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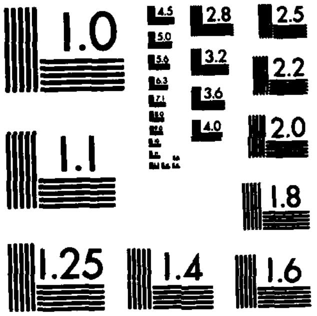

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Approaches to Computer Modeling of Phosphate Hide-Out

K. A. S. HARDY AND J. C. COOPER

Inorganic and Electrochemistry Branch
Chemistry Division

June 28, 1984

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Computer modeling of phosphate hide-out in high temperature boilers, if feasible, could predict and suggest corrective action. The feasibility of such modeling is dependent on the availability and accuracy of information concerning the species in boiler water and their reactions. Therefore, species present in boiler water were identified and information on their concentrations was summarized. Thermochemical data at high temperatures for these species were tabulated. Very few high temperature kinetic data were found. Available computer programs for modeling multi-species, high temperature solutions were obtained and modified and initial modeling attempts were made.

The sufficiency of the species and thermochemical data and the adequacy of the computer programs were evaluated. It is concluded that computer modeling of phosphate hide-out is feasible. The accuracy of the model could be improved by a more systematic and thorough analysis of boiler water under normal and hide-out conditions. High temperature thermochemical data for the formation and solubilization of metal phosphate species, especially iron, sodium-iron, and calcium should be measured.

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Approaches to Computer Modeling of Phosphate Hide-Out

CONTENTS

Approaches to Computer Modeling of Phosphate Hide-Out

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INTRODUCTION

Phosphate is used as a water treatment chemical in navy boilers. The main purpose of this treatment is to remove calcium from solution as soft nonadherent calcium phosphate sludge rather than as hard scale forming species such as calcium carbonate, calcium sulfate, or calcium silicate. The calcium phosphate formed can then be removed from the boiler by blowdown. Addition of Na_3PO_4 and Na_2HPO_4, called the coordinated phosphate or cophos treatment, also affords pH control as the phosphate acts as a buffer to keep pH at a value above which acid corrosion occurs and below which caustic corrosion becomes significant.

Difficulties are sometimes encountered in the use of this cophos treatment, and phosphate levels decrease below the desired values. Some of these decreases are due to contamination by shore or sea water, by outward leakage, or by carryover. Sometimes, however, decreased phosphate levels cannot be explained by these causes; this is called phosphate or chemical hide-out and it is characterized by a decrease in phosphate concentration at higher firing rates. The hide-out can be reversed by lowering the firing rate. This makes control of the phosphate levels very difficult because addition of phosphate at the higher firing rates to keep the phosphate levels within the established limits, causes the phosphate concentrations to increase beyond these limits upon decreasing the firing rate. In addition, pH control is lost and pH rises into the caustic region.

Computer modeling of phosphate hide-out in boiler water could predict when the phenomenon will occur and suggest

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corrective actions for prevention. The accuracy and predictive value of the computer model depends on the quality of the data and the validity of the mathematical alogrithms used in the computer program. Development of such a model requires, first, determination of the significant chemical species, information about their concentrations, and an assessment of available high temperature kinetic and thermodynamic data for these species. Given sufficient data, a modeling method can then be selected and complex software developed.

Summarized in this report is such a survey of available information. After reviewing the current understanding of phosphate hide-out, data on species and species concentrations were collected. High temperature thermodynamic data were compiled. Available computer programs, useful for modeling multi-species, high temperature solutions, were obtained and modified. The sufficiency of the data, and the adequacy of the programs were evaluated. Initial attempts made to develop a basic model using these data and programs are presented. Recommendations are made concerning collection of important data and further development of programs. The review of the current understanding of phosphate hide-out follows.

BACKGROUND ON PHOSPHATE HIDE-OUT

Several explanations are reported for phosphate hide-out. It has been suggested [1-5] that a form (or forms) of sodium phosphate exists which is less soluble at higher temperatures and that this causes phosphate to hide out at high temperatures and to redissolve at lower temperatures. Interaction of iron and phosphate as $NaFePO_4$ [4-7] and/or $Fe_3(PO_4)_2$ [1,7] has also been suggested to explain the loss of phosphate from solution. Hide-out has been seen to occur to a greater degree in recently cleaned boilers which were not sufficiently passivated [4]. Hide-out also occurs when waterside deposits are present [8], especially when these include such species as Fe, Cu, Ni, and Zn [4] and in areas where corrosion and concentrating films are found [9] such as crevices, pits and bends [8]. A better explanation of the hide-out may be obtained from computer modeling with the proper parameters. Such a model could be used to control and predict this unwanted phenomenon.

Several reports describe attempts to develop models of steam generating systems [10-13] and of industrial cooling water systems [14-17]. Purposes and orientations vary but the chief goal of all such models is to reduce the relationships of the species in a solution to mathematical terms, or equations, which can be used to simulate the operation and interrelationships of these species. These simulations can then be used as an approach to understand such things as corrosion [12] and scale formation [14], and to predict the changes which will be caused by such perturbations as the addition of chemicals and changes in temperature. This information can then be used to choose safe operating limits and appropriate water treatment. None of these reported attempts has focused on phosphate hide-out.

SPECIATION, CONCENTRATIONS, AND CONDITIONS

The first step necessary in preparing a model is to itemize the species in solution, especially those which will or may be important in phosphate hide-out. Sources of this information are discussed in Appendix A and a list of these species is available in Table A-1 of that Appendix. These are individual species and thermochemical data are needed for the combinations and reactions of them.

Besides information on the types of species found in a boiler, information is also needed on the concentrations, or ranges of concentrations, of those species. On the whole there is not much information available to us systematically summarizing the types and amounts of various species in boiler water. Appendix A summarizes the sources of such information and the data which are available. The quantitative data from these sources are presented in Table A-2 of that Appendix.

Although this information provides a starting place, it must be stated that a more comprehensive analysis of the species found in boiler water while operations are normal and while phosphate hide-out is occuring is desirable.

The conditions found in the boilers included a range of temperatures from 25°C to 300°C. If conductivity is kept within the suggested levels (less than 300 μmhos/cm), then ionic strength is low (probably less than 0.01 *M*). However, fault conditions such as inleakage or concentrating films can raise ionic strength significantly.

KINETIC AND THERMOCHEMICAL DATA

For a complete model of any solution both kinetic and equilibrium thermodynamic data are needed. It is important to include both approaches. For example, one reaction may be energetically favored but will still not occur within the given time frame because the process is very slow. Such a case is the precipitation of $Ca_5(PO_4)_3OH$, hydroxyapatite, which is the thermodynamically most stable calcium phosphate. However, depending on the pH, it is not always the first form to precipitate because kinetically it is a slower reaction. Nancollas [18] has studied the kinetics of these precipitations and has discussed the interplay of kinetics and thermodynamics for several calcium phosphate forms. However, the work was done at low temperature (37°C) and data for high temperatures are not available. Other data, also available only at low temperatures, include that on rust formation [19]. The rate data for complex and ion-pair formation and on the dissolution and precipitation reactions at high temperatures are not available.

This does not mean that modeling is impossible. Other models based on thermodynamics have been successful in making useful predictions for boiler water, cooling water, and natural waters [20]. It is also likely that at high temperatures most kinetics are sufficiently fast that good models can be developed using a thermodynamic approach. We decided to continue to evaluate the availability of the necessary high temperature thermodynamic data and to pursue modeling from this approach.

A large body of thermochemical data at 298°K (25°C) has been compiled. Data for the high temperatures found in boilers (up to 300°C), however, are spread throughout the literature. Water itself behaves very differently at high temperatures. It is, therefore, necessary to discuss the nature of water and of solutions at high temperature, and to summarize methods of dealing with various forms of available data before describing the collected data. These are discussed in Appendix B.

To model chemistry in boilers the availability of high temperature data for the species of interest in boilers must be assessed. A compilation of available data is presented in Appendix C; it includes sources of this thermochemcial data, a description of the forms in which these sources present data, and Tables C-1 through C-9 in which the actual data are organized by species type.

COMPUTER PROGRAMS AND MODELING

Having summarized the available data, a consideration of available programs and other modeling approaches led to the selection of two programs with which to begin initial modeling. The program COMICS, developed by Perrin and Sayce [20] and revised by Cooper [21] was already available in this laboratory. The program calculates the concentrations of free metals, free ligands and of the complex species in solution, including mixed species, such as $MM'L$, hydrolyzed species, such as $M(OH)_2$, protonated species such as MHL, and polynuclear species such as M_2L_2, where M and M' represent different metals and L represents some ligand. Using formation constants, total ligand and metal concentrations, and pH, the program calculates the concentrations of up to forty species derived from four different metal ions and four ligands, and will plot these results. The program makes no corrections for high temperature except of course that the formation constants used can be the high temperature values since they are input by the user. Also, no precipitation reactions can be included. The second program chosen for use is WATEQF [22] which is a Fortran program written for the calculation of the chemical equilibria in natural waters; it was developed for use by the United States Geological Survey (USGS). Included in the program are 193 reactions, both aqueous formation and precipitation reactions. The program includes corrections for higher temperatures in the calculation of activities from ionic strength, some high temperature equilibia data, and allowance for the change in concentrations due to the change in density as temperature changes.

