

AN ABSTRACT OF THE THESIS OF

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Hydrogen sulfide emissions from the smelt dissolving tank area of some kraft pulp mills exceed environmental limitations. There are two main factors to consider in determining the cause of these emissions: chemical equilibria and rate processes. This investigation considers the chemical equilibria in the smelt shatter jet area (system A) and the dissolving tank (system B) of a kraft pulp mill.

In each system, the chemical species and operating conditions are described. The thermodynamic constants, which include activity coefficients and equilibrium constants, are determined. A detailed analysis is made of the errors in these thermodynamic constants, particularly the activity coefficients in the dissolving tank. An iterative calculation procedure to calculate the equilibrium composition is given for each system. In both cases, the system of equations includes conservation of mass in each phase and equilibrium expressions describing the interactions between species. The calculated

equilibrium values are compared to measured values to determine if either system is at equilibrium.

The calculated equilibrium partial pressures of hydrogen sulfide for system A greatly exceed the measured values obtained from a kraft pulp mill. Thus, the evolution of hydrogen sulfide in system A is not limited by equilibrium, but by rate processes (i.e., kinetics or mass transfer). The major variables affecting hydrogen sulfide release are steam, carbon dioxide, and oxygen partial pressures.

In system B, the equilibrium partial pressure of hydrogen sulfide is stable over the typical range of operating conditions. The uppermost limit of calculated equilibrium partial pressures of hydrogen sulfide is slightly below the measured values.

As a result of these equilibrium calculations, it is concluded that the major source of hydrogen sulfide emissions is system A. Future work is recommended involving experimentation to determine the rate processes controlling the release of hydrogen sulfide. Process controls and modifications for a kraft pulp mill that may help decrease emissions are also presented.

A Study of Chemical Equilibria in the
Kraft Smelt Dissolving System

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NOMENCLATURE

<u>Symbol</u>	
a, b*	Empirical constants in equation (42).
a_i	Activity of species i.
a1, b1, c1, I1	Constants used in equation (23) to calculate the standard state change in the Gibbs function.
a2, b2, c2, θ , ω	Temperature independent coefficients specific to the solvent, used in equations (56) and (57).
A, B	Constants used in equation (44).
c	Empirical parameter defined by equation (41).
$C_{p,i}^\circ$	Standard heat capacity of species i.
$C_{p,i}^\circ]_{T_r}^T$	Average standard heat capacity of species i from temperature T_r to temperature T.
$C_{T,i}$	Number of moles of "species containing i" per kg solvent.
F	Degrees of freedom or number of independent variables.
I	Total ionic strength
I_i	Ionic strength for species i.
k_i	Salting out coefficient for species i.
K_i	Thermodynamic equilibrium constant.
m	Total molality.
m_i	Molality of species i.
N	Number of chemical species.
P	Number of chemical phases.
P_i	Partial pressure of species i.
pH	$-\log$ (moles H^+ /liter solution).
ppm	Parts per million.

Symbol

q	Empirical parameter defined by equation (39).
r	Number of restrictions or chemical reactions.
R	Gas constant, 1.9872 cal/gmol-°K.
S	Number of special constraints.
T	Temperature.
T_r	Reference temperature in degrees kelvin (298.15°K).
V_{ij}	Defined by equation (45).
W	Interaction parameter used in equation (21).
x	Liquid mole fraction.
y	Gas mole fraction.
z_i, z_j	Absolute values of cationic and anionic charge.
$\alpha', \beta', \lambda'$	Temperature independent coefficients characteristic of the reaction, used in equation (57).
γ_+, γ_-	Single ion activity coefficients.
γ_{ij}	Mean ionic activity coefficient of species ij in a multicomponent a solution.
γ_{ij}°	Mean activity coefficient for i (cation) and j (anion) in water.
$(\gamma_{ij})_{\text{eff}}$	Effective mean activity coefficient for ij in a ternary system.
Γ_{ij}	Reduced activity coefficient for an electrolyte ij in a multicomponent solution.
Γ_{ij}°	Reduced activity coefficient of electrolyte ij in water.
Γ^*	Value of Γ_{ij}° when I approaches a very small value; that is, Γ_{ij}° from the Debye-Hückel limiting equation (40).
ν_j, ν_ℓ	Stoichiometric coefficients for the products and reactants, respectively, used in equation (55).

$\Delta C_{p,r}^{\circ}$	Standard heat capacity change of reaction.
$\Delta C_{p,r}^{\circ}]_{T_r}^T$	Average standard heat capacity change of reaction from temperature T_r to temperature T.
ΔG°	Standard-state change in the Gibbs function.
ΔG^E	Excess change in the Gibbs function.
$\overline{\Delta G}_i$	Partial molar change in the Gibbs function.
$\overline{\Delta G}_i^E$	Excess partial molar change in the Gibbs function.
$\overline{\Delta G}_i^{id}$	Ideal partial molar change in the Gibbs function.
ΔH	Heat of mixing.
ΔH°	Standard-state change in enthalpy.
ΔH_r°	Standard enthalpy of reaction.
ΔH^E	Excess enthalpy change.
$\overline{\Delta H}_i$	Partial molal heat of mixing.
$\overline{\Delta H}_i^E$	Excess partial molar change in enthalpy.
ΔS_e°	Standard electrostatic entropy of dissociation.
ΔS_r°	Standard entropy of reaction.
ΔS^E	Excess entropy change.
[]	Molality (moles solute/kg solvent).

A STUDY OF CHEMICAL EQUILIBRIA IN THE KRAFT SMELT DISSOLVING SYSTEM

INTRODUCTION

In chemical pulping of wood, about half of the wood is recovered as fibers. The remainder of the wood is dissolved in an aqueous solution of pulping chemicals. The spent pulping liquor is burned to recover the heating value of the dissolved organics as steam and to separate the inorganic pulping chemicals for recovery.

The predominant chemical pulping process in the United States is the kraft process. This process uses a solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to pulp wood. The spent pulping liquor from the kraft process is concentrated to about 65 percent solids and burned in a recovery boiler. The recoverable inorganics consist mainly of sodium carbonate (Na_2CO_3) and Na_2S . This fraction falls to the bottom of the boiler where it forms a molten salt mixture (smelt).

Na_2S is produced in the lower region of the recovery boiler due to the reducing conditions that are maintained there. Sodium sulfate (Na_2SO_4) is usually present because of incomplete reduction to Na_2S in the recovery boiler. Na_2SO_4 enters the recovery boiler as makeup chemical and as recycled particulates from the recovery boiler stack. It is also formed from reoxidation of Na_2S as it contacts air when leaving the recovery boiler. The smelt is drained off through openings in the bottom of the boiler (smelt spouts). Steam jets (shatter jets) are then used to break up the molten smelt into droplets (Figure 1). These droplets then fall into the dissolving tank, which contains

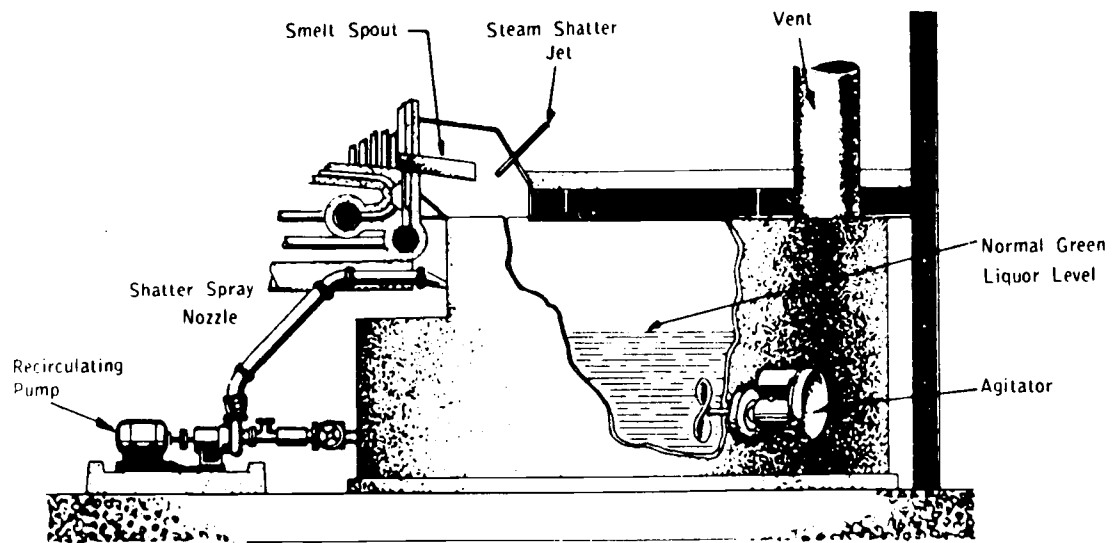


Figure 1. Smelt dissolving system (Smook, 1982).

a high temperature ionic solution. After leaving the dissolving tank, the solution is reconverted to fresh cooking liquor. The shatter jets and dissolving tank will be referred to as the dissolving tank system.

Reduced sulfur compounds, consisting mainly of hydrogen sulfide (H_2S), are released as gases in the smelt dissolving system. The measured level of H_2S emissions often exceeds environmental limits. It is important to determine the major parameters controlling the release of H_2S so that process controls or modifications can be implemented to reduce emissions.

To determine what controls or modifications are needed, we need first to understand what controls H_2S emissions in the shatter jet area and the dissolving tank. The overall problem has two main factors to consider: chemical equilibria and rate processes.

The first objective in solving the overall problem will be equilibrium studies at the shatter jet area (system A) and at the dissolving tank (system B). An equilibrium study at each area will identify the major variables affecting H_2S release. For a smelt of known composition, it will be possible to determine the equilibrium H_2S concentrations of system A and of system B. It must be determined whether either one of these equilibrium concentrations is equal to H_2S levels found in the dissolving tank system of a kraft mill. If not, then an experimental study will be necessary to determine which rate processes (e.g. mass transfer or kinetics) control the production of H_2S . Upon identification of the variables or rate processes controlling H_2S release, a control strategy or process modification can be recommended to reduce H_2S emissions.

The scope of this thesis is to carry out equilibrium analyses on system A and system B. The objective is to determine the composition of gases in equilibrium with a smelt of known composition. For system A the equilibrium H_2S concentration will be determined as a function of temperature, the partial pressures of water, carbon dioxide, and oxygen, and of the mole fraction of Na_2S in the smelt. For system B the equilibrium H_2S concentration will be determined as a function of temperature, pH, and initial concentrations of sodium carbonate, sodium sulfide, sodium sulfate, and sodium hydroxide. This will identify the major variables affecting H_2S release in each system. Measured H_2S concentrations from the dissolving tank system of a kraft pulp mill will then be compared to the calculated equilibrium H_2S concentrations from both systems. This will indicate if equilibrium has been attained or if rate processes are controlling the H_2S emissions.

If rate processes are controlling, an experimental study will be recommended. Control strategies or process modifications will also be recommended to reduce H_2S emissions.

SYSTEM A

A. Introduction

The shatter jets are high pressure steam (approximately 150 psia) jets directed at the liquid smelt flowing by gravity from the smelt spouts. The steam is moving at a high velocity and its kinetic energy "shatters" the molten smelt stream into small droplets. If the smelt were allowed to pour into the dissolving tank without first being fragmented, then explosions would result as the smelt boiled the aqueous solution (Reid, 1977).

The smelt leaves the kraft recovery boiler in the temperature range of 1025°K (Merriam et al, 1980) to just over 1100°K (Kelly et al, 1981). The melting range of the smelt varies considerably with smelt composition. The total pressure in the entire smelt dissolving system remains at approximately one atmosphere.

The first step in analyzing the chemical equilibrium of system A is to define the chemical species present. Next, we will discuss the equilibrium relationships and mass conservation equations used. Thermodynamic constants (i.e., equilibrium constants and activity coefficients) will then be calculated and employed in a computer program to determine the equilibrium concentrations of all species present. Those variables which have the largest effect on the partial pressure of H_2S will be determined. Comparisons to experimentally measured H_2S concentrations will also be made.

B. Chemical Species

The smelt consists mainly of Na_2CO_3 and Na_2S . Na_2SO_4 will also be considered because Grace (1979) has shown that the reoxidation of Na_2S to Na_2SO_4 can be very important in the temperature range from 800-1200°K. Reeve et al (1981) have also measured trace amounts of NaOH in kraft recovery boilers. Merriam et al (1980), however, have neglected the presence of NaOH in equilibrium analyses. In this study, we will examine the effect of NaOH on the release of H_2S .

System A also contains the following gaseous components: H_2S , H_2O , O_2 , N_2 , CO_2 , and SO_2 . H_2O , of course, enters the system to "shatter" the smelt into droplets. O_2 and N_2 enter the system as air through the ports in the smelt spout enclosure and auxiliary fans used to exhaust all gases up the dissolving-tank stack. Occasionally, carbon particles can be seen on the smelt surface as it flows out of the recovery boiler. CO_2 is included because Bauer and Dorland (1953) have shown that the oxidation of carbon is instantaneous in the temperature range from 800-1200°K. Borg et al (1974) have measured H_2S concentrations of 300 parts per million (ppm) directly above the smelt bed in kraft recovery boilers where O_2 concentrations are extremely low. Young (1977) has measured H_2S concentrations of 10 ppm just above the smelt spouts where O_2 concentrations are much higher. SO_2 is considered because some of the H_2S is probably oxidized to SO_2 . Bauer and Dorland (1953) have also shown this reaction to be instantaneous at such high temperatures.

C. Equilibrium Relationships and Conservation of Mass

In system A, there are two phases (liquid and gas) and ten components when NaOH is included in the analysis. The first step in defining the equilibrium is to determine the number of independent variables that must be arbitrarily specified to establish the state of the system. According to Smith and Van Ness (1979), the state of the system at equilibrium is fixed when the temperature, pressure, and composition in each phase is fixed. In this analysis there are, therefore, twelve phase rule variables: four liquid mole fractions, six gas mole fractions, temperature, and pressure. The power of the phase rule is that it will give the number of variables that, when specified, will establish the remaining variables in the system. This can be accomplished by employing the phase rule for reacting systems with special restraints:

$$F = 2 - P + N - r - S \quad (1)$$

where

F = degrees of freedom or number of independent variables

P = number of phases

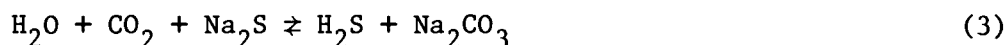
N = number of chemical species

r = number of restrictions or chemical reactions

S = number of special constraints

The main problem is to determine the maximum number of independent chemical reactions, r . Following the techniques described by Smith and Van Ness (1979), the formation equations are written for

each chemical compound present. Next the elements that are not present in the system are eliminated, one at a time, by combining the formation equations according to a fixed procedure. The final set of r equations that results is a complete set of independent reactions for the N species in the system. It should be noted that many such sets of reactions are possible, depending upon the order in which the reduction is carried out. All such sets of chemical reactions, however, will number r as long as all reacting chemical species are present at least once in that set of reactions. For the system we are concerned with containing ten species and two phases, the reduction analysis gives $r = 4$ (see Appendix 1 for the details). The four reactions that result are as follows:



It is important to remember that reactions (2-5) are not the only possible reactions; however, this set of reactions does in fact describe the actual system well. As noted earlier, Grace et al (1979) and Bauer and Dorland (1953) have found reactions (2) and (5) to be favored at high oxygen partial pressures and at high temperature. These conditions exist in the smelt dissolving system. Reaction (3) has been cited by Strohbeen and Grace (1982) and others as being significant in the liberation of H_2S .

Referring back to the overall phase rule analysis, a special constraint, that of constant sulfur to sodium ration (S/Na) in the liquid phase, was added to the analysis. Reasons for this restraint will be given in the next section.

The overall degrees of freedom for the system where $N = 10$, $r = 4$, $P = 2$, and $S = 1$ is 5 using equation (1). This means that we must fix five variables. We can specify temperature, pressure, and any three mole fractions. When we specify five of these variables, all other phase rule variables will be fixed.

In the analysis in which NaOH is neglected, one variable is eliminated ($N = 9$), as is reaction (4). This has no net effect upon the number of overall degrees of freedom which remains equal to 5.

Each of the reversible reactions listed above will now be considered. By applying thermodynamic principles, chemical reaction equilibria can be calculated as long as the necessary thermal data for the compounds are known.

The equilibrium state can be defined as the point where no further change will take place unless the reaction conditions are changed. The equilibrium constant, K , defines the equilibrium state. An equilibrium constant can be written for each of the four reactions.

$$K_2 = \frac{a_{\text{Na}_2\text{SO}_4}}{a_{\text{Na}_2\text{S}}^2 a_{\text{O}_2}^2} \quad (6)$$

$$K_3 = \frac{a_{\text{H}_2\text{S}} a_{\text{Na}_2\text{CO}_3}}{a_{\text{Na}_2\text{S}} a_{\text{H}_2\text{O}} a_{\text{CO}_2}} \quad (7)$$

$$K_4 = \frac{a_{\text{NaOH}}^2 a_{\text{H}_2\text{S}}}{a_{\text{Na}_2\text{S}} a_{\text{H}_2\text{O}}^2} \quad (8)$$

$$K_5 = \frac{a_{\text{H}_2\text{O}} a_{\text{SO}_2}}{a_{\text{H}_2\text{S}} a_{\text{O}_2}^{3/2}} \quad (9)$$

where a_i is the activity of species i in the equilibrium mixture. The activity of a gas is equal to its partial pressure (P_i) in this system because the reaction conditions are such that the ideal gas model is a valid approximation. For a liquid, the standard state is that of the pure component at the same temperature, pressure, and phase as the mixture. The activity for this choice of standard state is equal to the mole fraction, x_i , multiplied by its activity coefficient, γ_i . Rewriting equations (6-9) in these terms will yield:

$$K_2 = \frac{x_{\text{Na}_2\text{SO}_4} \gamma_{\text{Na}_2\text{SO}_4}}{x_{\text{Na}_2\text{S}} \gamma_{\text{Na}_2\text{S}} P_{\text{O}_2}^2} \quad (10)$$

$$K_3 = \frac{P_{\text{H}_2\text{S}} x_{\text{Na}_2\text{CO}_3} \gamma_{\text{Na}_2\text{CO}_3}}{x_{\text{Na}_2\text{S}} \gamma_{\text{Na}_2\text{S}} P_{\text{H}_2\text{O}} P_{\text{CO}_2}} \quad (11)$$

$$K_4 = \frac{x_{\text{NaOH}}^2 \gamma_{\text{NaOH}}^2 P_{\text{H}_2\text{S}}}{x_{\text{Na}_2\text{S}} \gamma_{\text{Na}_2\text{S}} P_{\text{H}_2\text{O}}^2} \quad (12)$$

$$K_5 = \frac{P_{H_2O} P_{SO_2}}{P_{H_2S} P_{O_2}^{3/2}} \quad (13)$$

These four equations can now be related back to the phase rule analysis. There are twelve phase rule variables: four liquid mole fractions, six gas mole fractions, temperature, and pressure. As mentioned earlier, we will be specifying five variables; therefore, seven will be unknown but fixed. This means that seven independent equations will be needed to determine these seven unknowns. Equations (10-13) can be used as can the mass conservation equations for each phase:

$$\sum_{i=1}^4 x_i = 1.0 \quad (14)$$

$$\sum_{i=1}^6 y_i = 1.0 \quad (15)$$

The seventh equation comes from the special constraint that was placed on the system, that of constant S/Na in the liquid phase.

Written in terms of mole fractions, S/Na is:

$$\frac{S}{Na} = \frac{x_{Na_2S} + x_{Na_2SO_4}}{x_{NaOH} + 2(x_{Na_2SO_4} + x_{Na_2S} + x_{Na_2CO_3})} \quad (16)$$

D. Thermodynamic Constants

Activity Coefficients

In order to solve the simultaneous equations developed in the previous section, we need to determine the activity coefficients for each of the liquid phase species. Rosen and Sillen (1960) and others conducting equilibrium studies considered the smelt as a binary mixture containing 50 to 80 percent Na_2CO_3 and 20 to 50 percent Na_2S . Na_2SO_4 and NaOH were trace species by comparison, and their mole fractions usually remained below 0.05. No data for the activities in ternary or quaternary melts of the four species, Na_2S , Na_2CO_3 , Na_2SO_4 , and NaOH , were found in the literature. We, therefore, decided to treat the smelt as a binary mixture as Rosen and Sillen (1960) did.

The two components Na_2S and Na_2CO_3 have the cation in common and anions of the same charge and approximately the same ionic radius. Rosen and Sillen (1960) determined that the binary mixture followed "regular" solution behavior as described by Hildebrand (1929). The assumption of "regular solution" behavior implies that the excess entropy change (ΔS^E) of mixing is zero. The excess entropy change is also related to changes in the excess enthalpy and Gibbs function as follows:

$$\Delta H^E = \Delta G^E + T\Delta S^E \quad (17)$$

With $\Delta S^E = 0$, then $\Delta H^E = \Delta G^E$. This is valid for mixtures such as Na_2S - Na_2CO_3 which have the cation in common, and anions of the same charge and roughly the same "ionic radius."

For a regular solution, the heat of mixing, ΔH varies parabolically with composition so the following equation can be developed:

$$\Delta H^E = \Delta H = Wx_i x_j \quad (18)$$

From the definition of partial molal quantities it follows that:

$$\overline{\Delta H}_j^E = Wx_i^2 \quad \text{and} \quad \overline{\Delta H}_i^E = Wx_j^2 \quad (19)$$

Hildebrand (1929) found that the excess partial molar change in the Gibbs function in transferring one mole of species i from an ideal solution to a regular one was equal to:

$$\overline{\Delta G}_i^E = \overline{\Delta G}_i - \overline{\Delta G}_i^{\text{id}} = RT \ln \frac{a_i}{x_i} \quad (20)$$

We can also define the activity coefficient as $\gamma_i = a_i/x_i$ and since $\overline{\Delta G}_i^E = \overline{\Delta H}_i^E$, equations (19) and (20) can be combined to yield:

$$RT \ln \gamma_i = Wx_j^2 \quad \text{and} \quad RT \ln \gamma_j = Wx_i^2 \quad (21)$$

The derivation of these expressions can be accomplished with the use of Van Ness and Abbott (1982).

Equation (21) relates the activity coefficient of species i to the mole fraction of species j , system temperature, and in interaction parameter, W . The interaction parameter can be computed from heat of mixing data or freezing point data. For the $\text{Na}_2\text{S}-\text{Na}_2\text{CO}_3$

system, Rosen and Sillen (1960) used freezing point data to obtain an average W equal to 3750 cal/mole. Since W is independent of temperature, as discussed in Lewis and Randall (1961), it is a straightforward calculation to relate the activity coefficient of Na_2S and the mole fraction of Na_2CO_3 .

Since no data were available for the activity coefficients for Na_2SO_4 and NaOH , an error analysis was done to determine the effect the range $\gamma_{\text{NaOH}} = \gamma_{\text{Na}_2\text{SO}_4} = 1 - 5$, would have upon equilibrium concentrations. Five is the maximum γ value generated by equation (21) as x approaches one. The results of this error analysis will be discussed in Section E.

Equilibrium Constants

In order to solve the set of simultaneous equations in part C, we need to calculate equilibrium constants for each of the chemical reactions. At equilibrium $\Delta G = 0$; therefore, it is possible to relate the standard-state change in the Gibbs function of each reaction to its corresponding equilibrium constant:

$$\Delta G^\circ = -RT \ln K \quad (22)$$

Bauer and Dorland (1953) used equations of the type:

$$\Delta G^\circ = \Delta H^\circ + a_1(T \log T) + b_1(T^2/1000) + c_1(1000/T) + I_1(T) \quad (23)$$

to calculate ΔG° for each chemical compound. The constants a_1 , b_1 , c_1 and I_1 were different, depending upon which compound was being studied. ΔG° and $\log K$ were then calculated for several high

temperature reactions. The equilibrium constants for reactions (2) and (3) above, were calculated directly at the temperature of interest (1000°K and 1200°K), by Bauer and Dorland (1953). In the case of reactions (4) and (5), the equilibrium constants were determined by combining formation reactions for the individual products and reactants where $\log K$ values were available. A listing of the equilibrium constants used in system A can be seen in Appendix 4.

E. Calculation Procedure

A computer program was written to solve the seven simultaneous equations developed in part C. In this program five of the twelve phase rule variables are arbitrarily specified. These five variables are: temperature, pressure, and the mole fractions of O_2 , CO_2 , and H_2O in the gas phase. The gas-phase mole fractions of O_2 , CO_2 , and H_2O were selected because preliminary investigations showed that they had the greatest influence on the partial pressure of H_2S . As noted earlier, the total pressure in all cases is one atmosphere; and

$$P_i = y_i P.$$

The first iterative section of the program assumes a value of $\gamma_{Na_2S} = 1.943$ which corresponds to a Na_2CO_3 mole fraction ($x_{Na_2CO_3}$) of approximately 0.65. This $x_{Na_2CO_3}$ value was chosen because preliminary calculations showed that $x_{Na_2CO_3}$ only varied from 0.55-0.75; therefore, the error in using approximately 0.65 for the initial guess was fairly small.

With $\gamma_{Na_2S} = 1.943$, the program does iterative calculations by incrementing the mole fraction of Na_2SO_4 ($x_{Na_2SO_4}$) until the fixed

S/Na is equal to its specified value. The lowest tolerance used in the S/Na calculations was one percent, because ten percent errors were found to exist in the equilibrium constants. Therefore, a more exact S/Na fit would have been meaningless.

After the S/Na iteration is complete, $\gamma_{\text{Na}_2\text{S}}$ is recalculated using the new value of $x_{\text{Na}_2\text{CO}_3}$ generated in the S/Na calculations. A successive substitution routine is used in this iterative section. The new $\gamma_{\text{Na}_2\text{S}}$ is then used back in the first iterative section that increments $x_{\text{Na}_2\text{SO}_4}$ until S/Na is at its fixed value. The whole process usually only takes two or three loops between section one and section two before the equilibrium calculations are within their one percent tolerance levels. The detailed logic can be seen on a flow diagram in Appendix 2, which also includes the computer program EQUIL and a sample printout.

The program prints out the equilibrium mole fractions in the liquid phase (x) and the equilibrium partial pressures (P_i) of all the gases present. The equilibrium composition corresponds to the temperature, pressure, and the mole fractions of O_2 , CO_2 , and H_2O in the gas phase that were initially specified. In this way, we can do a parametric analysis on the partial pressure of H_2S as a function of temperature, pressure, and the mole fractions of O_2 , CO_2 , H_2O , and Na_2S . This will both quantitatively and qualitatively identify the variables which have the greatest effect on the partial pressure of H_2S .

F. Results

It should be noted that liquid mole fractions will be denoted by x_i , gas mole fractions by y_i , and gas partial pressure as P_i .

The parametric analysis using program EQUIL was done for both 1200°K and 1000°K. These two temperatures represent the upper and lower temperature extremes that can be found in the molten smelt.

Figure 2A shows $-\log P_{\text{H}_2\text{S}}$ as a function of $-\log P_{\text{H}_2\text{O}}$ for various S/Na values and for the temperatures listed above. In these calculations, P_{O_2} was held constant at 10^{-18} atm (1000°K) or 10^{-14} atm (1200°K) depending upon temperature, while $P_{\text{CO}_2} = 0.05$ atm at both temperatures. In referring to Figure 2A it is clear that an increase in the $P_{\text{H}_2\text{O}}$ always leads to an increase in $P_{\text{H}_2\text{S}}$, regardless of S/Na or temperature. The change in S/Na from 0.16 to 0.10 at 1200°K appears to have little effect upon $P_{\text{H}_2\text{S}}$. In Figure 2B a drop in S/Na from 0.16 to 0.10 corresponds to a decrease in the equilibrium value of $x_{\text{Na}_2\text{S}}$ from 0.31 to 0.19.

