text{O}_{13}$  titrated with  $0.01255 M \text{HCl}$ ; the ionic strength of all the solutions was adjusted to unity by tetramethylammonium chloride and  $T = 25^\circ$ . Curve 2,  $0.001929 M$  tetraphosphate with  $0.01255 M \text{HCl}$  in presence of  $0.06944 M$  guanidinium chloride. Curve 3,  $0.02119 M$  tetraphosphate titrated with  $0.01255 M \text{HCl}$  in presence of  $0.2427 M$  guanidinium chloride. Curve 4,  $0.002111 M$  tetraphosphate titrated with  $0.01255 M \text{HCl}$  in presence of  $0.4167 M$  guanidinium chloride.

Since the values of the last two acidity constants of tetraphosphate play a fundamental role in the calculation these values were recalculated under the exact experimental conditions of this study. Typical results in the absence of guanidinium ion are given in Table I. These values agree closely with those previously reported and summarized in eq. 8 and 9.

The value of  $\log F_{1.5}$  obtained by iteration quickly converged to  $9.49 \pm 0.07$ . Since the value fluctuated only in a random manner within experimental error and independently of the guanidinium ion concentration, this proves the presence of only one protonated complex  $\text{C}(\text{NH}_2)_3\text{HP}_4\text{O}_{13}^{4-}$  having the following complexity constant.

$$\beta_{111} = \frac{[\text{C}(\text{NH}_2)_3\text{HP}_4\text{O}_{13}^{4-}]/[\text{C}(\text{NH}_2)_3^+](\text{H}^+) \times [\text{P}_4\text{O}_{13}^{6-}]}{10^{9.49} \pm 10^{0.07}} \quad (10)$$

This constant is converted to the following more meaningful form in terms of the protonated ligand as follows.

$$\beta_{\text{M}\cdot\text{HL}} = \frac{[\text{C}(\text{NH}_2)_3\text{HP}_4\text{O}_{13}^{4-}]}{[\text{C}(\text{NH}_2)_3^+][\text{HP}_4\text{O}_{13}^{5-}]} = \beta_{111} \div \beta_{011} = 10^{1.5} \pm 10^{0.07} \quad (11)$$

The right side of eq. 6 was then solved to yield  $F_{0.5}$  by using the above value for  $\beta_{11}$  and omitting the  $\beta_{211}$  term. As shown in Table I,  $F_{0.5}$  varied in a linear manner as a function of the free guanidine concentration within an experimental error of  $\pm 10^{0.10}$ . In the plot of  $F_{0.5}$  vs.  $[\text{C}(\text{NH}_2)_3^+]$  the intercept of 70 cor-

responds to  $\beta_{101}$  and the slope of 576 corresponds to  $\beta_{201}$ . Thus

$$\beta_{101} = [C(NH_2)_3P_4O_{13}^{5-}] \div [C(NH_2)_3^+][P_4O_{13}^{6-}] = 10^{1.84} \pm 10^{0.10} \quad (12)$$

$$\beta_{201} = [(C(NH_2)_3)_2P_4O_{13}^{4-}] \div [C(NH_2)_3^+]^2[P_4O_{13}^{6-}] = 10^{2.76} \pm 10^{0.10} \quad (13)$$

Models can be constructed in which the guanidinium ion is located in a plane above or below that of the phosphorus atoms in a coiled structure. This structure appears feasible because it can account for the ease of

bonding two guanidinium ions. In an alternate structure the tetraphosphate is coiled around the guanidinium ion in a plane perpendicular to that of the tetraphosphate ion. It is possible that the latter structure is predominant in the 1:1 complex and the former in the 1:2 complex. Either conventional linear hydrogen bonds or less localized bonds between nitrogen atoms and one or more oxygen atoms are possible. Related studies of various amine-polyphosphate systems are in progress.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

## High Molecular Weight Boron Sulfides. II. Identification, Relative Intensities, Appearance Potentials, and Origins of the Ions

