

10 CFR 50.90

October 19, 2007
5928-07-20202

U.S. Nuclear Regulatory Commission
Attn: Document Control Desk
Washington, DC 20555-0001

Three Mile Island, Unit 1 (TMI Unit 1)
Facility Operating License No. DPR-50
NRC Docket No. 50-289

Subject: Response To Request For Additional Information – Technical Specification Change Request No. 337: Reactor Building Emergency Sump pH Control System Buffer Change (TAC No. MD5963)

- References:
- (1) USNRC letter to AmerGen Energy Company, LLC dated October 4, 2007, "Request for Additional Information Regarding Proposed Reactor Building Emergency Sump System Buffer Change (TAC No. MD5963)"
 - (2) AmerGen Energy Company, LLC letter to NRC dated June 29, 2007 (5928-07-20097), "Technical Specification Change Request No. 337 – Reactor Building Emergency Sump pH Control System Buffer Change"

This letter provides additional information in response to the NRC request for additional information (RAI), issued October 4, 2007 (Reference 1), regarding TMI Unit 1 Technical Specification Change Request No. 337, submitted to NRC for review on June 29, 2007 (Reference 2). The additional information is provided in Enclosure 1.

Regulatory commitments established by this submittal are identified in Enclosure 3. If any additional information is needed, please contact David J. Distel at (610) 765-5517.

I declare under penalty of perjury that the foregoing is true and correct. Executed on the 19th day of October, 2007.

Respectfully,

gbr

Pamela B. Cowan
Director - Licensing & Regulatory Affairs
AmerGen Energy Company, LLC

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October 19, 2007

Page 2

Enclosures: 1) Response to Request for Additional Information
 2) Applicable Pages from C-1101-153-E410-040, Rev. 0, References 4.2 & 4.5
 3) List of Commitments

cc: S. J. Collins, USNRC Administrator, Region I
 P. J. Bamford, USNRC Project Manager, TMI Unit 1
 D. M. Kern, USNRC Senior Resident Inspector, TMI Unit 1
 File No. 07029

ENCLOSURE 1

TMI UNIT 1

**RESPONSE TO REQUEST FOR ADDITIONAL INFORMATION
TECHNICAL SPECIFICATION CHANGE REQUEST No. 337
Reactor Building Emergency Sump pH Control System Buffer Change**

**RESPONSE TO REQUEST FOR ADDITIONAL INFORMATION (RAI)
TMI UNIT 1 TECHNICAL SPECIFICATION CHANGE REQUEST No. 337
Reactor Building Emergency Sump pH Control System Buffer Change**

1. NRC Question

In section 7.1, page 15 of Attachment 2 the licensee listed eight chemicals which will exist in the sump water after a loss of coolant accident (LOCA). In its analysis the licensee assumed that each of them will dissociate or speciate into positive or negative ionic species. By balancing the resulting positive and negative charges, to obtain neutrality of the solution, the licensee could determine the amount of trisodium phosphate (TSP) required for obtaining a given value of pH. Provide a list of the ionic species.

Response

The description of the methodology stated above is correct as utilized in the referenced calculation. The Boron Speciation can be found in section 7.7 of the previously submitted Attachment 2 calculation (C-1101-153-E410-040, Rev. 0) (pages 22 to 24). The TSP Phosphate Speciation can be found in section 7.8 of the previously submitted Attachment 2 calculation (C-1101-153-E410-040, Rev. 0) (pages 24 to 26).

2. NRC Question

Describe the procedure for determining speciation of boron and TSP.

Response

The equilibrium concentrations of the boron species are determined by using the method described in reference 4.5 of the previously submitted Attachment 2 calculation (C-1101-153-E410-040, Rev. 0). The applicable pages of this reference are provided in Enclosure 2.

The equilibrium concentrations of the TSP species are determined by using the method described in reference 4.2 of the previously submitted Attachment 2 calculation (C-1101-153-E410-040, Rev. 0). The applicable page of this reference is provided in Enclosure 2. This paper is written in Russian, with an English abstract on the last page. The information in the abstract confirms the ionization constants as used in the above referenced pH calculation.

3. NRC Question

Explain the statement in section 2.6 on page 5 of Attachment 2 that "boron content will not be exceeded provided the power rate does not increase (2568 MWt) and the cycle duration (2 years) does not increase."

Response

TMI Unit 1 is currently licensed to operate at 2568 MWt with a 24-month cycle and these current licensing basis parameters have been utilized in the analysis referenced above. Any potential change to the TMI Unit 1 licensed power level or cycle duration would require additional evaluation of the impact on boron content. Potential changes to the licensed power level or operating cycle duration are not directly applicable to this license amendment application.

4. NRC Question

In section 6, on page 13 of Attachment 2, it is stated that water and boric acid in the sump is determined from a mass balance with two bounding conditions for water and boric acid. What are they and how were they determined?

Response

The two bounding conditions are Beginning of Cycle and End of Cycle chemistry configurations. Beginning of Cycle was chosen to maximize the boric acid concentration and mass. End of Cycle was chosen to minimize the boric acid concentration and mass. The values such as Borated Water Storage Tank (BWST) concentration are based upon Technical Specification limits.

5. NRC Question

According to Regulatory Guide 1.183, if the sump pH is controlled at the minimum values of 7, the molecular iodine is prevented from formation and release to the containment. However, during the engineered safety feature (ESF) recirculation phase, a higher pH is assumed to support iodine flashing fractions at 5 percent for the first 24 hours and 2 percent for the following 29 days. In the submittal the licensee specified the required pH ≥ 7.3 . Discuss: (1) the methodology for determining this pH value and (2) was the sump water pH buffered at this pH?

Response

The methodology for determining a minimum pH requirement of 7.3 utilized an overall approach of applying the Standard Review Plan (SRP) guidance with differences only in the use of pH values and application of a model for the mass transfer of iodine across the boundary layer between the liquid surface and the bulk gas space in the auxiliary building, as described in Calculation No. C-1101-900-E000-087, Rev. 2, previously submitted in Reference 2. This approach identified at pH values below 7.3 the TMI Unit 1 UFSAR flashing fraction requirements of 5% for the first 24 hours and 2% for the following 30 days, could not be met. Therefore, a limiting, minimum pH value of 7.3 was established.

At a pH of 7.3 the sump water is buffered utilizing TSP. This pH value is indicative of the maximum allowable amount of boron and the minimum amount of TSP in the sump water, resulting in the lowest achievable pH value after buffering.

6. **NRC Question**

Proposed insert C to technical specification (TS) page 4-2b describes the need to perform periodic solubility tests on the TSP to ensure adequate dissolution time. However, Insert D to the proposed TS surveillance requirements, TS page 4-10c, does not include solubility as one of the verifications performed on the TSP. Describe this apparent discrepancy between the TS bases and the TS surveillance requirement.

Response

Proposed insert D to the Technical Specification (TS) page 4-10c, describes the system surveillance requirements for the Reactor Building Emergency Sump pH Control System. Surveillance Test "b" of proposed insert D states, "Verify that a sample from the TSP baskets provides adequate pH adjustment of borated water." This surveillance requirement, specifically the statement "adequate pH adjustment," is determined by performing a two-part test, which includes sequential solubility and buffering verification, as described in the proposed TS Bases, insert C. Therefore, the scope of proposed insert D TS surveillance requirement includes solubility verification testing, in addition to buffering verification. The elements and methodology of the proposed TS surveillance testing will be clearly delineated in station surveillance procedures (Reference commitment in Enclosure 3).

7. **NRC Question**

When verifying the TSP buffering capability, solubility, and total mass, how is the sample obtained? How does the sampling account for the potential that the TSP on the interior of the basket may exhibit different properties (hydration, density, etc.) than samples taken from the basket periphery? Discuss the potential impact that variations in material properties within each basket may have on surveillance tests to determine buffer capability, solubility, and total mass of TSP available.

Response

TMI Unit 1 will quantify the total mass of TSP buffer present during each refueling outage as described in the Technical Specification Change Request No. 337, submitted June 29, 2007. The TSP basket sample will be obtained by taking a total of approximately 500 grams of material from the basket. Procedures will ensure that samples are taken within the basket at both interior and peripheral locations to obtain a representative sample (Reference commitment in Enclosure 3). The mass of TSP in each basket will be determined each refueling outage to ensure the TSP mass is as required. Weighing each basket eliminates potential variations due to settling and changes in density that may occur. The TSP form to be used is TSP dodecahydrate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$). The dodecahydrate form has the maximum water of hydration and will not absorb additional water and the water of hydration will remain constant during subsequent operating cycles. Use of the maximum hydrated form will eliminate variability in hydration and density as it is fully hydrated. Determining the total mass and use of the maximum hydrated form will eliminate sample variability that may exist in different areas of the baskets. Measuring the total mass present eliminates the requirement to determine density of the material in the baskets and potential differences of material density in different sections of the baskets.