It is obvious from Figure 2A that $P_{\text{H}_2\text{S}}$ is an order of magnitude greater when the temperature is 1000°K than it is for 1200°K. The maximum $P_{\text{H}_2\text{S}} = 0.00794$ ($-\log P_{\text{H}_2\text{S}} = 2.1$) occurs at 1000°K, S/Na = 0.16 and $P_{\text{H}_2\text{O}} = 0.900$ ($-\log P_{\text{H}_2\text{O}} = 0.046$). A value of $P_{\text{H}_2\text{S}} = 0.00794$ corresponds to an H_2S concentration of approximately 7940 ppm.

A sensitivity study was undertaken to determine the uncertainty in the calculated results. The standard deviations in each of the equilibrium constants and activity coefficients were combined to determine the maximum uncertainty. The error bars in Figure 2A for the S/Na curve at 1000°K correspond to this maximum uncertainty. In

Figure 2A. Variation of P_{H_2S} with P_{H_2O} and S/Na .

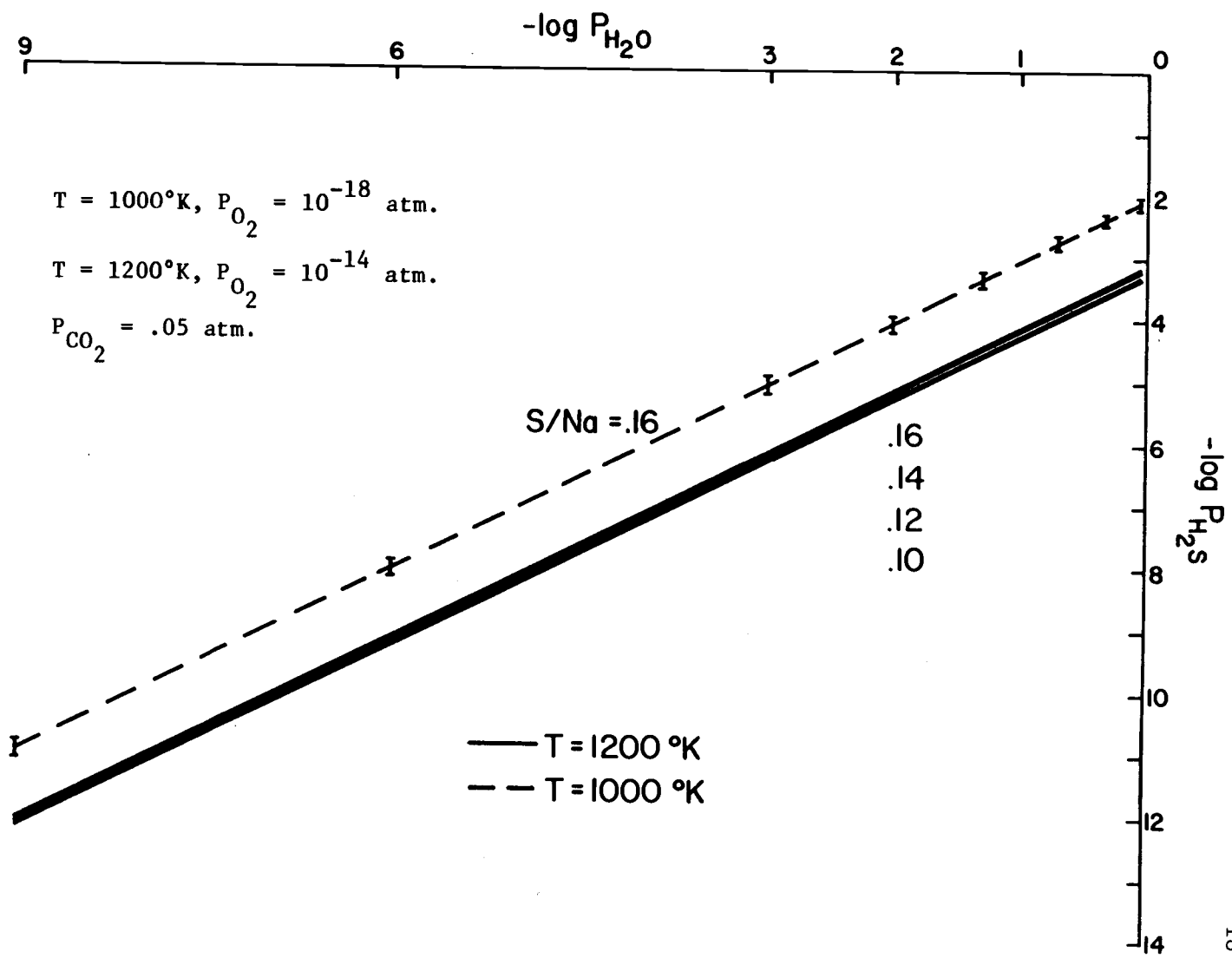


Figure 2B. Variation of X_{Na_2S} with P_{H_2O} and S/Na.

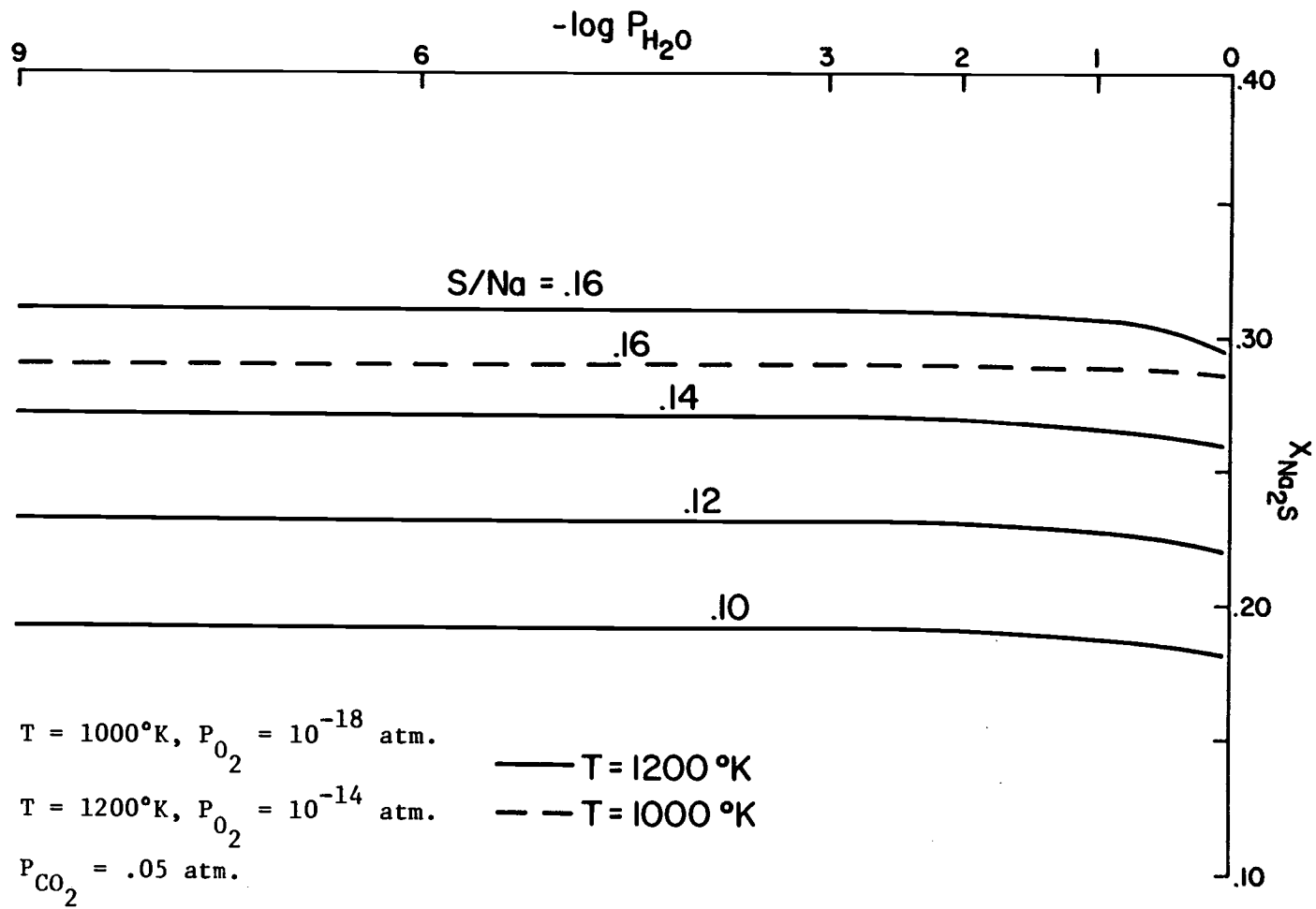


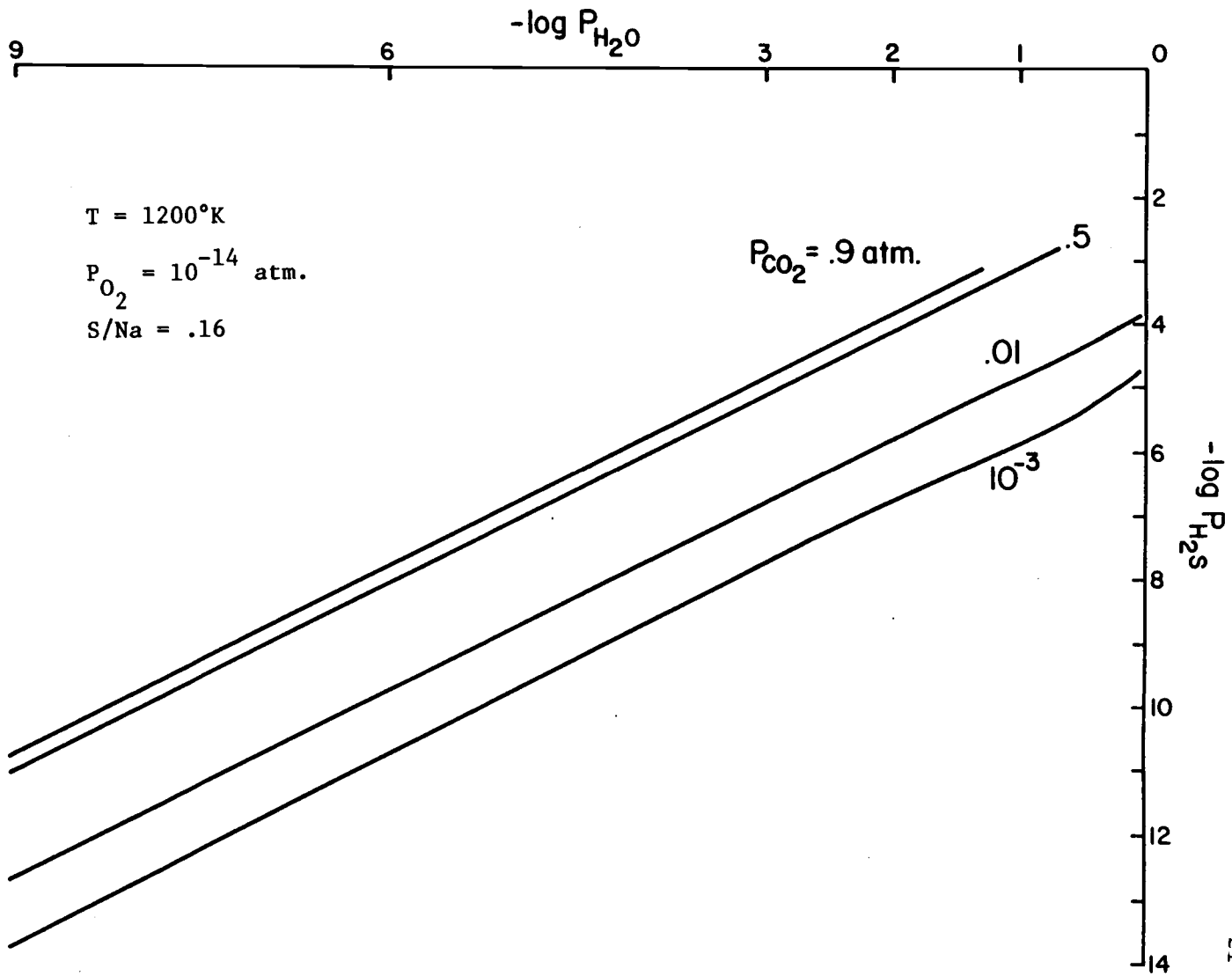
Figure 2A the maximum $P_{\text{H}_2\text{S}}$ value listed above is within an accuracy of ± 17 percent of the reported value. This uncertainty is applicable to all of the calculated equilibrium $P_{\text{H}_2\text{S}}$ values.

Figures 3A and 3B show $-\log P_{\text{H}_2\text{S}}$ as a function of $-\log P_{\text{H}_2\text{O}}$ at various P_{CO_2} and temperatures. In these calculations, P_{O_2} was held constant at 10^{-18} atm (1000°K) or 10^{-14} (1200°K) while $S/\text{Na} = 0.16$ at both temperatures. From Figures 3A and 3B, it is clear that an increase in P_{CO_2} causes a definite increase in $P_{\text{H}_2\text{S}}$ for all cases studied. The $P_{\text{H}_2\text{S}}$ is once again an order of magnitude greater at 1000°K than it is for 1200°K. Quantitatively, the $P_{\text{H}_2\text{S}}$ varies from 0.02 to 1.02×10^{-6} atmospheres in the $P_{\text{H}_2\text{O}}$ range from 0.9 to 0.1 atmospheres, depending upon temperature and P_{CO_2} . This corresponds to a change in H_2S concentration from 20,000 ppm to 1.02 ppm. It is clear that the highest concentration of H_2S occurs when high concentrations of H_2O and CO_2 are present. An increase in partial pressure of H_2S is once again seen to be directly proportional to a decrease in system temperature.

Figures 4A and 4B show $-\log P_{\text{H}_2\text{S}}$ as a function of $-\log P_{\text{H}_2\text{O}}$ at different P_{O_2} and temperatures. The P_{CO_2} and S/Na were held constant for this set of calculations at 0.05 atm and 0.16, respectively. At 1200°K, $P_{\text{H}_2\text{S}}$ increases linearly with $P_{\text{H}_2\text{O}}$ in all cases. As P_{O_2} is decreased, the $P_{\text{H}_2\text{S}}$ increases greatly until $P_{\text{O}_2} = 10^{-14}$. At this point, any further decrease in P_{O_2} has no further effect upon $P_{\text{H}_2\text{S}}$.

At 1000°K, the same linear relationship between H_2O and H_2S is evident, but $P_{\text{H}_2\text{S}}$ is an order of magnitude greater for the same P_{O_2} than it was for 1200°K. The $P_{\text{H}_2\text{S}}$ also becomes independent of P_{O_2} at a

Figure 3A. Variation of P_{H_2S} with P_{H_2O} and Y_{CO_2} at 1200°K.



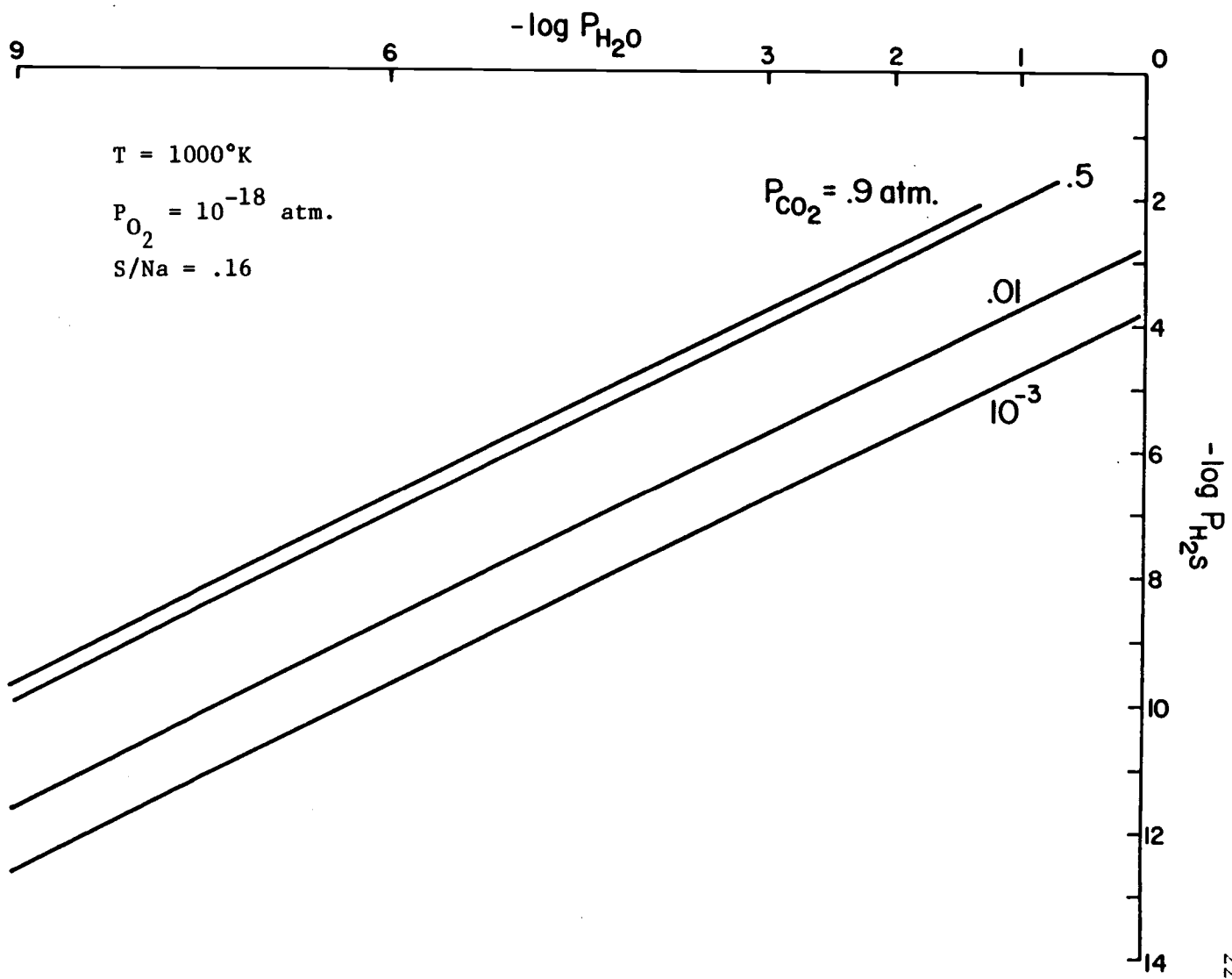


Figure 3B. Variation of $P_{\text{H}_2\text{S}}$ with $P_{\text{H}_2\text{O}}$ and Y_{CO_2} at 1000°K .

Figure 4A. Variation of P_{H_2S} with P_{H_2O} and Y_{O_2} at 1200°K.

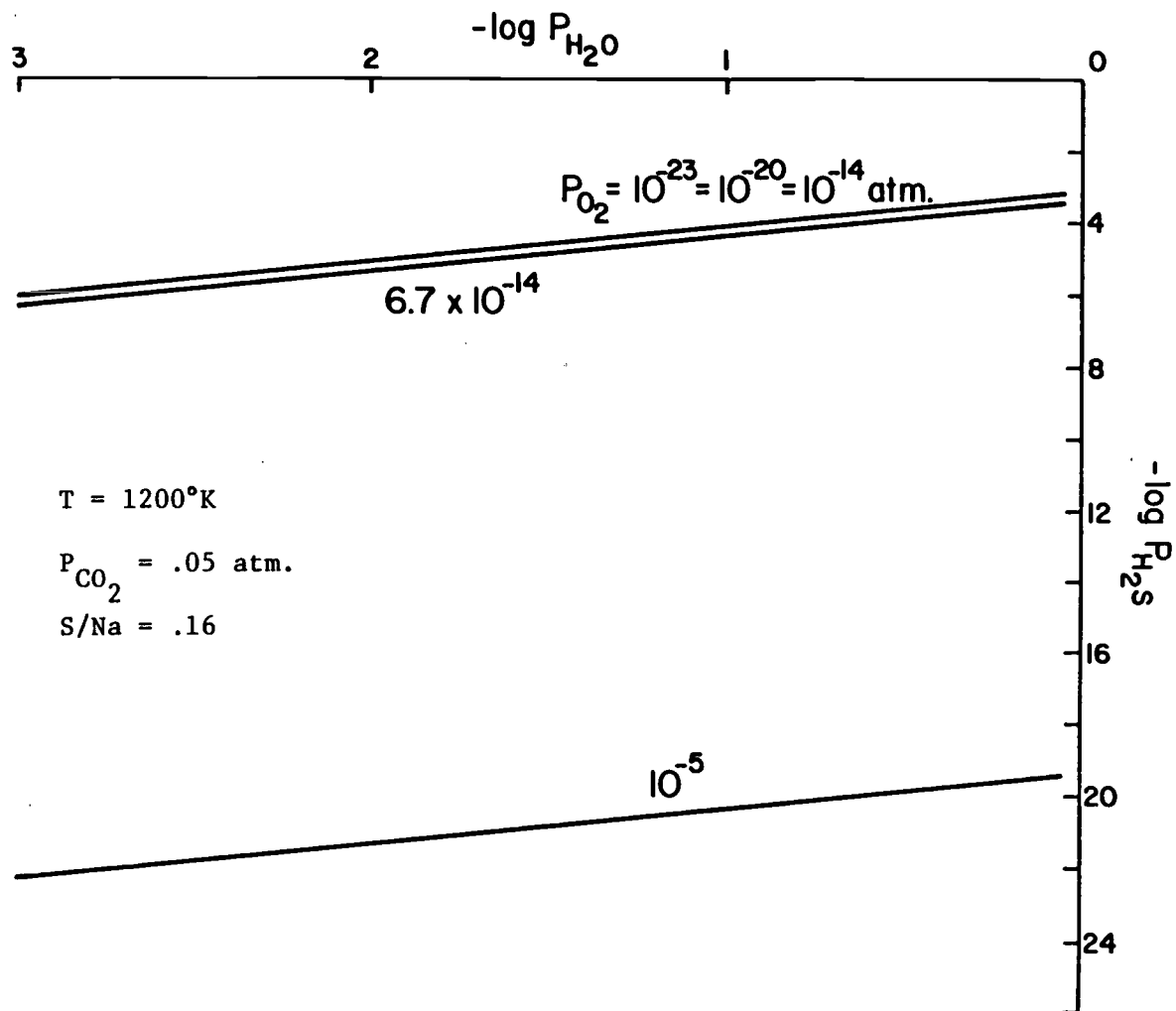
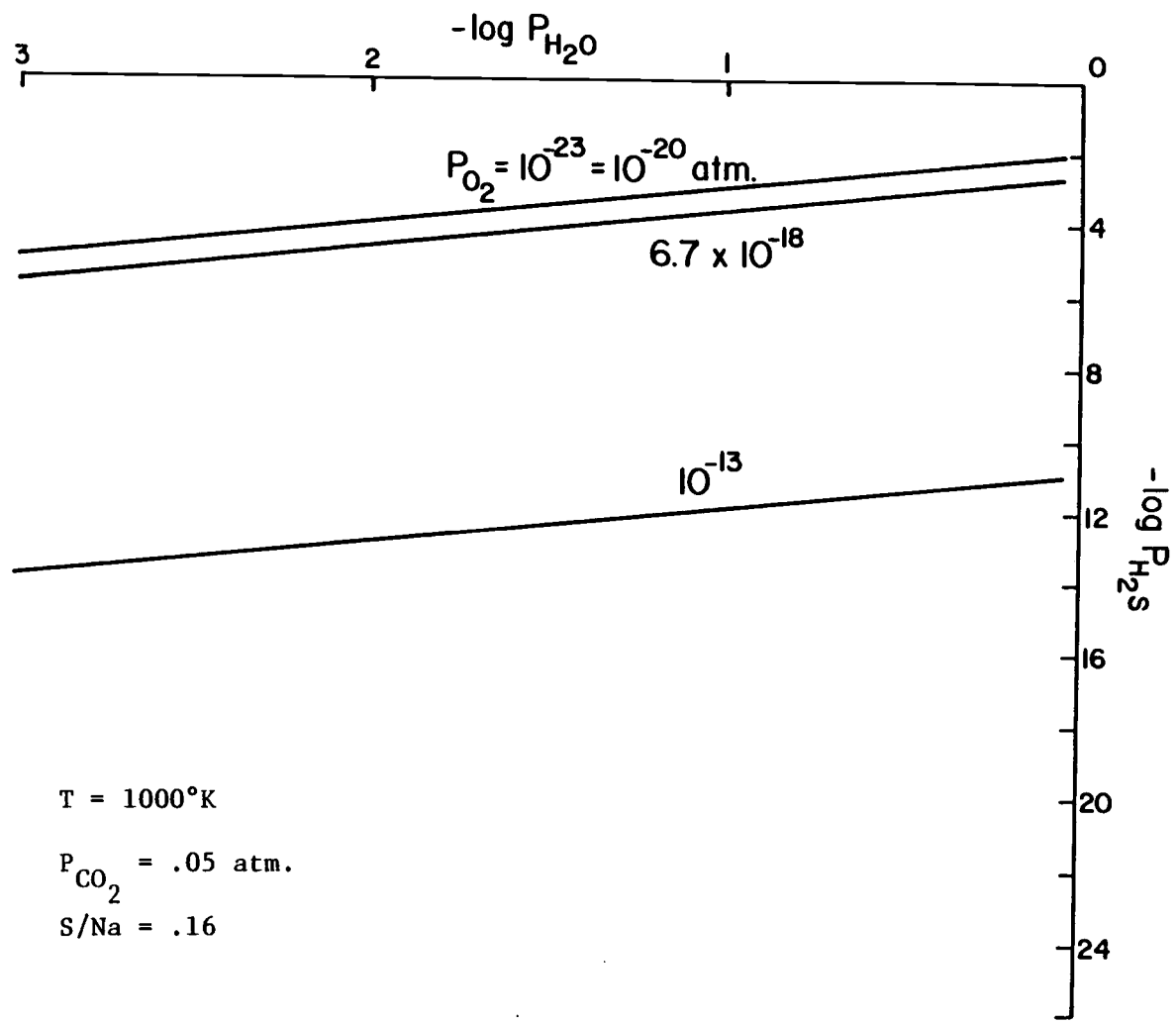


Figure 4B. Variation of P_{H_2S} with P_{H_2O} and y_{O_2} at 1000°K.



much smaller P_{O_2} , 10^{-20} , compared to 10^{-14} atmospheres calculated at 1200°K. For the 1000°K case, the maximum value of P_{H_2S} is about 0.01 atmospheres ($-\log P_{H_2S} = 2$) which occurs at $P_{H_2O} = 0.9$ atmospheres ($-\log P_{H_2O} = 0.046$) and P_{O_2} values less than or equal to 10^{-20} atmospheres.

Figures 5A and 5B show $-\log P_{H_2S}$ as a function of $-\log P_{O_2}$ at various P_{CO_2} and temperatures. P_{H_2O} and S/Na were held constant in these calculations at 0.5 atm and 0.16, respectively. Examination of the figures reveal that P_{H_2S} is constant until P_{O_2} is approximately 10^{-14} at 1200°K or 10^{-18} at 1000°K. The P_{H_2S} then decreases rapidly for both temperatures as P_{O_2} increases. At P_{O_2} from 0.1-1 atm, P_{H_2S} can be considered to be negligible (10^{-26} - 10^{-35} atmospheres).