Because COMICS was available and had the capacity to handle so many species in solution, initial calculations were done with it. The first calculations were made of the ionization of phosphoric acid at low (25°C) and high (300°C) temperature. Formation constant data were first calculated using the entropy and enthalpy data [23] in Table C-3 using equations (B-3 and B-4) and assuming a zero heat capacity. It is instructive to compare the log of the equilibrium constants so calculated with those measured by Mesmer and Baes [24,25] for reactions (1-3):

$$H^+ + H_2PO_4^- = H_3PO_4 \qquad (1)$$

$$H^+ + HPO_4^{2-} = H_2PO_4^- \qquad (2)$$

$$H^+ + PO_4^{3-} = HPO_4^{2-} \qquad (3)$$

For reaction (1) the calculated value at 25°C is 2.12, while the measured value is 2.145. At 300°C the calculated value is 2.78 while the measured constant is 4.40. For reaction (2) at 25°C the calculated value is 7.21 and the measured value is 7.197 while at 300°C the calculated constant is 6.93 while the measured is 8.946. Note that measured and calculated values are very close at 25°C but are not so at 300°C. The difference clearly demonstrates that heat capacity must be included at the higher temperatures, and that there is a greater degree of ion association at the higher temperatures. The value of the log of the third constant, reaction (3), is not given at 300°C because it was too difficult to extrapolate to solutions of low ionic strength. For the calculation with the COMICS program a value of 12.7 was assumed for reaction at 300°C as this represents a good approximation based on the data for 150°C [24]. The total concentration of phosphate was taken as 25 ppm or 2.6×10^{-4} M. Figures 1 and 2 summarize the calculations done at 25°C and 300°C. A comparison of the two plots indicates that at the higher temperature the phosphate stays bound to the proton up to higher pH values. This means that in the pH range of normally operating boilers the phosphate is found as HPO_4^{2-} or $H_2PO_4^-$. This is consistent with the decreased solvating capacity of water at high temperatures, such that a higher degree of ion association and complex formation is seen.

Conclusions which can be drawn from this COMICS calculation with the ion association constants for phosphate are: heat capacity must be included in the calculation of high temperature formation constants and at higher temperatures there are higher concentrations of the protonated forms of phosphate.

COMICS was also used for the calculation of metal bound phosphate using the constants reported for 25°C by Sillen and Martell [26,23] in Table C-3. The concentrations of dissolved metal ions were chosen based on reported values [20] shown in Table A-2. These values are: Ca, .03 ppm = $.7 \times 10^{-6}$ M;

Fe, .09 ppm = 1.6×10^{-6} M; Cu, .17 ppm = 2.7×10^{-6} M; Mg, .18 ppm = 7.4×10^{-6} M. A separate calculation was done with each metal and 25 ppm phosphate. Another calculation was then done for the mixture of all the metals with the phosphate using the same concentrations described above. The acid association values used were those of Martell and Sillen [23]. Figure 3 plots the calculated percentages of species for the calculation done with calcium and phosphate. The species $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} were calculated as per cent total phosphate whereas free Ca^{2+} and $CaHPO_4$ were calculated and plotted as per cent total calcium. Because phosphate is in such large excess (26 fold) over the calcium, the amount of calcium hydrogen phosphate present is very small and represents less than 1% of the total phosphate. The curves for the phosphate remain unchanged from that calculated without metal present as shown in Figure 1. The curves for the metal species in Figure 3 indicate that most (90%) of the calcium remains unbound to the phosphate. This holds true for magnesium and copper also. However, the calculation with iron shows that most (>90%) of the iron is bound as $FeHPO_4$.

The results for the mixture of all the metals with phosphate are plotted in Figures 4 and 5. For Figure 4 the results are calculated as per cent total phosphate. Again the curves remain essentially unchanged from Figure 1. The amount of phosphate bound to the metals remains small even for the mixture. This is due to the low concentration of the metals and to the fact that only iron binds phosphate very strongly. Figure 5 plots the results for each metal species in the mixture calculated as a per cent of that total metal concentration. The conclusion drawn from this is the same as that for the individual calculations; all of the metals are essentially free except iron. One further calculation was done with the species concentrations computed for calcium, phosphate, and pH. The most stable precipitate of calcium phosphate is $Ca_5(PO_4)_3(OH)$ and the solubility product for this at 25°C is (4):

$$K_{sp} = [Ca]^5[PO_4]^3[OH] = 10^{-56} \tag{4}$$

Using the computed concentrations at pH 10, with only calcium and phosphate present in solution, the above product was found to be 1.1×10^{-55}. When the other metals were present the calculated product is 1.1×10^{-52}. Thus precipitation will occur under these conditions and will be exaserbated by the competitive binding of phosphate by other metals. This emphasizes the need to include precipitation reactions; COMICS does not have this capability. Also only low temperature data are available for these metal phosphate species. It is expected, based on the nature of water at high temperature, that the degree of metal-hydrogen phosphate association will increase with increasing temperature. If corrections were also made for the higher concentrations of species found in crevices and below porous deposits then this iron hydrogen phosphate association could prove very important in phosphate hide-out.

Inasmuch as COMICS does not include precipitation reactions, present effort involves calculations with WATEQF. Although WATEQF includes many features necessary to the modeling of a system at high temperature as was mentioned before, some adaptations are required. The program does not include all of the high temperature data needed and these must be added. Modifications of this program for available computer systems and for applicability to high temperatures are in progress. It is expected that this program will offer a great deal of capability to the modeling of boiler water.

SUMMARY

The purpose of this study was to evaluate the feasibility of modeling phosphate hide-out in navy boilers. It was necessary to collect the available appropriate data, to obtain and modify computer programs which can accurately model multi-component equilibria at high temperatures, and to evaluate the sufficiency of the data and the adequacy of the programs.

Data on speciation and the concentrations of species are summarized in Tables A-1 and A-2. These data are probably sufficient, though a systematic and thorough analytical evaluation would increase the data base and insure the reliability of the calculated results. Such a study should evaluate the species and their concentrations in boiler water under normal operating conditions and under the condition of phosphate hide-out.

Very few applicable high temperature kinetic data are available. This does not mean that modeling is impossible as many systems have been successfully modeled using only a thermodynamic approach. The available high temperature thermochemical data are summarized in the Tables of Appendix C. The data which are not available and which may be of significance are the formation constants and solubility products for metal phosphate species. The compounds which may be of special importance are iron phosphates, sodium iron phosphate, and calcium phosphates at high temperature.

Two computer programs have been used that calculate concentrations of species in multi-component equilibria. Initial models were done with COMICS which does not include solubility products. Also, high temperature corrections such as one for ionic strength are not included in the program. WATEQF is still being modified for this problem, for high temperatures, and for the HP 1000 and VAX 11/750 computer systems. WATEQF has all of the necessary components for modeling boiler water, or can be modified.

Initial modeling done with COMICS led to several conclusions. First, calculation of high temperature formation constants using heat capacity information is essential. Second, there is a greater tendency for phosphate to be protonated at

higher temperatures. From the modeling done with metal ions and phosphate at 25°C, it can be concluded that iron has a much higher affinity for hydrogen phosphate than does calcium, magnesium, or copper. This affinity is expected to be even higher at high temperatures, although such thermochemical data are not available. The inclusion of solubilty data in these calculations, not presently possible with the program COMICS, is essential in a calculation with the large number of species expected for an accurate and predictive model of boiler water chemistry. Based on a rough calculation, it is expected that the presence of other metals will increase the tendency of calcium phosphate to precipitate. Data and computer programs have thus been collected and evaluated, and some initial modeling has been accomplished.

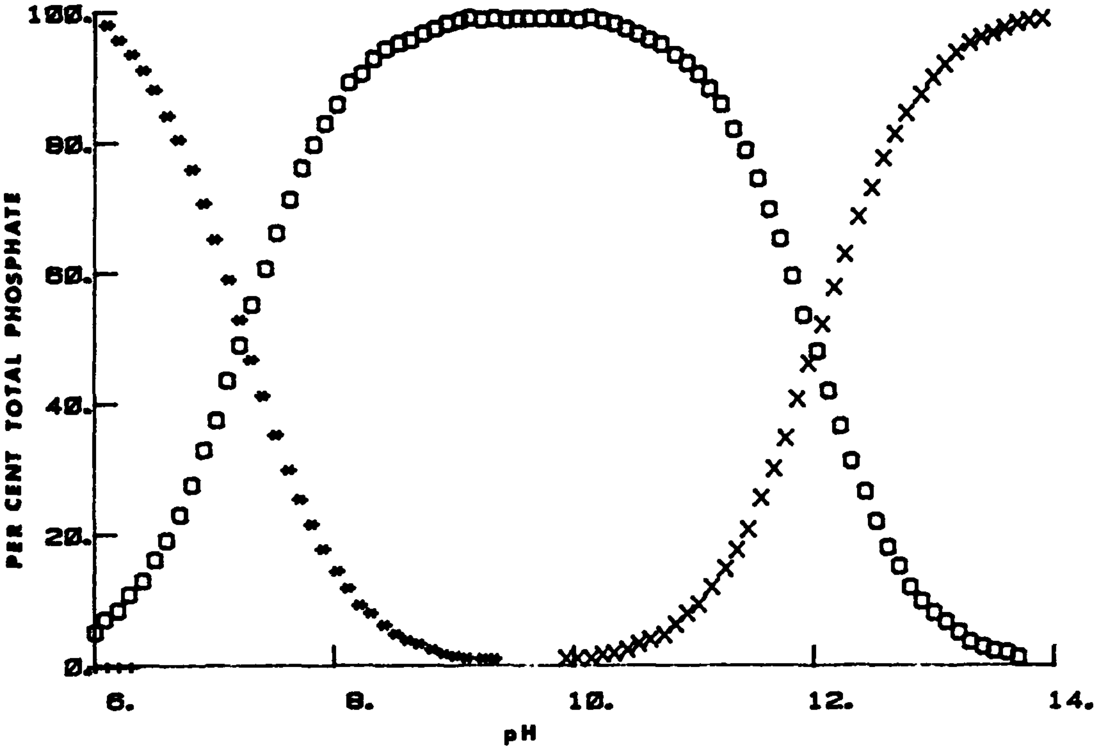

Fig. 1 - Speciation of phosphate at 25°C as a function of pH
(+, H_3PO_4; *, $H_2PO_4^-$; □, HPO_4^{2-}; ×, PO_4^{3-})