8. **NRC Question**

Proposed insert C to TS page 4-2b describes the need to periodically determine the mass of TSP because leaking valves and components may dissolve some of the TSP from the baskets. If a leaking valve or component were to result in a portion of the TSP being dissolved, how would the dissolved TSP be accounted for when adding additional TSP to the basket. If there is no mechanism for removing the dissolved TSP then addition of more TSP may result in a total mass that exceeds the TS limits. Discuss how the loss of TSP through operational dissolution is accounted for when determining the total mass of TSP.

Response

If a leaking valve or component were to result in a portion of the TSP being dissolved, the solution would drain to the Reactor Building Sump by running across the floor or through floor drains. The sump water is periodically drained (i.e., 1x per month and will be more frequent with the new sump design) to the Auxiliary Building sump for processing, thus removing the dissolved TSP from the Reactor Building. Any TSP residue remaining on the floor or sump would be insignificant. Initial TSP loading is approximately 27,000 lbs, which provides significant margin to the maximum allowable TSP quantity of 28,840 lbs to accommodate potential TSP residue remaining on the Reactor Building floor. Any TSP that has dissolved and is lost to the floor or sump is accounted for by determining the total mass of TSP in each basket. If there is no loss by dissolution the mass will remain constant. There is no mass lost from settling, only a volume change, which does not impact mass.

9. **NRC Question**

TMI-1 is proposing to switch to TSP as a buffering chemical. Testing indicates that TSP in the presence of dissolved calcium can result in rapid precipitation of calcium phosphate, which can create significant head loss across a sump strainer covered with a debris bed. Provide a list of all potential sources and amounts of calcium within the TMI-1 containment and provide the calculated dissolved calcium concentration in a post-LOCA pool. Provide the relative chemical precipitate loading predicted by the WCAP 16530-NP, ["Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191"], model for TMI-1 with TSP and at the maximum projected pH value (8) for the pool.

Response

TMI Unit 1 is evaluating chemical effects through alternate testing. However, use of the WCAP 16530-NP model is being considered, and if utilized, this issue will be addressed in the TMI Unit 1 Generic Letter 2004-02 response. The alternate testing program will estimate the contribution of chemical effects on strainer head loss performance. The key element of the program is small scale testing in a simulated post-LOCA containment environment in which the increase in head loss from chemical effects of materials (dissolution, leaching chemical compounds, and precipitate formation) is compared to head loss due to debris without chemical effects. The chemical effects head loss testing is intended to reproduce as close as possible the chemical interactions of materials (dissolution, leaching chemical compounds, precipitate and debris physical characteristics) in a post LOCA containment environment. This testing includes the effects of fibrous insulation installed at TMI Unit 1 and concrete.

TMI Unit 1 does not utilize calcium silicate insulation, which is the significant contributor of calcium in the industry. The water sources that will be present in the Reactor Building sump during building spray actuation (BWST, RCS) are less than 1 PPB calcium. Other potential calcium sources at TMI Unit 1 are insignificant and would not impact the overall calcium loading.

10. **NRC Question**

In Section 4.5 of Enclosure 1 to the proposed license amendment request, it is stated that the evaluation was based on utilizing and analyzing available industry and technical research data. The evaluation concluded that all environmentally qualified equipment located inside the Reactor Building (RB) are qualified for the revised RB spray chemical conditions resulting from the proposed change. Please provide details of the methodology, assumptions, regulatory provisions applied and analysis to support the above conclusion.

Response

Environmentally Qualified (EQ) equipment is currently qualified for Reactor Building (RB) spray with a pH range of 8.0 – 11.0. The proposed design alters the pH range to 4.0 – 10.0 over the initial 24 hours, with a long-term pH of 7.3 –8.0 (essentially a neutral solution). To assess the EQ impact of the revised RB spray, EQ equipment located inside the RB was evaluated for the effects of an acidic RB spray (low pH extreme). The current EQ evaluation bounds the high extreme of the revised RB spray. This evaluation is described below:

Regulatory Provisions

The EQ Program for TMI Unit 1 meets the requirements of 10 CFR 50.49. EQ equipment has been evaluated for compliance with either the Division of Operating Reactors (DOR) Guidelines or 10 CFR 50.49, with guidance from Regulatory Guide 1.89.

TMI Unit 1 equipment qualified to the DOR Guidelines relies on partial test and analysis. With regard to containment sprays, the DOR Guidelines, Section 5.3 states:

...[A]n item of Class IE equipment may be shown to be qualified for a complete spectrum of service conditions even though it was only type tested for high temperature, pressure and steam. The qualification for service conditions such as radiation and chemical sprays may be demonstrated by analysis (evaluation) Components enclosed entirely in corrosion resistant cases (e.g., stainless steel) may be shown to be qualified for a chemical environment by analysis of the effects of the particular chemicals on the particular enclosure materials. The effects of chemical sprays on the pressure integrity of any gaskets or seals present should be considered in the analysis.

TMI Unit 1 equipment qualified to 10 CFR 50.49 relies on sequential testing of a specimen that is identical or similar to installed equipment, with supplemental analysis. With regard to containment sprays, 10 CFR 50.49(e)(3) states:

The composition of chemical used [for qualification] must be at least as severe as that resulting from the most limiting mode of plant operation (e.g., containment spray, emergency core cooling, or recirculation from containment sump). If the composition of the chemical spray can be affected by equipment malfunctions, the most severe chemical spray environment that results from a single failure in the spray system must be assumed.

With regard to qualification methods, 10 CFR 50.49(f)(4) identifies the following as an acceptable method:

Analysis in combination with partial type test data that supports the analytical assumptions and conclusions.

Qualification per 10 CFR 50.49 is based on type testing that includes chemical spray, though for different pH ranges.

As shown by these excerpts, supplemental analysis of the effects of the revised RB spray is permitted for equipment qualified to either the DOR Guidelines or 10 CFR 50.49.

Methodology

The methodology for EQ evaluation of revised RB spray is to identify the age-sensitive and metallic materials wetted by the spray, and assess their resistance to chemical attack. The evaluation relied upon the original EQ test if it included a chemical spray that bounded the pH range of the revised RB spray. For cases not bounded by the EQ test, or in the absence of testing under spray conditions, evaluation relies upon available industry and technical research data, such as that published in Perry's Chemical Engineers' Handbook. This handbook rates the resistance of materials to various chemical agents using general descriptors such as excellent, very good, fair, poor, etc.

Assumptions

The only assumption in the EQ evaluation of revised RB spray is a conservative determination of TMI Unit 1 RB spray duration (52 hours post-DBE). There are no assumptions regarding material identification since EQ Binders identify wetted parts and materials. Similarly, there is no assumption regarding chemical effects since EQ test data or published literature is available in all cases.

Evaluation

The evaluation extends the current EQ basis with supplemental analysis of the resistance of materials to the effects of the revised RB spray. The low pH extreme (4.0) is addressed primarily by analysis. The high pH extreme (10.0) is bounded by the current qualification assessment and is justified by either analysis or EQ test data. The acceptability of the revised containment chemical spray pH range and duration, with respect to age sensitive materials and metal housings, is performed in accordance with the requirements of 10 CFR 50.49, "Environmental Qualification of Electric Equipment Important to Safety for Nuclear Power Plants." Age sensitive materials and metallic enclosures of the EQ equipment that will be exposed to chemical spray are identified. These materials are evaluated using available industry and technical/research data including chemical

resistance of materials, effect of aging on materials exposed to spray, and the overall spray duration. The evaluation acceptance criteria are based on determination of age sensitive materials and metallic enclosures exposed to the chemical spray. The chemical resistance of the exposed age sensitive materials and metallic enclosures is determined utilizing Perry's Chemical Engineer's Handbook, Sixth Edition, and Harper's Handbook of Physics, Elastomers and Composites, Second Edition. The applicability of acceptance criteria to aged components and at elevated temperatures was evaluated and determined that the revised containment chemical spray at TMI Unit 1 does not exacerbate any significant adverse effect on aged components the acceptance criteria remains applicable to the EQ components located in the TMI Unit 1 containment.

Surface conductivity of sprays was evaluated for potential effects on conducting material/terminal blocks. At TMI Unit 1 this is not a concern since terminations are either sealed or not directly exposed to the chemical spray. Deposition of boron/foreign material, if any, will be washed away by the longer duration spray solution.

Cables installed in conduits, jacketed cables, splices, and terminations were evaluated. The spray evaluations for these materials determined that there is no effect due to the revised spray condition.