Once again there is a large increase in P_{H_2S} as the temperature goes from 1200°K to 1000°K. The largest concentration of H_2S is approximately 0.03 atmospheres (30,000 ppm) for all P_{O_2} less than 10^{-18} atmospheres at 1000°K and $P_{CO_2} = 0.4$.

The calculations for Figures 2-5 were done with and without consideration of NaOH as a species. The results when considering NaOH are listed in Table 1. It can be seen from the table that in the P_{H_2O} range of 0.2-0.9 atmospheres, P_{H_2S} was usually less than ten percent different when considering NaOH. For the case when P_{H_2O} is less than 0.2 atmospheres, P_{H_2S} is essentially the same for all calculations, with or without the presence of NaOH.

G. Discussion

The results illustrated in Figures 2-5 indicate that the P_{CO_2} and P_{H_2O} both have a strong effect upon H_2S release. In all cases,

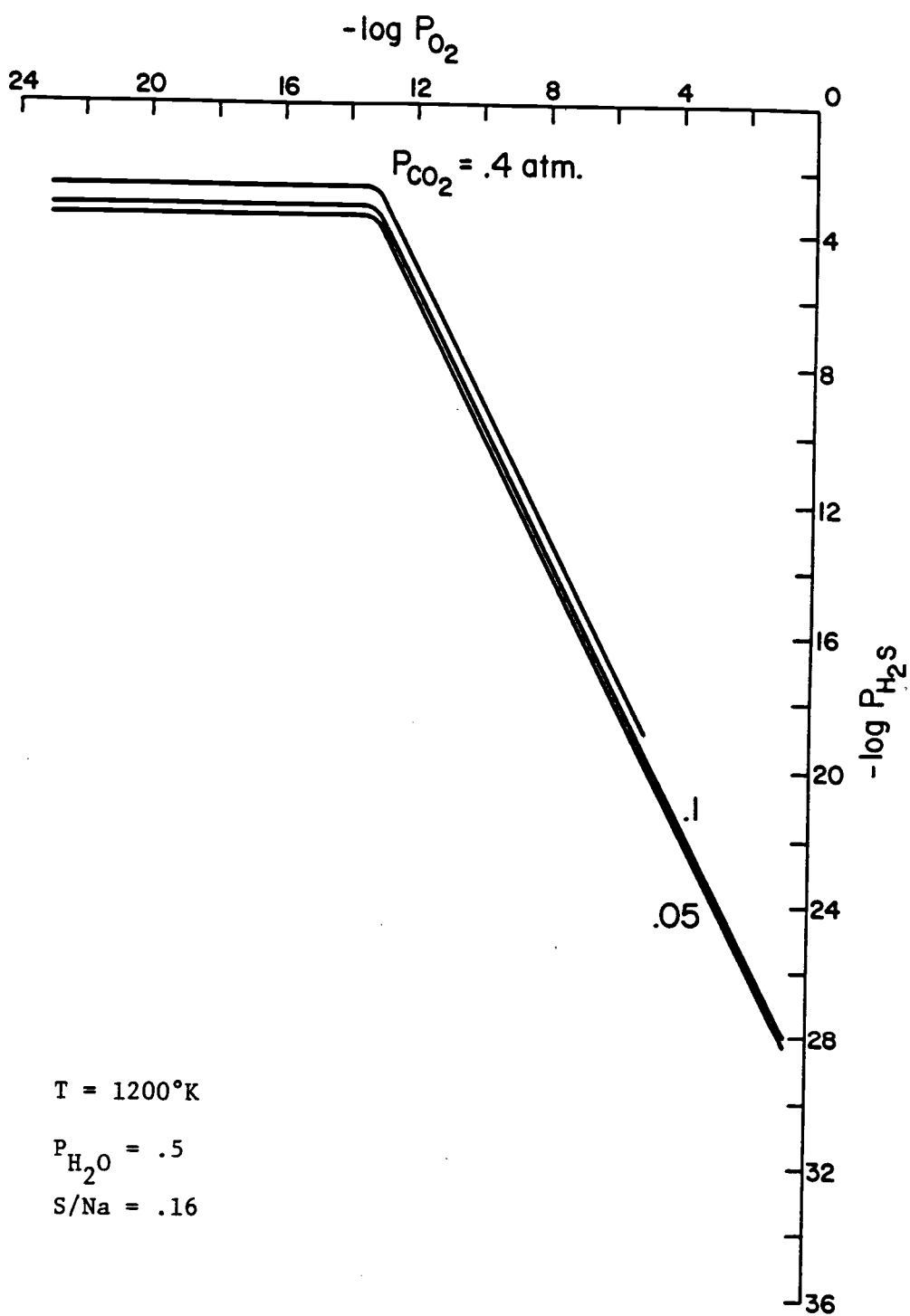


Figure 5A. Variation of $P_{\text{H}_2\text{S}}$ with P_{O_2} and y_{CO_2} at 1200°K .

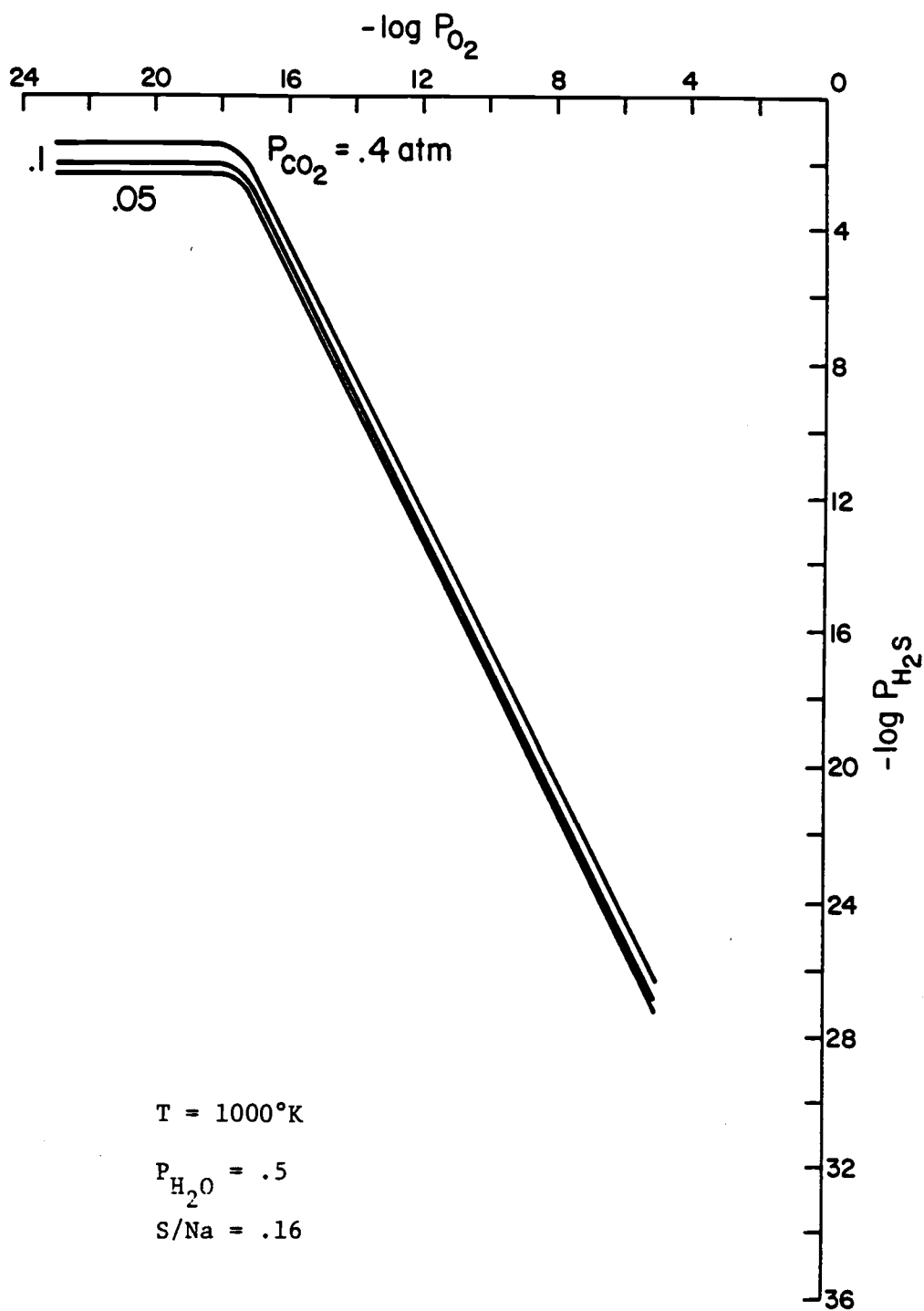


Figure 5B. Variation of $P_{\text{H}_2\text{S}}$ with P_{O_2} and y_{CO_2} at 1000°K .

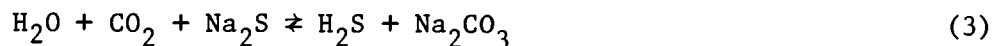
Table 1. The effect NaOH has upon P_{H_2S} .

P_{H_2O} (atm.)	P_{H_2S} atm. (NaOH) present	x_{NaOH}	P_{H_2S} atm. (no NaOH)	Difference in P_{H_2S} (%)
S/Na = 0.16, $P_{O_2} = 10^{-14}$ atm., T = 1200°K				
($P_{CO_2} = 0.05$ atm.)				
0.9	6.52×10^{-4}	1.32×10^{-1}	7.04×10^{-4}	7.8
0.5	3.68×10^{-4}	1.01×10^{-1}	3.91×10^{-4}	5.8
0.2	1.50×10^{-4}	6.54×10^{-2}	1.57×10^{-4}	4.0
10^{-3}	7.80×10^{-7}	4.84×10^{-3}	7.83×10^{-7}	0.3
10^{-6}	7.83×10^{-7}	1.53×10^{-4}	7.83×10^{-5}	0
($P_{CO_2} = 0.5$ atm.)				
0.2	1.54×10^{-3}	2.14×10^{-2}	1.57×10^{-3}	2
10^{-3}	7.83×10^{-6}	1.53×10^{-3}	7.83×10^{-6}	0
10^{-6}	7.83×10^{-9}	4.85×10^{-5}	7.83×10^{-9}	0
($P_{CO_2} = 10^{-3}$ atm.)				
0.9	1.86×10^{-5}	5.55×10^{-1}	1.41×10^{-5}	24
0.5	8.67×10^{-6}	4.76×10^{-1}	7.83×10^{-6}	9.7
0.2	2.99×10^{-6}	3.54×10^{-1}	3.13×10^{-6}	4.5
10^{-3}	1.53×10^{-8}	3.35×10^{-2}	1.57×10^{-8}	2.5
10^{-6}	1.57×10^{-11}	1.08×10^{-3}	1.57×10^{-11}	0
($P_{CO_2} = 0.05$ atm., $P_{O_2} = 10^{-18}$ atm.)				
0.9	6.62×10^{-4}	1.32×10^{-1}	7.16×10^{-4}	7
0.5	3.73×10^{-4}	1.01×10^{-1}	3.98×10^{-4}	6
0.2	1.52×10^{-4}	6.56×10^{-2}	1.58×10^{-4}	4.6
10^{-3}	7.93×10^{-7}	4.85×10^{-3}	7.96×10^{-7}	0.4
($P_{O_2} = 10^{-5}$ atm.)				
0.9	3.99×10^{-20}	1.24×10^{-1}	3.55×10^{-20}	11
0.5	2.14×10^{-20}	9.45×10^{-2}	1.97×10^{-20}	8
0.2	8.30×10^{-21}	6.12×10^{-2}	7.90×10^{-21}	5
10^{-3}	3.98×10^{-23}	4.49×10^{-3}	3.95×10^{-23}	0.7

Table 1. Continued.

P_{H_2O} (atm.)	P_{H_2S} atm. (NaOH) present	x_{NaOH}	P_{H_2S} (atm.) (no NaOH)	Difference in P_{H_2S} (%)
T = 1000°K				
(P _{O₂} = 10 ⁻¹⁸ atm.)				
0.9	7.68 x 10 ⁻³	3.13 x 10 ⁻²	7.95 x 10 ⁻³	3.4
0.5	4.31 x 10 ⁻³	2.34 x 10 ⁻²	4.42 x 10 ⁻³	2.5
0.2	1.74 x 10 ⁻³	1.49 x 10 ⁻²	1.77 x 10 ⁻³	1.7
10 ⁻³	8.82 x 10 ⁻⁶	1.06 x 10 ⁻³	8.83 x 10 ⁻⁶	0.1
10 ⁻⁶	8.83 x 10 ⁻⁹	3.37 x 10 ⁻⁵	8.83 x 10 ⁻⁹	0
10 ⁻⁹	8.83 x 10 ⁻¹²	1.06 x 10 ⁻⁶	8.83 x 10 ⁻¹²	0
(P _{CO₂} = 0.5 atm.)				
0.2	1.76 x 10 ⁻²	4.75 x 10 ⁻³	1.77 x 10 ⁻²	0.6
10 ⁻³	8.82 x 10 ⁻⁵	3.37 x 10 ⁻⁴	8.83 x 10 ⁻⁵	0
10 ⁻⁶	8.83 x 10 ⁻⁸	1.06 x 10 ⁻⁵	8.83 x 10 ⁻⁸	0
(P _{CO₂} = 10 ⁻³ atm.)				
0.9	1.39 x 10 ⁻⁴	1.94 x 10 ⁻¹	1.59 x 10 ⁻⁴	15
0.5	7.83 x 10 ⁻⁵	1.50 x 10 ⁻¹	8.83 x 10 ⁻⁵	11
0.2	3.24 x 10 ⁻⁵	9.91 x 10 ⁻²	3.53 x 10 ⁻⁵	8.2
10 ⁻³	1.75 x 10 ⁻⁷	7.49 x 10 ⁻³	1.77 x 10 ⁻⁷	0.1
10 ⁻⁶	1.76 x 10 ⁻¹⁰	2.38 x 10 ⁻⁴	1.76 x 10 ⁻¹⁰	0
(P _{CO₂} = 0.05 atm., P _{O₂} = 10 ⁻²³ atm.)				
0.9	8.15 x 10 ⁻³	3.18 x 10 ⁻²	8.47 x 10 ⁻³	3.8
0.5	4.57 x 10 ⁻³	2.38 x 10 ⁻²	4.70 x 10 ⁻³	2.7
0.2	1.85 x 10 ⁻³	1.52 x 10 ⁻²	1.88 x 10 ⁻³	1.6
10 ⁻³	9.39 x 10 ⁻⁶	1.08 x 10 ⁻³	9.41 x 10 ⁻⁶	0.2
(P _{O₂} = 10 ⁻⁵ atm.)				
0.9	1.06 x 10 ⁻²⁷	2.90 x 10 ⁻²	1.01 x 10 ⁻²⁷	4.7
0.5	5.68 x 10 ⁻²⁸	2.17 x 10 ⁻²	5.58 x 10 ⁻²⁸	1.8
0.2	2.26 x 10 ⁻²⁸	1.38 x 10 ⁻²	2.23 x 10 ⁻²⁸	1.3
10 ⁻³	1.12 x 10 ⁻³⁰	9.84 x 10 ⁻⁴	1.12 x 10 ⁻³⁰	0

an increase in P_{CO_2} or P_{H_2O} always leads to an increase in P_{H_2S} at equilibrium. The support for these results comes from reaction (3) where H_2O and CO_2 combine with Na_2S to produce H_2S . Reaction (3) is as follows:



In Figures 4 and 5, the P_{H_2S} is constant until $P_{O_2} = 10^{-14}$ atmospheres for 1200°K or 10^{-18} atmospheres for 1000°K. At this point, P_{H_2S} declines rapidly with increasing P_{O_2} . This can best be attributed to the combined effect of reactions(2) and (3). Reaction (2) is:



At 1200°K, the equilibrium constant for reaction (2), K_2 , is approximately 10^{26} . Therefore, from equation (10):

$$K_2 = 10^{26} = \frac{x_{Na_2SO_4} \gamma_{Na_2SO_4}}{x_{Na_2S} \gamma_{Na_2S} P_{O_2}^2} \quad (10)$$

as $P_{O_2}^2$ increases, x_{Na_2S} decreases causing $x_{Na_2SO_4}$ to increase in order to keep K_2 constant. Physically, this corresponds to the oxidation of Na_2S to Na_2SO_4 as P_{O_2} increases to values greater than 10^{-14} atmospheres. The same phenomena occurs at 1000°K, except the oxidation occurs as P_{O_2} increases above 10^{-18} atmospheres.

As Na_2S is oxidized to Na_2SO_4 , the equilibrium H_2S concentration is affected by reaction (3). For similar values of H_2O , CO_2 , and Na_2CO_3 , the decrease in Na_2S on the left hand side of reaction (3)

causes a corresponding decrease in H_2S on the right hand side. Hence, the rapid decline in P_{H_2S} as seen in Figure 5.

In Figures 2-5, another significant result is the consistently higher P_{H_2S} at $1000^\circ K$ compared to that at $1200^\circ K$. In all cases, the P_{H_2S} is at least an order of magnitude greater at $1000^\circ K$. Reaction (3) is probably responsible for this effect. The equilibrium constant for this reaction, K_3 , increases an order of magnitude from 0.01928 at $1200^\circ K$ to 0.203 at $1000^\circ K$. The increase in K_3 causes a direct increase in the calculated equilibrium H_2S concentration. May (1952) and Bauer and Dorland (1954) have documented this increase in K_3 with a decrease in temperature. This is an important result for system A, because the smelt cools off as it drops from the smelt spouts to the dissolving tank. It is logical that any cooling that occurs would cause a greater release of H_2S in a system tending toward equilibrium.

In examining Table 1 we can see that NaOH has little effect upon the formation of H_2S . This result is supported by reaction (4):



The equilibrium constant, K_4 , is approximately 10^{-5} both at $1200^\circ K$ and at $1000^\circ K$. This is at least three orders of magnitude smaller than K_3 in all cases. The equilibrium concentration of H_2S is therefore controlled by reaction (3). Thus, the overall effect of neglecting NaOH and reaction (4) is probably minimal.

In order to determine if system A is at equilibrium, a comparison to actual data taken from a kraft pulp mill is necessary. The gas phase composition was measured at the smelt-stream shatter jet

location in the dissolving tank area at Weyerhaeuser Company's Springfield, Oregon, mill. The following species were measured:

Species	P (atm) (dry gas basis)
O ₂	0.209
CO ₂	trace (approximately 0.004)
H ₂ S	5.2 x 10 ⁻³
CO	0

Based on actual measurements of smelt composition by Merriam et al (1980), and rough estimates of the gas composition the following variables were approximated:

Species	Concentration (atm or mole fraction)
P _{SO₂}	9.0 x 10 ⁻⁴
P _{H₂O}	0.5
P _{N₂}	0.39
x _{Na₂S}	0.31
x _{Na₂CO₃}	0.67
x _{Na₂SO₄}	0.02

After neglecting the presence of NaOH and omitting reaction (4), we calculated the apparent equilibrium constants for reactions (2), (3), and (5) using the above values in equation (10), (11), and (13). An order of magnitude estimate was desired; therefore, activity coefficients were kept at unity. The results are listed in Table 2 along with the actual thermodynamic equilibrium constants from Bauer and Dorland (1954) that were used in program EQUIL.

Table 2. Measured versus theoretical equilibrium constants.

	Measured and estimated values	Bauer and Dorland (1954) (1000°K)
K_2	5.91	4.2170×10^{34}
K_3	5.62	0.203
K_5	5.12	1.1220×10^{23}

These calculations, although not exact, are important in pointing out how far the system is from equilibrium. The Na_2S is obviously not well mixed with the bulk O_2 , otherwise it would all be oxidized according to equation (2). These results indicate that rate processes (e.g., mass transfer) are probably controlling the oxidation of both Na_2S and H_2S . The H_2S concentration is also limited by these rate processes rather than by equilibrium considerations.

The results depicted in Figure 5B can also be used to show that the system is not at equilibrium. For the mill data where $P_{\text{O}_2} = 0.1045$, $P_{\text{CO}_2} = 0.002$, and $P_{\text{H}_2\text{O}} = 0.5$, the equilibrium $P_{\text{H}_2\text{S}}$ from Figure 5B is less than 10^{-30} atmospheres. The measured amount at Springfield is 10^{-3} atmospheres, indicating the system is far from equilibrium.

It should be noted that the SO_2 , CO_2 , and H_2O partial pressures used in this comparison of K_2 , K_3 , and K_5 were reasonable estimates. If these estimates were two or three orders of magnitude in error the results would still point to a non-equilibrium situation.

H. Summary

System A, the smelt shatter jet area of the smelt dissolving system, is a high temperature mixture of molten salts and the following gases: SO_2 , H_2O , H_2S , CO_2 , O_2 , and N_2 . By employing the phase rule for reactive systems, four reactions were found to be necessary to characterize the system at equilibrium. The actual reactions selected were based on their relation to the physical system. Equilibrium constants were calculated from thermal data, and the activity coefficients were approximated by assuming a binary mixture of Na_2S - Na_2CO_3 which followed "regular" solution behavior. Along with the four chemical reaction equations, equations for the conservation of mass in each phase and an equation requiring S/Na to be constant in the liquid phase were chosen in order to calculate the chemical equilibrium. An iterative program which solved the equations simultaneously was written, and the results yielded the equilibrium $P_{\text{H}_2\text{S}}$ as a function of temperature, $x_{\text{Na}_2\text{S}}$, P_{CO_2} , $P_{\text{H}_2\text{O}}$, and P_{O_2} .

Results indicated that any increase in P_{CO_2} or $P_{\text{H}_2\text{O}}$ causes a corresponding increase in equilibrium $P_{\text{H}_2\text{S}}$. In addition, high P_{O_2} causes oxidation of Na_2S and H_2S , thereby lowering $P_{\text{H}_2\text{S}}$ at equilibrium. The presence of NaOH had a negligible effect upon $P_{\text{H}_2\text{S}}$ in all cases except high $P_{\text{H}_2\text{O}}$, where there was approximately a ten percent difference. Lastly, equilibrium H_2S concentrations were found to be ten times greater for 1000°K than they were for 1200°K .

The equilibrium calculations were compared to measured values obtained from the smelt dissolving system of a kraft pulp mill. It was determined that system A was not at equilibrium and, as a result, that rate processes probably control the rate of H_2S release.

SYSTEM B

A. Introduction

In system A the smelt is "shattered" into small droplets to avoid explosions in the dissolving tank and to aid in the dissolving process. The smelt must first be dissolved in order to recover the inorganic salts contained in it. As it dissolves it forms an aqueous solution of sodium salts (green liquor).

System B includes all dissolved species in the concentrated alkaline green liquor and also the gases above the liquor surface. The green liquor is normally close to its boiling point (90-105°C). The gases above the green liquor are at a total pressure of approximately one atmosphere.

In studying the equilibria for system B we will follow the same general procedure that we did for system A. All of the relevant chemical species will be discussed along with their chemical equilibrium relationships. Mass conservation equations for the liquid phase sodium, carbonate, sulfide, and sulfate ions will be combined with an electroneutrality expression and the equilibrium equations. This set of equations will be solved simultaneously in a computer program which generates the equilibrium composition. Included in this program will be a subroutine which calculates the activity coefficients for all required species.

Results of the equilibrium program will be illustrated as a function of temperature and composition. The results will be compared to the actual mill data to determine if the system is at equilibrium.

B. Chemical Species

The chemical species in system B include components in the green liquor and the gas phase in contact with its surface. The aqueous green liquor includes the following species in solution: Na^+ , H^+ , OH^- , S^{2-} , HS^- , $\text{H}_2\text{S}(\text{aq})$, CO_3^{2-} , HCO_3^- , $\text{H}_2\text{CO}_3^*(\text{aq})$, $\frac{1}{2}\text{SO}_4^{2-}$, and HSO_4^- . The gas phase in contact with the green liquor includes the following compounds: CO_2 , H_2S , N_2 and O_2 .

In order to do the equilibrium analysis, mass balances on Na^+ , CO_3^{2-} , S^{2-} , and SO_4^{2-} are required. To determine the total mass of each of these ions a sample of green liquor was obtained at Weyerhaeuser Company's Springfield, Oregon mill. The standard titration procedure in TAPPI Standards (1968) was followed to determine these concentrations. The results are listed in Table 3. The results in Table 3 will be used as initial inputs in the equilibrium program. In order to determine the accuracy of these values and also to determine an appropriate concentration range for each of the ions, mill data from Grace (1975) were studied. Grace (1975) tabulated white liquor concentrations for over 40 mills. The only major difference between green liquor and white liquor is that in white liquor, the Na_2CO_3 has been converted into NaOH . The average values and range of variance

^{1/}The concentration of hydrated carbon dioxide, $\text{CO}_2(\text{aq})$ predominates over the concentration of carbonic acid, H_2CO_3 . However, it is difficult to distinguish between $\text{CO}_2(\text{aq})$ and H_2CO_3 by analytical procedures, such as acid base titration, therefore, a hypothetical species (H_2CO_3^*) is used to represent H_2CO_3 plus $\text{CO}_2(\text{aq})$ (Shoeyink and Jenkins, 1980).

Table 3. Results of green liquor titration. Sample obtained from the mill at T = 93.3°C,
P = 1 atm.

Species	Molarity ($\frac{\text{moles solute}}{\ell \text{ solution}}$)	Molality ($\frac{\text{moles solute}}{\text{kg solvent}}$)	Mass concentration ($\frac{\text{g solute}}{\ell \text{ solution}}$)
Na ⁺	4.60	4.77	106.0
Total S ²⁻ = S ²⁻ + HS ⁻ + H ₂ S(aq)	0.535	0.555	17.2
Total CO ₃ ²⁻ = CO ₃ ²⁻ + HCO ₃ ⁻ + H ₂ CO ₃ [*] (aq)	1.43	1.48	85.8
Total SO ₄ ²⁻ = SO ₄ ²⁻ + HSO ₄ ⁻	0.0944	0.0980	9.07
OH ⁻	0.481	0.499	8.18

for Grace's data are listed in Table 4. These results will be used in deciding the range of concentrations to be used in the equilibrium program discussed later.

Table 4. White liquor analysis.

Species	Molarity	Mass concentration	Approximate molarity range
Na ⁺	4.33	99.6	1.50 -5.367
S ²⁻	0.424	13.6	0.243-0.640
CO ₃ ²⁻	0.263	15.8	0.160-0.462
SO ₄ ²⁻	0.051	4.9	0-0.15

C. Conservation of Mass, Equilibrium Relationships
and Electroneutrality Expression

As described above, system B contains 13 unknown quantities. They are the concentrations of SO₄²⁻, HSO₄⁻, S²⁻, HS⁻, H₂S(aq), H₂S(g), CO₃²⁻, HCO₃⁻, H₂CO₃^{*}(aq), CO₂(g), Na⁺, H⁺ and OH⁻. In order to determine this set of concentrations, 13 independent equations are required. To determine this set of equations, we followed the methods outlined in Snoeyink and Jenkins (1980) for solving aqueous equilibrium problems. The first step is to define the equilibrium mass balances on Na⁺, CO₃²⁻, S²⁻ and SO₄²⁻.

$$C_{T,Na} = [Na^+] \frac{2}{\quad} \quad (24)$$

$\frac{2}{\quad} [\]$ refers to molality (moles solute/kg solvent).

$$C_{T,CO_3} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad (25)$$

$$C_{T,S} = [H_2S] + [HS^-] + [S^{2-}] \quad (26)$$

$$C_{T,SO_4} = [HSO_4^-] + [SO_4^{2-}] \quad (27)$$

$C_{T,i}$ in this case refers to the number of moles of "species containing i " per kg solvent. For each set of calculations $C_{T,Na}$, C_{T,CO_3} , $C_{T,S}$, and C_{T,SO_4} will be fixed at a value within the range described in the previous section. It should be noted that in fixing C_{T,CO_3} and $C_{T,S}$ we are making the assumption of a closed system. In system B, the pH is always greater than ten. As a result of this, the totally protonated species, $H_2CO_3^*(aq)$ and $H_2S(aq)$ will be negligible in the mass balance equation.

