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~~UC-80 Reactor Technology~~
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THE CALCULATED pH OF AQUEOUS
BORIC ACID SOLUTIONS
AS A FUNCTION OF TEMPERATURE AND
ADDED BASE CONTENT

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Chemical Development

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Table of Contents

	<u>Page</u>
List of Figures	iii
Abstract	v
Introduction	1
Derivation of Equations	1
Use of Figures	3
Appendix I - Fortran Program	26
Appendix II - Data Used in Computations	27

LIST OF FIGURES

<u>Figure Number</u>	<u>Title</u>	<u>Page Number</u>
1	Computer Program Flow Diagram	6
2	Ionization Constants (K_w , K_{11} , and K_{13}) as a Function of Temperature	7
3	Ionization Constants of Weak Bases (K_{LiOH} , K_{NH_4OH}) as a Function of Temperature	8
4	pH as a Function of Total Nitrogen Concen- tration and Total Boron Concentration at 75°F	9
5	pH as a Function of Total Nitrogen Concen- tration and Total Boron Concentration at 400°F	10
6	pH as a Function of Total Nitrogen Concen- tration and Total Boron Concentration at 500°F	11
7	pH as a Function of Total Nitrogen Concen- tration and Total Boron Concentration at 530°F	12
8	pH as a Function of Total Nitrogen Concen- tration and Total Boron Concentration at 572°F	13
9	pH Versus Total Boron Concentration at Various Total Nitrogen Concentrations at 530°F	14
10	pH Versus Total Pure Nitrogen Concentration at Various Temperatures	15
11	pH Versus Temperature at (N_{tot}) = 10^{-4} Molal and Various (B_{tot}) Concentrations	16
12	pH as a Function of Total Base Ion Concentration and Total Boron Concentration at 75°F	17
13	pH as a Function of Total Base Ion Concentration and Total Boron Concentration at 400°F	18
14	pH as a Function of Total Base Ion Concentration and Total Boron Concentration at 500°F	19
15	pH as a Function of Total Base Ion Concentration and Total Boron Concentration at 530°F	20

LIST OF FIGURES (Continued)

<u>Figure Number</u>	<u>Title</u>	<u>Page Number</u>
16	pH as a Function of Total Base Ion Concentration and Total Boron Concentration at 572°F	21
17	pH Versus Temperature at a Total Base Ion Concentration of 10^{-4} Molal and Various Total Boron Concentrations	22
18	pH as a Function of Total Lithium and Total Boron Concentration at 530°F	23
19	Ammonium Ion Concentration as a Function of Total Nitrogen and pH at 530°F	24
20	pH Versus Pure Total Boron Concentration at Various Temperatures	25

ABSTRACT

Calculations of pH of chemical shim solutions at various temperatures are made using the equilibrium equations, the equations for conservation of total boron, charge and total base. The pH is plotted as a function of total boron concentration and concentration of total base ion, and as a function of the total base (lithium or ammonia) and total boron concentration. Crossplots of pH versus total boron concentration at constant base concentration are presented. Plots of pH versus temperature at constant base and boron concentration are also presented.

A method is described for an iterative graphical solution for the pH of a solution of boron and a neutralizing mixture of bases at constant temperature.

INTRODUCTION

The theory of the pH of boric acid solutions with added strong base has been discussed and some calculations of the pH of such solutions presented in WCAP-3713 "Some Physico-chemical Studies of Boric Acid Solutions at High Temperatures" by D. E. Byrnes. The data presented there is of interest in elucidating the properties and expected behavior of solutions of interest in chemical shim plants. The increased interest in and importance of the effect of pH on plant reactivity in chemical shim solutions with either strong base or ammonia additions has made it desirable to carry out more detailed pH calculations to higher accuracy.

The tedious and repetitive nature of the required calculations is ideally suited to machine computation, hence, the procedure has been coded and the calculations performed on the IBM 7090. The results are presented graphically to an accuracy suitable for use in the study of pH reactivity effects in atomic power reactors. It is recommended that all future reactivity pH studies be based on the figures presented here.

DERIVATION OF EQUATIONS

The work repeats and expands upon part of the work of Dr. D. E. Byrnes ^{/1} described in WCAP-3713. It also uses the assumptions that the only boron species present in significant amounts are boric acid (H_3BO_3) a singly charged monoborate ion ($(B(OH)_4)^-$) and a singly charged triborate ion ($(B_3O_3(OH)_4)^-$), and that the activity coefficients can be assumed to be constant and the value unity. Boric acid, the monoborate ion and the triborate ion will hereafter be abbreviated as (HB), (B^-) and ($B\bar{3}$) respectively.