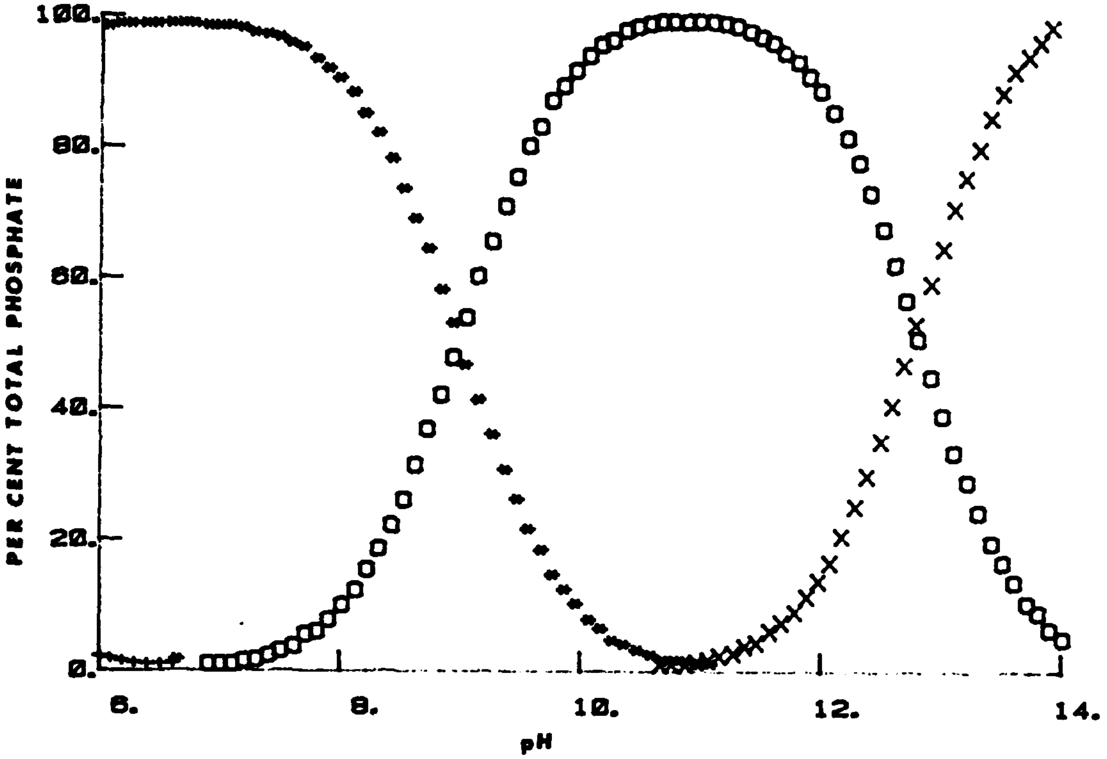

Fig. 2 – Speciation of phosphate at 300°C as a function of pH (+, H_3PO_4; *, $H_2PO_4^-$; □, HPO_4^{2-}; ×, PO_4^{3-})

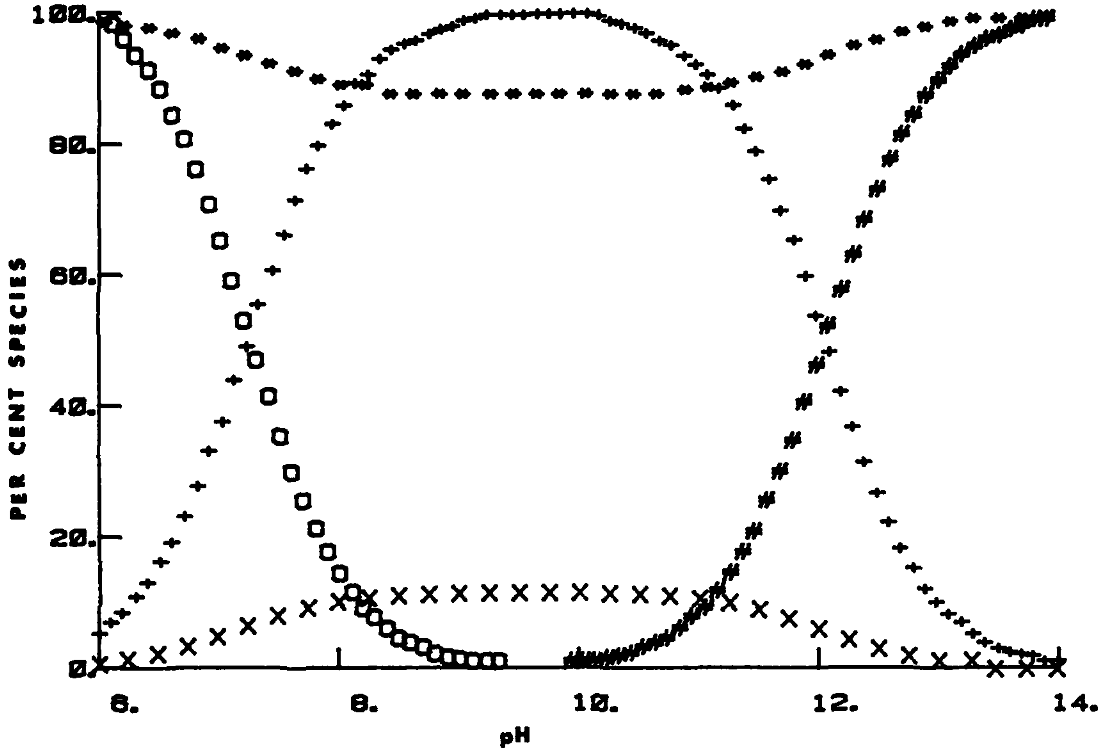

Fig. 3 – Speciation of calcium and phosphate as a function of pH (□, $H_2PO_4^-$; +, HPO_4^{2-}; #, PO_4^{3-}; these three species are calculated as per cent total phosphate; x, $CaHPO_4$; ✱, Ca^{2+}; these two species are calculated as per cent total calcium)

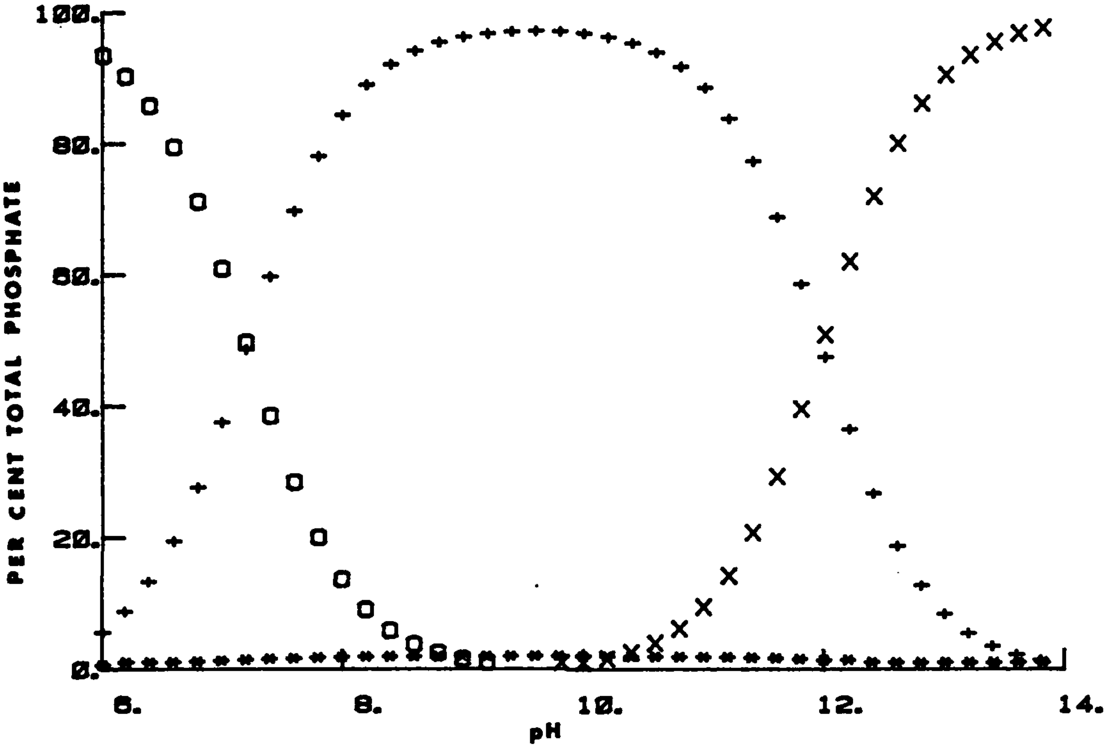

Fig.4 – Speciation of calcium, magnesium, iron, copper, and phosphate as a function of pH
(□, $H_2PO_4^-$; +, HPO_4^{2-}; ×, PO_4^{3-}; ✻, sum of $MHPO_4$ where M is Ca, Mg, Fe, and Cu)