Conclusion

This evaluation demonstrated that the EQ equipment located inside containment at TMI Unit 1 remains qualified by the existing EQ files, as supplemented by the revised containment chemical conditions. No specific actions are required to physically protect equipment from spray contact.

11. NRC Question

Please confirm that the temperature profile inside the RB remains unchanged due to the proposed design change.

Response

The Reactor Building temperature profile remains unchanged due to the proposed buffer design change.

ENCLOSURE 2

Applicable Pages from C-1101-153-E410-040, Rev. 0, References 4.2 & 4.5

REFERENCE 4.2

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L. A. Pavlyuk, P. A. Kryukov

SPECTROPHOTOMETRIC DETERMINATION OF THE FIRST AND OF THE SECOND IONIZATION CONSTANTS OF PHOSPHORIC ACID FROM 25 TO 175°C

The first and the second ionization constants, K_{a1} and K_{a2} , of phosphoric acid have been determined at various temperatures between 25 and 175°C from spectrophotometric data with 2,6-dinitrophenol and *p*-nitrophenol as indicators.

The results expressed as a function of absolute temperature are given by the equations:

$$pK_{a1} = 583,01/T - 2,715 + 0,009801 \cdot T$$

$$\text{and } pK_{a2} = 1272,7/T - 1,154 + 0,01368 \cdot T.$$

TABLE II
EXTENT OF REACTION: QUENCHING
vs. SPECTROPHOTOMETRY*

10 ³ [Sn(II)], M	10 ³ [H ₂ O ₂], M	10 ³ [Cu(II)], M	% complete	
			Quenching	Spectro- photometry
2.43	1.22	0.00	88 ± 3	38 ± 0.5
1.17	2.34	0.00	71 ± 3	58 ± 1
1.17	1.17	0.00	57 ± 3	48 ± 1
1.17	1.17	1.40	46 ± 3	50 ± 1

* Conditions: [HClO₄] = 1.00 M, μ = 2.00 (LiClO₄), 25°, λ = 255 nm.

Cahill and Taube⁵ have demonstrated that isotope fractionation studies of hydrogen peroxide reactions can be used to gain information about the mechanism. An initial 1-equiv step should yield a value of 1.00 for the fractionation factor, as defined by Cahill and Taube, and a value of 0.940 for an initial 2-equiv step. The value observed by Cahill and Taube for the Sn(II)-H₂O₂ reaction in hydrochloric acid was 0.943 indicative of a 2-equiv step.

The results of some fractionation experiments are shown in Table III. The values of the fractionation

TABLE III RESULTS OF ISOTOPIC FRACTIONATION EXPERIMENTS					
10 ³ [Sn(II)], M	10 ³ [H ₂ O ₂], M	10 ³ [Cu(II)], M	[HClO ₄], M	[HCl], M	Fractionation factor ^a
2.1	3.0	0.0	1.24	0.0	0.972
1.9	3.0	6.0	1.29	0.0	0.965
1.5	3.0	0.0	0.00	0.96	0.957

^a As defined in ref 3.

factors lie between those expected for a 1-equiv or a 2-equiv mechanism and suggest that both types of processes are operative. Our value obtained from HCl solutions does not agree with that reported by Cahill

and Taube. A brief series of kinetic experiments indicates that marked deviation from second-order behavior occurs in HCl solutions. Adherence to a second-order rate law should have been observed if the mechanism was a single, 2-equiv step.

Higginson has used the induced reduction of K₂Co(C₂O₄)₂ as a test for the presence of Sn(III) as an intermediate in the oxidation of Sn(II). In experiments where the initial concentration of the cobalt complex was about equal to the Sn(II) and H₂O₂ concentrations, no induced reduction of K₂Co(C₂O₄)₂ could be detected.

Conclusions and Summary

In perchlorate solutions the reaction between Sn(II) and H₂O₂ is complicated. Significant discrepancies in the apparent extent of reaction as determined by spectrophotometry compared to results obtained *via* quenching and titration techniques suggest the existence of a non-steady-state intermediate which absorbs in the wavelength region used to follow the disappearance of tin(II). The addition of Cu(II) ion appears to eliminate the reaction pathway giving rise to the intermediate, which probably is the result of a 1-equiv reduction of H₂O₂. However, even at high concentrations of Cu(II) ion the reaction still takes place and then obeys a second-order rate law which is consistent with a 2-equiv mechanism. It seems likely that the reaction takes place by parallel pathways involving 1- and 2-equivalent mechanisms. Isotope fractionation factors intermediate between those expected for the two mechanisms lend support to the dual nature of the mechanism.

Acknowledgment.—This work was supported by National Science Foundation Grant GP-13900.

REFERENCE 4.5

CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY,
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Acidity Measurements at Elevated Temperatures. VI. Boric Acid Equilibria¹

By R. E. MESMER,^{*} C. F. BAES, JR., AND F. H. SWEETON

Received May 17, 1971

Boric acid-borate equilibria have been studied by means of a hydrogen electrode concentration cell from 50 to 290°. The equilibrium in dilute boric acid solution, B(OH)₃ + OH⁻ = B(OH)₄⁻, was studied as a function of KCl concentration from 0.13 to 1.0 m. A small ionic strength (*I*) dependence of the equilibrium quotient (*Q*_{1,1}) was observed which decreases slightly with temperature. The pressure dependence of the equilibrium quotient is very small up to 2000 psi. Values of *Q*_{1,1} are given to better than 0.01 log unit by the expression

$$\log Q_{1,1} = \frac{1573.21}{T} + 28.6059 + 0.012078T - 13.2258 \log T + (0.3250 - 0.00033T)I - 0.0912I^{1/2}$$

for values of *I* from 0 to 1 m and *T* from 273 to 573°K. Results for more concentrated boric acid solutions (up to 0.6 m) in 1.0 m KCl have indicated the formation of the polynuclear species B₂(OH)₇⁻ and B₃(OH)₁₀⁻ and minor amounts of either B₄(OH)₁₃⁻ or B₅(OH)₁₆⁻. The trimeric species is needed to fit the data at all temperatures studied (and previous data at 25°). The dimeric species, which has not been reported previously, is indicated quite strongly by the present results at 200° while the need for a fourth (tetrameric or pentameric) species is indicated by the results at 50°. The two alternative schemes—B(OH)₃⁻, B₂(OH)₇⁻, B₃(OH)₁₀⁻, and B₄(OH)₁₃⁻ or B₅(OH)₁₆⁻—are both consistent with the data of Ingri at 25° and give as good a fit as the four-species scheme which he chose. Thermodynamic parameters have been derived for all the species in 1 m KCl and for B(OH)₃⁻ at infinite dilution.

Introduction

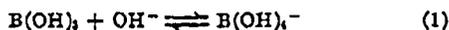
Boric acid-borate buffer mixtures serve as pH standards, occur in natural aqueous systems and in de-

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp.

tergent solutions, and are used as burnable nuclear poisons in the coolants of pressurized water nuclear reactors. It is not surprising, therefore, that the equilibria which occur in various aqueous solutions of boric acid and borate have been extensively studied,

although only at temperatures near room temperature. From the results it is clear that, in addition to the mononuclear boric acid and orthoborate ion, which have been well established by infrared and Raman spectroscopy²⁻⁵ to be trigonal $\text{B}(\text{OH})_3$ and tetrahedral $\text{B}(\text{OH})_4^-$ species, a number of polyborate ions also are formed.

Manov, *et al.*,⁷ and Owen⁸ have carried out careful measurements of the equilibrium



at boron concentrations as low as 0.01 *m* where interference from polyborates is insignificant. The two sets of measurements, both made over the temperature range 0–60° in cells without liquid junction and containing hydrogen and Ag–AgCl electrodes, are in excellent agreement. They also show that borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) reacts quickly in dilute solution to produce the mononuclear species in the equilibrium amounts.

The equilibria occurring in more concentrated boric acid–borate solutions have been carefully studied in several media by Ingri.^{9–13} The species formed appear to be as well established as can be expected considering the number which evidently are formed and the relatively large medium change which must be introduced in order to study them. Ingri found his extensive data to be most consistent with formation of the polymeric species $\text{B}_3(\text{OH})_{10}^-$, $\text{B}_3(\text{OH})_{11}^{2-}$, and $\text{B}_4(\text{OH})_{14}^{2-}$. Ingri also has shown by means of a "self-medium" study¹² that no species are formed with a hydroxide-to-boron ratio greater than 4 in the presence of as much as 0.1 *m* hydroxide. This demonstrates convincingly that the equilibrium constants given by Konopik and Leberl¹⁴ for dissociation of the second and third protons from boric acid (equivalent to the formation of $\text{B}(\text{OH})_4^{2-}$ and $\text{B}(\text{OH})_5^{3-}$) are much too high.