The equilibrium equations are then given by:

$$(H^+) (B^-) = K_{11} (HB) \quad (1)$$

$$(H^+) (B\bar{3}) = K_{13} (HB)^3 \quad (2)$$

$$(H^+) (OH^-) = K_w \quad (3)$$

$$(MeI^+) (OH^-) = K_{Base} (MeIOH) \quad (4)$$

(MeI^+) and (MeIOH) are respectively the concentration of base ion and undissociated base.

The equation for conservation of total boron is:

$$(HB) + (B^-) + 3(B\bar{3}) = (B_{tot}) \quad (5)$$

^{/1} D. E. Byrnes, WCAP-3713 - "Some Physicochemical Studies of Boric Acid Solutions at High Temperatures", September, 1962.

The equation for conservation of charge is:

$$(\text{OH}^-) + (\text{B}^-) + (\text{B}_3^-) = (\text{H}^+) + (\text{MeI}^+) \quad (6)$$

The equation of the conservation of total base is:

$$(\text{MeI}^+) + (\text{MeIOH}) = (\text{Base}) \quad (7)$$

Substituting equations (1) and (2) in equation (5) yields:

$$\begin{aligned} (\text{HB}) + \frac{K_{11} (\text{HB})}{(\text{H}^+)} + \frac{3 K_{13} (\text{HB})^3}{(\text{H}^+)} &= (\text{B}_{\text{tot}}) \\ \text{or } (\text{HB})^3 + \frac{(K_{11} + (\text{H}^+))(\text{HB})}{3 K_{13}} - \frac{(\text{B}_{\text{tot}})(\text{H}^+)}{3 K_{13}} &= 0 \end{aligned}$$

Solving this cubic for (HB) by Cardan's method (picking an arbitrary value of (H^+) and (B_{tot})):

$$\begin{aligned} \text{XH} &= \frac{(K_{11} + (\text{H}^+))}{9 K_{13}} & \text{XG} &= \frac{-(\text{B}_{\text{tot}})(\text{H}^+)}{3 K_{13}} \\ U &= \sqrt[3]{\frac{-\text{XG} + \sqrt{(\text{XG})^2 + 4 (\text{XH})^3}}{2}} \\ (\text{HB}) &= U - \frac{\text{XH}}{U} \end{aligned}$$

The remaining species can now be evaluated from the equations:

$$(\text{B}^-) = \frac{K_{11} (\text{HB})}{(\text{H}^+)} \quad (1a)$$

$$(\text{B}_3^-) = \frac{K_{13} (\text{HB})^3}{(\text{H}^+)} \quad (2a)$$

$$(\text{MeI}^+) = (\text{OH}^-) + (\text{B}^-) + (\text{B}_3^-) - (\text{H}^+) \quad (6)$$

Substituting equation (4) in (7), the equation used to calculate the total amount of a specific base required to produce a given ion concentration M_n^+ is obtained:

$$(\text{Base}_n) = (M_n^+) + \frac{(M_n^+) (\text{OH}^-)}{K_{\text{Base}}} \quad (8)$$

$$\text{or } (\text{Base}_n) = (M_n^+) \left(1 + \frac{K_w}{K_{\text{Base}} (\text{H}^+)} \right) \quad (9)$$

$$\text{where total base ion} = (\text{MeT}^+) = \sum_{n=1}^n (M_n^+)$$

In order to solve for pH at a given temperature, total boron concentration and base concentration, it is necessary to interpolate on graphs plotted from the above equations, as the direct solution of pH as a function of (Base), (B_{tot}) and temperature is feasible only on a computer.

A program was written in FORTRAN II for the 7090 computer to perform the calculations using the above equations. A flow diagram and copy of the program are given in Figure 1 and Appendix I respectively.

The equilibrium constants used in the calculations are listed in Appendix II.

USE OF FIGURES

The use of the computer was necessary to calculate the values of total base ion given in Figures 12 - 16. The total concentration of a weak base is then calculated by equation (9) which is simple enough to allow hand computation.

Thus, Figures 12 - 16 are the most fundamental and all other calculations or crossplots can be made from them by hand, although the computer program allowed the computation of the concentration of a pure weak base.

Examples of the use of tables are given below.