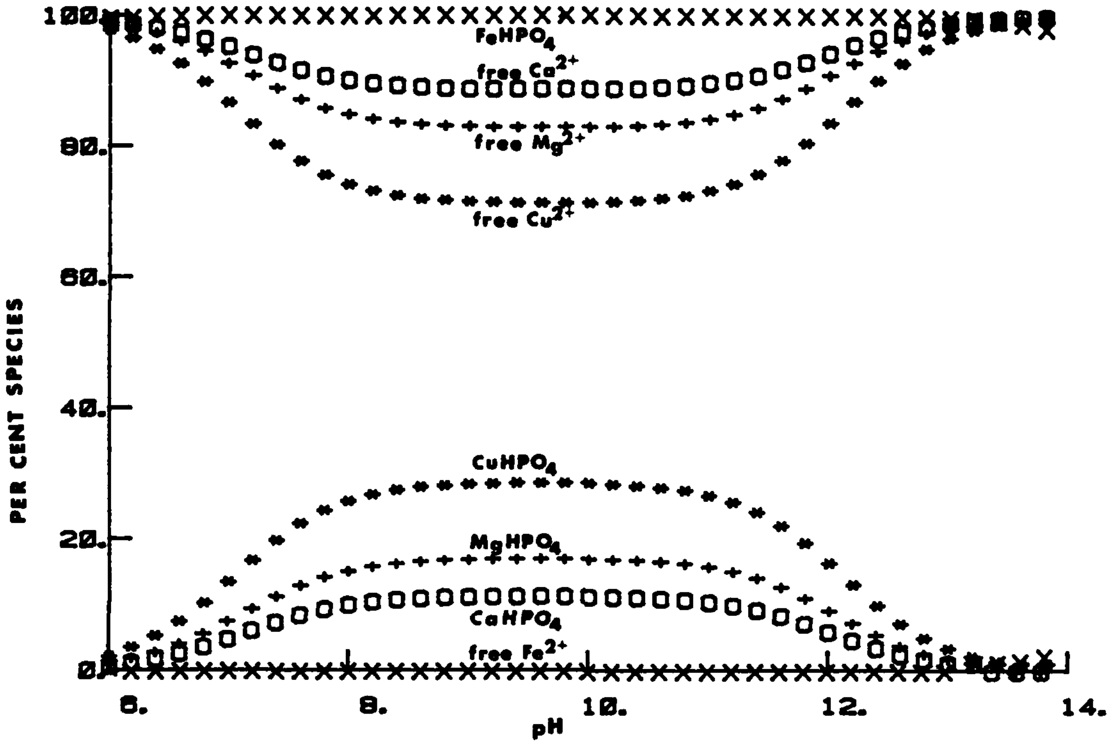

Fig. 5 – Speciation of calcium, magnesium, iron, copper, and phosphate as a function of pH (each metal species is calculated as a per cent of that total metal concentration)

APPENDIX A

SPECIATION AND SPECIES CONCENTRATIONS

Essential to the development of a good model is a compilation of the species found in boiler water. From the suggestions of possible causes for phosphate hide-out described in the section on BACKGROUND, the species phosphate, iron, sodium, copper, nickel, and zinc are considered to be important. A Naval Ship's Technical Manual (NSTM) [8] lists other contaminant metals and anions found in source water and in the analysis of sludge. Other species were discussed at a workshop of the American Society of Mechanical Engineers (ASME) [27]. In other reported models [12,13,28] other contaminants are mentioned. Two reports [29,30] include still other species found in navy boilers. A list of all of these species is given in Table A-1.

Also essential is information on the concentrations of these species. The same sources with qualitative information [8,29,30,27] as well as ships' logs provide some quantitative data. These data are summarized in Table A-2.

Additional qualitative and quantitative data on boiler scale is useful. Deposits on boilers were analyzed and found to include Fe, Si, Ca, Mg, S, Pb, Cu, Zn, Ni, and P [29]. The quantitative analysis of this deposit showed that 0.2% was Pb and the authors suggest that the probable components of the deposit are as follows: Na_2SO_4, 99 ppm; NaCl, 146 ppm; K_2CO_3, 36 ppm; K_2SO_4, 13 ppm; SiO_2, 5 ppm; NaOH, 37 ppm; HCO_3-, present. The NSTM also defines the individual contribution made to boiler water conductivity by the species Cl-, $SO_4{}^{2}-$, HCO_3-, Na+, $Ca^{2}+$, $Mg^{2}+$, and OH- [8].

TABLE A-1

SPECIES PRESENT IN BOILER WATER *

ANIONS	CATIONS	NEUTRAL
PO_4^{3-}	H^+	O_2
CO_3^{2-}	Ca^{2+}	CO_2
Cl^-	Fe^{2+}, Fe^{3+}	N_2
SiO_4^{4-}	Mg^{2+}	SiO_2
SiO_3^{2-}	Cu^{2+}, Cu^+	(NH_3)
OH^-	Na^+	(H_2)
SO_4^{2-}	Zn^{2+}	
O^{2-}	Ni^{2+}	
HO_2^-	Mn^{2+}	
	(Cr^{2+})	
	(Ti^{2+})	
	(Sn^{2+})	
	(Pb^{2+})	
	(Al^{3+})	
	(K^+)	

* Those in parentheses are expected to be less important.

TABLE A-2

CONCENTRATIONS OF SPECIES IN BOILER WATER

Reference Footnote	8 a	8 b	8 c	29 d	29 e	29 f	USS Brooke (standards)	USS Brooke (3/10/83)	30	27 g	27 h
pH			9.8-10.2	11.0	10.9	10.7	8.5-10.2	8.1-9.0		9-10	
Conductivity (μmhos/cm)	25.0 (max)		400	368	800	700	300(max)	40-45			
$[PO_4^{3}-]$ (ppm)			25-60	30	30	.3/2 (i)	10-30	20-25	10-25	3-10	
Hardness as $[CO_3^{2}-]$ (ppm)		0.10 (max)				1		.04-.08	.05-.17		
$[SiO_2]$ (ppm)	0.20 (max)	0.20 (max)	5 (max)								
[Cl-] (epm)			1.00 (max)			88.5 (ppm)	1.00		2.0		
Alkalinity						.93/1.1 (j)					
TDS						364					

TABLE A-2 (CONT'D)

CONCENTRATIONS OF SPECIES IN BOILER WATER

Reference Footnote	8 a	8 b	8 c	29 d	29 e	29 f	USS Brooke (standards)	USS Brooke (3/10/83)	30	27 g	27 h
NH_3						1.1					
Ca(ppm)						<0.03			.10		
Mg(ppm)						0.18			.38		
Zn(ppm)									.56		
Cu(ppm)						0.17			.08		
Ni(ppm)									2.5		
Fe(ppm)						0.09			1.13		
Na(ppm)						110					
SO_4^{2-} (ppm)						75.7					
K(ppm)						24					
O_2(ppb)			15							15	
CO_2(ppb)											50-100

Footnotes: a, shore steam standards; b, processed shore water standards; c, boiler water standards (all are 1977 standards)
d, analysis 9/26/63; e, analysis 10/4/63; f, analysis 10/22/63
g, Pocock talk; h, Gould talk
i, .3 by gravimetric and 2 by Navy colorimetric;j,.93 by phenol and 1.1 by methyl purple

APPENDIX B

DISCUSSION OF WATER AND SOLUTIONS AT HIGH TEMPERATURE AND SUMMARY OF METHODS FOR DEALING WITH VARIOUS FORMS OF HIGH TEMPERATURE THERMOCHEMICAL DATA

WATER

The highly structured nature of water at room temperature due to hydrogen bonding is lost at higher temperatures as the kinetic energy increases. This change in the degree of structure causes dramatic changes in several properties. Density decreases (.9971 at 25°C, .7125 at 300°C). Viscosity decreases. The dielectric constant decreases (78.381 at 25°C, 20.052 at 300°C) showing a change from a very polar medium to one that is similar to non-polar liquids. The solvating nature of water thus changes. At 25°C water hydrates ions and polar molecules easily, fitting them into the structure. At higher temperature water is not as good at hydrating species and there is not as much structure for them to fit into. Electrolytes thus become weaker. This affects the thermodynamic functions of solute species and this change is reflected in the heat capacity function. A similar change in heat capacity is not seen for homogeneous solutions in non-polar solvents. For the aqueous solutions found in boilers, these changes must be included and heat capacity data at high temperatures must be available. It is essential that conclusions not be based on low temperature data.