BY FRANK T. GREENE AND PAUL W. GILLES

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The new boron sulfides having molecular weights extending to above 850 have been further investigated by mass spectrometric techniques. Slightly sulfur-rich  $B_2S_3$  samples were prepared from natural and  $B^{10}$ -enriched boron, were chemically analyzed, and were vaporized in a mass spectrometer at temperatures between 300 and 600°. Ions were formed by electron impact and were identified by mass number, isotopic intensity distribution, and isotopic shift. The ions are in three series. Series I consists of 37 ions containing boron and sulfur alone; series II, 20 ions containing also a third element, tentatively identified as silicon; and series III, 15 ions containing a different third element, probably oxygen. Time, temperature, and electron energy dependences indicated that several neutral molecules vaporized from the sample and that on electron impact each produced an ion which decomposed predominantly without boron loss to produce the observed ions. It is suggested that the  $BS_2$  polymers  $B_3S_{16}$ ,  $B_7S_{14}$ ,  $B_{10}S_{20}$ ,  $B_9S_{18}$ , and  $B_8S_{12}$  are the neutral parent molecules and that they are obtained in equilibrium with the viscous  $B_2S_3$  liquid containing 0.5 to 1.0% excess sulfur, about 1% silicon, and about 1% excess oxygen. Approximate values for the appearance potentials for many of the ions were obtained. The heat of vaporization of  $B_2S_3$  was measured as  $36 \pm 5$  kcal./mole. The partial molal heats of vaporization of the higher molecular weight neutral parents from the sample are about  $55 \pm 10$  kcal./mole, appreciably higher than the heat of vaporization of  $B_2S_3$ .

### Introduction

The authors have recently reported the discovery of two new classes of boron sulfides with molecular weights up to 850 mass units.<sup>1</sup> Further mass spectrometric investigations using both normal and  $B^{10}$ -enriched boron have supported the original conclusions as to the existence of polymeric boron sulfides and have provided information on the appearance potentials of the ions, and on the identity and heats of vaporization of the neutral substances arising in the vaporization reaction. A third class of boron sulfide ions has also been detected. It is the purpose of this paper to present the new information for these complex systems.

### Experimental

The condensed boron sulfide samples were prepared in silica tubing by the reaction between boron and dry, flowing  $H_2S$  at about 700° to form  $HBS_2$ , which was then thermally decomposed to  $B_2S_3$  and  $H_2S$ . The latter reaction was performed in silica or graphite containers under vacuum at a maximum temperature of 300°. The resulting sample was a glass and contained an excess of sulfur compared to stoichiometric  $B_2S_3$ . In a few cases a part of this excess sulfur was removed by reaction with  $H_2$  followed by a thorough flushing with purified He. The normal boron was from a high purity crystalline sample furnished by the U. S. Borax Company; the 93%  $B^{10}$ -enriched boron was an amorphous sample obtained from the Oak Ridge National Laboratory.

The boron sulfide samples were analyzed by allowing them to react with a large excess of water to form  $H_2S$ , S, and  $H_3BO_3$ . The  $H_2S$  was flushed from the solution with nitrogen and trapped

in a train containing 4% ammoniacal hydrogen peroxide. The resultant solution was heated to destroy the peroxide and to complete the conversion of sulfide to sulfate, which was precipitated as  $BaSO_4$ .

The original solution could have been divided for the free sulfur, boric acid, and impurity analyses, but in actual practice fresh samples were used for the three analyses. The free sulfur was in colloidal form; it could be readily oxidized to sulfate with heated ammoniacal peroxide after which it was also determined as  $BaSO_4$ . Treatment of the  $BaSO_4$  with HF followed by igniting and weighing showed that the precipitate did not carry  $SiO_2$ . The boric acid was analyzed by titration with 0.1 N NaOH using mannitol as a complexing agent. Silicon was determined as  $SiO_2$  by the standard method involving heating to dryness twice with HCl, filtering, igniting, weighing, heating to dryness with HF, igniting, and weighing.

For the mass spectrometric measurements, the boron sulfide samples were placed in previously outgassed graphite Knudsen cells having 1.0-mm. orifices and heated by radiation from a W filament to between 300 and 600°. Temperatures were measured by a Pt-Pt, Rh thermocouple. At the lower end of this temperature range the sample is a glass and at the higher end, a viscous liquid. The effusing molecules were ionized by electron impact and analyzed with a Nuclide Analysis Associates HT series, 12 in., 60°, single focusing mass spectrometer having a resolution of about 1000. An electron multiplier was used as the detector. Most of the spectra were obtained with 50–70-v. electrons, and all were obtained with moderately rapid magnetic scans. The crucible region and ion source were operated at pressures of less than  $5 \times 10^{-6}$  and  $1 \times 10^{-6}$  torr, respectively, and were separated by a movable slit or shutter which could be used to stop the beam or to scan it. Shutter profiles and spectra taken with different ion source potentials revealed that the observed ions were produced from neutral molecules which had been vaporized from the sample in the crucible.

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