Ammonium Hydroxide - Boric Acid Solutions

Values of pH in ammonium hydroxide - boric acid solutions can be taken directly from Figures 4 - 8. For example, at 530°F in Figure 7, the pH at $(B_{\text{tot}}) = 10^{-2}$ and $(N_{\text{tot}}) = 10^{-3}$ is 6.45. It should be observed that at the

higher temperatures and higher pH, the normal reactor conditions, the constant pH lines are approximately equally spaced, making accurate interpolation possible. The same pH can be taken from the crossplot (Figure 9) which may be more convenient for some uses. Plots at the limiting case of pure ammonia ($B_{tot} = 0$) are given in Figure 10 at various temperatures. The effect of temperature on the pH at constant ratios of (B_{tot}) and (N_{tot}) can be seen in Figure 11.

Potassium Hydroxide - Boric Acid Solutions

Values of pH in potassium hydroxide - boric acid solutions or any base assumed to be completely ionized can be taken directly from the curves for pH versus total base ion and boron concentration (Figures 12 - 16). For example, at 75° the pH in a solution 10^{-4} molal in (B_{tot}) and 5×10^{-5} molal in potassium hydroxide is 8.89. The effect of temperature on the pH at constant ratios of (B_{tot}) and strong base concentration is presented in Figure 17.

Lithium Hydroxide - Boric Acid Solutions

Values of pH in pure lithium hydroxide - boric acid solutions at 530°F are presented in Figure 18. At $Li = 10^{-2}$ and (B_{tot}) = 10^{-1} the pH is 8.75. At the higher temperatures given, the lithium is essentially completely ionized below pH 8. At 75°, it is completely ionized for all values of pH given.

Ammonium Hydroxide, Potassium Hydroxide - Boric Acid Solutions

A simple iterative procedure for the calculation of the pH of a solution of a mixture of bases and boric acid is possible, as illustrated in the following example:

T	(N_{tot})	(K_{tot})	(B_{tot})
530°F	10^{-4}	10^{-3}	10^{-1}

Select an arbitrary nominal value of pH, i.e., (6.5). Then calculate the ammonium ion concentration from equation (9) or Figure 19. At $N = 10^{-4}$, the ammonium ion concentration is found to be 1.76×10^{-6} . Since potassium is assumed to be completely ionized ($K_{tot} = (K^+) = 10^{-3}$). The total base ion concentration is then found to be (MeI^+) = $10^{-5} + 1.72 \times 10^{-6} = 1.172 \times 10^{-5}$. From Figure 15 the pH at this (MeI^+) and 10^{-1} (B_{tot}) is found to be 5.92. This pH is then taken back to Figure 17 or equation (9) to recompute the ammonium ion concentration. The cyclical process is continued until the pH no longer changes. In this case, the pH will converge to approximately 6.01.

All concentrations are given in molal units. They may be converted to parts per million (ppm) by the following factors:

$$\text{K ppm} = \text{K molal} \times 39100$$

$$\text{NH}_3 \text{ ppm} = \text{N molal} \times 17032$$

$$\text{Li ppm} = \text{Li molal} \times 6940$$

$$\text{B ppm} = \text{B molal} \times 10820$$

Figure 2 - Ionization Constants (K_w , K_{11} , and K_{13}) as a Function of Temperature

Figure 3 - Ionization Constants of Weak Bases (K_{LiOH} , K_{NH_4OH}) as a Function of Temperature

Figure 4 - pH as a Function of Total Nitrogen Concentration and Total Boron Concentration at 75°F

T = 400°F

Figure 5 - pH as a Function of Total Nitrogen Concentration and Total Boron Concentration at 400°F

T = 500°F

Figure 6 - pH as a Function of Total Nitrogen Concentration and Total Boron Concentration at 500°F

T = 530°F

Figure 7 - pH as a Function of Total Nitrogen Concentration and Total Boron Concentration at 530°F

T = 572°F

Figure 8 - pH as a Function of Total Nitrogen Concentration and Total Boron Concentration at 572°F

Figure 9 - pH Versus Total Boron Concentration at Various Total Nitrogen Concentrations at 530°F

- 15 -

Figure 10 - pH Versus Total Pure Nitrogen Concentration at Various Temperatures

Figure 11 - pH Versus Temperature at $(N_{tot}) = 10^{-4}$ Molal and Various (B_{tot}) Concentrations

Figure 12 - pH as a Function of Total Base Ion Concentration and Total Boron Concentration at 75°F

Figure 13 - pH as a Function of Total Base Ion Concentration and Total Boron Concentration at 400°F

Figure 14 - pH as a Function of Total Base Ion Concentration and Total Boron Concentration at 500°F

530°F

Figure 15 - pH as a Function of Total Base Ion Concentration and Total Boron Concentration at 530°F

Figure 16 - pH as a Function of Total Base Ion Concentration and Total Boron Concentration at 572°F