In addition to the mass balance equations listed above there are also eight reactions. Each reaction is listed below with its corresponding equilibrium equation containing equilibrium constants (K_i) and single ion activity coefficients (γ_i). All species are aqueous (aq), unless otherwise noted with the subscript g (for gas). The system pressure is approximately one atmosphere, therefore, the activities of all gases are equivalent to partial pressures.

The dissolution of hydrogen sulfide:

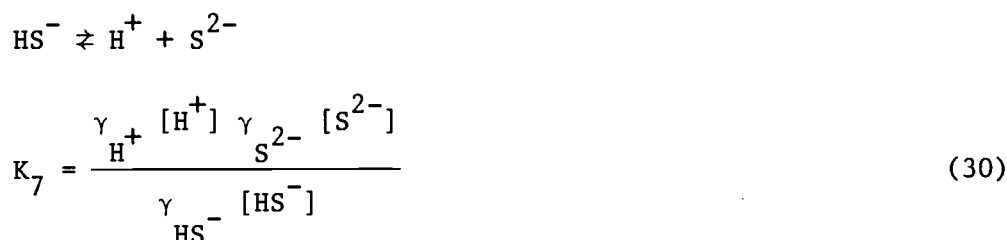
$$H_2S(g) \rightleftharpoons H_2S(aq)$$

$$K_5 = \frac{\gamma_{H_2S} [H_2S]}{P_{H_2S}} \quad (28)$$

The dissociation of aqueous hydrogen sulfide:



The dissociation of the bisulfide ion:



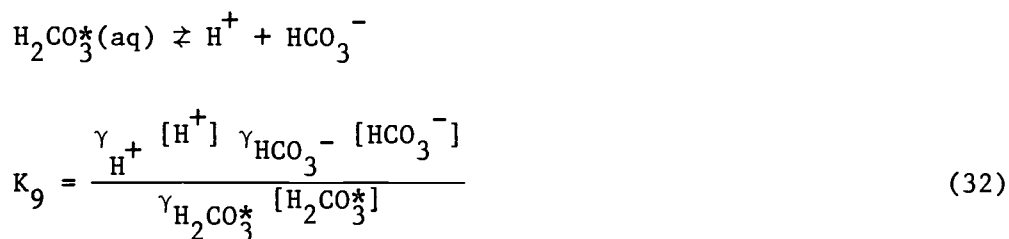
The dissolution of carbon dioxide:



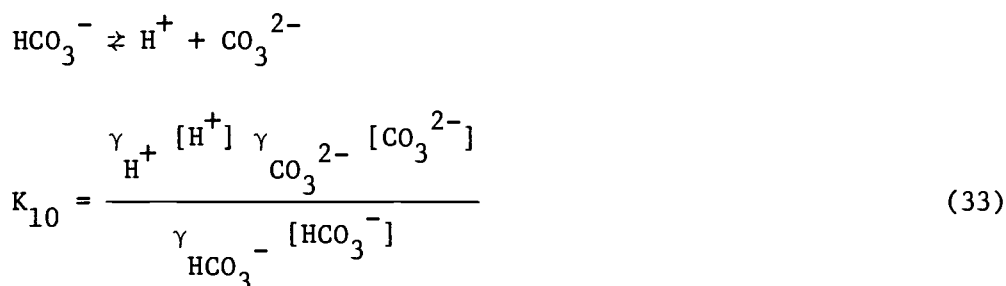
For the solvent, water, γ_i approaches one as the solution becomes more dilute. The parameter x refers to the mole fraction. In most cases where $x_{\text{H}_2\text{O}}$ is approximately equal to one, the activity, $\{ \text{H}_2\text{O} \} = x_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}$ can also be assumed equal to one. Equation (31) then becomes:

$$K_8 = \frac{\gamma_{\text{H}_2\text{CO}_3^*} [\text{H}_2\text{CO}_3^*]}{P_{\text{CO}_2}} \quad (31)$$

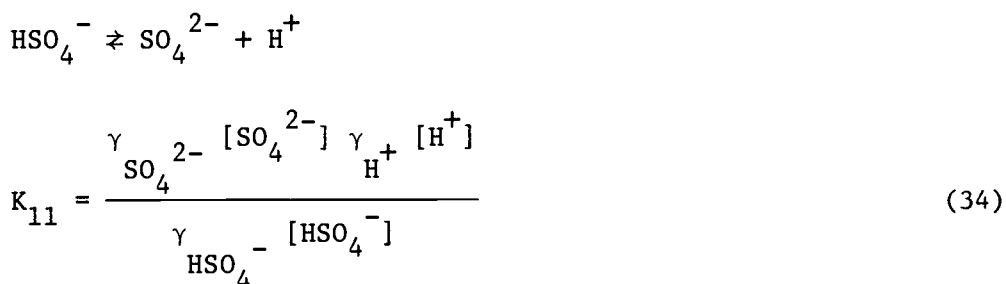
The dissociation of carbonic acid:



The dissociation of the bicarbonate ion:



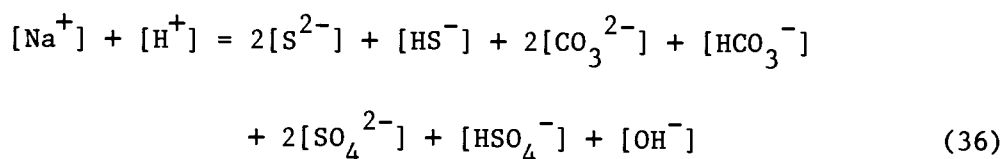
The dissociation of the bisulfate ion:



The dissociation of water:



The last equation needed is the charge balance or electro-neutrality equation. The basis of the electroneutrality equation is that all solutions must be electrically neutral. In every solution the total number of positive charges must equal the total number of negative charges. For this system, the result is



D. Thermodynamic Constants

Activity Coefficients

The mean activity coefficients of all species must be determined in order to calculate the equilibrium composition for system B. The accurate estimation of activity coefficients in the ionic solution of the dissolving tank is difficult because of the electrostatic charges of attraction and repulsion between the ions. A method for calculating activity coefficients which accounts for these interactions was developed by Kusik and Meissner (1977, 1975, 1973, 1972). This method has been accurately summarized and evaluated by Gokcen (1979) who recommends it be used only when direct experimental results are not available.

The following variables will be used frequently in the following section:

I = total ionic strength

I_i = ionic strength for species i

γ_{ij}° = mean activity coefficient for i (cation) and j (anion) in water

γ_{ij} = mean activity coefficient for ij in a multicomponent solution

Γ_{ij}° = reduced activity coefficient of electrolyte ij in water

Γ_{ij} = reduced activity coefficient for an electrolyte ij in a multicomponent solution

z_i, z_j = absolute values of cationic and anionic charge

The basis of the Kusik and Meissner method is that when $\log \gamma_{12}^\circ$ is plotted as a function of I for various electrolytes the curves cross one another; however, when $\log \Gamma_{12}^\circ = (1/z_1 z_2) \log \gamma_{12}^\circ$, as a function of I is plotted for the same electrolytes very few of the curves cross each other (Gokcen, 1979). Figure 6 is an example of some actual curves of $\log \Gamma_{12}^\circ$ vs. I (Gokcen, 1979).

In binary solutions Γ_{12}° is equal to

$$\Gamma_{12}^\circ = (\gamma_{12}^\circ)^{1/z_1 z_2} \quad (37)$$

For multicomponent solutions the reduced activity coefficient, Γ_{12} is defined similarly as

$$\Gamma_{12} = (\gamma_{12})^{1/z_1 z_2} \quad (38)$$

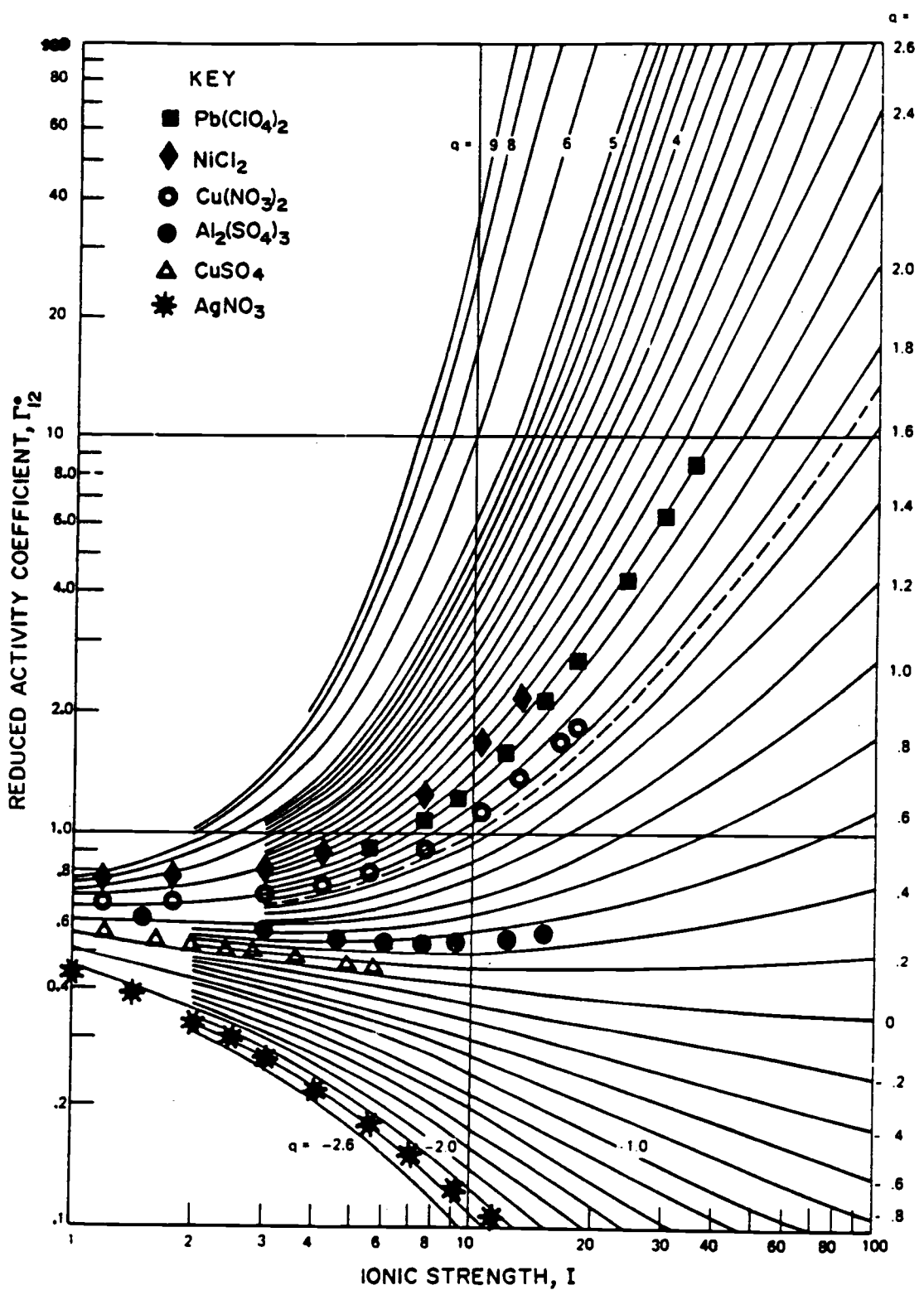


Figure 6. Variation of Γ_j^0 with I . Reproduced by permission from Gocken, 1979. ^{1j}

In theory only one $\log \Gamma_{12}^{\circ}$ at a high ionic strength is required to fix the entire curve and the parameter q , as defined below, for a given species. The empirical parameter q depends upon temperature and the specific electrolyte. In this system several of the species do not have previously calculated q values; therefore, it is necessary to generate them. Using $\log \Gamma_{12}^{\circ}$ vs I (for I greater than one) data, it is possible to calculate an average value for q by solving the following equations simultaneously with an available subroutine.

$$\Gamma_{12}^{\circ} = [1 + (0.75 - 0.065q)(1 + 0.1I)^q - (0.75 - 0.065q)]\Gamma^* \quad (39)$$

where Γ^* is given by

$$\log \Gamma^* = \frac{-0.5107\sqrt{I}}{1 + c\sqrt{I}} \quad (40)$$

and c is given by

$$c = 1 + 0.55q \cdot e^{-0.023 \cdot I^3}$$

The constants prior to Γ^* in equation (39) represent empirical corrections to the Debye-Hückel equation as given by equation (40). These coefficients have been obtained by trial and error using activity coefficients of as many electrolytes as possible (Gokcen, 1979).

As mentioned previously the parameter q is temperature dependent. However, if $q(25^{\circ}\text{C})$ is known, $q(T)$ can be calculated from

$$q(T) = (T-25)[a \cdot q(25^\circ\text{C}) + b^*] + q(25^\circ\text{C}) \quad (42)$$

where T is the temperature in degrees celsius. In equation (42) $a = -0.0079$ and $b^* = 0.0029$ for sulfates and $a = -0.005$ and $b^* = 0.0085$ for all other electrolytes. The accuracy of equation (42) has been questioned by Gokcen (1984). It was recommended for use only in the event that high temperature activity coefficient data was unavailable.

In system B mean activity coefficients are needed for the following electrolytes: Na_2S , Na_2CO_3 , Na_2SO_4 , NaOH , NaHS , and NaHCO_3 . To convert these mean coefficients into single-ion activity coefficients, mean activity coefficient data is also needed for KCl and NaCl . The method used in this conversion will be discussed later.

Gokcen (1979) listed q values at 25°C for NaOH and Na_2SO_4 . These values are given in Table 5 along with their corresponding standard deviations. Without concentrated high-temperature activity data, the q values in Table 5 had to be used in equation (42) to generate high temperature values for q . With ionic strength and q known, reduced activity coefficients in water (Γ_{ij}°) can be calculated by solving equations (39-41). The calculation procedure is described in Section E.

For Na_2CO_3 , mean activity coefficients as a function of concentration and temperature were measured by Taylor (1955). With these data, equation (37) was used to calculate the reduced activity coefficients of Na_2CO_3 in water, (Γ_{ij}°). The total ionic strengths were calculated from,

$$I = \frac{1}{2} \sum_{i=1}^2 m_i z_i^2 \quad (43)$$

where z_i refers to the charge of species i . By using the data for Γ_{12}° as a function of I , q was determined at 95°C by solving equations (39-41) simultaneously. By using these high temperature data, the error in using the empirical equation (42) was eliminated.

Table 5. Average q values for electrolytes.

Species	$q^{1/}$	$I(\text{max})^{2/}$	$s^{3/}$
NaOH	3.000	6.0	0.066
Na ₂ SO ₄	-0.190	12.0	0.029

^{1/} Value of q from equation (39).

^{2/} Maximum value of the ionic strength at which equation (39) compared against experimental data.

^{3/} Estimated standard deviation in $[\Gamma[\text{equation (39)}]/\Gamma(\text{experimental})] - 1$.

To determine q for NaHCO₃, only one activity coefficient (from Peiper and Pitzer, 1981) could be found at a molality greater than one. This value was used to generate q at 25°C by the same method employed for Na₂CO₃.

The data involving the sulfide compounds was meager at best. The only Na₂S system for which data were found involved a study of the ternary system, Na₂S-NaOH-H₂O, by Khvorostin et al (1975). The Kusik and Meissner method requires activity coefficients of each electrolyte in water, $\gamma_{\text{Na}_2\text{S}}^\circ$; however, Khvorostin only listed effective values $(\gamma_{\text{Na}_2\text{S}})_{\text{eff}}$. These effective activity coefficients

include the effects of NaHS and NaOH. Since no other data were available, the $(\gamma_{\text{Na}_2\text{S}})_{\text{eff}}$ data were used to generate q values as above. The uncertainty involved with this assumption will be discussed later in Section F.

In calculating NaHS activity coefficients, similar problems were encountered. The only available data were by Herr and Heltz (1976) for the ternary system NaHS-H₂S-H₂O. The measurements were done at low concentrations (maximum $m = 0.2$) and mean activity coefficients were represented by the Guggenheim equation for low $P_{\text{H}_2\text{S}}$ ($P_{\text{H}_2\text{S}} < 0.01$).

$$\log \gamma_{\text{NaHS}} = \frac{-Am^{1/2}}{1+m^{1/2}} + Bm \quad (44)$$

where the constant A is from the Debye-Hückel theory and accounts for all nonspecific ionic interactions. Herr and Heltz (1976) determined the parameter B by a linear regression analysis of the values for the standard potential E_{NaHS}° . The B coefficient accounts for the short range ion-ion interactions specific to NaHS.

According to Pytkowicz (1983), however, the Guggenheim equation has a limit of usefulness in the ionic strength range of 0.1-0.5. In system B, the ionic strength is greater than five. At such high ionic strengths, ion pairing and specific interactions need to be considered to obtain accurate activity coefficient predictions (Pytkowicz, 1983). Such studies require years of experimentation which is beyond the scope of this thesis. As with the Na₂S ternary system, the $(\gamma_{\text{Na}_2\text{S}})_{\text{eff}}$ data were used to generate q values at 25°C with values of the constants A and B generated by Herr and

Heltz (1976). The range of q values was tested in a sensitivity study (discussed in Section F) to determine the effect changes in γ_{NaHS} have upon the equilibrium value of $P_{\text{H}_2\text{S}}$.

For NaCl and KCl, high temperature data of the activity coefficient as a function of molality were calculated by Silvester and Pitzer (1977) and Holmes et al (1978), respectively. As with Na_2CO_3 , equation (42) was avoided and q was determined by solving equations (39-41).

Along with the numerous errors already mentioned in determining q , the high ionic strengths in system B also slightly exceeded the maximum limitations listed in Table 5 for NaOH. In order to determine the uncertainty that exceeding the ionic strength limits could introduce upon $P_{\text{H}_2\text{S}}$, a wide variation in q for NaOH was studied. The results of this testing are discussed in Section F.

In system B there are also two non-electrolytes, dissolved hydrogen sulfide, $\text{H}_2\text{S}(\text{aq})$ and the approximate species $\text{H}_2\text{CO}_3^*(\text{aq})$. To estimate the mean activity coefficients for these two species the "salting out" method as described by Randall and Failey (1927) was employed. "Salting out" implies an increase of the internal pressure of the solution caused by electrolytes. The effect caused by electrolytes upon non-electrolytes (especially dissolved gases) can be approximated by the salting out coefficient, $k = \log(\gamma_i/I)$. This parameter is practically constant even at high ionic strengths for a given temperature. Failey and Randall (1927) suggest using an arithmetic mean value for k from their eight tables of data, for several dissolved gases over a range of ionic strength from almost

zero to ten. In an effort to increase the accuracy, an arithmetic mean was determined for dissolved H_2S and CO_2 separately. Data were available for $15^\circ C$ and $25^\circ C$, but nothing for $100^\circ C$. On the average, a 20 percent decrease in k occurred for an increase in temperature from $15^\circ C$ to $25^\circ C$. In the sensitivity study k values in excess of ± 200 percent from the arithmetic mean were tested to determine the effect upon equilibrium P_{H_2S} .

After calculating or estimating q values for all of the compounds it is necessary to determine the mean reduced activity coefficients of each species in the actual mixture. The following equation was proposed by Kusik and Meissner and also summarized in Gokcen's (1979) review

$$\log \Gamma_{ij} = \frac{z_i}{z_i + z_j} (V_{i2} I_2 \log \Gamma_{i2}^\circ + V_{i4} I_4 \log \Gamma_{i4}^\circ + \dots) I^{-1} \\ + \frac{z_j}{z_i + z_j} (V_{j1} I_1 \log \Gamma_{j1}^\circ + V_{j3} I_3 \log \Gamma_{j3}^\circ + \dots) I^{-1} \quad (44)$$

where even numbered subscripts represent anions and odd subscripts are cations. The values of Γ_{ij}° for binary solutions depend upon temperature and total ionic strength (I) of the actual mixture.

The parameters V_{ij} and I_i and given by

$$V_{ij} = 0.5 \frac{(z_i + z_j)^2}{z_i z_j} \quad (45)$$

and

$$I_i = 0.5 m_i z_i^2 \quad (46)$$

where I_i is the ionic strength of the individual species (Gokcen, 1979).

Kusik and Meissner (1977) have found that the overall error in estimating activity coefficients for various mixed electrolytes in aqueous solutions is generally less than 20 percent. In the sensitivity study discussed in later sections the maximum deviation of 20 percent for the mean activity coefficients in the mixtures, γ_{ij} , will be tested to determine the effect such a change in γ_{ij} causes upon equilibrium P_{H_2S} .

After determining the mean activity coefficients by Kusik and Meissner's method, we calculate the single ion activity coefficients for each relevant ion in the system. The single ion activity coefficients are needed in the equilibrium equations (28-35) in order to calculate the molal composition of each chemical species.

By using equations (39-41) of Kusik and Meissner's method and the q values generated earlier, it is possible to calculate the mean activity coefficients for potassium chloride (KCl) and sodium chloride (NaCl) at the ionic strengths in system B. Garrels and Christ (1965) suggest making the assumption that $\gamma_+ = \gamma_-$ for a standard univalent electrolyte. The behavior of KCl in solution is often the standard basis for obtaining these individual ion activity coefficients (Lewis and Randall, 1961). MacInnes (1919) suggests that γ_{K^+} and γ_{Cl^-} are equal in a pure solution of KCl, therefore it is a reasonable approximation that

$$\gamma_{KCl} = [(\gamma_{K^+})(\gamma_{Cl^-})]^{1/2} = \gamma_{K^+} = \gamma_{Cl^-} \quad (47)$$

According to Garrels and Christ (1965), the quantity a_1 , which is

related to the diameter of the ion in solution, is equal to 3.0×10^{-8} cm for the potassium and chloride ions. Ions of the same "effective" diameter are more likely to behave similarly in solution, thereby supporting the MacInnes assumption.

From the q values for NaCl generated earlier we can next determine the mean activity coefficient of NaCl in the ionic strength range of system B. The single ion activity coefficient for sodium can then be determined as follows:

$$\gamma_{\text{NaCl}} = [(\gamma_{\text{Na}^+})(\gamma_{\text{Cl}^-})]^{1/2} = [(\gamma_{\text{Na}^+})(\gamma_{\text{KCl}})]^{1/2} \quad (48)$$

$$\gamma_{\text{Na}^+} = \frac{\gamma_{\text{NaCl}}^2}{\gamma_{\text{KCl}}} \quad (49)$$

This is the mean salt method as described by Garrels and Christ (1965). It can be used to calculate the individual ion activity coefficients for the ions of system B. Thus, for NaOH the hydroxide anion is calculated as follows

$$\gamma_{\text{OH}^-} = \frac{\gamma_{\text{NaOH}}^2}{\gamma_{\text{Na}^+}} \quad (50)$$

For polyvalent species such as Na_2S the sulfide ion activity coefficient is calculated similarly:

$$\gamma_{\text{Na}_2\text{S}} = [(\gamma_{\text{Na}^+}^2)(\gamma_{\text{S}^{2-}})]^{1/3} \quad (51)$$

$$\gamma_{S^{2-}} = \frac{\gamma_{Na_2S}^3}{\gamma_{Na^+}^2} \quad (52)$$

The same techniques are employed to calculate the carbonate, sulfate, bicarbonate and bisulfide ions in system B.

The errors in the mean salt method are difficult to estimate, but become greater as the bridge becomes longer (e.g., for sulfides, carbonates). The best check is always against experimental data. For example, a given combination of single ion activity coefficients should give fair results when compared to experimentally derived mean activity coefficients. The mean activity coefficients are also dependent upon the ionic strength, and therefore, single ion activity coefficients are also dependent upon ionic strength. We are making the assumption that the activity coefficient of a given ion depends only upon the ionic strength. This may be true in dilute solutions but the assumption breaks down as the concentration increases. Certain models, such as Pitzer's equations (Chen et al, 1979), which include interaction coefficients between ions have proven to be more accurate when studying concentrated mixtures of electrolytes. These more advanced models are beyond the scope of this thesis. They will, however, be applied to equilibrium problems such as this in the near future.

Equilibrium Constants

The equilibrium constants used in equations (28-35) are all calculated from the data of Helgeson (1969). In the temperature

range applicable to this study (approximately 90-105°C) the standard state for the aqueous phase is a hypothetical one molal solution at one atmosphere and any specified temperature. For the gases and solids the standard state is unit activity for the pure ideal gas at one atmosphere and for the pure solid at any specified temperature.

The fundamental thermodynamic equation describing the equilibrium constant as a function of temperature is

$$\ln K(T) = \ln K(T_r) - \frac{\Delta H_r^\circ(T_r)}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) - \frac{1}{RT} \int_{T_r}^T \Delta C_{p,r}^\circ(T) dT + \frac{1}{R} \int_{T_r}^T \Delta C_{p,r}^\circ(T) d \ln T \quad (53)$$

where ΔH_r° and $\Delta C_{p,r}^\circ$ are, respectively, the standard enthalpy change and the change in heat capacity of reaction, R is the gas constant, K the equilibrium constant, T the absolute temperature of interest (in °K), and T_r the reference temperature (298.15°K) (Helgeson, 1969).

The integrals in equation (53) are approximated as follows when average heat capacity data can be computed for all reactants and products:

$$\ln K(T) = \ln K(T_r) - \frac{\Delta H_r^\circ(T_r)}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) - \frac{\Delta C_{p,r}^\circ \int_{T_r}^T (T-T_r)}{RT} + \frac{\Delta C_{p,r}^\circ \int_{T_r}^T \ln T/T_r}{R} \quad (54)$$

and

$$\Delta C_{p,r}^{\circ}]_{T_r}^T = \sum_j \nu_j C_{p,j}^{\circ}]_{T_r}^T - \sum_{\ell} \nu_{\ell} C_{p,\ell}^{\circ}]_{T_r}^T \quad (55)$$

where j and ℓ represent the products and reactants, respectively (Helgeson, 1969). Equation (54) was used to calculate equilibrium constants for equations (29) and (30).

In many cases it is common to find no heat capacity data for one or more of the reactants or products under consideration. The dissociation constants can still be approximated accurately up to 200°C by evaluating the following equation (Helgeson, 1967a).

$$\ln K(T) = \frac{\Delta S_r^{\circ}(T_r)}{RT} \left[T_r - \frac{\theta}{\omega} \left(1 - \exp[\exp(b_2 + a_2 T) - c_2 + \frac{T - T_r}{\theta}] \right) \right] - \frac{\Delta H_r^{\circ}(T_r)}{RT} \quad (56)$$

when θ , ω , a_2 , b_2 , and c_2 are temperature independent coefficients which are specific to the solvent. For aqueous solutions these coefficients are 219, $1.0032^{\circ}\text{K}^{-1}$, $0.01875^{\circ}\text{K}^{-1}$, -12.741, and 7.84×10^{-4} , respectively (Helgeson, 1967a). The method of approximation by equation (56) involves the assumption that $\Delta C_{p,r}^{\circ}(T)$ changes monotonically but nonlinearly with temperature (Helgeson, 1969).