The recent work of Spessard¹⁵ on the derivation of equilibrium quotients for several assumed species from data up to 90° unfortunately does not contribute to the identification of the actual species present since the total boron concentration was not varied and his technique provided data of very limited accuracy. This latter point is illustrated by the poor agreement of his data with the more precise data of Owen and King³ in 3 *M* NaCl and the irregular variation of log *Q* with temperature for several of his assumed species in several of the media studied.

Information on the rates of formation of some of the

polyborates has been obtained by Anderson, *et al.*,¹⁶ and Osugi, *et al.*,¹⁷ using temperature-jump and pressure-jump techniques. They are in agreement and assign a rate constant of about $3 \times 10^3 \text{ M}^{-2} \text{ sec}^{-1}$ for the reaction



Momii and Nachtrieb¹⁸ found evidence for a slightly slower approach to equilibrium at concentrations of boron between 0.6 and 2.0 *M* at 25° in solutions made up from $\text{Na}_2\text{B}_4\text{O}_7$. Two separate ¹¹B resonance peaks with variable relative intensity were observed also by Onak, *et al.*¹⁹ The former authors interpreted their data in terms of equilibria involving pentaborate ion $\text{B}_5\text{O}_6(\text{OH})_4^-$ although no unique assignment could be made. Equilibria were attained in these studies during the time of mixing. All species in tetraborate solutions ($\text{M}_2\text{B}_4\text{O}_7$) exchange rapidly giving a single nmr line. The surprising observation of apparent slow changes in the infrared spectra of supersaturated boric acid–borate solutions reported by Valyashko and Vlasova²⁰ was not confirmed by Raman spectra and pH measurements taken by us over a 10-week period at 25° for solutions containing 0.6–0.3 *m* boron in boric acid–borate mixtures.

Because of the importance of borates in general and some of their uses which involve high temperatures, we have employed the high-temperature potentiometric techniques developed recently in this laboratory²¹ to examine the hydrolysis of boric acid. The results of such a study in dilute borate solutions should be especially useful in extending the temperature range of pH buffer mixtures and in estimating the pH and other chemical properties of nuclear reactor coolants. Results in more concentrated borate solutions at elevated temperatures should establish more firmly the identity of the polyborate species which are formed in aqueous solutions.

Experimental Section

Materials.—A stock solution of 3.3 *m* KCl prepared from J. T. Baker analyzed reagent was purified by acidifying to pH 3.5 and purging with N_2 to remove CO_2 . The fluoride content of the neutralized stock was $7 \times 10^{-4} \text{ m}$ as determined by the lanthanum fluoride electrode. The protolytic impurities in a 1 *m* solution made from the stock were ca. 10^{-4} m as determined by titration between pH values of 5 and 9.

The KOH solutions were prepared from KOH pellets and a small stoichiometric amount of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was added to precipitate the CO_3^{2-} present. The base solutions were stored in paraffin-lined vessels under hydrogen.

The boric acid solutions were prepared from reagent boric acid which had been recrystallized from water. The stock solution was standardized by titration in the presence of mannitol.

Ultrahigh-purity hydrogen (99.999%) from J. T. Baker was used throughout this study.

Potentiometric Apparatus and Techniques.—The pressure cell and electrode assembly employed for this work were described in detail in a previous paper.²¹ At the beginning of each experiment the air was removed from the cell by successively pressurizing with hydrogen to 500 psi and venting to the atmosphere. This cycle was repeated three times before addition of hydrogen

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(3) D. E. Bethell and N. Sheppard, *Trans. Faraday Soc.*, **51**, 9 (1955).

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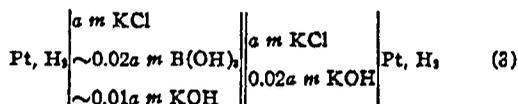
(21) R. E. Mesmer, C. F. Baes, Jr., and F. H. Sweeton, *J. Phys. Chem.*, **74**, 1037 (1970).

for the equilibration. In the titration experiments, the titrant was delivered from a Zircaloy vessel through platinum capillary tubing to the cell compartment by means of a pressure generator.

Corrections were applied to the data for the small amount of solvent in the gas phase at the higher temperatures. The correction was limited to less than 1% at 200° since the gas-to-liquid volume ratio was small in both compartments.

From the data of Byrnes²² on the distribution coefficient of boric acid between the aqueous and gas phases, the amount in the gas phase under any of the conditions of the present measurements is expected to be <0.1%. This was verified by analysis of the gas phase over a 1 m boric acid solution in 1 m KCl at 248°.

Potentiometric Measurements.—The cell representation for experiments conducted in dilute boric acid solutions (< 0.02 m) is



The electrode compartment on the right contains the reference electrode. In these experiments the concentration of KCl was varied from 0.13 to 1 m, and the KOH concentration was generally kept at about 1/10th of the KCl concentration. The solution on the left contains boric acid and KOH in an approximate ratio of 2:1. The emf was observed as a function of temperature. The resulting values of the equilibrium quotient for reaction 1 ($Q_{1,1}$) are summarized in Table I and Figure 1, wherein

TABLE I
DATA FOR LOG $Q_{1,1}$ AS A FUNCTION OF TEMPERATURE AND IONIC STRENGTH IN KCl SOLUTIONS*

t, °C	I	m _B	n	log Q _{1,1}	log Q _{1,1}
99.90	1.02	0.01992	0.873	2.423	0.009
100.42	1.01	0.01994	0.752	2.722	0.008
202.22	1.02	0.01994	0.815	2.344	0.008
230.44	1.02	0.02004	0.714	2.234	0.008
290.02	1.02	0.02009	0.650	1.967	0.008
30.34	1.02	0.01999	0.901	4.254	0.008
100.42	1.02	0.02009	0.882	4.212	0.004
150.77	1.02	0.02001	0.840	2.791	0.004
202.11	1.02	0.02000	0.734	2.344	0.003
236.24	1.02	0.02009	0.598	2.011	0.003
49.54	0.51	0.01000	0.904	4.270	0.005
99.60	0.51	0.01006	0.847	3.349	0.004
150.12	0.51	0.01001	0.791	2.759	0.003
200.25	0.51	0.01003	0.709	2.730	0.003
30.34	0.51	0.01000	0.936	4.260	0.003
99.60	0.51	0.01006	0.879	3.307	0.004
150.12	0.51	0.01001	0.791	2.759	0.003
200.25	0.51	0.01003	0.709	2.730	0.003
236.24	0.51	0.01006	0.577	2.022	0.007
290.25	0.51	0.01007	0.516	1.944	0.007
49.79	0.264	0.01002	0.879	4.224	0.003
99.65	0.264	0.01002	0.817	3.219	0.003
150.12	0.264	0.01003	0.779	2.720	0.003
200.42	0.264	0.01000	0.742	2.293	0.004
236.24	0.264	0.01006	0.676	2.002	0.007
290.42	0.264	0.01009	0.612	1.824	0.008
30.19	0.264	0.01002	0.879	4.226	0.003
99.20	0.264	0.01003	0.797	3.259	0.003
149.39	0.264	0.01001	0.779	2.720	0.003
200.25	0.264	0.01003	0.671	2.291	0.006
231.06	0.264	0.01007	0.572	1.991	0.004
50.54	0.129	0.01203	0.918	4.201	0.004
99.25	0.129	0.01203	0.772	3.240	0.004
149.42	0.129	0.01204	0.723	2.721	0.003
199.57	0.129	0.01200	0.672	2.290	0.003
235.42	0.129	0.01209	0.594	1.995	0.004
290.08	0.129	0.01210	0.512	1.820	0.007
49.29	0.129	0.004239	0.879	4.224	0.003
99.27	0.129	0.004462	0.739	3.241	0.003
150.24	0.129	0.004614	0.592	2.715	0.007
190.23	0.129	0.004824	0.507	2.304	0.008
231.20	0.129	0.004967	0.396	2.006	0.010

* $Q_{1,1}$ is the molal equilibrium quotient for reaction 1, I is the ionic strength, m_B is the boron molality, and n is the number of OH⁻ ions bound per B(OH)₃ group in solution.

I is the ionic strength, m_B is the total boron molality, and n is the ligand number, i.e., the number of OH⁻ ions bound per B(OH)₃ group in solution.