The equilibrium for the ionization of water has been well studied at high temperatures:

$$H_2O = H^+ + OH^- \qquad \text{(B-1)}$$

Measured pK_w values are available up to 350°C. The value of K_w decreases as temperature increases, demonstrating the change of water from a very polar and ionizable solvent to one which is less so. This change in K_w also means that the values of pH also vary greatly with temperature and modeling must include this.

IONIC STRENGTH

The effect of ionic strength on solution equilibria increases with increasing temperature due to changes in the nature of water. One way to include this in calculations is to use an extended form of the Debye-Huckel equation (B-2) to evaluate the activity coefficient, $\gamma_\pm$, which measures the non-ideality of the electrolyte:

$$\log \gamma_\pm = - A|Z+Z-| * I^{1/2}/(1 + a * I^{1/2}) + B * m \qquad \text{(B-2)}$$

Values for A, the Debye-Huckel limiting slope, increase with temperature and are known [25,31]. The values of Z are the charges of the ions, I is the ionic strength, and a and B are constants for which empirical values (frequently unity) are assigned [25,31].

HEAT CAPACITIES

High temperature data, especially heat capacities, for aqueous reactions are available in several forms. Various approaches which are used to obtain and manipulate these data will be summarized, so that all data can be in the same form for systematic use. The equations which define the important relationships of equilibria and thermodynamic functions are:

$$-RT \ln K(T) = \Delta \bar{G}^{\circ}_{T} \qquad \text{(B-3)}$$

$$\Delta \bar{G}^{\circ}_{T} = \Delta \bar{H}^{\circ}_{T} - T \Delta \bar{S}^{\circ}_{T} = \qquad \text{(B-4)}$$

$$\Delta \bar{G}^{\circ}_{298} - \Delta \bar{S}^{\circ}_{298} \Delta T + \int_{298}^{T} \Delta \bar{C}_p \, dT - \int_{298}^{T} \Delta \bar{C}_p \, d \ln T \qquad \text{(B-5)}$$

The equilibrium constant, K, at temperature, T, can thus be calculated with the free energy at T, $\Delta \bar{G}^{\circ}_{T}$, or with the values for enthalpy, $\Delta \bar{H}^{\circ}_{T}$, and entropy, $\Delta \bar{S}^{\circ}_{T}$, at that temperature. The equilibrium constant can also be calculated with the more accessible values of free energy at 298°K, and the standard state entropy change at 298°K, if the value for the change in heat capacity, $\Delta \bar{C}_p$, is known for the temperatures of interest.

For most systems, heat capacity is variable and values are least accessible at high temperatures. Where data are available, C_p is usually defined over a temperature range (specific to the compound in question) by:

$$\Delta \bar{C}_p = a + bT^{\pm 1} + cT^{\pm 2} \qquad \text{(B-6)}$$

As these data are frequently not available, three means of making estimates are used [25,32]. These are the zero heat capacity assumption, the constant heat capacity method, and the correspondance principle. Over the wide range of temperatures occurring in boilers it is unlikely that ΔC°_p will be zero. However, if two chemical reactions are combined such that like charges are balanced it is occassionally possible that the changes in heat capacity will cancel, yielding a situation where the overall change in heat capacity is zero. This is true for the ionization of dihydrogen phosphate:

$$H_2PO_4^- = H^+ + HPO_4^{2-} \qquad K \qquad \text{(B-7)}$$

$$H^+ + OH^- = H_2O \qquad 1/K_w \qquad \text{(B-8)}$$

$$\overline{\hspace{20em}}$$

$$H_2PO_4^- + OH^- = HPO_4^{2-} + H_2O \qquad K/K_w \qquad \text{(B-9)}$$

Such zero heat capacity treatment is rarely possible. It is much more likely that the combination of two chemical reactions will lead to a constant, non-zero heat capacity. In this constant heat capacity approach, the equations are combined so that the ionic charges are balanced. This is more likely to result in constant values of ΔC_p if the species are similar. The validity of this approach can be verified by plotting known values and those that are calculated in this way. There is, however, no general test of this method. It is thus used with the greatest confidence to extrapolate values to higher temperatures where some higher temperature measurements have been made.

The third approach to estimating heat capacity values is the correspondence principle described by Criss [32] and Cobble [33]. For this approach a heat capacity function is defined:

$$C^\circ_T = \Delta T * \bar{S}^\circ_T - \int_{298}^{T} \bar{S}^\circ_T \, dT \qquad \text{(B-10)}$$

where $\bar{S}^\circ_T$ is defined as:

$$\bar{S}^\circ_T = a_T + b_T \bar{S}^\circ_{298} \qquad \text{(B-11)}$$

This heat capacity term can then be used to approximate standard free energy by:

$$\bar{G}^\circ_T = \bar{G}^\circ_{298} - \Delta T * \bar{S}^\circ_{298} + C^\circ_T \qquad \text{(B-12)}$$

Evaluations of this approach [32] have demonstrated that it is satisfactory up to 250°C; at 300°C there is still considerable uncertainty.

APPENDIX C

HIGH TEMPERATURE THERMOCHEMICAL DATA

To model boiler water it is necessary to compile and assess the available high temperature thermochemical data. A wide variety of sources were used to collect these data; as a result the data are given in a variety of forms. For example, the United States Geological Survey (USGS) [34] compiled data on the energy for the reactions of formation from the elements of many species of interest here. Values for $\Delta H°$, $S°$, $\Delta G°$, and $\log K_f$ at temperatures ranging from 298°K up to 1800°K for some compounds are given. Additionally, Helgeson [35] has compiled ion dissociation equilbria for aqueous species, solubility products, heat capacity values, and enthalpies, entropies, and average heat capacities for the formation of aqueous ions; data are given up to 300°C where they are available.

Data are also included in reports of modeling done of boiler chemistry [10-12,31] and of natural waters [22,36]. Most of these data are presented as values of the formation constant or the solubility product at a specific temperature. However, some of the data are presented in the more general form:

$$\log K = a + bT^{\pm 1} + cT^{\pm 2} \qquad \text{(C-1)}$$

Three further sources [25,37,38] include values of heat capacities and of log K at different temperatures. Finally, some applicable thermodynamic data are available in the form of phase diagrams [3,5].

The data found in these sources have been summarized in tables of Appendix C, for the purposes of this work, by species type. As water is the medium in which all solution reactions in the boiler take place, data for the ionization of water are essential. Many sources of these data are available and the reported values are in Table C-1. Data for other species follow in several tables; to make these tabulations easier to use, Table C-2 includes common general information. There are few data pertinent to phosphoric acid and phosphate species, although the first two ionization constants have been carefully measured [25,31]. Other pertinent data are in Table C-3. One different source of data is available, that is, phase diagrams for sodium phosphate [3,5]. A study of the available data leads to the conclusion that there is not much high temperature data for metal phosphate species. Because of the possible implication of iron phosphate species involvement in phosphate hide-out [5] and because of the known interaction of phosphate with iron in natural water systems [39], these missing data may be important to the development of a complete model. Consideration of various phosphate forms is apparently unnecessary as they are converted to orthophosphates at high temperatures [40].

Data for CO_2, bicarbonate, and carbonate reactions are widely available. They are summarized in Table C-4. Table C-5 includes data for the reactions of SiO_2, silicic acid, silicate, and metal silicates. Data for hydroxide species and metal hydrolysis reactions are in Table C-6. Reactions involving sulfuric acid, hydrogen sulfate, and metal sulfates have been well studied; data are in Table C-7. Data for species involving chloride which are mainly ion pair dissociation reactions, have been presented in Table C-8. These data are more important at high temperatures than at low because there is a greater tendency for ion pair association due to the decreasing solvating capacity of water. The energies of formation of metal oxides are available [34,35] for FeO, Fe_2O_3, Fe_3O_4, $MgFe_2O_4$, and Cu_2O. The only reported solubility data for metal oxides are for magnetite, Fe_3O_4 [31]. Enthalpies of formation, with entropy and average heat capacities are available for the formation of aqueous metal ions and a variety of anions [35]. These ions are: Ag+, Cu+, $Cu^{2}+$, $Pb^{2}+$, $Zn^{2}+$, $Fe^{2}+$, $Fe^{3}+$, $Ca^{2}+$, $Mg^{2}+$, $Ba^{2}+$, K+, Na+, $Al^{3}+$, HS-, $S^{2}-$, F-, $SO_4{}^{2}-$, $CO_3{}^{2}-$, OH-, Cl-, and H+. These data are useful in deriving other values for aqueous media. Notably absent in this source are data for $PO_4{}^{3}-$. Included in Table C-9 are data for all other species which did not fit the above classifications.