When dissociation constants are known over a restricted temperature range, experimental $\log K(T)$ values can be fit by the method of least squares according to

$$\begin{aligned}
\ln K(T) = & \frac{\Delta S_e^\circ(T_r)}{RT} \left[T_r - T - \frac{\theta}{\omega} \left(1 - \exp[\exp(b2+a2T) - c2 + \frac{T-T_r}{\theta}] \right) \right] \\
& - \frac{\Delta H_r^\circ(T_r)}{RT} + \frac{\Delta S_r^\circ(T_r)}{R} + \frac{\alpha'}{R} \left(\ln \frac{T}{T_r} - 1 + \frac{T_r}{T} \right) \\
& + \frac{\beta'(T-T_r)^2}{2.303RT} + \frac{\lambda'}{2.303RT} \left(\frac{T^3}{3} - \frac{T_r^3}{3} - T_r^2 T + T_r^3 \right) \quad (57)
\end{aligned}$$

where θ , ω , a , b , and c are coefficients with the values given above. The parameter $\Delta S_e^\circ(T_r)$ is the electrostatic entropy of dissociation at T_r and α' , β' and λ' are temperature independent coefficients characteristic of the reaction (Helgeson, 1967a). Equation (57) was used to generate dissociation constants for equations (32), (33) and (35).

In order to determine the equilibrium constants for the dissolution reactions [equations (28) and (31)], either a combination of average and actual heat capacities or the method of least squares was applied. The reader is referred to Helgeson (1969) for details. The errors associated with the individual equilibrium constants will be discussed later in the sensitivity study.

Applying the techniques listed above, Helgeson (1969) calculated equilibrium constants for equations (28-35) as a function of temperature; however, he listed data points at 50°C intervals. In system B equilibrium constants are needed at 90, 95, 100, and 105°C. In order to determine equilibrium constants at these four temperatures $\log K$ values at 50, 100, 150, and 200°C were used as base points from Helgeson's data. Newton's forward formula as described in Carnahan et al (1969) was then used to interpolate $\log K$ values at each of

the intermittent temperatures listed above. The final equilibrium constants for equations (28-35) are listed in Table 6 and Appendix 4.

Table 6. Equilibrium constants for equations (28-35) in the temperature range 90-105°C. $\log K(T)$.

Equation number	Reaction	90°C	95°C	100°C	105°C
(28)	$\text{H}_2\text{S}_{(g)} \rightleftharpoons \text{H}_2\text{S}$	- 1.40	- 1.41	- 1.43	- 1.44
(29)	$\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+$	- 6.64	- 6.63	- 6.63	- 6.63
(30)	$\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-}$	-12.03	-11.91	-11.78	-11.66
(31)	$\text{CO}_{2(g)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3^*$	- 1.93	- 1.95	- 1.97	- 1.99
(32)	$\text{H}_2\text{CO}_3^* \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	- 6.41	- 6.43	- 6.45	- 6.47
(33)	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	-10.15	-10.16	-10.16	-10.16
(34)	$\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$	- 2.84	- 2.92	- 2.99	- 3.06
(35)	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	-12.43	-12.34	-12.26	-12.18

E. Calculation Procedure

A computer program (AQS), was written to calculate activity coefficients by the Kusik and Meissner method and to solve the equations developed earlier. A sequential description of the calculation procedure for AQS is as follows:

1. Enter the total mass balances (C_T 's) listed in Section C as equations (24-27). Next, enter the initial guess of the molalities for sodium, sulfide, carbonate, sulfate, hydroxide, bisulfide, bicarbonate, and hydrogen ions.

2. AQS calculates the individual ionic strengths (equation 46), total ionic strength and V factors (equation 45). The program uses the IMSL subroutine ZSPOW to simultaneously solve the nonlinear Kusik and Meissner equations (39-41) and generate reduced activity coefficients for the pure electrolytes. These calculations correspond to the total ionic strength calculated in step 2.
3. Program AQS determines the reduced activity coefficients in the electrolyte mixture using equation (44) and converting them to mean activity coefficients with equation (38). Next, AQS calculates single ion activity coefficients by employing the MacInnes assumption as described in Section D.
4. With the single ion activity coefficients and temperature dependent equilibrium constants, AQS calculates the equilibrium composition of all species in terms of molalities and partial pressure. In this step the mass balance equations (24-27) and the equilibrium equations (28-35) are solved simultaneously.
5. Program AQS then checks the equilibrium composition with the charge balance or electroneutrality equation to within a specified tolerance. If the electroneutrality equation does not check within the specified tolerance, then AQS corrects the molality of the hydrogen ion ($[H^+]$) and goes back to step 4. This iterative procedure continues until the tolerance on the electroneutrality expression reaches its specified limit.

At this point there is a new equilibrium concentration, different from the original guess.

6. AQS then checks the new concentrations against the initial guesses used in step 2. If the difference is greater than tolerance 2, the program goes back and repeats steps 2-5 with the new concentrations. This is a successive substitution routine. It insures that the final equilibrium concentration that satisfies the electroneutrality equation tolerance is also the same concentration that is used to calculate the activity coefficients within tolerance 2.
7. AQS prints out the equilibrium concentration of system B along with the pH and temperature. The detailed logic of program AQS can be seen on a flow diagram in Appendix 3, which also includes the program and a sample printout.

The calculation procedure has a tolerance of 0.01 percent in the electroneutrality expression and in the successive substitution section. This tolerance limit insures convergence to within three decimal places on the equilibrium concentrations, thus eliminating errors in convergence.

The program AQS determines the equilibrium concentration as a function of the initial concentration of Na_2S , Na_2CO_3 , Na_2SO_4 , and NaOH concentrations and of the system temperatures. A parametric analysis can be done to determine the effect, if any, that a change in the initial concentrations has upon the equilibrium partial pressure of H_2S . The effect of temperature, if any, on the equilibrium partial pressure of H_2S can also be determined. This type of analysis

can once again pinpoint the variables that have an important effect upon the release of H_2S . It will also generate equilibrium concentrations of H_2S which can be compared to actual mill data to determine if system B is in fact at equilibrium.

F. Results

A sensitivity study was undertaken to determine the uncertainty in the equilibrium P_{H_2S} calculations. First, the standard deviations for the equilibrium constants in equations (28-35) were determined. The reactions and standard deviations are listed in Table 7. Each equilibrium constant was then used in program AQS, individually, at its maximum and minimum while keeping all other constants fixed at their mean values. These calculations generated an equilibrium P_{H_2S} for each maximum and minimum equilibrium constant separately. These values will be used later to help determine the overall uncertainty in P_{H_2S} .

In assigning standard deviations to the mean activity coefficients, it was not possible to assign a fixed value for each coefficient in system B. Exact quantitative values defining the uncertainty for activity coefficients in the mixture are not available.. Kusik and Meissner (1977) stated that most activity coefficients in mixtures can be predicted to less than 20 percent uncertainty using equation (44); however, further errors could arise when using equation (42) over large temperature ranges. To test the effect that each activity coefficient had upon the mean equilibrium P_{H_2S} , a trial and error process was used.

Table 7. Standard deviations for each equilibrium constant in system B.

Equation number	Equilibrium constant	Reaction	Percent deviation ($\pm\%$)	Reference
(28)	K_5	$H_2S(g) \rightleftharpoons H_2S(aq)$	3	Kozintseva (1964)
(29)	K_6	$H_2S(aq) \rightleftharpoons HS^- + H^+$	1.5	Ellis and Milestone (1967)
(30)	K_7	$HS^- \rightleftharpoons H^+ + S^{2-}$	1.68	Ellis and Milestone (1967)
(31)	K_8	$CO_2(g) + H_2O \rightleftharpoons H_2CO_3^*(aq)$	2.0	Signet et al (1962)
(32)	K_9	$H_2CO_3^*(aq) \rightleftharpoons H^+ + HCO_3^-$	2.0	Ryzhenko (1963)
(33)	K_{10}	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	2.0	Ryzhenko (1963)
(34)	K_{11}	$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$	3.5	Marshall and Jones (1966)
(35)	K_{12}	$H_2O \rightleftharpoons H^+ + OH^-$	1-3	Harnad and Hamer (1933)

Each electrolyte is characterized by a specific fixed q value which when combined with ionic strength and temperature determines the mean activity coefficient in the mixture, γ_{ij} . The parameter q was changed for each electrolyte, individually, and the corresponding percent change this caused on its mean activity coefficient and equilibrium P_{H_2S} tabulated. The program AQS, described in Section E, was used in these calculations. The process was continued until plus and minus 20 percent uncertainty was reached in the mean activity coefficients for Na_2CO_3 , Na_2SO_4 , $NaOH$, and $NaHCO_3$ in the mixture. These calculations also generated equilibrium P_{H_2S} values corresponding to the maximum and minimum mean activity coefficients. It was then possible to associate these γ_{ij} changes with either a negative or positive change in P_{H_2S} at equilibrium. The P_{H_2S} at these minimum and maximum activity coefficients could also be compared to the mean P_{H_2S} value to determine which γ_{ij} 's had the greatest effect upon equilibrium P_{H_2S} .

The two sulfide compounds, Na_2S and $NaHS$ were treated differently due to the absence of reliable activity data. For example, Table 8 lists some data from Khvorostin's article on $(\gamma_{Na_2S})_{eff}$ as a function of molality. Also listed is the ionic strength and reduced activity coefficient. To generate q values for the electrolytes, data for the reduced activity coefficients, Γ_{ij}° 's as a function of ionic strength, I are needed to solve equations (39-41). Due to the questionable accuracy of the data for Na_2S , the lowest ionic strength was given the highest reduced activity coefficient to calculate a value of q . Similarly, the highest ionic strength was

given the lowest reduced activity coefficient to generate a second extreme in q . Because the range in q was so wide, it meant that potentially, any given molality could correspond to any given activity coefficient for Na_2S in the system. The minimum and maximum values of q were used in program AQS to calculate corresponding equilibrium $P_{\text{H}_2\text{S}}$ values. This allowed a comparison to be made to the mean $P_{\text{H}_2\text{S}}$ in order to determine the effect Na_2S activity coefficients had upon the overall equilibrium $P_{\text{H}_2\text{S}}$.

Table 8. Selected activity coefficients of sodium sulfide as a function of molality.

$m_{\text{Na}_2\text{S}}$	$(\gamma_{\text{Na}_2\text{S}})_{\text{eff}}$	I (from equation 43)	$\Gamma_{\text{Na}_2\text{S}}^\circ$ (from equation 37)
0.4	0.985	1.2	0.992
0.5	1.081	1.5	1.040
0.6	1.179	1.8	1.086
0.8	1.379	2.4	1.174
1.0	1.582	3.0	1.258
1.2	1.791	3.6	1.338
1.4	2.004	4.2	1.416
1.8	2.460	5.4	1.568
2.0	2.698	6.0	1.643
2.5	3.472	7.5	1.863

Because of the uncertainty in the NaHS data, the same approach was employed to determine minimum and maximum q values over the range of activity data as was used for Na_2S . The corresponding $P_{\text{H}_2\text{S}}$ values were also compared to the mean $P_{\text{H}_2\text{S}}$ to determine the effect of NaHS activity coefficients upon the mean $P_{\text{H}_2\text{S}}$ value. The mean q values and the percent deviation caused in γ_{ij} and $P_{\text{H}_2\text{S}}$ are listed in Table 9 for all species. The calculations for the sensitivity studies all used the following initial conditions:

$$T = 100^{\circ}\text{C}$$

$$C_{T,S} = 0.5552$$

$$C_{T,\text{CO}_3} = 1.484$$

$$C_{T,\text{SO}_4} = 0.098$$

$$C_{T,\text{Na}} = 4.7734$$

Table 9. The effect of uncertainty in activity coefficients upon equilibrium $P_{\text{H}_2\text{S}}$.

Species	Mean q	min q	$P_{\text{H}_2\text{S}}$ (ppm)	γ_{ij}	max q	$P_{\text{H}_2\text{S}}$ (ppm)	γ_{ij}
Na_2S	4.144	2.073	9.52	0.5598	7.714	18.6	2.001
Na_2CO_3	0.070	-0.566	14.92	0.2657	0.666	14.89	0.4395
Na_2SO_4	-0.190	-0.228	14.89	0.3219	-0.152	14.89	0.3284
NaOH	3.000	0.800	22.73	0.5338	4.900	10.35	0.8037
NaHS	0.120	-1.418	12.00	0.5096	1.339	17.50	0.6628
NaHCO_3	-0.128	-0.91	14.89	0.5794	9.00	14.89	1.183

The nonelectrolytes were tested individually, by entering the lowest and highest values of the salting out coefficient. Both extremes, for $\text{H}_2\text{S}(\text{aq})$ and $\text{H}_2\text{CO}_3^*(\text{aq})$ had a negligible effect upon the equilibrium $P_{\text{H}_2\text{S}}$ when tested in AQS.

To determine the overall maximum uncertainty in $P_{\text{H}_2\text{S}}$, all equilibrium constants and q's which increased $P_{\text{H}_2\text{S}}$ when tested individually, were combined together in AQS. This combined effect

produced the highest possible P_{H_2S} when compared to the mean P_{H_2S} . The overall minimum uncertainty was determined by combining all equilibrium constants and q 's that caused P_{H_2S} to decrease below the mean value. Although the chances of all maximum or minimum deviations occurring at once in all equilibrium constants and q 's are slim, the results do provide an upper and lower limit to the calculated equilibrium P_{H_2S} values. The overall maximum was found to be 35.6 ppm (+138 percent) and the overall minimum 4.83 ppm (-67 percent).

Examination of Table 9 indicates that the variables that most affect P_{H_2S} are the activity coefficients for Na_2S , $NaHS$ and $NaOH$. Because of the uncertainty in the activity data for these compounds, especially the sulfide species, further error analysis was necessary.

For $NaOH$, Na_2S and $NaHS$, the mean activity coefficients in the mixture, γ_{ij} , were changed more drastically (by changing q values), in order to compare the effect these changes had on the maximum and minimum P_{H_2S} values of 35.6 ppm and 4.83 ppm respectively. Table 10 lists the changes in the mean activity coefficients for Na_2S , $NaHS$ and $NaOH$, and their effects upon the maximum and minimum equilibrium P_{H_2S} .

In examining Table 10 it can be seen that γ_{NaHS} has a great effect upon equilibrium P_{H_2S} . A 55.6 percent decrease in γ_{NaHS} caused a corresponding 64 percent decrease in P_{H_2S} from the minimum value of 4.83 ppm. Similarly, for Na_2S a 44.9 percent decrease in γ_{Na_2S} caused a 59.3 percent decrease in the minimum P_{H_2S} .

In testing the maximum uncertainty in P_{H_2S} , changes in γ_{NaHS} had a very large effect upon P_{H_2S} . A 112 percent change in γ_{NaHS} caused

a 250 percent change in maximum P_{H_2S} . Changes in both γ_{Na_2S} and γ_{NaOH} had a negligible effect upon P_{H_2S} .

Table 10. The effect large changes in γ_{Na_2S} , γ_{NaHS} and γ_{NaOH} have upon P_{H_2S} .

Species	γ_{ij}	Difference from mean γ_{ij} (%)	q	P_{H_2S} (ppm)	Difference from mean P_{H_2S} (%)
Na_2S	0.5712	--	2.073	4.83	--
Na_2S	0.3235*	- 43.4	0.100	2.06*	- 57.3
Na_2S	0.3148*	- 44.9	0.010	1.96*	- 59.3
NaHS	0.5183	--	-1.418	4.83	--
NaHS	0.3569*	- 31.1	-5.000	3.13*	- 35.2
NaHS	0.2302*	- 55.6	-7.50	1.74*	- 64.0
NaOH	0.8704	--	4.90	4.83	--
NaOH	0.9191*	+ 5.60	5.50	4.22*	- 12.7
NaOH	1.004 *	+ 15.4	6.50	3.36*	- 30.4
Na_2S	1.391	--	7.714	35.6	--
Na_2S	2.180**	+ 56.7	10.00	36.2**	+ 1.91
Na_2S	3.460**	+149.	15.00	36.4**	+ 2.39
NaHS	0.4806	--	1.339	35.6	--
NaHS	0.6730**	+ 40.	5.000	62.9**	+ 77.0
NaHS	1.019**	+112.	10.00	124.4**	+250.
NaHS	1.226**	+155.	15.00	166.9**	+369.
NaOH	0.4596	--	0.800	35.6	--
NaOH	0.4273**	- 7.03	0.100	40.1**	+ 12.7
NaOH	0.4233**	- 7.90	0.0100	40.7**	+ 14.5
NaOH	0.4229**	- 7.98	0.0010	40.8**	+ 14.7

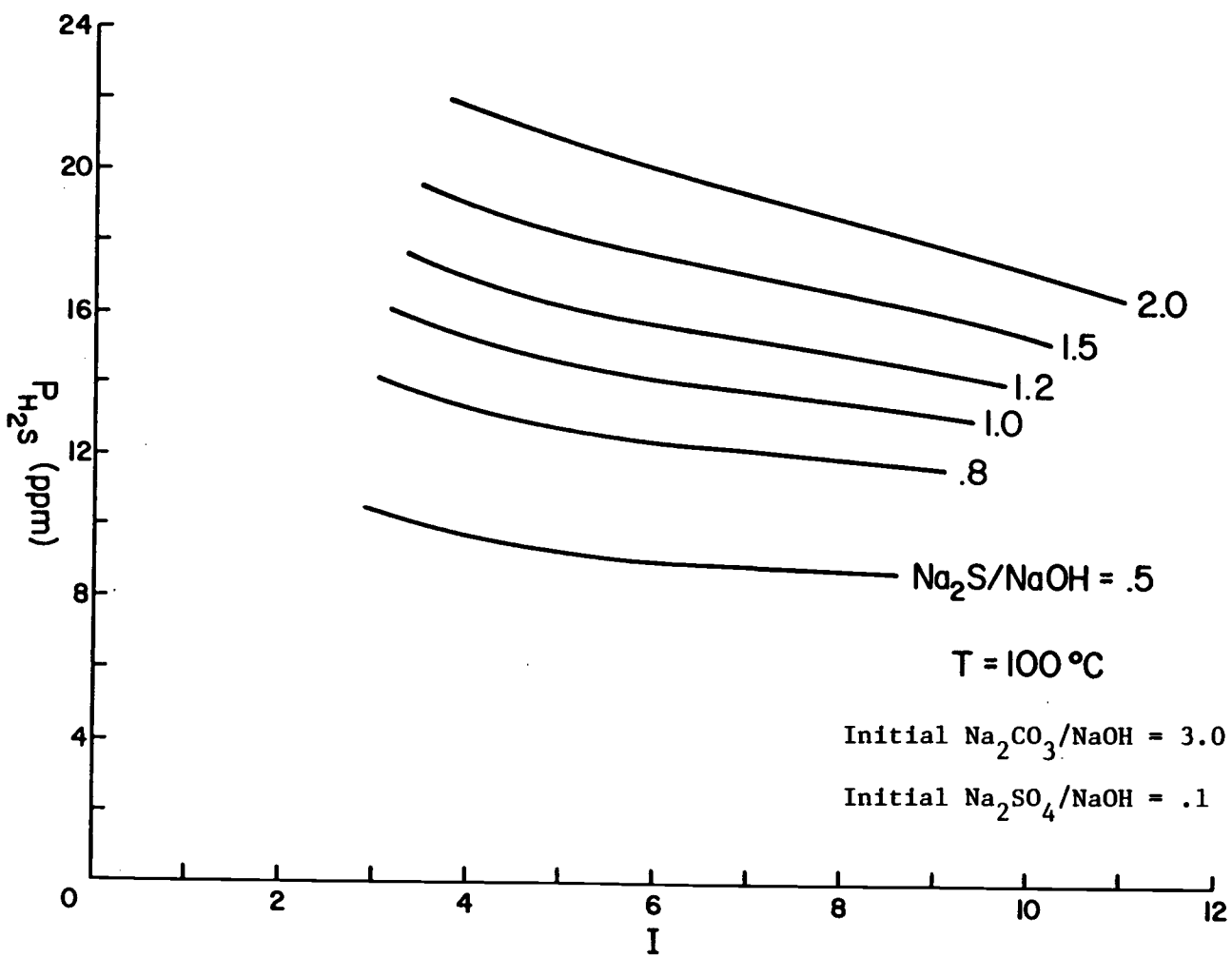
* Deviation from the minimum.

** Deviation from the maximum.

Parametric Analysis

Program AQS was used following the calculation procedure described in Section E to generate all results for the system B parametric analysis. Figure 7 (Test I) shows P_{H_2S} as a function of

Figure 7. Variation of P_{H_2S} with I and initial $Na_2S/NaOH$ ratio.



ionic strength at fixed initial Na_2S to NaOH ratio. The calculations were done for 100°C , which is approximately 5°C below the boiling point of green liquor. Figure 7 illustrates that at any fixed initial $\text{Na}_2\text{S}/\text{NaOH}$ ratio, the $P_{\text{H}_2\text{S}}$ decreased with increasing ionic strength. In all cases as the initial $\text{Na}_2\text{S}/\text{NaOH}$ ratio was increased from 0.5 to 2.0, $P_{\text{H}_2\text{S}}$ increased proportionately. The highest equilibrium $P_{\text{H}_2\text{S}}$ value was approximately 22 ppm and occurred at an ionic strength of approximately 3.75. The lowest $P_{\text{H}_2\text{S}}$ value was about 8.5 ppm occurring at an ionic strength of 8.6. In Test I, the ratio of initial Na_2CO_3 to NaOH ($\text{Na}_2\text{CO}_3/\text{NaOH}$) and the ratio of initial Na_2SO_4 to NaOH ($\text{Na}_2\text{SO}_4/\text{NaOH}$) were both held constant at 3.0 and 0.1 respectively.

The results of the sensitivity study can be applied directly to the parametric analysis. Figure 8 represents the Test I run where $\text{Na}_2\text{S}/\text{NaOH} = 1$, with the (---) line calculated from the sensitivity study. The maximum uncertainty for each $P_{\text{H}_2\text{S}}$ is +138 percent, which was determined earlier in this section. The minimum uncertainty in the figure represents a 67 percent decrease in all $P_{\text{H}_2\text{S}}$ values. All calculated $P_{\text{H}_2\text{S}}$ values are assumed to contain the same degree of uncertainty, therefore (---) lines such as those in Figure 8 apply to all calculated results.

In Test II the $P_{\text{H}_2\text{S}}$ was calculated as a function of ionic strength for fixed initial ratios of $\text{Na}_2\text{CO}_3/\text{NaOH}$ from 2.4 to 3.6. The following ratios were held constant for this set of analyses: initial $\text{Na}_2\text{S}/\text{NaOH} = 1.1$ and initial $\text{Na}_2\text{SO}_4/\text{NaOH} = 0.1$. Less than a five percent change in $P_{\text{H}_2\text{S}}$ resulted as initial $\text{Na}_2\text{CO}_3/\text{NaOH}$ ratio was increased from 2.4 to 3.6. The results can be seen in Table 11.

Figure 8. Uncertainty in the variation of P_{H_2S} with I.

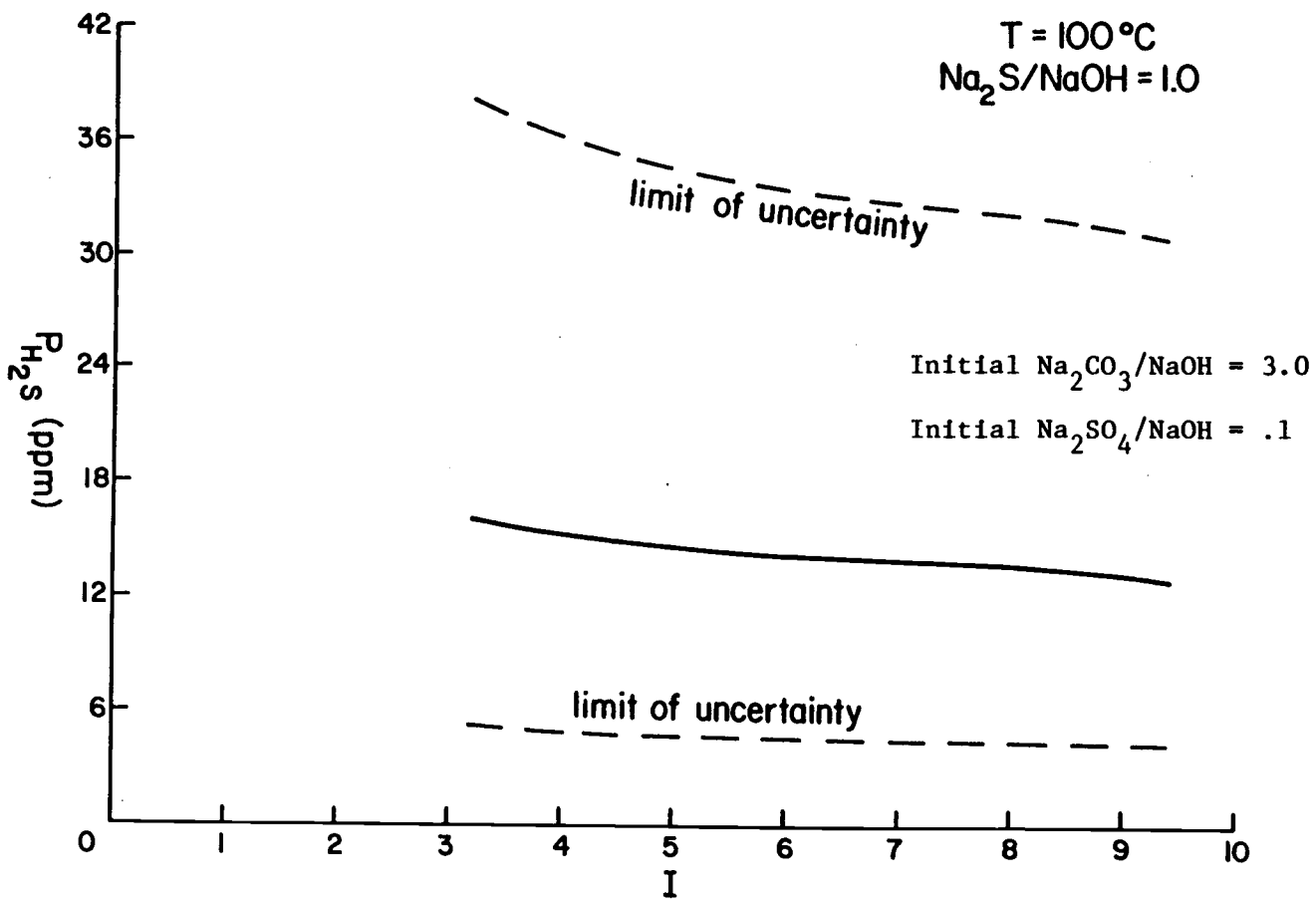


Table 11. Results of Test II, varying initial $\text{Na}_2\text{CO}_3/\text{NaOH}$ ratio.

$\text{Na}_2\text{CO}_3/\text{NaOH}$ (molalities)	$\text{P}_{\text{H}_2\text{S}}$ (ppm)	Ionic strength
2.4	16.89	2.78
3.0	16.88	3.23
3.6	16.85	3.67
2.4	14.59	5.60
3.0	14.82	6.46
3.6	14.89	7.32
2.4	13.83	8.29
3.0	13.65	9.57
3.6	13.25	10.86

In Test III the $\text{P}_{\text{H}_2\text{S}}$ was calculated as a function of ionic strength for fixed initial ratios of $\text{Na}_2\text{SO}_4/\text{NaOH}$ equal to 0.1 and 0.2. The initial $\text{Na}_2\text{S}/\text{NaOH}$ and $\text{Na}_2\text{CO}_3/\text{NaOH}$ ratios were held constant at 1.1 and 3.0 respectively. As with Test II, an increase in initial $\text{Na}_2\text{SO}_4/\text{NaOH}$ ratio from 0.1 to 0.2 had a negligible effect (less than one percent) upon $\text{P}_{\text{H}_2\text{S}}$. The results can be seen in Table 12.