At higher concentrations of boron (0.02–0.8 m), where the objective was to determine the species present, titration experiments were conducted in which the KCl concentration was kept at 1.0 m and the amount of base added was limited arbitrarily to about 8% of the KCl concentration. Some medium change is inherent in such studies where the equilibria can be observed only at relatively high concentrations. Data were obtained from titrations at 80.3, 100.0, and 199.8°. These results are summarized in Table II and Figure 2.

(22) D. E. Byrnes, "Some Physicochemical Studies of Boric Acid Solutions at High Temperatures," Report No. 3713, Westinghouse Corp., Atomic Power Division, 1962.

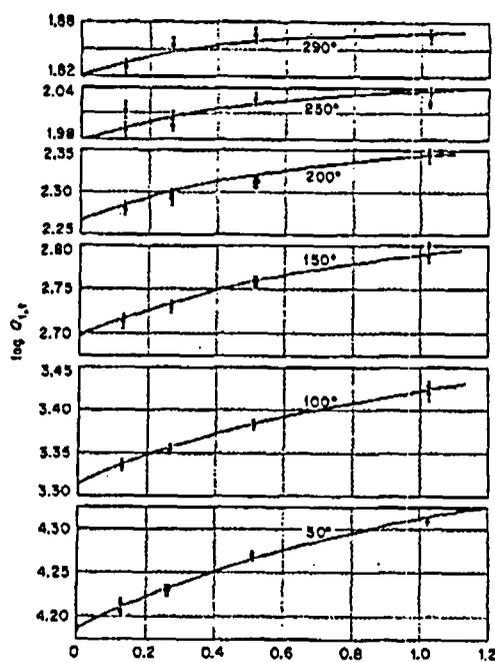


Figure 1.—Log $Q_{1,1}$ as a function of ionic strength. The curves were drawn using the equation in Table III. The dark rectangle at the intercept at 50° is taken from the data of ref. 7.

TABLE II
POTENTIOMETRIC DATA ON BORIC ACID SOLUTIONS IN 1 m KCl*

I × 10	m _B × 10	50.3°			100.0°			199.8°		
		-log[OH ⁻]	n	m _B × 10	-log[OH ⁻]	n	m _B × 10	-log[OH ⁻]	n	m _B × 10
0.0021	0.2486	7.730	0.0032	0.2433	6.341	0.0092	0.3201	6.519		
0.251	0.2682	7.799	1.203	0.2423	4.222	0.007	0.3299	4.242		
1.645	0.2616	7.519	2.212	0.2413	2.999	0.041	0.3167	2.492		
3.361	0.2632	4.490	2.466	0.2400	2.791	0.218	0.3269	2.100		
3.969	0.2629	4.474	4.846	0.2387	2.448	1.228	0.3221	2.866		
2.244	0.2634	4.244	6.126	0.2374	2.227	1.227	0.3222	2.692		
4.363	0.2609	4.205	7.285	0.2362	2.012	1.874	0.3222	2.598		
7.749	0.2595	2.722	8.507	0.2348	2.722	4.899	0.3190	2.205		
9.545	0.2581	2.261	9.806	0.2335	2.490	3.780	0.3164	2.205		
9.900	0.2565	2.768	9.223	0.2321	2.181	4.722	0.3111	2.023		
9.972	0.2552	2.240	9.722	0.2308	1.971	2.123	0.3098	1.874		
10.01	0.2538	2.124	9.218	0.2294	1.772	2.035	0.3052	1.692		
10.21	0.2520	1.923	0.0015	1.0000	7.200	0.877	0.2997	1.824		
9.94	0.2493	1.741	0.322	0.9913	5.011	0.739	0.2922	1.428		
0.0020	1.0001	4.448	0.649	0.9960	4.682	0.000	1.0048	2.368		
0.130	0.9979	6.922	1.299	0.9791	4.226	0.191	1.0020	4.137		
0.491	0.9920	5.728	2.928	0.9510	2.915	0.470	0.9964	2.821		
1.133	0.9816	3.202	3.292	0.9194	2.626	0.948	0.9880	3.242		
1.940	0.9688	4.917	3.177	0.9203	2.269	1.472	0.9794	1.820		
2.017	0.9519	4.644	4.647	0.9022	2.127	2.079	0.9691	2.940		
4.042	0.9387	4.411	7.729	0.8800	2.776	3.080	0.9280	2.786		
3.117	0.9214	4.342	6.790	0.8622	2.207	2.022	0.9049	1.823		
6.277	0.9044	4.018	5.370	0.8461	2.187	4.227	0.9124	2.463		
7.347	0.8921	3.008	5.394	0.8473	1.970	3.263	0.9140	2.259		
9.126	0.8806	2.290	9.711	0.8327	1.750	5.510	0.9019	2.028		
9.519	0.8687	1.125	0.0010	1.976	7.194	7.397	0.9728	1.844		
9.753	0.8577	2.722	0.0010	1.976	7.194	7.397	0.9728	1.844		
9.861	0.8460	2.222	0.990	1.972	5.720	0.822	0.9649	1.823		
9.994	0.8393	1.908	0.263	1.961	5.247	0.000	0.9524	1.516		
0.0017	1.977	8.212	1.063	1.911	4.227	0.872	1.982	4.610		
0.0011	1.971	6.992	1.820	1.877	4.267	0.709	1.949	4.022		
0.239	1.959	6.227	2.210	1.844	4.066	0.324	1.923	3.721		
0.816	1.949	5.022	2.824	1.809	2.828	0.712	1.927	2.648		
1.020	1.912	2.222	3.294	1.779	2.743	1.409	1.906	2.212		
1.820	1.882	2.228	3.920	1.750	2.614	1.908	1.886	2.042		
2.210	1.868	2.204	4.215	1.719	2.464	2.293	1.857	2.002		
2.764	1.819	4.812	4.120	1.691	2.368	2.923	1.807	2.723		
3.244	1.766	6.664	2.120	1.661	2.268	3.923	1.807	2.723		
3.827	1.736	4.213	0.0014	2.844	2.391	3.291	1.780	2.661		
4.424	1.724	4.260	0.042	2.825	4.403	4.499	1.719	2.424		
4.997	1.697	4.227	0.126	2.812	3.866	5.030	1.699	2.327		
5.554	1.672	4.118	0.262	2.782	2.408	5.030	1.699	2.327		
6.087	1.647	9.014	0.621	2.899	0.272	0.000	3.862	6.088		
6.641	1.613	7.558	0.826	2.829	4.846	0.950	3.810	4.943		
6.922	1.590	6.859	1.162	2.879	4.663	0.390	3.808	4.277		
6.621	1.562	6.415	1.416	2.822	4.216	0.442	3.814	3.923		
6.722	1.529	6.045	1.710	2.664	4.508	0.707	3.693	3.741		
1.079	1.596	5.772	2.012	2.466	4.237	0.992	3.618	2.210		
1.611	1.515	5.244	2.327	2.344	4.109	1.374	3.617	3.349		
1.763	1.433	5.140	2.701	2.278	0.976	1.226	3.212	3.212		
2.120	1.384	5.160	0.0022	0.940	0.022	0.822	3.212	3.112		
2.424	1.320	5.099	0.029	0.923	0.907	2.717	3.279	2.847		
2.904	1.258	4.844	0.245	0.909	0.806	0.001	3.664	4.644		
0.0020	1.236	9.215	0.422	0.700	5.266	0.020	3.918	4.609		
0.022	1.217	8.122	0.606	3.604	0.226	0.127	3.891	4.794		
0.120	1.261	7.480	0.794	3.207	1.144	0.209	3.790	4.241		
0.492	1.265	6.648	1.194	3.412	0.976	0.461	3.679	4.092		
0.974	1.216	6.121	1.465	3.214	0.820	0.651	3.602	3.912		
1.192	1.209	5.928	1.624	3.117	0.646	0.842	3.503	3.757		
1.419	1.209	5.722	1.826	3.026	0.429	1.109	3.283	3.670		
1.620	1.112	5.594	1.926	2.926	0.226	1.311	3.183	3.523		
						1.522	3.082	3.249		

* n is the ligand number and m_B is the boron molality.

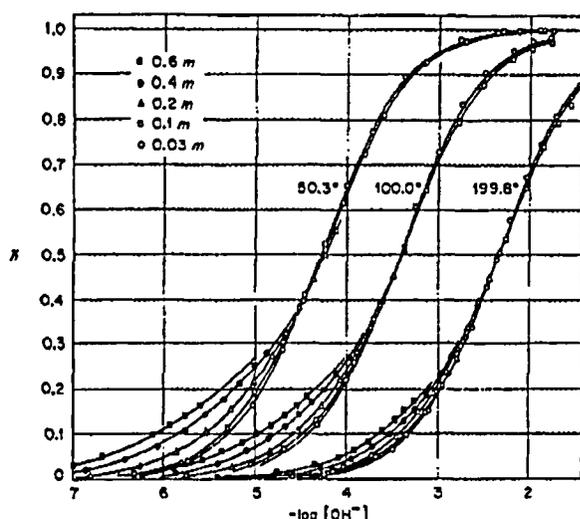


Figure 2.—The effect of boron concentration and temperature on the hydrolysis of boric acid in 1 *M* KCl. The approximate boron concentrations are listed above and the curves were calculated from the equilibrium quotients given by scheme II in Table VI.