TABLE C-1

DATA ON THE IONIZATION OF WATER ($-\log K_w$)

Reaction: $H_2O = H^+ + OH^-$

Temperature (°C)	pK_w[41]	pK_w[44]	pK_w[42]	pK_w[43]	pK_w[45]	pK_w[46]
0	14.94		11.			14.938
25	13.99			14.00		13.995
50	13.27			13.27		13.275
60				13.03		
75	12.71					12.712
100	12.26			12.26		12.265
125	11.91	11.942	11.907		11.905	11.912
150	11.64	11.675	11.634	11.64	11.671	11.638
175	11.44	11.477	11.420		11.461	11.432
200	11.30	11.352	11.254	11.27	11.302	11.289
225	11.22	11.261	11.131		11.196	11.208
250	11.20	11.230	11.049	11.13	11.138	11.191
275	11.22	11.245	11.012		11.132	11.251
300	11.30	11.300	11.034	11.39	11.193	11.406
325						11.71
350		11.521*	11.42			12.30
352			11.15			15.74
374.15		11.674*	11.997*			

* Extrapolated beyond the range of the data.

$$\log([H^+][OH^-]) = -151.713/T - 111.491 - 0.03685\,T + 44.077\log T + (2\,A * I^{1/2}/(1 + 1.5*I^{1/2})) - (0.6356 - 0.001078)\,I$$

(from reference 12)

TABLE C-2

SUMMARY INFORMATION FOR THE THERMODYNAMIC DATA TABLES

All species are assumed to be dissolved, aqueous species unless otherwise noted.

* indicates that data at other temperature values are available in the reference. Usually the value at the highest temperature is presented.

$a(T) = \Delta T + T_2 \ln(T_2 / T_1)$

• in a chemical formula signifies a dissolved ion pair.

Dimensions are: ΔH, cal/mole; ΔG, cal/mole; ΔS, cal/mole-deg; C_p, cal/mole-deg.

Formation data available are: ΔH, S°, ΔG, C°_p, and log K_f for reactions of formation from the elements in their satandard states.

Temperatures used are all °C; thus log K(200) signifies the formation constant at 200°C.

Subscript s = solid.

TABLE C-3

THERMOCHEMICAL DATA FOR PHOSPHORIC ACID AND PHOSPHATES

Reference	Reaction	Data
23	$H^+ + PO_4^{3-} = HPO_4^{2-}$	$\Delta H_1 = -3.50 \quad \Delta S_1 = 43$
23	$H^+ + HPO_4^{3-} = H_2PO_4^-$	$\Delta H_{12} = -0.80 \quad \Delta S_{12} = 30.3$
23	$H^+ + H_2PO_4^- = H_3PO_4$	$\Delta H_{13} = 1.88 \quad \Delta S_{13} = 16.0$
25,31	$H_3PO_4 = H^+ + H_2PO_4^-$	pK (300) = 4.400*
25,31	$H_2PO_4^- = H^+ + HPO_4^{2-}$	pK (300) = 8.946*
25	$OH^- + H_2PO_4^- =$ $HPO_4^{2-} + H_2O$	$\Delta G_{298} = -9271 \quad \Delta S_{298} = -11.0$ ΔC_p (0–300°C) = −0.1
25	$H_3PO_4 + OH^- =$ $H_2PO_4^- + H_2O$	$\Delta G_{298} = -16163 \quad \Delta S_{298} = -3$ ΔC_p (0–300°C) = 11
34	H_3PO_4	formation data to 700°C
31	Na_3PO_4	solubilty 1500 ppm (350°C)
2,4	sodium phosphate	phase diagrams
34	$Ca_3(PO_4)_2$	formation data to 1300°C
34	$Ca_5(PO_4)_3OH$	formation data to 1200°C
26	$Fe^{2+} + HPO_4^{2-} = FeHPO_4$	log β(30) = 7.3
26	$Mg^{2+} + HPO_4^{2-} = MgHPO_4$	log β(25) = 2.91
26	$Ca^{2+} + HPO_4^{2-} = CaHPO_4$	log β(25) = 2.70
26	$Ca^{2+} + H_2PO_4^{2-} = CaH_2PO_4^+$	log β(25) = 1.08
26	$Cu^{2+} + HPO_4^{2-} = CuHPO_4$	log β(25) = 3.2
26	$Na^+ + HPO_4^{2-} = NaHPO_4^-$	log β(25) = 0.60
26	$K^+ + HPO_4^{2-} = KHPO_4^-$	log β(25) = 0.49

TABLE C-4

THERMOCHEMICAL DATA FOR CO_2, HCO_3^-, and CO_3^{2-} SPECIES

Reference	Reaction	Data
25	$CO_{2(aq)}$	C_p^o (25-300°C) = 45
34	$CO_{2(g)}$	formation data to 1500°C
25	$CO_{2(g)} = CO_{2(aq)}$	$\Delta G = 1992 + 23.0\ \Delta T$ $+ 36.0\ a(T)$
25	$CO_2 + OH^- = HCO_3^-$	$\Delta G = -10406 + 3.7\ \Delta T$ $- 19.5\ a(T)$
25	$HCO_3^- + OH^- =$ $CO_3^{2-} + H_2O$	$\Delta G = -5010 + 16.1 \Delta T$ $- 21.0\ a(T)$
22	$CO_3^{2-} + H^+ = HCO_3^-$	$\log K = - 6.4980 + 0.02379\ T$ $+ 2902.39/T$ (valid 0-50°C)
11	$HCO_3^- = H^+ + CO_3^{2-}$	$\log K(250) = -11.34$ $\log K(300) = -11.98$
35	$HCO_3^- = H^+ + CO_3^{2-}$	$\log K(250) = -11.43$ $\log K(300) = -13.38$
22	$HCO_3^- + H^+ = H_2CO_3$	$\log K = -14.8435 + 0.03279\ T$ $+ 3403.71/T$ (valid 0-50°C)
11	$H_2CO_3 = H^+ + HCO_3^-$	$pK(250) = 7.88$ $pK(300) = 8.58$
35	$H_2CO_3 = H^+ + HCO_3^-$	$pK(250) = 7.63$ $pK(300) = 8.86$
10	$H_2CO_3 = H^+ + HCO_3^-$	$\log K(300) = -8.55$
12	$H_2CO_3 = H^+ + HCO_3^-$	$\log K = -2382.2/T + 8.153$ $- 0.02194\ T$
35	$CO_3^{2-}{}_{(aq)}$	formation data up to 300°C
34	$CaCO_{3(s)}$	formation data up to 900°C
22,36	$CaCO_{3(s,calcite)} =$ $Ca^{2+} + CO_3^{2-}$	$\log K = 13.543 - 0.0401\ T$ $-3000/T$* (valid 0-50°C)
36	$CaCO_{3(s,argonite)} =$ $Ca^{2+} + CO_3^{2-}$	$\log K = -10.21 + 0.0217\ T$ -5.17 x $10^{-5}\ T^2$
35	$CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}$	$\log K(300) = -14.10$
11	$CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}$	$\log K(250) = -12.72$ $\log K(300) = -14.10$
22	$Ca^{2+} + CO_3^{2-} = CaCO_3^o$	$\log K = -27.393 + 4114/T$ $+ 0.05617\ T$ (valid 10-50°C)
35	$CaCO_3 = Ca^{2+} + CO_3^{2-}$	$\log K(200) = -5.2$
35	$CaCO_3 + 2\ H^+ =$ $Ca^{2+} + H_2O + CO_2$	$\log K(300) = 8.73$
22	$Ca^{2+} + HCO_3^- = CaHCO_3^+$	$\log K = - 2.95 + 0.0133\ T$ (valid 0-50°C)
25	$Ca^{2+} + HCO_3^- = CaHCO_3^+$	$pK(250) = -2.94$ $pK(300) = -3.43$

(* if $CaHCO_3$ is deleted this value will change)

TABLE C-4 (CONT'D)

THERMOCHEMICAL DATA FOR CO_2, HCO_3^-, and CO_3^{2-}

Reference	Reaction	Data
34	$CaMg(CO_3)_{2(s)}$	formation data to 800°C
34	$MgCO_{3(s)}$	formation data to 700°C
22	$Mg^{2+} + HCO_3^- = MgHCO_3^+$	$\log K = 2.319 - 0.011056\ T + 2.298 \times 10^{-5}\ T^2$ (valid 10-90°C)
25	$Mg^{2+} + HCO_3^- = MgHCO_3^+$	$pK(250) = -2.56$ $pK(300) = -2.97$
22	$Mg^{2+} + CO_3^{2-} = MgCO_3^\circ$	$\log K = 0.991 + 0.0066\ T$ (valid 10-90°C)
25	$M^{2+} + HCO_3^- = MHCO_3^+$	log K at various T for Ni, Mn, Cu, Zn, Fe