Table 12. Results of Test III, varying initial $\text{Na}_2\text{SO}_4/\text{NaOH}$ ratio.

$\text{Na}_2\text{SO}_4/\text{NaOH}$	$\text{P}_{\text{H}_2\text{S}}$ (ppm)	Ionic strength
0.1	16.88	3.23
0.2	16.88	3.30
0.1	14.82	6.46
0.2	14.84	6.60
0.1	13.65	9.57
0.2	13.60	9.78

The effect of temperature was studied by redoing sections of Test I at 90°C and noting the change in $P_{\text{H}_2\text{S}}$. The results can be seen in Figure 9. At 90°C for a constant initial ratio of $\text{Na}_2\text{S}/\text{NaOH} = 1.0$ all $P_{\text{H}_2\text{S}}$ values were lower by approximately 30 percent. Similar results were obtained for initial ratios of $\text{Na}_2\text{S}/\text{NaOH}$ equal to 0.5 and 1.5.

G. Discussion

In referring to Figure 7 it is clear that increasing initial concentrations of Na_2S always correspond to larger equilibrium $P_{\text{H}_2\text{S}}$ results. This is because there is more total sulfur in the system. The total amount of dissolved sulfide species, $C_{\text{T,S}}$, is greater and there is also more hydrogen sulfide gas released. The decrease in $P_{\text{H}_2\text{S}}$ with increasing ionic strength for fixed initial $\text{Na}_2\text{S}/\text{NaOH}$ ratios corresponds to an increase in the system pH. There are more hydroxide ions in solution causing the system pH to shift to the right on a pC-pH diagram, resulting in a decrease of dissolved hydrogen sulfide. More of the initial sulfide ends up as sulfide and bisulfide ions rather than the totally protonated $\text{H}_2\text{S}(\text{aq})$ species.

A closer look at equation (28) is necessary in order to justify the overall decrease in equilibrium $P_{\text{H}_2\text{S}}$.

$$P_{\text{H}_2\text{S}} = \frac{\gamma_{\text{H}_2\text{S}} [\text{H}_2\text{S}]}{K_5} \quad (28)$$

The equilibrium constant K_5 is fixed because it is only a function of temperature, which is set at 100°C for this study. The activity

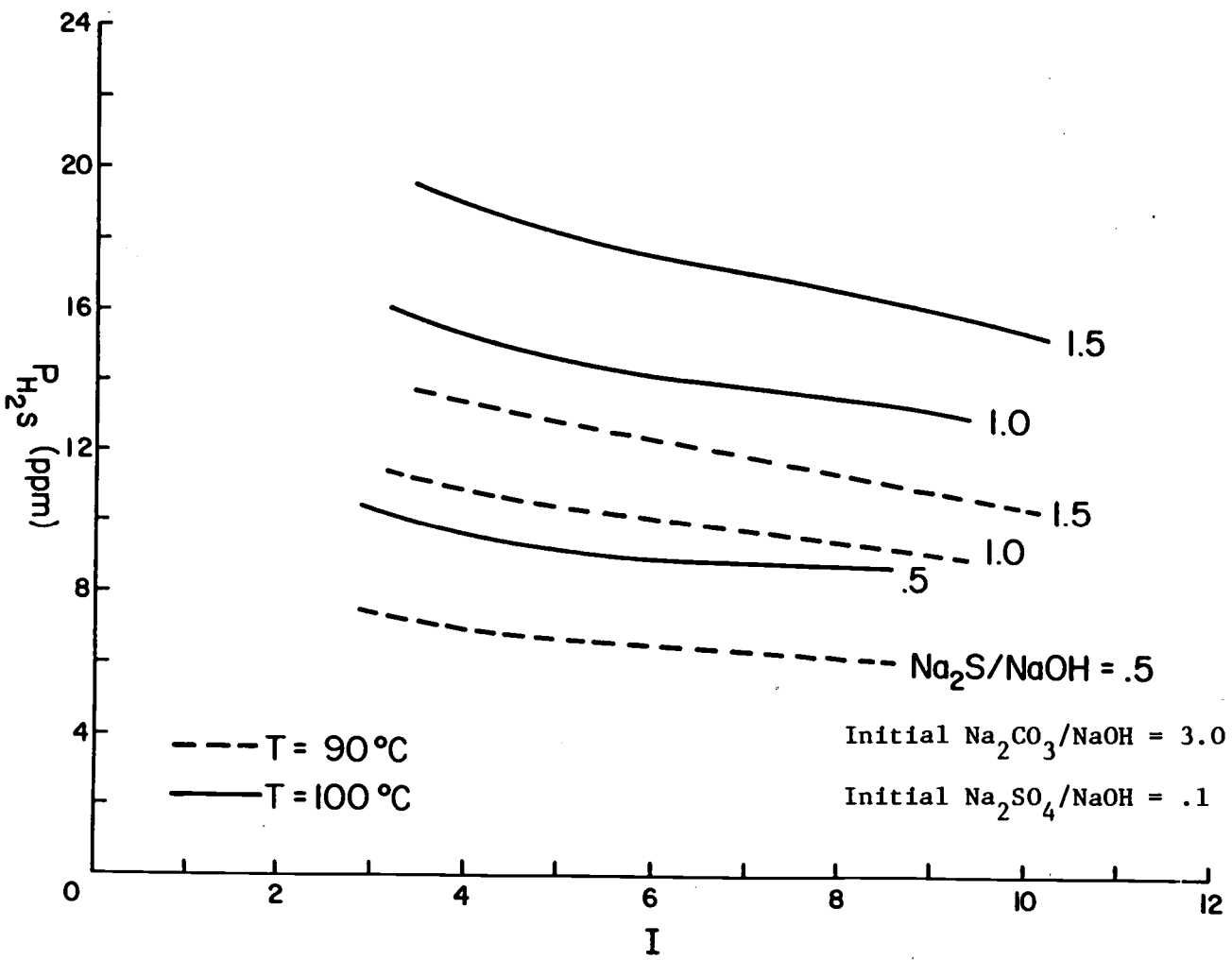


Figure 9. Variation of $P_{\text{H}_2\text{S}}$ with I, initial $\text{Na}_2\text{S}/\text{NaOH}$ ratio, and temperature.

coefficient of hydrogen sulfide, $\gamma_{\text{H}_2\text{S}}$, increases with increasing ionic strength, but at a slower rate than the decrease in dissolved hydrogen sulfide, $[\text{H}_2\text{S}]$. The net effect, therefore, causes a slight decrease in $P_{\text{H}_2\text{S}}$ in all cases as the ionic strength and pH increase.

In reference to Figure 8 it is important to note that the results of the sensitivity study allow us to bracket each equilibrium $P_{\text{H}_2\text{S}}$ value between the minimum and maximum values. For example, Figure 8 shows that at an ionic strength of 6.34, the $P_{\text{H}_2\text{S}}$ is somewhere in the range of 4 to 33 ppm. In spite of this rather large range in $P_{\text{H}_2\text{S}}$, rough comparisons to measured values can still be accomplished.

Table 3 of Section B listed titration results from Weyerhaeuser's Springfield, Oregon mill. These results correspond to the following initial ratios:

$$\text{Na}_2\text{S}/\text{NaOH} = 1.15$$

$$\text{Na}_2\text{CO}_3/\text{NaOH} = 3.0$$

$$\text{Na}_2\text{SO}_4/\text{NaOH} = 0.2$$

The ionic strength for such a solution is approximately 6.5. With $\text{Na}_2\text{S}/\text{NaOH} = 1.15$ and $I = 6.5$, Figure 9 gives a mean value for equilibrium $P_{\text{H}_2\text{S}}$ of approximately 12 ppm. Considering the uncertainty in these calculations (+138 percent and -67 percent) the real $P_{\text{H}_2\text{S}}$ could actually be as low as 4 ppm or as high as 29 ppm. As discussed earlier the initial $\text{Na}_2\text{CO}_3/\text{NaOH}$ and $\text{Na}_2\text{SO}_4/\text{NaOH}$ ratios have a negligible effect upon $P_{\text{H}_2\text{S}}$, therefore they need not be exactly equal to the constants in Figure 9.

According to Young (1984), for the green liquor conditions listed in Table 3, the measured P_{H_2S} at the Springfield mill was 35 ± 5 ppm. The upper limit of uncertainty in the calculated equilibrium P_{H_2S} is close to the measured P_{H_2S} value. However, there are insufficient data at this time to prove that the system is actually at equilibrium.

The highest equilibrium P_{H_2S} value generated in the parametric analysis is approximately 22 ppm at an ionic strength of 3.75 (Figure 7). This corresponds to an initial $Na_2S/NaOH$ ratio of 2.0, which is in fact, too high for most kraft green liquors. The lowest P_{H_2S} in the analysis is 6 ppm at an ionic strength of 8.5 and a temperature of $90^\circ C$ (Figure 9). This value corresponds to an initial $Na_2S/NaOH$ ratio of 0.5 which is too low for most green liquors. With negative 67 percent uncertainty applied to the low value of 6 ppm and the positive 138 percent uncertainty applied to 22 ppm, the hydrogen sulfide equilibrium concentration could be anywhere from 1.98 to 52.0 ppm.

For typical changes in process variables such as the initial $Na_2S/NaOH$ ratio or temperature, the equilibrium P_{H_2S} will fall within this range. The overall range in system B is a factor of 20. In system A the equilibrium P_{H_2S} range varies by a factor of 20,000 for typical changes in process variables such as P_{H_2O} or P_{CO_2} . It can be concluded that system B is quite stable compared to system A. Process changes in system B probably will not affect hydrogen sulfide emissions, whereas process changes in system A may have a drastic effect upon them.

H. Summary

System B, the aqueous high-temperature solution of sodium salts consists of $\text{H}_2\text{S}(\text{g})$ and $\text{CO}_2(\text{g})$ in equilibrium with the following ions: Na^+ , H^+ , OH^- , S^{2-} , HS^- , $\text{H}_2\text{S}(\text{aq})$, CO_3^{2-} , HCO_3^- , $\text{H}_2\text{CO}_3^*(\text{aq})$, SO_4^{2-} , and HSO_4^- . Four mass conservation equations, for liquid phase sodium, carbonate, sulfide and sulfate ions, were combined with eight equilibrium equations and an electroneutrality expression to characterize the system at equilibrium.

High temperature equilibrium constants were interpolated from the data of Helgeson (1969). The mean activity coefficients for all electrolytes were calculated using the Kusik and Meissner method. The mean salt method was then used to convert these values into single ion activity coefficients. Due to the inaccuracies inherent in these methods, as well as the errors in the activity data, a sensitivity study was done to define the uncertainty in the $P_{\text{H}_2\text{S}}$ calculations.

An iterative program was written to solve all of the equations simultaneously and yield results of $P_{\text{H}_2\text{S}}$ as a function of ionic strength, pH and initial molar ratios of $\text{Na}_2\text{S}/\text{NaOH}$, $\text{Na}_2\text{CO}_3/\text{NaOH}$ and $\text{Na}_2\text{SO}_4/\text{NaOH}$. The results indicated that increases in initial $\text{Na}_2\text{S}/\text{NaOH}$ ratio caused slight increases in $P_{\text{H}_2\text{S}}$, while increases in initial $\text{Na}_2\text{CO}_3/\text{NaOH}$ and $\text{Na}_2\text{SO}_4/\text{NaOH}$ ratios had a negligible effect upon $P_{\text{H}_2\text{S}}$. In all cases, equilibrium $P_{\text{H}_2\text{S}}$ decreased with increasing ionic strength and pH. The $P_{\text{H}_2\text{S}}$ also decreased slightly with temperature; however, the practical temperature variation in green liquor

is small, hence limiting the overall importance of temperature as a controlling variable.

The equilibrium results were compared to hydrogen sulfide measurements taken just above the green liquor surface at a kraft pulp mill. The $P_{\text{H}_2\text{S}}$ measurements were found to be close to the uppermost limit of calculated equilibrium $P_{\text{H}_2\text{S}}$.

Overall, the calculated equilibrium $P_{\text{H}_2\text{S}}$ proved to be rather stable under typical operating ranges and solution concentrations found in a kraft green liquor dissolving tank. This leads us to believe that excesses in hydrogen sulfide emissions are probably caused in system A where $P_{\text{H}_2\text{S}}$ increased drastically with small changes in major process variables such as steam and carbon dioxide.

OVERALL CONCLUSIONS

The variables which have the most effect upon equilibrium P_{H_2S} in system A (the smelt shatter jet area) are P_{CO_2} , P_{H_2O} , P_{O_2} , and system temperature. An increase in P_{H_2O} or P_{CO_2} causes a proportional increase in equilibrium P_{H_2S} . An increase in P_{O_2} causes the oxidation of Na_2S and H_2S , thereby lowering equilibrium P_{H_2S} . Changes in temperature also have a large effect upon equilibrium P_{H_2S} . For example, a decrease in system temperature from 1200°K to 1000°K causes the equilibrium P_{H_2S} to increase by a factor of ten.

The results of the equilibrium calculations for system A were compared to measured values obtained from the smelt dissolving system of a kraft pulp mill. When the smelt is starved for oxygen (10^{-18} ppm at 1000°K), the calculated equilibrium P_{H_2S} can be as high as 20,000 ppm. At the pulp mill the bulk P_{H_2S} was equal to 50 ppm. From these results, it is concluded that rate processes (i.e., kinetics or mass transfer) must be controlling the release of hydrogen sulfide.

In system B (the alkaline green liquor solution) the controlling variables are the initial $Na_2S/NaOH$ ratio, pH and temperature. Results indicate that increases in the initial $Na_2S/NaOH$ ratio or temperature cause a slight increase in the equilibrium P_{H_2S} . Increases in the green liquor pH always lead to a decrease in the equilibrium P_{H_2S} .

When compared to system A, where variations in the process variables have a large effect on equilibrium P_{H_2S} , changes over the

full range of operating conditions in system B do not have any significant impact upon equilibrium P_{H_2S} . In system B, the upper limit of calculated equilibrium P_{H_2S} is slightly less than measured P_{H_2S} found in the smelt dissolving system; however, there are not enough data to prove whether the system is actually at equilibrium.

As a result of these calculations it is concluded that the major source of H_2S emissions is system A. Since rate processes appear to control the amount of hydrogen sulfide that is released, experimentation is now necessary to determine whether kinetics or mass transfer effects are more dominant.

FUTURE WORK

It is clear that hydrogen sulfide emissions are generated from system A (the smelt shatter jet area). Since the emissions are rate controlled, it is important to conduct an experimental investigation that will determine if mass transfer effects or kinetics are dominant. Experimentation needs to be done at high temperature in order to generate the needed results. Upon finding the rate controlling step, specific control strategies or process modifications can be instituted to lower hydrogen sulfide emissions.

In system B, the Kusik and Meissner method was used to determine mean activity coefficients for each electrolyte in solution. This method was not very accurate, and when it was combined with the mean salt method to calculate single ion activity coefficients, the uncertainty increased even more. If more accurate equilibrium results are desired, a better method for calculating activity coefficients is needed.

Pitzer's model, which uses interaction coefficients for each set of electrolytes, predicts single ion activity coefficients directly. In order to apply this model to system B, high temperature interaction coefficients are needed for some of the electrolytes, particularly Na_2S and NaHS . Once these data are available, a subroutine can be formulated which solves the equations of Pitzer's model directly for use in an equilibrium program such as AQS.

At present, the data for sulfides is meager, at best. In spite of the many problems in working with aqueous sulfides, the

experimental work is necessary in order to reduce the uncertainty in equilibrium calculations such as those carried out for system B.

CONTROL STRATEGIES AND PROCESS MODIFICATIONS

Based upon the overall conclusions of this study, the following control strategies and process modifications can be implemented at the kraft pulp mill to reduce H_2S emissions:

1. Install efficient steam shatter jet nozzles which minimize the steam required to break up the smelt stream adequately. This may require some design effort and experimentation with new nozzles if currently available designs are not adequate.
2. The nozzle position and orientation relative to the smelt stream should be chosen to break up the smelt adequately with a minimum steam flow rate. According to Clay (1984), shatter jets are usually operated for the maximum surge flows of smelt, therefore, they usually overshatter the smelt stream. The smelt must be broken-up sufficiently, so that the risk of dissolving tank explosions is negligible. Since the use of green liquor recirculation sprays below the shatter jets reduces the degree of break up required, it should also reduce the shatter jet stream requirements.
3. Scrub the dissolving tank flue gas with alkaline green liquor or weak wash with a pH of 12 or greater. The equilibrium analysis of system B showed that most of the green liquor exists as sulfide and bisulfide ions. Scrubbing with green liquor or weak wash could, therefore, dissolve most of the gaseous hydrogen sulfide.

4. Replace steam as the fluid used to "shatter" the smelt. There are two possible substitutes; nitrogen and weak wash. According to Clay (1984), weak wash shatter jets would be a better alternative. The energy cost to pressurize the weak wash, and the cost of the fluid are both less than for nitrogen.
5. Eliminate the shatter jets completely and design a different system. This system would have to cool the smelt enough to avoid explosions, while still allowing it to be dissolved in green liquor for reconversion back to fresh pulping liquor.

In Lyons Falls, New York such a system has already been implemented by Georgia Pacific Corporation on a sodium bisulfite liquor smelter. The smelt flows to a flaker and is compressed between two water-cooled rolls and solidified into thin sheets. The sheets are broken up into small pieces and sent to a storage silo (Farin, 1975).

Process modifications such as this one, may indeed lead to the elimination of H_2S emissions from the smelt shatter jet area.

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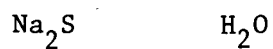
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APPENDICES

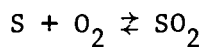
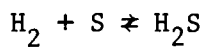
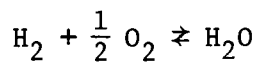
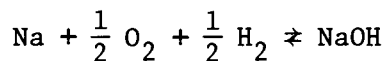
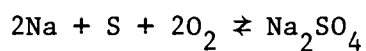
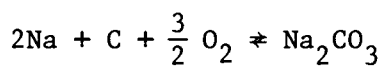
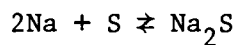
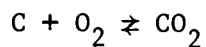
APPENDIX 1

Reduction Analysis to Determine the Number
of Reactions Needed in System A

1. Species present:

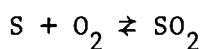
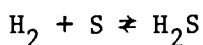
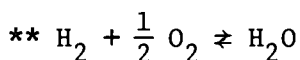
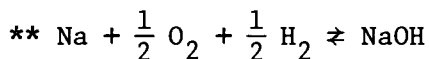
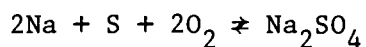
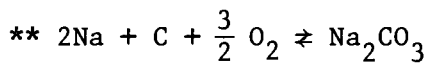
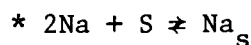
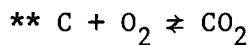


2. Formation reactions for each species:



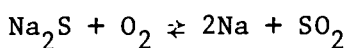
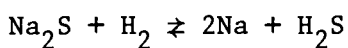
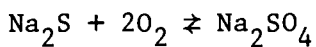
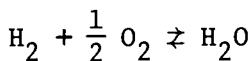
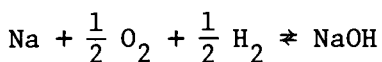
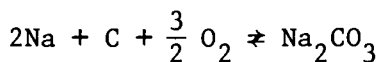
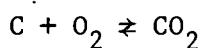
We must eliminate all species not present in the system, that is,
S, C, H₂, and Na.

3. Eliminate S first.

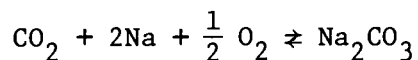
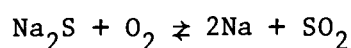
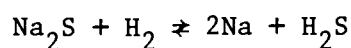
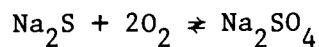
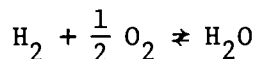
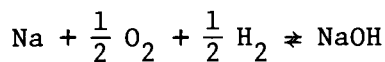


* Choose this reaction for combination with each of the others.

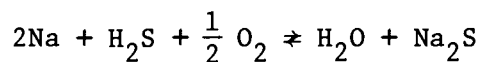
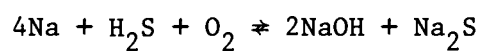
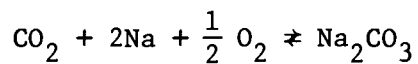
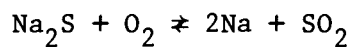
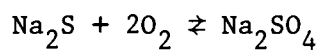
** No S in reaction; simply carry forward.



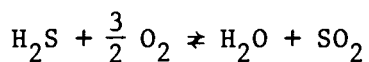
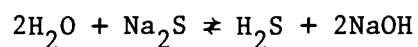
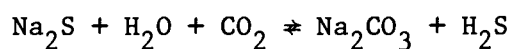
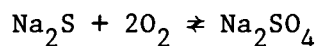
4. Following the same technique eliminate C.



5. Eliminate H_2 .



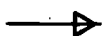



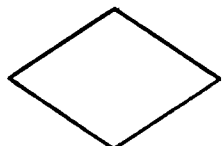



6. Eliminate Na.

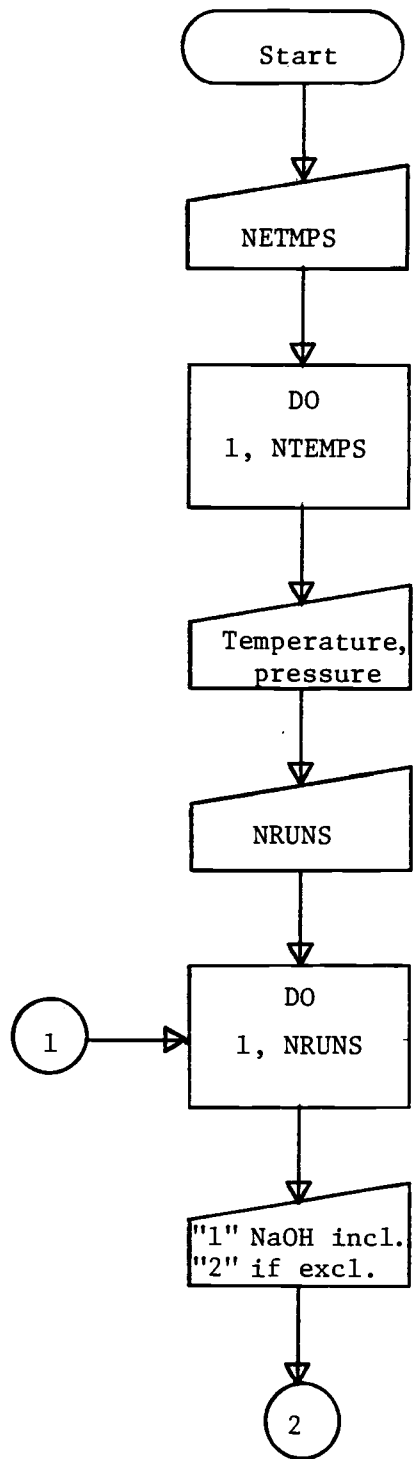


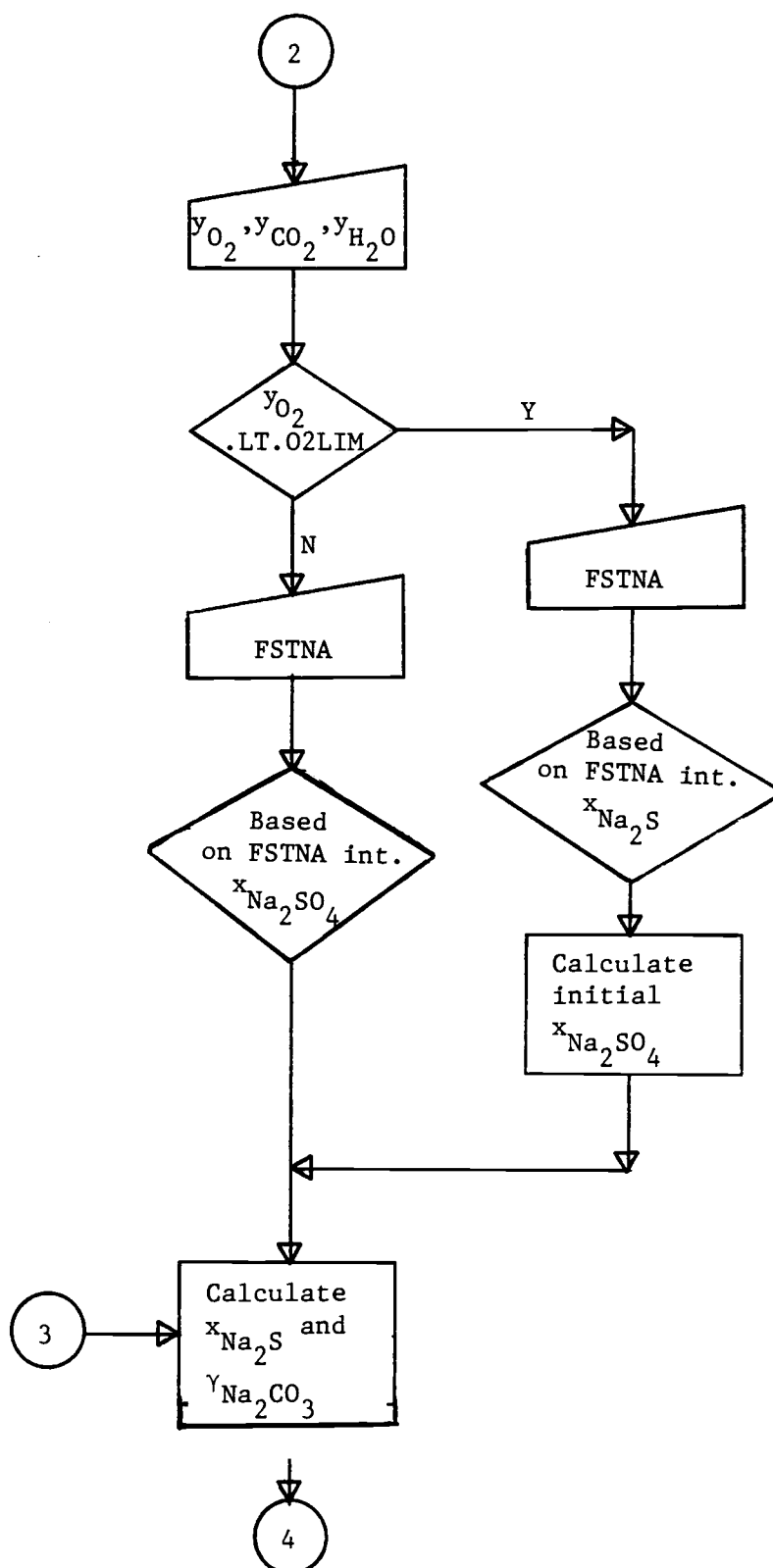
We now have a set of reactions which contains only those reacting species in the system. There are four reactions, therefore r is equal to four.