Figure 17 - pH Versus Temperature at a Total Base Ion Concentration of 10^{-4} Molal and Various Total Boron Concentrations

Figure 18 - pH as a Function of Total Lithium and Total Boron Concentration at 530°F

Figure 19 - Ammonium Ion Concentration as a Function of Total Nitrogen and pH at 530°F

Figure 20 - pH Versus Pure Total Boron Concentration at Various Temperatures

PROGRAM TO DETERMINE THE RELATIONSHIPS BETWEEN TOTAL BORON AND

7/14/64

```

C  AMMONIA CONCENTRATION AND OTHER SPECIES
    DIMENSION HB(50),R(50)
    8  READ INPUT TAPE 5,10,XKW,XKN,XK11,XK13,N,M
    10 FORMAT(4E10.0,2I2)
    IF(XKW)50,51,50
    50 IF(N)51,60,12
    60 N=NA
    M=MA
    GO TO 16
    12 READ INPUT TAPE 5,14,(HB(I),I=1,N),(R(J),J=1,M)
    14 FORMAT(10E8.0)
    16 DO 49 J=1,M
    WRITE OUTPUT TAPE 6,20,XKW,XKN,XK11,XK13,R(J)
200FORMAT(/43X45HCONCENTRATION DEPENDENCE OF BORON AND AMMONIA//9X,
    14HKW =,1PE10.3, 9X,4HKN =,E10.3, 7X,5HK11 =,E10.3,7X,5HK13 =,E10.3
    2,10X,3HR =,E10.3//126H      B      HB      BM1
    3      BM3      PH      MEI      N      BM1/
    48      NE BM3/8)
    22 DO 49 I= 1,N
    B=HB(I)
    H=EXPFF(-2.302585*R(J))
    XH=(XK11+H)/9.0/XK13
    XG=-B*H/3.0/XK13
    XU3=(-XG+SQRTF(XG**2+4.0*XH**3))/2.0
    XU=EXPFF(.33333333*LOGF(XU3))
    XHB=XU-XH/XU
    NE=0
    IF(B-XHB)23,21,26
    23 NE=2
    GO TO 46
    21 NE=1
    26 BM1 = XK11*XHB /H
    28 BM3 = XK13*XHB **3/H
    30 OH = XKW/H
    31 XMEI = OH + BM1 + BM3 -H
    33 XN = XMEI + XMEI*OH/XKN
    PH=R(J)
    41 Y2 = BM1/ B
    NA=N
    MA=M
    46 WRITE OUTPUT TAPE 6,47,8,XHB ,BM1,BM3,PH,XMEI,XN,Y2,NE
    47 FORMAT(1PE15.7,E10.3,6E15.7,I5)
    49 CONTINUE
    GO TO 8
    51 CALL EXIT
    52 END

```

FORTRAN PROGRAM

APPENDIX I

APPENDIX II

DATA USED IN COMPUTATIONS

Temp. (°F)	K_w /2	K_n /2	K_{11} /1	K_{13} /1
75 *	1.0×10^{-14}	1.79×10^{-5}	1.0×10^{-9}	1.0×10^{-7}
400	5.02×10^{-12}	2.83×10^{-6}	3.3×10^{-10}	1.4×10^{-9}
500	6.05×10^{-12}	$.6 \times 10^{-6}$	1.26×10^{-10}	3×10^{-10}
530	6.31×10^{-12}	$.345 \times 10^{-6}$	9.0×10^{-11}	2.0×10^{-10}
572	5.76×10^{-12}	$.162 \times 10^{-6}$	5.0×10^{-11}	1.1×10^{-10}

T (°F)	120	160	200	240	260	320	360	400	440	480	520
K_{Li} /3	.128	.0685	.0742	.0456	.0310	.0435	.0396	.0414	.0255	.0234	.0172

/1 D. E. Byrnes, WCAP-3713 - "Some Physicochemical Studies of Boric Acid Solutions at High Temperatures", September, 1962.

/2 M. E. Jones, KAPL-M-MEJ-1 - "The pH of Pure Water and of Ammonium, Lithium, and Potassium Hydroxide Solutions", 1950.

/3 J. M. Wright, W. T. Lindsay, Jr., and T. R. Druga, WAPD-TM-204 - "The Behavior of Electrolytic Solutions at Elevated Temperatures as Derived From Conductance Measurements", 1961.

* NOTE: The values of K_w , K_{11} , and K_{13} at 75°F were rounded by D. E. Byrnes to simplify desk calculations and were used for comparison with his work.