Data Reduction and Analyses.—The potentials *E* for the cell (3) are given by the expression²¹

$$E = (RT/F) \ln ([OH^-]/[OH^-]_r) - D_{OH}([OH^-]_r - [OH^-]) - zD_i([i]_r - [i]) \quad (4)$$

where [OH] and [i] denote, respectively, the concentration of hydroxide ion and of each other ionic species in the solution. The subscript *r* refers to the reference solution.

The liquid junction potential is given by the terms on the right containing *D*_{OH} and *D*_{*i*} which are calculated from the Henderson equation.²¹ The limiting equivalent conductances at high temperatures needed for the calculation of *D*_{OH} and *D*_{*i*} were obtained from Quist and Marshall.²³ Also the approximation that the equivalent conductance of B(OH)₃ equals that of Cl⁻ was used, with a large allowance (20%) for error from this assumption in the error analysis. The differences ([OH⁻]_r - [OH⁻]) and ([i]_r - [i]) were all small compared to the ionic strength and as a result the maximum liquid junction potentials were about 1 mV.

The data were analyzed and interpreted according to the treatment presented previously for similar studies²⁴ but here in terms of the average number of OH⁻ ions, \bar{n} , bound to a central moiety (B(OH)₃). This was derived from the data using eq 5

$$\bar{n} = ([H^+] + m_{OH} - [OH^-])/m_B \quad (5)$$

where *m*_{OH} and *m*_B are the stoichiometric concentrations of base and boron in solution. The OH⁻ concentration in the solution was obtained by a reiterative solution of eq 4. The H⁺ concentration, usually a small or negligible contribution to \bar{n} , was then obtained from the estimated value of the dissociation quotient for water.²¹

For the evaluation of *Q*_{1,1} from dilute boric acid experiments (Table I) the following relationship was used

$$\log Q_{1,1} = \log \left[\frac{\bar{n}}{(1 - \bar{n})[OH^-]} \right] \quad (6)$$

The error introduced by neglect of small amounts of polymers on this calculation of the value of log *Q*_{1,1} was less than the assigned experimental errors in Table I.

The analysis of the data from more concentrated boron solutions in terms of polymeric species was performed by the usual procedure: (1) A set of equilibria



was chosen, corresponding to a scheme of hydrolysis products. (2) Trial values of the corresponding equilibrium quotients

(23) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **69**, 2984 (1965).

(24) C. F. Baes, Jr., N. J. Meyer, and C. E. Roberts, *Inorg. Chem.*, **4**, 518 (1965); R. E. Mesmer and C. F. Baes, Jr., *ibid.*, **6**, 1951 (1967).

*Q*_{*z,y*} were used to calculate a value of \bar{n} for each data point by means of the expression

$$\bar{n}_c = (\sum y Q_{z,y} [B(OH)_3]^z [OH^-]^y) / m_B \quad (8)$$

wherein the free boric acid concentration was obtained by reiterative solution of the material balance expression

$$[B(OH)_3] = m_B - \sum z x Q_{z,y} [B(OH)_3]^z [OH^-]^y \quad (9)$$

(3) The *Q*_{*z,y*} values were adjusted until the best agreement was obtained between calculated and observed \bar{n} values for all the data. As will be described in the Discussion, a scheme was sought containing a minimum number of species B_{*z*}(OH)_{*3z+y*}^{*y-*} which gives a satisfactory fit to the data.

Weighting of Data.—The data used in the least-squares analyses were weighted according to the assigned experimental errors. Estimated errors were assigned to 17 independently measured quantities involved in solution makeup and in volume, potentiometric, and temperature measurements. The effect of these errors on the quantity ($\bar{n} - \bar{n}_c$) for each data point was obtained by numerical differentiation. Weights (*W*) were then obtained for use in the least-squares procedure by summing all 17 variances which could then be calculated to obtain the variance in ($\bar{n} - \bar{n}_c$) for each point.

The agreement factor defined in eq 10 was then used as the criterion for the schemes tested. The weight *W* is the reciprocal

$$\sigma(\bar{n}) = [\sum (W(\bar{n} - \bar{n}_c)^2) / (N_o - N_v)]^{1/2} \quad (10)$$

of the variance for the data point and (*N*_o - *N*_v) is the difference in the number of observations and the number of variables. The $\sigma(\bar{n})$ should be unity when the weights are accurately set and the data fit the model exactly.

Discussion

B(OH)₃-B(OH)₃⁻ Equilibrium.—Figure 1 shows the dependence of log *Q*_{1,1} for equilibrium 1 on *I* up to an ionic strength of unity at rounded temperatures.²⁵ The equilibrium quotient has a small dependence on ionic strength and this dependence decreases as the temperature increases.

A relatively small dependence of the equilibrium quotient on ionic strength was expected since it depends only on the ratio $\gamma_{OH^-} / \gamma_{B(OH)_3^-}$. For this ratio we have elected to use the two-term expression

$$\log (\gamma_{OH^-} / \gamma_{B(OH)_3^-}) = aI + bI^{1/2} \quad (11)$$

This simple relationship results when the usual Debye-Hückel expression for this ratio is expanded as a power series in *I*.²⁶ This expression is not to be construed as a uniquely significant form but simply an adequate description of the data.

A complete analysis of the temperature dependence of the log *Q*_{1,1} requires a knowledge of the pressure coefficient of the equilibrium quotient since the total pressure in these experiments varies from about 500 to 1900 psi. By experiment it was found that within the experimental error of the measurements (~0.004 unit in log *Q*) there was no effect of a change of 1300 psi at 50° and 1400 psi at 200°. The upper limit for the absolute magnitude of ΔV for the reaction based on these data is 3-4 cm³/mol. The pressure coefficient is therefore not a factor in setting the standard state for reaction 1 when expressing thermodynamic quantities at pressures below about 150 atm.

Table III shows the least-squares results of analyses

(25) The small correction for temperature (less than 2°) was made by fitting the data at a given ionic strength to the expression $\log Q_{1,1} = -A/T + B + CT - D \log T$ and then using the derivative ($d \log Q/d(1/T)$) to calculate the correction in log *Q*_{1,1}.

(26) If the ionic strength dependence for the activity coefficient of each ion has the form $\log \gamma_i = -a_i I^{1/2} / (1 + \beta_i I^{1/2}) + c_i$ from Debye-Hückel theory and if β and *c* are different for the two ions by $\Delta\beta$ and Δc , then $\log (\gamma_{OH^-} / \gamma_{B(OH)_3^-}) = (\Delta c - \alpha \Delta\beta)I + (2\alpha\beta\Delta\beta + \alpha\Delta\beta^2)I^{3/2} + \dots$

TABLE III
FITS TO THE $Q_{1,1}$ DATA OBTAINED WITH SEVERAL ASSUMPTIONS
FOR THE FORM OF THE TEMPERATURE DEPENDENCE

Case	ΔC_p	I	Agreement factor
1	c	$(i_1 + i_2 T)I + i_3 I^{1/2}$	2.02
2	cT	$(i_1 + i_2 T)I + i_3 I^{1/2}$	1.96
3*	$c_1 + c_2 T$	$(i_1 + i_2 T)I + i_3 I^{1/2}$	0.97
4	$c_1 + c_2 T$	$i_4 I + i_5 I^{1/2}$	1.78

* Case 3 gives $\log Q_{1,1} = 1573.21/T + 28.8059 + 0.012078T - 13.2258 \log T + (0.3250 - 0.00033T)I - 0.0912I^{1/2}$.

according to several assumptions for the form of the temperature dependence ΔC_p , and for the temperature dependence of the ionic strength terms. The agreement factors (from eq 10) shown are in terms of the estimated experimental error in $\log Q$. Case 3, where the ΔC_p is given linear dependence on temperature and one of the ionic strength terms is made temperature dependent, gives a satisfactory fit to the data. The other cases give poorer fits with pronounced systematic deviations.