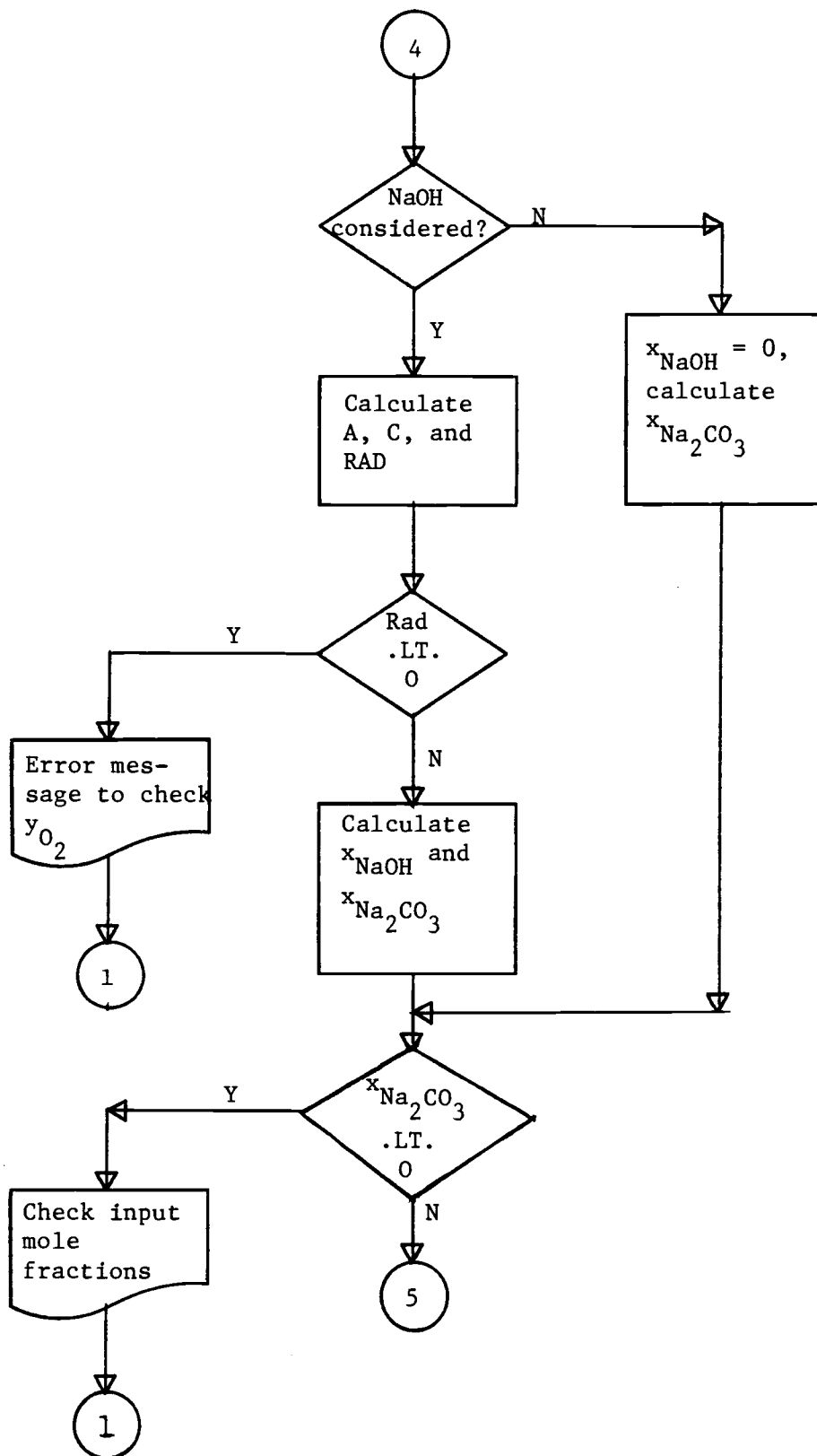
APPENDIX 2

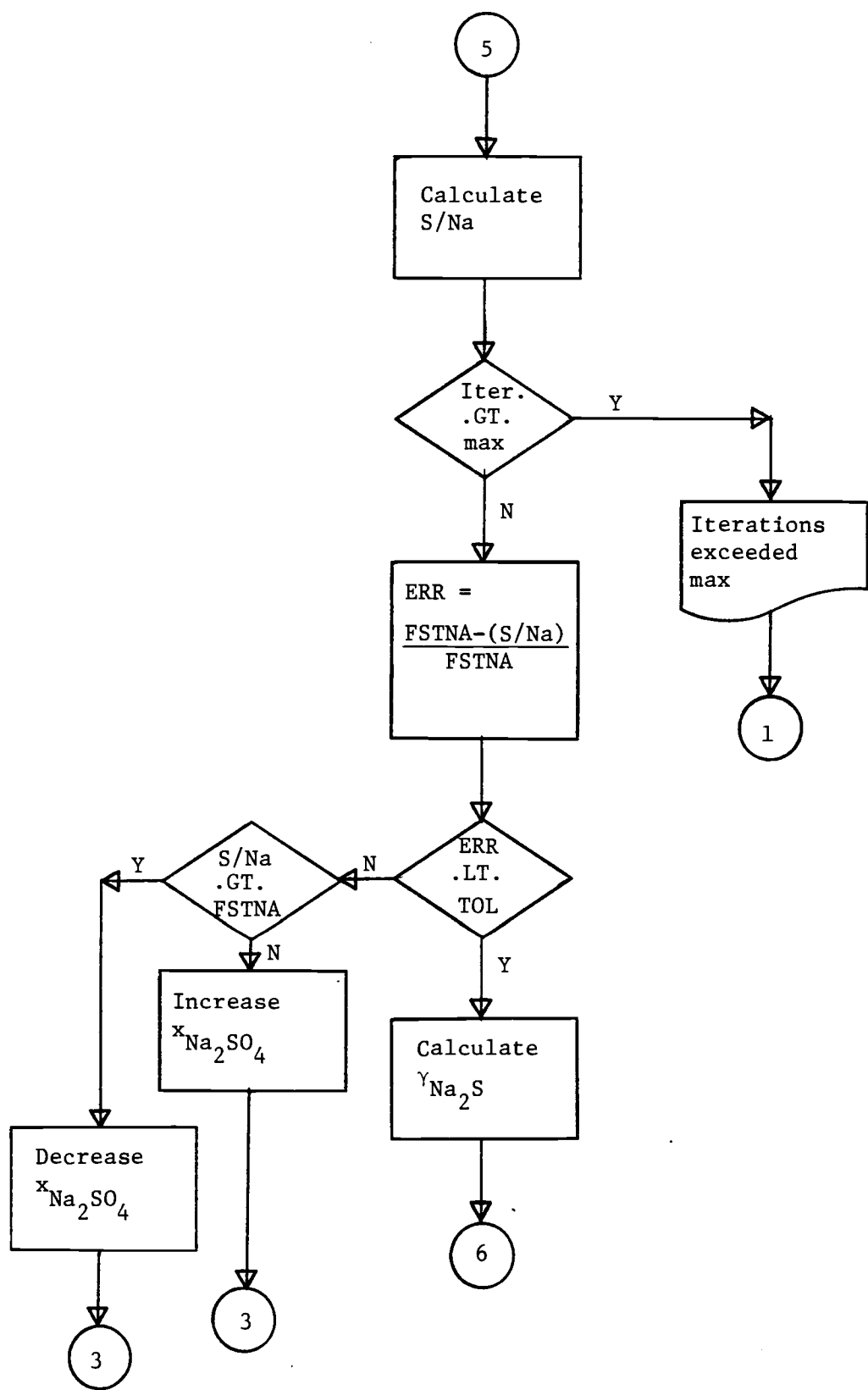
Flow Diagram for Program EQUILSymbols

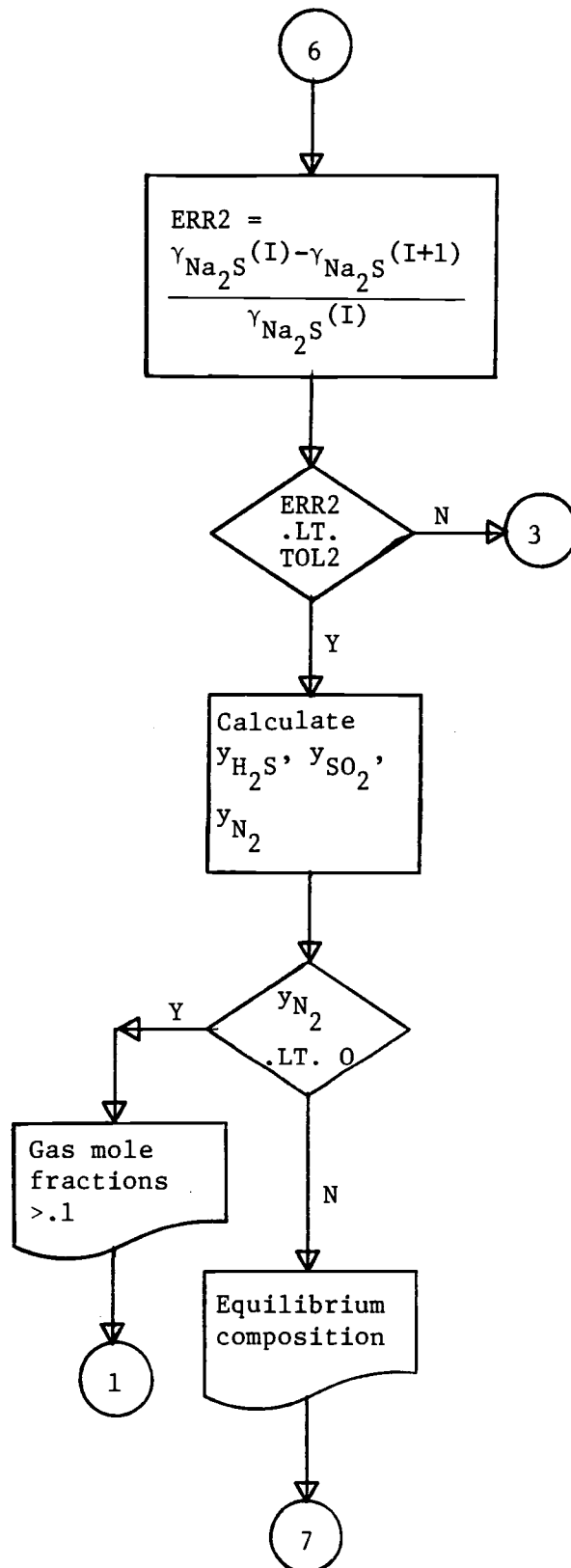
	Direction of Flow
	Terminal Symbol (stop or start)
	Manual Input (keyboard)
	Processing Symbol (arithmetic operations)
	Decision Symbol
	Predefined Process (subroutine)
	Printed Output (document)
	Connector or Junction

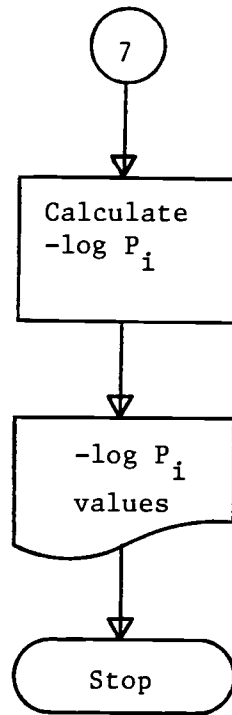












Program EQUIL

```

C
C   VARIABLE DECLARATIONS
C
C   INTEGER ITER,MAXIT,I,NRUNS,M,LOG,J,NTEMPS
C   REAL  X(4),Y(6),PAR(8),TOL,CORR,TEMP,PRES,PTOL
C   REAL  GAC,B,STNA,FSTNA,ACT(300),ERR2,TOL2
C   REAL  GD(5),R,A,C,RAD
C
C   VARIABLE DESCRIPTIONS
C
C   ITER= # OF ITERATIONS PROGRAM USES
C   MAXIT= MAX # OF ITERATIONS PROGRAM CAN BE
C   ALLOWED, USUALLY 1000
C   I= COUNTER IN DO LOOP FOR NRUNS
C   M= COUNTER USED IN SUCCESSIVE SUBSTITUTION
C   TO FIND CORRECT XNA2CO3 AND ACTIVITY COEFF.
C   FOR NA2S
C   NRUNS= # OF RUNS SELECTED BY USER
C   LOG= FLAG THAT INDICATES WHETHER NAOH IS
C   CONSIDERED IN THE ANALYSIS
C   J=COUNTER IN OUTER DO LOOP
C   NTEMPS= # OF TEMPS, "1" OR "2" THAT RUNS
C   WILL BE DONE AT
C   TOL= ALLOWABLE ERROR IN S/NA RATIO, .01
C   TOL2= ALLOWABLE ERROR IN SUCCESSIVE SUBS-
C   TITUTION DETERMINATION OF NA2S ACTIVITY
C   COEFF., .01
C   CORR= CORRECTOR TO EITHER * OR / XNA2SO4
C   UNTIL IT MEETS TOL, SET AT 1.005
C   TEMP= SYSTEM TEMPERATURE
C   PRES= SYSTEM PRESSURE, 1 ATM.
C   PTOL= % ERROR IN S/NA EQN.
C   GAC= GAS CONSTANT, 1.987 CAL/G-K
C   B= 3750 CAL/G
C   STNA= SULFUR(S) TO SODIUM(NA) RATIO
C   FSTNA= FIXED S/NA RATIO; .16,.14,.12 OR.10
C   ACT(300)= ARRAY FOR NA2S ACTIVITY COEFF.
C   CALCULATED VIA SUCCESSIVE SUBSTITUTION
C   ERR= DIFFERENCE BETWEEN STNA AND FSTNA
C   ERR2= DIFFERENCE BETWEEN NA2S ACTIVITY
C   COEFF. M AND ACTIVITY COEFF. M+1
C   GD(5)= -LOG(PARTIAL PRES.) OF EACH OF THE GASES
C   R= RATIO OF N2 TO REACTIVE GASES
C   A,C= VARIABLES IN QUADRATIC EQN. AX**2+BX+C
C   RAD= SQUARE ROOT TERM IN QUADRATIC EQN.
C   O2LIM1,O2LIM2= TEMP. DEPENDENT CONSTANTS USED
C   TO GET A GOOD FIRST APPROXIMATION OF XNA2SO4
C   SO ITERATION TIME IS LOW AND SUCC. SUBST.
C   CAN BE USED. THEY ARE DETERMINED MAINLY
C   FROM KA1, S/NA AND RXN.1

```

```

C
C   X(1)= MOLE FRACTION NAOH
C   X(2)= MOLE FRACTION NA2SO4
C   X(3)= MOLE FRACTION NA2S
C   X(4)= MOLE FRACTION NA2CO3
C
C   Y(1)= MOLE FRACTION O2
C   Y(2)= MOLE FRACTION CO2
C   Y(3)= MOLE FRACTION H2O
C   Y(4)= MOLE FRACTION SO2
C   Y(5)= MOLE FRACTION H2S
C   Y(6)= MOLE FRACTION N2
C
C   PAR(1)= NA2S ACTIVITY COEFF.,= F(XNA2CO3)
C   PAR(2)= NA2CO3 ACTIVITY COEFF.,= F(XNA2S)
C   PAR(3)= NAOH ACTIVITY COEFF.= 1.
C   PAR(4)= NA2SO4 ACTIVITY COEFF.= 1.
C   PAR(5)= EQUILIBRIUM CONST. FOR RXN. 1
C   PAR(6)= EQUILIBRIUM CONST. FOR RXN. 2
C   PAR(7)= EQUILIBRIUM CONST. FOR RXN. 3
C   PAR(8)= EQUILIBRIUM CONST. FOR RXN. 4
C
C
C
C   READ IN NTEMPS TO BE STUDIED, "1" OR "2". THIS
C   IS THE OUTERMOST LOOP.
C
C   WRITE(6,400)
400  FORMAT(/,'ENTER 1 FOR ONLY ONE TEMP. TO BE STUDIED',/,
1    'OR 2 FOR BOTH TEMPS. TO BE STUDIED',/)
C   READ(5,*) NTEMPS
C   DO 500 J=1,NTEMPS
C   WRITE(6,401)
401  FORMAT(/,'ENTER SYSTEM TEMP(DEGREES K) AND PRES(ATM.):',/)
C   READ(5,*) TEMP,PRES
C   IF(TEMP .EQ. 1000.) GO TO 505
C
C   INITIALIZE 4 EQUIL. CONST. FOR 1200 K.
C
C   PAR(5)=1.1324E26
C   PAR(6)=.01928
C   PAR(7)=2.858E-5
C   PAR(8)=3.3266E18
C
C   INITIALIZE TEMP. DEPENDENT XNA2SO4 PREDICTOR
C   CONSTANTS.
C
C   O2LIM1=1.25E-14
C   O2LIM2=7.94E-13
C   GO TO 506

```

```
C
C   INITIALIZE 4 EQUIL. CONST. AND XNA2SO4 PREDICTOR
C   CONST. FOR 1000. K
C
505  PAR(5)=4.2170E34
      PAR(6)=.203
      PAR(7)=1.442E-5
      PAR(8)=1.1220E23
      O2LIM1=1.25E-18
      O2LIM2=7.94E-17

C
C   INITIALIZE REGULAR SOLUTION CONSTANTS
C
506  GAC=1.987
      B=3750.

C
C
C   LET'S READ IN NRUNS AND LOOP UNTIL COMPLETE.
C
      WRITE(6,39)
39   FORMAT(/,'ENTER THE NUMBER OF RUNS:',/)
      READ(5,*) NRUNS
      DO 51 I=1,NRUNS
      WRITE(6,301)
301  FORMAT(/,'IS NAOH A POSSIBLE SPECIES?',/,
1     'ENTER 1 FOR YES OR 2 FOR NO',//)
      READ(5,*) LOG
      WRITE(6,81)
81   FORMAT(/,'ENTER O2,CO2 AND H2O MOLE FRACTIONS:',/)
      READ(5,*) Y(1),Y(2),Y(3)
      PAR(3)=PAR(4)=1.

C
      IF (Y(1) .LT. O2LIM1) GO TO 201
      IF (Y(1) .GT. O2LIM2) GO TO 205

C
C   WHEN YO2 IS SQUARED IT IS CLOSE IN
C   VALUE TO KA1. XNA2SO4 WILL BE CLOSE
C   IN MAGNITUDE TO .01.
C
C
      WRITE(6,98)
98   FORMAT(/,'FSTNA IS:',//)
      READ(5,*) FSTNA
      X(2)=.01
      GO TO 249
201  WRITE(6,202)
202  FORMAT(/,'FSTNA IS:',/)
      READ(5,*) FSTNA

C
C   BASED ON FSTNA PICK A PRELIMINARY
C   XNA2S, WHICH THEN ALLOWS FOR AN
C   ESTIMATE OF XNA2SO4
C
```



```

IF(FSTNA .EQ. .16) X(3)=.3
IF(FSTNA .EQ. .14) X(3)=.25
IF(FSTNA .EQ. .12) X(3)=.20
IF(FSTNA .EQ. .10) X(3)=.17

C
C   CALCULATE INITIAL GUESS OF XNA2SO4
C
PAR(1)=1.943
X(2)=X(3)*PAR(1)*Y(1)**2*PAR(5)/PAR(4)
GO TO 249
205 WRITE(6,206)
206 FORMAT(/,'FSTNA IS:',/)
READ(5,*) FSTNA

C
C   BASED ON FSTNA PICK AN INITIAL MOLE
C   FRACTION OF XNA2SO4 BECAUSE IF FULFILLS
C   THE S TO NA RESTRICTION, NOT XNA2S.
C
IF(FSTNA .EQ. .16) X(2)=.30
IF(FSTNA .EQ. .14) X(2)=.25
IF(FSTNA .EQ. .12) X(2)=.20
IF(FSTNA .EQ. .10) X(2)=.17
GO TO 249

C
C
C
C
249 CORR=1.005
TOL=.01
MAXIT=1000

C
C
C   INITIALIZE ITERATIONS TO 0,CALCULATE PTOL
C
ITER=0
PTOL=100.*TOL

C
C   DO ITERATIVE CALCULATIONS FOR NA2SO4 MOLE FRACTIONS
C
C   CALCULATE XNA2S AND XNA2CO3 WITH FIXED
C   ACTIVITY COEFS. FOR NA2S
C
TOL2=.01
M=1
ACT(1)=1.943
PAR(1)=1.943
105 X(3)=X(2)*PAR(4)/(PAR(1)*Y(1)**2*PAR(5))
PAR(2)=EXP(B*X(3)**2/(GAC*TEMP))
IF(LOG .EQ. 2) GO TO 302
A=PAR(6)*Y(2)*PAR(3)/(PAR(7)+PAR(2)*Y(3))
C=X(3)+X(2)-1.
RAD=(1.-4.*A*C)**.5

```

```

IF (RAD .LT. 0.) GO TO 179
X(1)=(-1.+RAD)/(2.*A)
X(4)=A*X(1)**2
GO TO 310
302 X(1)=0.
X(4)=1.-X(1)-X(3)-X(2)
310 IF(X(4) .LT. 0.) GO TO 89
C
C CALCULATE S TO NA RATIO AND COMPARE TO
C FIXED VALUE
C
C
181 STNA=(X(3)+X(2))/(X(1)+2.*X(4)+
1 2.*X(3)+2.*X(2))
ITER=ITER+1
IF(ITER .GT. MAXIT) GO TO 19
ERR=ABS(STNA-FSTNA)
ERR=ERR/FSTNA
IF (ERR .LT. TOL) GO TO 103
IF (STNA .GT. FSTNA) GO TO 63
X(2)=X(2)*CORR
GO TO 105
63 X(2)=X(2)/CORR
GO TO 105
C
C
C CALCULATE ACTIVITY COEFF. FOR NA2S AND
C MOLE FRACTIONS FOR H2S, CO2 AND N2.
C
103 PAR(1)=EXP(B*X(4)**2/(GAC*TEMP))
M=M+1
ACT(M)=PAR(1)
ERR2=ABS(ACT(M)-ACT(M-1))/ACT(M)
IF(ERR2 .LT. TOL2) GO TO 104
GO TO 105
104 Y(5)=X(3)*PAR(1)*Y(3)*PAR(6)*Y(2)/
1 (X(4)*PAR(2))
Y(4)=Y(5)*Y(1)**1.5*PAR(8)/Y(3)
Y(6)=1.-Y(3)-Y(2)-Y(1)-Y(4)-Y(5)
IF (Y(6) .LT. 0.) GO TO 191
GO TO 17
C
C CONVERGENCE IS OK, WRITE RESULTS
C
17 WRITE(6,18) TEMP,PRES
18 FORMAT(/,'THE TEMPERATURE OF THE SYSTEM IS ',F6.1,/,
1 ' DEGREES KELVIN AND THE PRESSURE IS ',F3.1,/,
1 'ATM.',//)
WRITE(6,13)X(3),X(4),X(1),X(2)
13 FORMAT(' THE LIQUID MOLE FRACTIONS ARE:',//,
1 'NA2S=',E10.3,/, 'NA2CO3=',E10.3,/,
1 'NAOH=',E10.3,/, 'NA2SO4=',E10.3,//)
WRITE(6,3)Y(3),Y(2),Y(1),Y(4),Y(5),Y(6)

```

```

3   FORMAT(' THE GAS PHASE MOLE FRACTIONS ARE:',//,
1   'H2O=',E10.3,/, 'CO2=',E10.3,/,
1   'O2=',E10.3,/, 'SO2=',E10.3,/,
1   'H2S=',E10.3,/, 'N2=',E10.3,/)

C
C   CALCULATE PLOTTING INFORMATION
C
R=Y(6)/(Y(3)+Y(2)+Y(1)+Y(4)+Y(5))
GD(1)=-LOG10(Y(3))
GD(2)=-LOG10(Y(2))
GD(3)=-LOG10(Y(1))
GD(4)=-LOG10(Y(4))
GD(5)=-LOG10(Y(5))

C
C
WRITE(6,58)GD(1),GD(2),GD(3),GD(4),GD(5)
58  FORMAT(//,'THE -LOGP FOR EACH GAS IS:',//,
1   'H2O=',F7.3,/, 'CO2=',F7.3,/,
1   'O2=',F7.3,/, 'SO2=',F7.3,/,
1   'H2S=',F7.3,/)

C
WRITE(6,59) R
59  FORMAT(/,'THE RATIO OF N2 TO REACTIVE GASES IS',E10.3,/)

C
C
GO TO 51
89  WRITE(6,90)
90  FORMAT(/,'SELECTION OF INITIAL MOLE FRACTIONS',/, '
1   WAS WRONG',/, 'IT IS NOT PHYSICALLY POSSIBLE',/)
GO TO 51

C
191 WRITE(6,192)
192 FORMAT(/,'GAS MOLE FRACTIONS > 1.,NOT POSSIBLE',/)
GO TO 51

C
179 WRITE(6,199)
199 FORMAT(/,'RAD IS NEGATIVE,CHECK O2 AND OTHERS',/)
GO TO 51

C
C
19  WRITE(6,20) MAXIT
20  FORMAT(/,'THE NUMBER OF ITERATIONS HAS EXCEEDED',/,
1   'THE MAXIMUM NUMBER OF',15,' CHOSEN IN THE START.',/)

51  CONTINUE
500 CONTINUE
RETURN
END

```

Sample Output from Program EQUIL

IS NAOH A POSSIBLE SPECIES?
ENTER 1 FOR YES OR 2 FOR NO

? 1

ENTER O2,CO2 AND H2O MOLE FRACTIONS:

? 6.7E-18,.05,.01

FSTNA IS:

? .16

THE TEMPERATURE OF THE SYSTEM IS 1000.0
DEGREES KELVIN AND THE PRESSURE IS 1.0
ATM.