TABLE C-5

THERMOCHEMICAL DATA FOR SILICA, SILICIC ACID, AND SILICATE SPECIES

Reference	Reaction	Data
25	$SiO_{2(s)} + 2\ H_2O = H_4SiO_4$	$\Delta G(298) = 5494\ \Delta S(298) = 5.26$ $\Delta C_p(0-300) = -11.9$
35	$SiO_{2(s)} + 2\ H_2O = H_4SiO_4$	$\log K(300) = -1.94$*
25	$SiO_{2(s)} + 2\ H_2O = H_4SiO_{4(aq)}$	$\Delta G = 5494 - 5.26\ \Delta T$ $-11.9\ a\ (T)$ $pK(300) = 2.00$ *
25	$SiO_{2(s)} + 2\ H_2O = H_3SiO_4{}^-{}_{(aq)}$	$pK(300) = 11.22$*
25	$H_4SiO_4 + OH^- = H_2SiO_3^- + H_2O$	$\Delta G(298) = -5687\ \Delta S(298) = 5.14$ $\Delta C_p(0-300) = 12$
25	$H_4SiO_4 + OH^- = H_2SiO_3^- + H_2O$	$\log K = 2346.69/T + 2.47979 \ln T - 18.4014$
25	$H_4SiO_4 = H^+ + H_3SiO_4^-$	$pK(300) = 9.22$*
22	$H_4SiO_4 = H^+ + H_3SiO_4^-$	$\log K = 6.3680 - 0.0163\ T - 3405.8999/T$
22	$H_4SiO_4{}^{\circ} = 2\ H^+ + H_2SiO_4{}^{2-}$	$\log K = 39.4780 - 0.0659\ T - 12355.0977/T$
35	H_4SiO_4	formation data to 300°C
25	$M_2SiO_{4(s)} = MO_{(s)} + MSiO_{3(s)}$	
	M = Mg	$pK(300) = 2.182$*
	M = Ca	$pK(300) = 4.265$*
	M = Fe	$pK(300) = 0.426$*
25	$MSiO_{3(s)} = MO_{(s)} + SiO_{2(s,quartz)}$	
	M = Mg	$pK(300) = 3.242$*
	M = Ca	$pK(300) = 8.115$*
	M = Fe	$pK(300) = 2.068$*
25	$MSiO_{3(s)} + H_2O = M^{2+} + SiO_{2(s,quartz)} + 2\ OH^-$	
	M = Mg	$pK(300) = 16.5$*
	M = Ca	$pK(300) = 14.2$*
	M = Fe	$pK(300) = 19.1$*
25	$M_2SiO_{4(s)} + H_2O = 2M^{2+} + SiO_{2(s,quartz)} + 4\ OH^-$	
	M = Mg	$pK(300) = 31.9$*
	M = Ca	$pK(300) = 24.6$*
	M = Fe	$pK(300) = 36.7$*
35	$Mg_2SiO_{4(s)} + 4\ H^+ = 2\ Mg^{2+} + H_4SiO_4$	$\log K(300) = 12.61$*

TABLE C-5 (CONT'D)

THERMOCHEMICAL DATA FOR SILICA, SILICIC ACID, AND SILICATE SPECIES

25	$MSiO_{3(s)} + H_2O + H^+ = M^{2+} + H_3SiO_4^-$	
	M = Mg	pK(300) = 5.112*
	M = Ca	pK(300) = 2.864*
	M = Fe	pK(300) = 7.786*
25	$M^{2+} + N_2SiO_{4(s)} = N^{2+} + MNSiO_{4(s)}$	
	M = Fe, N = Ca	pK(300) = -6.949*
	M = Ca, N = Fe	pK(300) = 5.102*
	M = Mg, N = Ca	pK(300) = -5.211*
	M = Ca, N = Mg	pK(300) = 2.026*
34	$CaMg(SiO_3)_{2\ (s)}$	formation data to 1300°C
34	$CaSiO_{3(s)}$	formation data to 1100°C
34	$Ca_2SiO_{4(s)}$	formation data to 1500°C
34	$Ca_3Mg(SiO_4)_{2\ (s)}$	formation data to 1300°C
34	$Fe_2SiO_{4\ (s)}$	formation data to 1500°C
34	$MgSiO_{3(s)}$	formation data to 1300°C
34	$Mg_2SiO_{4(s)}$	formation data to 1500°C
12	$Ca_3Si_2O_{7(s)} + 7\ H_2O = 3Ca^{2+} + 6\ OH^- + 2\ H_4SiO_4^{\circ}$	log K(275) = -43.16
12	$CaSiO_{3(s)} + 3\ H_2O = Ca^{2+} + 2\ OH^- + H_4SiO_4^{\circ}$	log K(275) = -15.70
12	$Ca_2SiO_{4(s)} + 4\ H_2O = 2\ Ca^{2+} + 4\ OH^- + H_4SiO_4^{\circ}$	log K(275) = -25.33
12	$Ca_3SiO_{5(s)} + 5\ H_2O = 3\ Ca^{2+} + 6\ OH^- + H_4SiO_4^{\circ}$	log K(275) = -29.6
12	$MgSiO_{3(s)} + 3\ H_2O = Mg^{2+} + 2\ OH^- + H_4SiO_4^{\circ}$	log K(275) = -18
12	$Mg_3Si_2O_7.2H_2O_{(s)} + 5\ H_2O = 3\ Mg^{2+} + 6\ OH^- + H_4SiO_4^{\circ}$	log K(275) = -52.14
12	$Mg_2SiO_{4(s)} + 4\ H_2O = 2\ Mg^{2+} + 4\ OH^- + 2\ H_4SiO_4^{\circ}$	log K(275) = -32.77
12	$CaMgSi_2O_{6(s)} + 6\ H_2O = Ca^{2+} + Mg^{2+} + 4\ OH^- + 2\ H_4SiO_4^{\circ}$	log K(275) = -35.47
12	$Ca_2MgSi_2O_{7(s)} + 7\ H_2O = 2\ Ca^{2+} + Mg^{2+} + 6\ OH^- + 2\ H_4SiO_4^{\circ}$	log K(275) = -45.46
12	$CaMgSiO_{4(s)} + 4\ H_2O = Ca^{2+} + Mg^{2+} + 4\ OH^- + H_4SiO_4^{\circ}$	log K(275) = -30.68

TABLE C-6

THERMOCHEMICAL DATA FOR HYDROXIDES AND METAL HYDROLYSIS REACTIONS

Reference	Reaction	Data
35	$OH^-_{(aq)}$	formation data to 300°C
31,12	$Ca(OH)_{2(s)} = Ca^{2+} + 2\ OH^-$	$\log K_{sp} = -25.7085$ $+ 12.9722 \log T$ $- 530.49/T$ $- 0.032331\ T$ $+ (6A\ I^{1/2}/1 + A_k\ I^{1/2})$ $- BI - CI^2$ (see 26 for parameters, valid to critical T of water)
11	$Ca(OH)_{2(s)} = Ca^{2+} + 2\ OH^-$	$pK(250) = 8.37$ $pK(300) = 9.38$
25	$Ca(OH)_{2(s)} = Ca^{2+} + 2\ OH^-$	$pK(300) = 10.48$*
10	$Ca(OH)_{2(s)} = Ca^{2+} + 2\ OH^-$	$\log K(300) = -9.39$
12	$Ca(OH)_{2(s)} = Ca^{2+} + 2\ OH^-$	$\log K(275) = -8.88$
25	$Ca^{2+} + 2\ H_2O = Ca(OH)_{2(s)} + 2\ H^+$	$pK(300) = 12.12$*
34	$Ca(OH)_{2(s)}$	formation data to 400°C
34	$Mg(OH)_{2(s)}$	formation data to 600°C
25	$Mg(OH)_{2(s)} = Mg^{2+} + 2\ OH^-$	$pK(300) = 14.54$*
11	$Mg(OH)_{2(s)} = Mg^{2+} + 2\ OH^-$	$pK(250) = 13.97$ $pK(300) = 14.98$
31	$Mg(OH)_{2(s)} = Mg^{2+} + 2\ OH^-$	$pK(300) = 14.98$*
10	$Mg(OH)_{2(s)} = Mg^{2+} + 2\ OH^-$	$\log K(300) = -14.25$
12	$Mg(OH)_{2(s)} = Mg^{2+} + 2\ OH^-$	$\log K = \log [Ca^{2+}][OH^-]^2 - 5.6$
12	$Mg(OH)_{2(s)} = Mg^{2+} + 2\ OH^-$	$\log K(275) = -14.48$
35	$Mg(OH)^+ = Mg^{2+} + OH^-$	$pK(200) = 4.1$*
10	$Mg(OH)^+ = Mg^{2+} + OH^-$	$pK(250) = 5.0$ $pK(300) = 5.7$
22	$Mg^{2+} + OH^- = Mg(OH)^+$	$\log K = 0.684 + 0.0051\ T$ (valid 10-90°C)
25	$Mg^{2+} + 2\ H_2O = Mg(OH)_2(s) + 2\ H^+$	$pK(300) = 8.06$*
12	$NH_4OH = NH_4^+ + OH^-$	$\log K = -2.8 \times 10^{-5}\ T^2$ $+ 0.018\ T - 7.63$ $+ A\ I^{1/2}/ (1 + 1.5\ I^{1/2})$
31	$NH_4OH = NH_4^+ + OH^-$	$pK_B(300) = 6.466$*
10	$NH_4OH = NH_4^+ + OH^-$	$\log K(300) = -6.21$

TABLE C-6 (CONT'D)