Thermodynamic Quantities at Infinite Dilution.—The thermodynamic quantities (Table IV) for reaction 1

TABLE IV
THERMODYNAMIC PARAMETERS AT INFINITE
DILUTION DERIVED FOR THE EQUILIBRIUM*

Temp. °C	ΔH° , kcal mol ⁻¹	ΔS° , cal deg ⁻¹ mol ⁻¹	ΔC_p° , cal deg ⁻¹ mol ⁻¹
0	-10.25 ± 0.13	-12.85 ± 0.46	3.9 ± 2.6
25	-10.12 ± 0.08	-12.13 ± 0.27	6.7 ± 2.1
50	-9.92 ± 0.05	-11.54 ± 0.16	9.4 ± 1.6
75	-9.65 ± 0.05	-10.73 ± 0.13	12.2 ± 1.2
100	-9.31 ± 0.05	-9.79 ± 0.14	15.0 ± 0.8
125	-8.90 ± 0.06	-8.73 ± 0.15	17.7 ± 0.7
150	-8.42 ± 0.06	-7.57 ± 0.16	20.5 ± 0.8
175	-7.88 ± 0.06	-6.32 ± 0.18	23.3 ± 1.2
200	-7.28 ± 0.08	-4.98 ± 0.18	26.0 ± 1.6
225	-6.58 ± 0.11	-3.57 ± 0.23	28.8 ± 2.1
250	-5.82 ± 0.15	-2.09 ± 0.32	31.5 ± 2.6
275	-5.00 ± 0.22	-0.58 ± 0.43	34.3 ± 3.0
300	-4.11 ± 0.29	1.04 ± 0.58	37.7 ± 3.5

* The uncertainties listed correspond to 3σ , wherein σ is based on the fit obtained with the expression in Table III, derived from case 3.

were derived from the values of $Q_{1,1}$ at $I = 0$ (i.e., the equilibrium constant $K_{1,1}$) as given by the expression from case 3 in Table III. The uncertainties are three standard deviations as calculated from the experimental errors assigned to individual determinations of $\log Q_{1,1}$. This should allow for any systematic errors in the derived thermodynamic quantities introduced by the restriction that ΔC_p changes linearly with temperature.

The value of ΔH°_{298} in Table IV is -10.12 ± 0.08 kcal mol⁻¹. Although there have been no precision calorimetric measurements of this quantity, Harries²⁷ has recently reported the nearly identical value of -10.2 ± 0.2 kcal mol⁻¹ based on a thermometric titration procedure. As is general for weak acids this heat is less than the heat of neutralization of a strong acid (-13.34 kcal mol⁻¹).²⁸ The formation of borate is opposed by the ΔS° and favored by the ΔH° . Since the addition of an OH⁻ ion to boric acid does not lead to a charge neutralization whereas the neutralization of the hydronium ion does, this probably accounts for

(27) R. J. N. Harries, *Talanta*, **8**, 1345 (1961).

(28) C. B. Vandervee and J. A. Swanson, *J. Phys. Chem.*, **67**, 2608 (1963).

the much more negative value of the ΔS for the former reaction compared to the latter (-12.2 vs. 19.3 cal deg⁻¹ mol⁻¹). The ΔC_p values calculated for reaction 1 using the expression from case 3, Table III, change from 3.9 cal deg⁻¹ mol⁻¹ at 0° to 37.7 cal deg⁻¹ mol⁻¹ at 300° .

Polyborate Equilibria.—That polyborates do exist in aqueous solutions is clearly evident in Figure 2 from the dependence of the n vs. $-\log [\text{OH}^-]$ curves on boron concentration above about 0.03 *m* at each of the three temperatures shown. This was also shown by the previous work at 25° and especially by the extensive work of Ingri in a number of different salt media. Trends with increasing temperature can be seen (Figure 2) in the shift of equilibria to higher hydroxide concentrations and also in the decreasing spread of the curves with boron concentration; these reflect a decreasing amount of polymerization.

The principal species which have been invoked by Ingri in analysis of his data are $\text{B}(\text{OH})_4^-$, $\text{B}_2\text{O}_2(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_6^{2-}$, and $\text{B}_4\text{O}_4(\text{OH})_8^{3-}$. In discussing such species we will use the notation (x,y) to represent the species according to the formula $\text{B}_x(\text{OH})_{x+y}^{y-}$. Hence, the polyborate species of Ingri become $(3,1)\text{-B}_3(\text{OH})_{10}^-$, $(3,2)\text{-B}_3(\text{OH})_{11}^{2-}$, and $(4,2)\text{-B}_4(\text{OH})_{14}^{3-}$. Of course, since no information can be derived from potentiometric studies alone regarding the hydration of such species, it is optional whether one writes $\text{B}_2\text{O}_2(\text{OH})_4^-$ or $\text{B}_2(\text{OH})_{10}^-$, etc.

Because the present data are of a precision comparable to that of Ingri and, in particular, because they cover a wide temperature range, it should be possible to test rather sensitively for the best scheme of polyborate species. By "best scheme" we mean the simplest scheme consistent with all the data. If such a scheme involves a sufficiently small number of species, it is likely to be the correct one, since an incorrect scheme with the same small number of species is not likely to fit data covering a wide range of conditions. In short, the simplest consistent scheme has the best chance of being the correct one.

The data of Ingri at 25° and our own data indicate that the maximum value of n is 1 and hence that no species exists which has a y/x ratio greater than unity. In addition, Ingri's self-medium study at very high concentrations of boron (2.5 *M*) show that at $n > 0.9$ the predominant polyborate species has an $x - y$ difference of 2.0.

Applying these constraints we have limited our analysis to the following array of 14 possible polymeric species: $(x,y) = (2,0), (2,1), (2,2); (3,0), (3,1), (3,2), (3,3); (4,0), (4,1), (4,2), (4,3); (5,1), (5,2), (5,3)$. In each scheme tested we have, of course, included $\text{B}(\text{OH})_4^-$, $(1,1)$, which has been well established as the only mononuclear borate species by the data in dilute solutions.

Least-squares analyses of the data at 50° , wherein we assumed that only one polymeric species was formed, not surprisingly failed in every case to give a satisfactory fit, thus indicating agreement with Ingri that at least two polymeric species are formed.

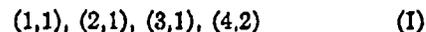
Least-squares analyses were next performed for all the possible pairs from the above array with the data at each of the three temperatures. The results as represented by the agreement factors for the four best

TABLE V
FIT OF THREE-SPECIES MODELS EACH
INCLUDING THE (1,1) AND (3,1) SPECIES ALONG WITH A THIRD

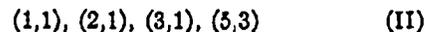
Third species (x,y)	$\sigma(A)$			Third species (x,y)	$\sigma(A)$		
	50.3°	100.0°	199.8°		50.3°	100.0°	199.8°
2,1	2.66	1.60	1.44	4,2	2.37	2.18	2.48
3,2	2.02	1.92	2.12	5,3	1.96	2.19	2.56

schemes are shown at each temperature in Table V. The important outcome of this analysis is that the (3,1) species is common to all the best schemes and that at the higher temperatures the (2,1) gives a much better fit as the second polymeric species than does any of the other three species ((4,2), (3,2), and (5,3)). At the lowest temperature, 50.3°, each of the last three species gives a significantly better fit than does the (2,1) species.

of the present data should be in terms of the scheme



or the scheme



wherein we expect that the fourth species will be minor at the higher temperatures while the second species will be minor at the lower temperatures.

This expectation is borne out by the least-squares analysis in terms of schemes I and II given in Table VI. The relative importance of each species in fitting the data may be judged by the uncertainty generated for its stability constant. It is noteworthy that the contributions of the (4,2) and the (5,3) species are so similar that replacement of one by the other has no

TABLE VI
LOG $Q_{s,v}$ VALUES FROM DATA IN 1 M KCl

	25°	50.3°	100.0°	199.8°
Scheme I				
1,1	5.278 ± 0.004	4.301 ± 0.004	3.428 ± 0.002	2.332 ± 0.002
2,1	5.95 ± 0.06	3.8 ± 0.4	3.45 ± 0.06	2.47 ± 0.04
3,1	7.319 ± 0.002	5.98 ± 0.01	4.707 ± 0.008	2.98 ± 0.04
4,2	13.29 ± 0.07	10.75 ± 0.11	8.1 ± 0.2	5.2 ± 0.6
$\sigma(A)$		2.38	1.55	1.45
Scheme II				
1,1	5.279 ± 0.003	4.296 ± 0.003	3.427 ± 0.002	2.332 ± 0.002
2,1	6.02 ± 0.04	3.7 ± 0.4	3.43 ± 0.05	2.47 ± 0.04
3,1	7.378 ± 0.003	5.997 ± 0.008	4.712 ± 0.008	2.98 ± 0.04
5,3	19.20 ± 0.08	16.43 ± 0.07	12.9 ± 0.1	8.6 ± 0.5
$\sigma(A)$		1.95	1.47	1.45

Analytical Expressions

$$\log Q_{1,1}^d = \frac{1573.21}{T} + 28.8397 + 0.011748T - 13.2258 \log T$$

$$\log Q_{2,1}^d = \frac{2756.1}{T} - 18.966 + 5.835 \log T$$

$$\log Q_{3,1}^d = \frac{3339.5}{T} - 8.084 + 1.497 \log T$$

$$\log Q_{4,2}^d = \frac{12820}{T} - 134.56 + 42.105 \log T$$

$$\log Q_{5,3}^d = \frac{14099}{T} - 118.115 + 36.237 \log T$$

* These values are derived from Ingri in 3 M NaClO₄. Because of the difference in medium, these quotients are not included in the derivation of the analytical expressions. ^b Based on data from Tables I and II. ^c Based on scheme I. ^d Based on scheme II.