THE LIQUID MOLE FRACTIONS ARE:

NA2S= .574E-01
NA2CO3= .680E+00
NAOH= .312E-02
NA2SO4= .260E+00

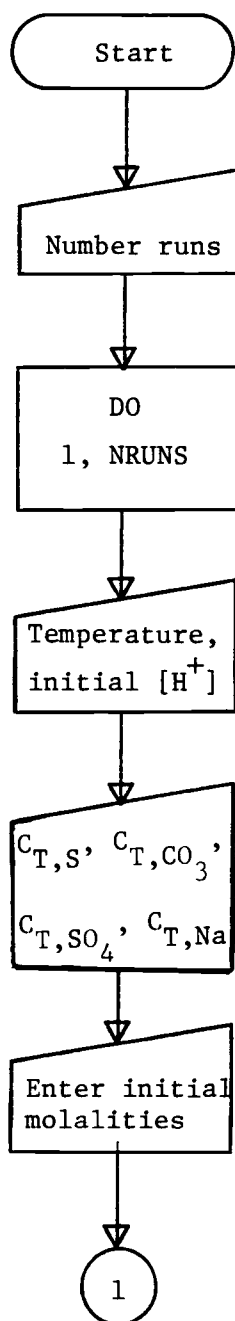
THE GAS PHASE MOLE FRACTIONS ARE:

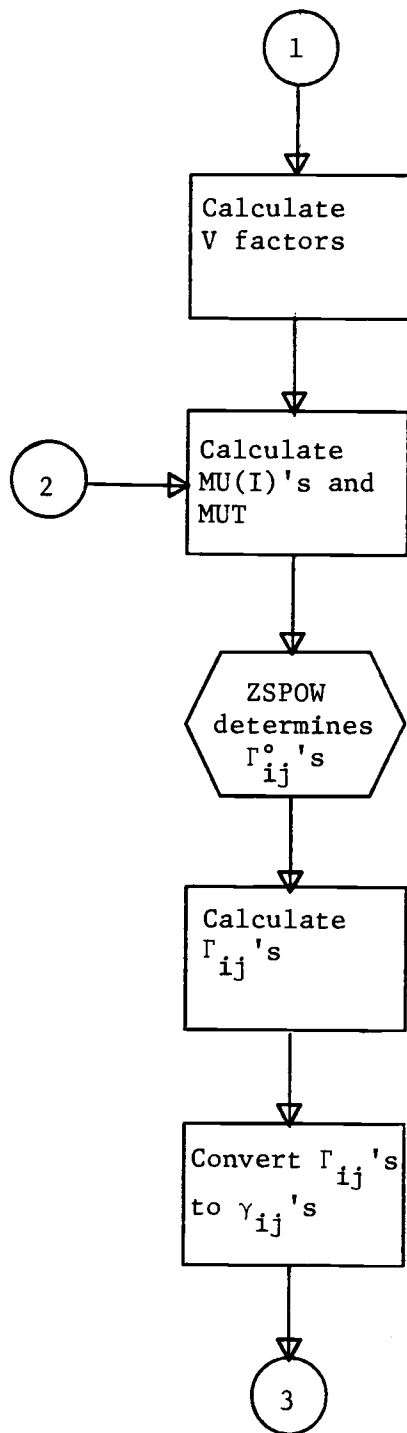
H2O= .100E-01
CO2= .500E-01
O2= .670E-17
SO2= .396E-05
H2S= .204E-04
N2= .940E+00

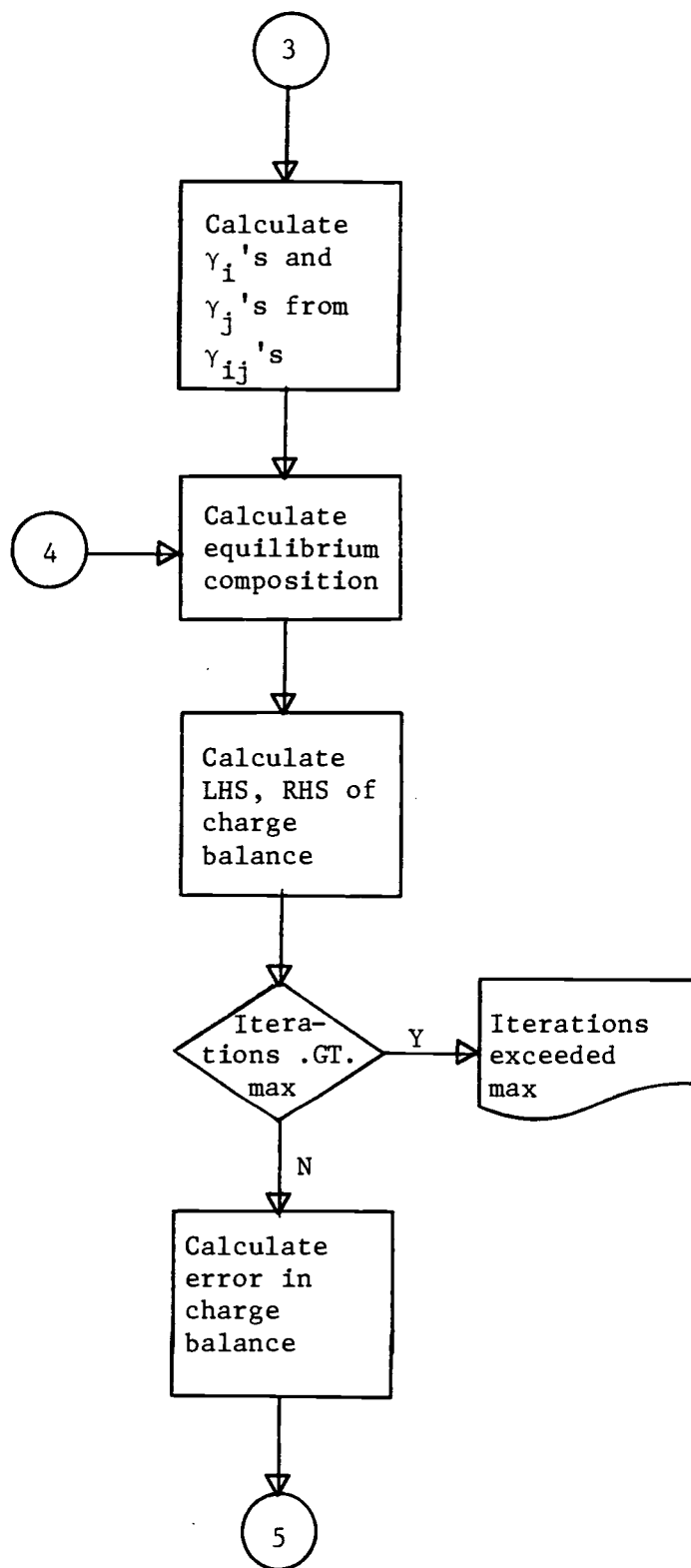
THE -LOGP FOR EACH GAS IS:

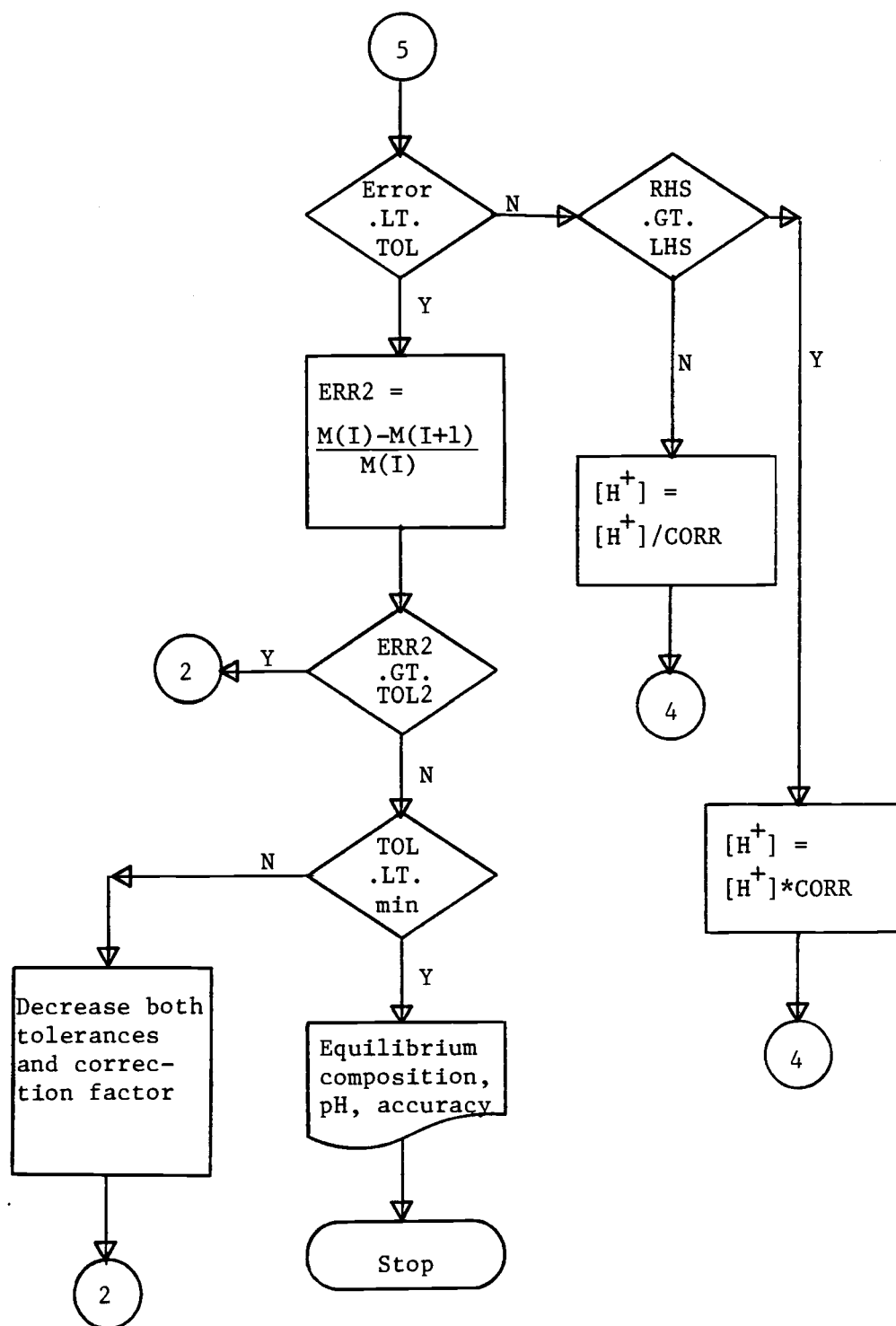
H2O= 2.000
CO2= 1.301
O2= 17.174
SO2= 5.402
H2S= 4.691

APPENDIX 3

Flow Diagram for Program AQS







Program AQS

```

C
C   VARIABLE DECLARATIONS
C
  INTEGER ITER,MAXIT,I,J,NRUNS,N,NSIG,ITMAX,IER,NPT,L,SPEC,MM
  INTEGER II,IS,IQ,IZ,IX,ID,IC,IT,JJ,JJJ
  REAL X(3),MB(4),K(12),AC(20),TOL,CORR,Y,F(3),PAR(2)
  REAL LHS,RHS,ERR,PTOL,Z(20),MUT,SECC1,SECC2,SUM3,MU(20)
  REAL RP(20,20),R(2,20),A(2,20),POE,M(1000,20),ITERR,PH
  REAL FNORM,WK(36),TOL2,T,ERR2(20),V(20,20),MIN,SC05,SC09
  EXTERNAL FCN
C
C   VARIABLE DESCRIPTIONS
C
  ITER= MAX # OF ITERATIONS
  I= COUNTER IN NRUNS LOOP
  J= COUNTER IN RP ARRAY
  NRUNS= NUMBER OF RUNS
  N= # EQUATIONS= # UNKNOWN IN ZSPOW
  NSIG= # SIGNIFICANT FIGURES IN ZSPOW
  ITMAX= MAX ITERATIONS IN ZSPOW
  IER= ERROR INDICATOR IN ZSPOW
  L= USED IN MOLALITY ARRAY FOR SUCC. SUBST. LOOP
  SPEC= # SPECIES RED. ACT. COEFF. WILL BE CALC. FOR
  II= COUNTER IN DO LOOP FOR ZSPOW
  IS= COUNTER IN MEAN ACT. COEFF. DO LOOP
  IX= COUNTER IN RED. ACT. COEFF. CALC.
  ID= COUNTER FOR SECC1
  IC= COUNTER IN MU DETERMINATION
  IT= COUNTER N V CALC.
  X(1),X(2),X(3)=  $\Gamma^*$ , C,  $\Gamma_j^*$  USED IN KUSIK AND MEISSNER
  METHOD
  TOL= MAX TOLERANCE IN ELECTRONEUTRALITY EQUATION
  TOL2= MAX TOLERANCE IN SUCC. SUBS. CALCS.
  CORR= CORRECTOR TO [H+] TO MAKE E.N. EQN. WORK
  F(3)= EQUATION DENOMINATOR NEEDED IN ZSPOW
  PAR(2)= CONSTANTS: MUT, Q USED IN K AND M METHOD
  LHS,RHS= VARIABLES FOR PARTS OF E.N. EQUATION
  ERR= DEVIATION IN E.N. EQUATION
  MUT= TOTAL IONIC STRENGTH
  SECC1,SECC2= PARTS OF EQUATION 41, K AND M METHOD
  SUM3= USED TO GET MUT
  POE= TWO CHARGES MULTIPLIED TOGETHER
  ITERR= # OF ITERATIONS IN E.N. LOOP
  PH= -LOG[H+]
  FNORM= USED IN ZSPOW
  WK(36)= USED IN ZSPOW
  T= TEMPERATURE
  MIN= SMALLEST ALLOWABLE TOLERANCE

```

C MB(1)= CTS=
 C MB(2)= CTCO3=
 C MB(3)= CTSO4=
 C MB(4)=CTNA+

C EQUILIBRIUM CONSTANTS FOR EACH DISSOCIATION RXN.

C K(5)= KH FOR H2S
 C K(6)= K1 FOR S= SYSTEM
 C K(7)= K2 FOR S= SYSTEM
 C K(8)= KH FOR CO2
 C K(9)= K1 FOR CO3= SYSTEM
 C K(10)= K2 FOR CO3= SYSTEM
 C K(11)= K2 FOR SO4= SYSTEM
 C K(12)= KW FOR H2O

C MOLALITIES

C M(L,1)= NA+
 C M(L,2)= S=
 C M(L,3)= PH2S
 C M(L,4)= CO3=
 C M(L,5)= HS04-
 C M(L,6)= S04=
 C M(L,7)= H2S(AQ)
 C M(L,8)= OH-
 C M(L,9)= H2CO3*
 C M(L,10)= HS-
 C M(L,11)= PCO2
 C M(L,12)= HCO3-
 C Y= H+

C SINGLE ION ACTIVITY COEFFICIENTS

C AC(1)= NA+
 C AC(2)= S=
 C AC(3)= HS04-
 C AC(4)= CO3=
 C AC(5)= H2S(AQ)
 C AC(6)= S04=
 C AC(7)= H2S(G)
 C AC(8)= OH-
 C AC(9)= H2CO3*
 C AC(10)= HS-
 C AC(11)= CO2(G)
 C AC(12)= HCO3-
 C AC(13)= H+

```

C
C   RP(2,20)= ARRAY FOR PURE REDUCED ACT. COEFF.
C   R(2,20)= ARRAY FOR REDUCED ACT. COEFF. IN THE MIXTURE
C   A(2,20)= ARRAY FOR MEAN ACT. COEFF.
C   Z(20)= ARRAY FOR ION CHARGES
C   V(20)= VARIABLE USED IN K AND H METHOD, F(CHARGES)
C   MU(20)= ARRAY FOR INDIVIDUAL SPECIES' IONIC STRENGTH
C   ERR2(20)= DEVIATION OF EACH SPECIES IN SUCC. SUBS. CALC.
C
C   INITIALIZE VARIABLES
C   AC(6)=AC(3)=AC(2)=AC(10)=AC(5)=1.
C   AC(7)=AC(4)=AC(12)=AC(9)=AC(11)=1.
C   AC(1)=AC(13)=AC(8)=1.
C
C   L=1
C   ITERR=0
C   MAXIT=1000
C   SC05=.0473
C   SC09=.0220
C
C   READ IN NRUNS AND LOOP TILL COMPLETE
C
C   WRITE(6,20)
20  FORMAT(/,'ENTER THE NUMBER OF RUNS:',/)
C   READ(5,*) NRUNS
C   DO 51 I=1,NRUNS
C   ITERR=0
C   WRITE(6,613)
613  FORMAT(/,'ENTER TEMPERATURE:',/)
C   READ(5,*) T
C   IF (T .EQ. 90.) GO TO 617
C   K(5)=4.00E-2
C   K(6)=2.34E-7
C   K(7)=1.660E-12
C   K(8)=1.00E-2
C   K(9)=3.55E-7
C   K(10)=6.918E-11
C   K(11)=1.02E-3
C   K(12)=5.495E-13
C   GO TO 619
617  K(5)=4.00E-2
C   K(6)=2.31E-7
C   K(7)=9.28E-13
C   K(8)=1.17E-2
C   K(9)=3.90E-7
C   K(10)=7.004E-11
C   K(11)=1.44E-3
C   K(12)=3.75E-13

```

```

619 WRITE(6,21)
21  FORMAT(/,'ENTER [H+]:',/)
    READ(5,*) Y
    MIN=2.E-4
    CORR=1.0125
    TOL=TOL2=.05
    WRITE(6,23)
23  FORMAT(/,'ENTER CTS,CTCO3,CTSO4,CTNA:',/)
    READ(5,*) MB(1),MB(2),MB(3),MB(4)
C
    WRITE(6,101)
101  FORMAT(/,'ENTER INITIAL GUESS OF MOLALITIES FOR:',/
1    'NA+,S=,CO3=,SO4=,OH-,HS- AND HCO3-',/)
    READ(5,*) M(1,1),M(1,2),M(1,4),M(1,6),M(1,8),
1    M(1,10),M(1,12)
    Z(1)=Z(8)=Z(10)=Z(12)=1.
    Z(2)=Z(4)=Z(6)=2.
    DO 203 IT=2,12,2
        V(1,IT)=(.5*(Z(1)+Z(IT))**2)/(Z(1)*Z(IT))
        V(IT,1)=V(1,IT)
203  CONTINUE
C
    CALCULATE IONIC STRENGTHS
C
300  MU(1)=.5*M(L,1)*Z(1)**2
    SUM3=0.
    DO 205 IC=2,12,2
        MU(IC)=.5*M(L,IC)*Z(IC)**2
        SUM3=SUM3+MU(IC)
205  CONTINUE
    MUT=MU(1)+SUM3
C
    CALCULATE ACTIVITY COEFFICIENTS FOR THE
    NONELECTROLYTES, H2S(AQ) AND H2CO3(AQ)
C
    FOR H2S(AQ)
    AC(5)=EXP(2.303*SC05*MUT)
C
    FOR H2CO3(AQ)
    AC(9)=EXP(2.303*SC09*MUT)
C

```

```

C
C   USE ZSPOW TO GET REDUCED ACTIVITY COEFFS.
C   FOR PURE ELECTROLYTES
C
      J=0
      N=3
      NSIG=4
      ITMAX=100
      X(1)=.42
      X(2)=1.
      REWIND 11
      SPEC=8
      DO 105 II=1,SPEC
        X(3)=.9
        PAR(1)=MUT
        READ(11,*) PAR(2)
        IF(PAR(2) .EQ. -.190) GO TO 129
        IF(PAR(2) .EQ. -.228) GO TO 129
        IF(PAR(2) .EQ. -.152) GO TO 129
        IF (PAR(2) .EQ. .0700) GO TO 134
        IF (PAR(2) .EQ. 2.049) GO TO 134
        IF (PAR(2) .EQ. .703) GO TO 134
        IF (PAR(2) .EQ. .666) GO TO 134
        IF (PAR(2) .EQ. -.566) GO TO 134
        IF (PAR(2) .EQ. 1.440) GO TO 134
        IF (PAR(2) .EQ. 2.551) GO TO 134
        IF (PAR(2) .EQ. .0315) GO TO 134
        IF (PAR(2) .EQ. 1.302) GO TO 134
        A1=-.005
        B1=.0085
        GO TO 133
129      A1=-.0079
        B1=.0029
133      PAR(2)=(T-25.)*(A1*PAR(2)+B1)+PAR(2)
134      CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
        J=J+2
        RP(1,J)=X(3)
        RP(J,1)=RP(1,J)
105     CONTINUE
C
C

```

```

C
C   CALCULATE THE REDUCED ACTIVITIES COEFF. FOR
C   EACH ELECTROLYTE IN THE SOLN.
C
      DO 209 IX=2,12,2
        SECC1=SECC2=0.
        DO 213 ID=2,12,2
          SECC1=SECC1+V(1,ID)*MU(ID)*LOG10(RP(1,ID))
213    CONTINUE
        SECC2=V(IX,1)*MU(1)*LOG10(RP(IX,1))
        R(1,IX)=EXP(2.303*((Z(1)/(Z(1)+Z(IX)))*SECC1/MUT
1    +(Z(IX)/(Z(1)+Z(IX)))*SECC2/MUT))
209    CONTINUE
C
C   CONVERT REDUCED ACTIVITY COEFFS. TO MEAN
C   ACTIVITY COEFF.
C
      DO 119 IS=2,12,2
        POE=Z(1)*Z(IS)
        A(1,IS)=R(1,IS)**POE
119    CONTINUE
C
C   USE THE MEAN SALT METHOD AND MACINNES
C   ASSUMPTION TO CALCULATE SINGLE ION ACTIVITY
C   COEFFICIENTS
C
      AC(14)=RP(1,14)
      AC(1)=RP(1,16)**2/AC(14)
      AC(2)=A(1,2)**3/(AC(1)**2)
      AC(4)=A(1,4)**3/(AC(1)**2)
      AC(6)=A(1,6)**3/(AC(1)**2)
      AC(8)=A(1,8)**2/AC(1)
      AC(10)=A(1,10)**2/AC(1)
      AC(12)=A(1,12)**2/AC(1)
C

```

```

C
C DO ITERATIVE CALCS. TO FIND CORRECT
C PH AND EQUILIBRIUM COMPOSITION.
C
C
L=L+1
30 M(L,6)=MB(3)/(1.+AC(6)*AC(13)*Y/(AC(3)*K(11)))
M(L,2)=MB(1)/(1.+AC(13)*AC(2)*Y/(AC(10)*K(7))+
1 AC(13)**2*AC(2)*Y**2/(AC(5)*K(6)*K(7)))
M(L,4)=MB(2)/(1.+AC(13)*AC(4)*Y/(AC(12)*K(10))+
1 Y**2*AC(4)*AC(13)**2/(AC(9)*K(9)*K(10)))
M(L,5)=AC(6)*AC(13)*M(L,6)*Y/(AC(3)*K(11))
M(L,8)=K(12)/(AC(13)*AC(8)*Y)
M(L,10)=AC(13)*AC(2)*Y*M(L,2)/(AC(10)*K(7))
M(L,7)=AC(10)*AC(13)*M(L,10)*Y/(AC(5)*K(6))
M(L,12)=AC(13)*AC(4)*Y*M(L,4)/(AC(12)*K(10))
M(L,9)=AC(13)*AC(12)*Y*M(L,12)/(AC(9)*K(9))
M(L,3)=AC(5)*M(L,7)/(AC(7)*K(5))
M(L,11)=AC(9)*M(L,9)/(AC(11)*K(8))
M(L,1)=M(1,1)

C
C
LHS=MB(4)+Y
RHS=2.*M(L,2)+M(L,10)+2.*M(L,4)+M(L,12)+2.*M(L,6)+M(L,5)+M(L,8)
ITERR=ITERR+1
IF(ITERR .GT. MAXIT) GO TO 100
ERR=ABS((LHS-RHS)/LHS)
IF(ERR .LT. TOL) GO TO 90
IF(RHS .GT. LHS) GO TO 11
Y=Y/CORR
GO TO 30
11 Y=Y*CORR
GO TO 30

C
90 DO 121 IQ=1,12
ERR2(IQ)=ABS(M(L,IQ)-M(L-1,IQ))/(M(L,IQ))
IF(ERR2(IQ) .GT. TOL2) GO TO 300
121 CONTINUE

C
C MAKE CORR, TOL, TOL2 SMALLER, UNTIL
C EQUIL. COMP. IS CONSTANT AT MIN.
C
IF(TOL .LT. MIN) GO TO 500
CORR=CORR/2.
CORR=CORR+.5
TOL=TOL/2.
TOL2=TOL2/2.
ITERR=0.
GO TO 300

```

```

C
C   PRINT RESULTS
C
500 WRITE(6,688) T
688 FORMAT(/,'THE TEMPERATURE IS',F6.1,' DEGREES CELSIUS',/)
    WRITE(6,88)
88  FORMAT(/,'THE COMPOSITION IS:',/)
    WRITE(6,91) M(L,2),M(L,4),M(L,6),M(L,8)
1   ,M(L,10),M(L,12),M(L,5)
91  FORMAT(/,'[S]=',E9.4,/, '[CO3]=',E9.4,/,
1   '[SO4]=',E9.4,/, '[OH-]=',E9.4,/,
1   '[HS-]=',E9.4,/, '[HCO3-]=',E9.4,/,
1   '[HSO4]=',E9.4,/)
    WRITE(6,92) M(L,7),M(L,9),M(L,3),M(L,11),M(L,1),Y
92  FORMAT(/,'[H2S]=',E9.4,/, '[H2CO3*]=',E9.4,/,
1   '[PH2S]=',E9.4,/, '[PCO2]=',E9.4,/,
1   '[NA+]=',E9.4,/, '[H+]=',E9.4,/)
    PH=-LOG10(Y)
    WRITE(6,701)PH
701 FORMAT(/,'THE PH IS',F6.2,/)
    PTOL=TOL*100.
    WRITE(6,40)PTOL
40  FORMAT(/,'RESULTS IN ELECTRONEUTRALITY EQN.',/,
1   'ARE ACCURATE TO',F7.4,'% ',/)
    WRITE(6,173) MUT
173 FORMAT(/,'THE TOTAL IONIC STRENGTH IS',F7.2,/)
    IF(TOL .GT. MIN) GO TO 300
    DO 899 JJ=1,13
        WRITE(6,901) AC(JJ)
901  FORMAT(E10.4)
899  CONTINUE
    R(1,14)=RP(1,14)
    A(1,14)=RP(1,14)
    R(1,16)=RP(1,16)
    A(1,16)=RP(1,16)
    DO 905 JJJ=2,16,2
        WRITE(6,903)RP(1,JJJ),R(1,JJJ),A(1,JJJ)
903  FORMAT(3E10.4)
905  CONTINUE
    GO TO 51

C
100 WRITE(6,181)
181 FORMAT(/,'ITERR .GT. MAXIT',/)
    GO TO 51

C
C
51  CONTINUE
    RETURN
    END

C

```


C

```
SUBROUTINE FCN(X,F,N,PAR)
INTEGER N
REAL X(3),F(3),PAR(2)
F(1)=(1.+(.75-.065*PAR(2))*(1+.1*PAR(1))**PAR(2)-
1 (.75-.065*PAR(2)))*X(1)-X(3)
F(2)=-LOG10(X(1))-((.5107*PAR(1)**.5)/
1 (1.+X(2)*PAR(1)**.5))
F(3)=-X(2)+1.+55*PAR(2)*EXP(-.023*PAR(1)**3)
RETURN
END
```

Sample Output from Program AQS

ENTER THE NUMBER OF RUNS:

? 1

ENTER TEMPERATURE:

? 90.

ENTER [H+]:

? 1.E-11

ENTER CTS,CTCO3,CTS04,CTNA:

? .6875,1.875,.0625,5.375

ENTER INITIAL GUESS OF MOLALITIES FOR:
NA+,S=,CO3=,SO4=,OH-,HS- AND HCO3-

? 5.375,.3,1.8,.0625,.1,.3,.01

THE TEMPERATURE IS 90.0 DEGREES CELSIUS

THE COMPOSITION IS:

[S-]=.1355E+00
[CO3-]=.1874E+01
[SO4-]=.6250E-01
[OH-]=.6774E+00
[HS-]=.5520E+00
[HCO3-]=.1402E-02
[HSO4-]=.3299E-12

[H2S]=.3324E-06
[H2CO3*]=.7343E-09
PH2S=.1870E-04
PCO2=.9152E-07
[NA+]=.5375E+01
[H+]=.2127E-11

THE PH IS 11.67

RESULTS IN ELECTRONEUTRALITY EQN.
ARE ACCURATE TO .0195%

THE TOTAL IONIC STRENGTH IS 7.45

APPENDIX 4

Thermodynamic Constants used in System A and System BEquilibrium Constants for System A

Equation	log K T = 1000°K	log K T = 1200°K
(10)	34.625	26.054
(11)	-0.693	-1.715
(12)	-4.841	-4.544
(13)	23.050	18.522

Equilibrium Constants for System B

Equation	log K T = 90°C	log K T = 100°C
(28)	- 1.40	- 1.43
(29)	- 6.64	- 6.63
(30)	-12.03	-11.78
(31)	- 1.93	- 1.97
(32)	- 6.41	- 6.45
(33)	-10.15	-10.16
(34)	- 2.84	- 2.99
(35)	-12.43	-12.26

Mean q Values used in Program AQS

Species	Mean q
Na ₂ S	4.144
Na ₂ CO ₃	0.070
Na ₂ SO ₄	-0.190
NaOH	3.000
NaHS	0.120
NaHCO ₃	-0.128