THERMOCHEMICAL DATA FOR HYDROXIDES AND METAL HYDROLYSIS REACTIONS

Reference	Reaction	Data
31	$NaOH = Na^{+} + OH^{-}$	K(218) = 0.55
10	$NaOH = Na^{+} + OH^{-}$	log K(300) = -1.10
31	$LiOH = Li^{+} + OH^{-}$	K(350) = 0.007
35	$FeOH^{+} = Fe^{2+} + OH^{-}$	pK(200) = 5.7*
25	$Fe^{2+} + H_2O = Fe(OH)^{+} + H^{+}$	ΔG(298) = 12700 ΔS(298) =1.7 ΔC_p(0-300) =-7
42	$2\ Cu^{2+} + 2\ H_2O = Cu_2(OH)_2^{2+} + 2\ H^{+}$	log K = 2.497 - 3833/T
25	$M^{2+} + H_2O = M(OH)^{+} + H^{+}$	pK(300)
	M = Mn	5.77*
	M = Fe	4.92*
	M = Co	5.10*
	M = Ni	5.22*
	M = Cu	4.22*
25	$M^{2+} + 2\ H_2O = M(OH)_2^{\circ} + 2\ H^{+}$	pK(300)
	M = Mn	11.9*
	M = Fe	10.9*
	M = Co	10.2*
	M = Ni	11.6*
	M = Cu	9.2*
25	$M^{2+} + 3\ H_2O = M(OH)_3^{-} + 3\ H^{+}$	pK(300)
	M = Mn	21.0*
	M = Fe	18.2*
	M = Co	19.3*
	M = Ni	18.1*
	M = Cu	17.4*

TABLE C-7

THERMOCHEMICAL DATA FOR SULFURIC ACID, AND SULFATE SPECIES

Reference	Reaction	Data
35	SO_4^{2-}	formation data to 300°C
25	$HSO_4^- = H^+ + SO_4^{2-}$	pK(300) = 6.324*
10	$HSO_4^- = H^+ + SO_4^{2-}$	log K(300) = -7.06
11	$HSO_4^- = H^+ + SO_4^{2-}$	pK(250)= 4.98 pK(300)= 5.71
35	$HSO_4^- = H^+ + SO_4^{2-}$	log K(300) = -7.06*
31,12	$HSO_4^- = H^+ + SO_4^{2-}$	$\log K = - 33.0024 \log T + 91.471 - 3520.3/T$
22	$H^+ + SO_4^{2-} = HSO_4^-$	$\log K = -5.3505 + 557.2461/T + 0.0183412\ T$ (valid 25-225°C)
25	$SO_4^{2-} + H_2O = HSO_4^- + OH^-$	pK(300) = 4.977*
10	$H_2SO_4 = H^+ + HSO_4^-$	log K(300) = 0.70
35	$H_2SO_4 = H^+ + HSO_4^-$	log K(300) = 0.50*
25	$HSO_4^- + HPO_4^{2-} = H_2PO_4^- + SO_4^{2-}$	pK(300) = 2.622*
31,12	$CaSO_{4(s)} = Ca^{2+} + SO_4^{2-}$	$\log K = - 133.207 + 3569.6/T + 53.5472 \log T + 0.0529025\ T$
25	$CaSO_{4(s)} = Ca^{2+} + SO_4^{2-}$	pK(300) = 5.917*
10	$CaSO_{4(s)} = Ca^{2+} + SO_4^{2-}$	log K(300) = - 9.05
10	$CaSO_4 = Ca^{2+} + SO_4^{2-}$	log K(300) = - 5.36
35	$CaSO_4 = Ca^{2+} + SO_4^{2-}$	log K(200) = - 3.6*
12	$CaSO_{4(s)} = Ca^{2+} + SO_4^{2-}$	log K(275) = - 9.03
11	$CaSO_{4(s)} = Ca^{2+} + SO_4^{2-}$	pK(250) =8.03 pK(300) =9.25
25	$BaSO_{4(s)} = Ba^{2+} + SO_4^{2-}$	pK(300) = 10.155*
25	$BaSO_{4(s)} + Ca^{2+} = CaSO_{4(s)} + Ba^{2+}$	pK(300) = 4.238*
31	$MgSO_4^{\circ} = Mg^{2+} + SO_4^{2-}$	$\log K = -158.540 + 4180.6/T + 62.160 \log T - 0.046298\ T$
10	$MgSO_4 = Mg^{2+} + SO_4^{2-}$	log K(300) = -7.92
11	$MgSO_4(s) = Mg^{2+} + SO_4^{2-}$	pK(250) =5.56 pK(300) =7.33
35	$MgSO_4 = Mg^{2+} + SO_4^{2-}$	log K(200) = -4.8*
31	$Na^+ + SO_4^{2-} = NaSO_4^-$	pK(300) = 2.84*
10	$NaSO_4^- = Na^+ + SO_4^{2-}$	log K(300) = - 3.64
10	$Na_2SO_4 = 2\ Na^+ + SO_4^{2-}$	log K(300) = 2.40
11	$Na_2SO_4 = 2\ Na^+ + SO_4^{2-}$	pK(250) =5.01 pK(300) =5.34
10	$NaHSO_4 = Na^+ + HSO_4^-$	log K(300) = -0.30
22	$K^+ + SO_4^{2-} = KSO_4^-$	$\log K = 3.1060 - 673.5999/T$ (valid 10-50°C)
31	$K^+ + SO_4^{2-} = KSO_4^-$	pK(250) = 2.45
35	$KSO_4^- = K^+ + SO_4^{2-}$	log K(200) = -1.94*
35	$KHSO_4 = K^+ + HSO_4^-$	log K(250) = 0.8 log K(300) = - 0.3
10	$NH_4SO_4^- = NH_4^+ + SO_4^{2-}$	log K(300) = -0.30
35	$MnSO_4 = Mn^{2+} + SO_4^{2-}$	log K(200) = -4.3*
35	$ZnSO_4 = Zn^{2+} + SO_4^{2-}$	log K(200) = -4.6*

TABLE C-8

THERMOCHEMICAL DATA OF CHLORIDE SPECIES

Reference	Reaction	Data
35	$Cl^-_{(aq)}$	formation data up to 300°C
34	$CaCl_{2\,(s)}$	formation data up to 700°C
34	$FeCl_{2\,(s)}$	formation data up to 1000°C
34	$FeCl_{3\,(s)}$	formation data up to 400°C
34	$HCl_{(g)}$	formation data up to 1500°C
34	$NH_4Cl_{(s)}$	formation data up to 400°C
10	$HCl = H^+ + Cl^-$	log K(300) = -1.23
35	$HCl = H^+ + Cl^-$	log K(300) = -1.24*
31	$HCl = H^+ + Cl^-$	log K(360) = -2.98*
10	$NaCl = Na^+ + Cl^-$	log K(300) = -1.10
35	$NaCl = Na^+ + Cl^-$	log K(300) = -0.8*
31	$NaCl = Na^+ + Cl^-$	log K(360) = -1.88*
11	$NaCl_{(s)} = Na^+ + Cl^-$	log K(250) =.9 log K(300)=.3
11	$CaCl_{2(s)} = Ca^{2+} + 2Cl^-$	log K(250) = 2.4
		log K(300) = 1.6
11	$MgCl_{2(s)} = Mg^{2+} + 2Cl^-$	log K(250) = 1.4
		log K(300) = 0.6
35	$KCl = K^+ + Cl^-$	log K(300) = -0.6*
35	$FeCl^{2+} = Fe^{3+} + Cl^-$	log β(150) = -3.98*
35	$FeCl_2^+ = Fe^{3+} + 2Cl^-$	log β(150) = -4.72*
35	$FeCl_3 = Fe^{3+} + 3Cl^-$	log β(150) = -4.30*
35	$FeCl_4^- = Fe^{3+} + 4Cl^-$	log β(150) = -3.23*

TABLE C-9

THERMOCHEMICAL DATA FOR OTHER SPECIES

Reference	Reaction	Data
34	$O_{2(g)}$	formation data to 1500°C
25	$O_{2(aq)}$	$C_p(25-300) = 45$
25	$O_{2(g)} = O_{2(aq)}$	$\Delta G_T = 3944 + 22.9\ \Delta T + 39\ a(T)$
22	$H_2S = H+ + HS-$	$\log K = 11.17 - 0.02386T - 3279.0/T$ (valid 25–300°C)
35	$HS- = H+ + S^{2}-$	$\log K(300) = -7.72$*
34	$H_2S = H+ + HS-$	$\log K(300) = -8.06$*
34	$NH_{3(g)}$	formation data to 1500°C
25	$NH_{3(g)} = NH_{3(aq)}$	$\Delta G_T = -2410 + 19.4\ \Delta T + 5.9\ a(T)$
10	$NH_{3(aq)} = NH_{3(g)}$	$\log D(300) = 0.7$
11	$NH_4+ = NH_3 + H+$	$\log K(250) = -5.14$ $\log K(300) = -4.57$
22	$NH_4+ = NH_3° + H+$	$\log K = 0.6322 - 2835.7598/T - 0.001225\ T$
25	$NH_{3(aq)}$	$C_p(25-300) = 14$
25	$NH_3 + H_2O = NH_4+ + OH-$	$pK(300) = 6.694$*
25	$NH_3 + H+ = NH_4+$	$pK(300) = -4.607$*
25	$NH_{3(g)} + H_2O = NH_4+ + OH-$	$pK(300) = 7.582$*
25	$H_{2(aq)}$	$C_p = 36$
25	$H_{2(g)} = H_{2(aq)}$	$\Delta GT = 4238 + 17.5\ \Delta T + 29\ a(T)$
25	$N_{2(aq)}$	$C_p = 46$
25	$N_{2(g)} = N_{2(aq)}$	$\Delta G_T = 4340 + 23.0\ \Delta T + 39\ a(T)$

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