The conclusion to be drawn from this analysis then is that while two polymeric species can account for the data at a single temperature, quite clearly more than two are required to account for all the data. Moreover, the identity of the correct species at the highest temperature seems quite clear in view of the uniquely good fit given by the scheme (1,1), (2,1), (3,1). At 50°, however, an additional polymeric species evidently becomes important while the (2,1) species becomes less important. Since it is known from Ingri's "self-medium" results that a polymeric species is formed at high \bar{n} values in which the difference $x - y$ equals 2.0, it is not surprising that improved fits to the lower temperature data are obtained when the (4,2) or the (5,3) species replaces the (2,1) species. Thus it seems clear that the best overall interpretation

significant effect on the formation quotients of the other species.

Schemes I and II were also used to fit Ingri's unweighted data in 3 M NaClO₄ at 25°. Both schemes I and II were found to give fits as good as Ingri's—(1,1), (3,1), (3,2), and (4,2). The values for log $Q_{s,v}$, however, are somewhat higher than expected based on our results in the chloride medium. Regarding the question of which one of these alternative four-species schemes is the correct one, we believe that scheme I or II is a better choice than Ingri's scheme because each is consistent with all the present data and Ingri's is not.

The analytical expression for the temperature dependence of the log $Q_{s,v}$ for each species is also given in Table VI. Thermodynamic parameters calculated

from these expressions at 298°K are given in Table VII (uncertainties are 1σ). The variations of the polymer distribution with concentration of boron and with temperature are shown in Figure 3 at 50 and 200°.

TABLE VII
THERMODYNAMIC QUANTITIES FOR BORATE EQUILIBRIA AT
298° IN 1 M KCl

$x\text{B}(\text{OH})_3 + y\text{OH}^- \rightleftharpoons \text{B}_x(\text{OH})_{3x+y}^{y-}$					
x,y	ΔH_{298}° , kcal mol ⁻¹	ΔS_{298}° , eu	x,y	ΔH_{298}° , kcal mol ⁻¹	ΔS_{298}° , eu
1,1	-10.3 ± 0.2	-12.0 ± 0.6	4,2	-34 ± 6	-55 ± 19
2,1	-9.2 ± 1	-9.1 ± 3	5,3	-43 ± 4	-58 ± 14
3,1	-14.4 ± 0.3	-17.1 ± 1			

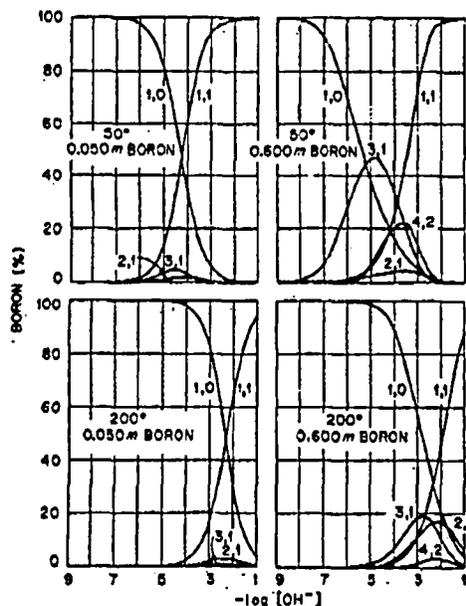
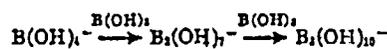


Figure 3.—Distribution of species calculated for solutions containing 0.05 and 0.60 M boron at 50 and 200°. The species are represented by the notation (x,y) for the formula $\text{B}_x(\text{OH})_{3x+y}^{y-}$.

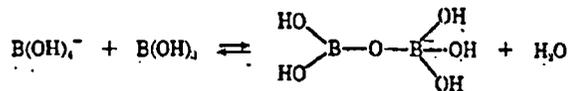
As the temperature increases, there is a decrease in the amount of polyborates at a given boron concentration and β value, as was evidenced by the reduction in spread of the curves in Figure 2.

Stability of Polyborates.—The reality of the species $\text{B}(\text{OH})_4^-$ can scarcely be doubted in view of the extensive data here, as well as elsewhere, which support equilibrium 1. The reality of the (3,1) species, while somewhat less certain, is nonetheless highly probable since it was found in all the better schemes at all temperatures in the present study and had previously been proposed by Ingri to interpret his data at 25°. The (2,1) species also seems highly probable in view of the fact that it, along with the (1,1) and the (3,1) species, is uniquely sufficient to explain the present data above 100°. The identity of the fourth species (e.g., (4,2) or (5,3)) is relatively much less certain.

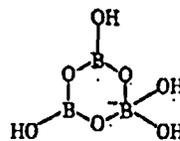
While the sequence of the first two polynuclear species might suggest the successive addition of $\text{B}(\text{OH})_3$ groups to the orthoborate ion



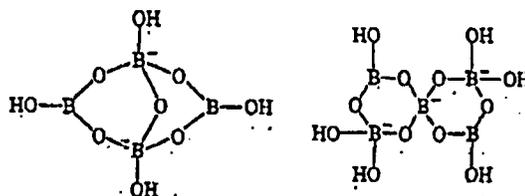
by -OH- bridging, the positive ΔS associated with the first step (2.9 ± 3 eu from Table VII) is in contrast to the negative ΔS associated with the combination of OH^- ion and $\text{B}(\text{OH})_3$ (-12.0 ± 0.9 eu) and hence would seem more consistent with the formation of an -O- bridge



since this is accompanied by the additional entropy contributed by the molecule of water liberated. Moreover, the triborate species is more stable than would be predicted from the stability of the dimer if a stepwise addition process were all that was occurring. This stability of the trimer led Ingri to suggest that it has the ring structure



Such a structure is consistent with the following rules proposed by Edwards and Ross¹⁹ for the structures of crystalline hydrated polyborates. (i) Boron atoms exist in threefold and fourfold coordination, the former having a neutral charge and the latter a 1- charge. (ii) The basic structure of the polyborates is a six-membered ring with alternate boron and oxygen atoms. (iii) To be stable the ring must contain one or two tetrahedral boron atoms. (iv) Other discrete anions may be formed by the fusion of two rings at a tetrahedral boron atom. (v) Long-chain polyanions may be formed from the rings by repeated dehydration. When applied to the polyborate ions which appear to exist in aqueous solution, these rules lead to the above structures for the dimer and trimer and to the following structures for the remaining alternative species



Finally, rule (iii) is consistent with the absence of a cyclic trimer of boric acid ($\text{B}_3\text{O}_3(\text{OH})_3$) in aqueous solution.

(19) J. O. Edwards and V. Ross, *J. Inorg. Nucl. Chem.*, 18, 229 (1960).

ENCLOSURE 3

LIST OF COMMITMENTS

SUMMARY OF AMERGEN COMMITMENTS

The following table identifies regulatory commitments made in this document by AmerGen. (Any other actions discussed in the submittal represent intended or planned actions by AmerGen. They are described to the NRC for the NRC's information and are not regulatory commitments.)

COMMITMENT	COMMITTED DATE OR "OUTAGE"	COMMITMENT TYPE	
		ONE-TIME ACTION (Yes/No)	PROGRAMMATIC (Yes/No)
The elements and methodology of the proposed TS Table 4.1-5, Item 2.b surveillance testing will be clearly delineated in station surveillance procedures.	Upon implementation of amendment.	No	Yes
Procedures will ensure that samples are taken within the basket at both interior and peripheral locations to obtain a representative sample.	Upon implementation of amendment.	No	Yes
Use of the WCAP 16530-NP model is being considered, and if utilized, this issue (ref Q.9) will be addressed in the TMI Unit 1 Generic Letter 2004-02 response.	Upon implementation of amendment.	Yes	No