

PROGRESS REPORT NO. 7

FOR THE PERIOD OF AUGUST 27, 1965 TO FEBRUARY 15, 1966

TO

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THE INSTITUTE OF PAPER CHEMISTRY

INVESTIGATION OF SMELT-WATER REACTIONS

Submitted by:

*Project 2419* THE BABCOCK & WILCOX COMPANY  
RESEARCH CENTER  
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PROGRESS REPORT NO. 7 OF THE BABCOCK & WILCOX COMPANY  
ACTIVITIES ON INVESTIGATION OF SMELT-WATER REACTIONS

INTRODUCTION

This report summarizes the work accomplished between August 27, 1965 and February 15, 1966. Our objectives during this work period were as follows:

1. To determine if elemental sodium can be formed in smelt under laboratory-simulated furnace conditions.
2. To investigate the smelt-liquid water reactions.
3. To report the results of a second test of the proposed emergency shut-down procedure.

SUMMARY

1. The smelt-water (liquid) reaction was studied experimentally. The results, as found under the experimental conditions employed, are summarized as follows:
  - (a) At 1500°F and 1600°F, normal smelts ranging from 25.0 - 39.7% Na<sub>2</sub>S required multiple 2-cc injections of water before explosions occurred. Explosions were observed in three out of four cases in this temperature range. The fourth experiment was terminated prior to explosion in order to analyze the smelt in its pre-explosive condition. In every case 1.3 - 2.1% NaOH was found.
  - (b) At 1800°F, two of four normal smelts exploded at one or two water injections, a third exhibited a blurrp at the first injection, and the fourth did not explode

after six injections. The sodium hydroxide content of the smelts after the experiments ranged from 0.2 - 4.4%, with the lowest hydroxide level found in the smelt that did not explode.

- (c) When sodium hydroxide at a level of 5%, was added to the identical (39.7%  $\text{Na}_2\text{S}$ ) smelt sample investigated in (a), at 1600°F in four out of five cases the smelt exploded at the first water addition. In the fifth case the experiment was terminated after two water injections and no explosion took place.
- (d) The observed explosions exhibited maximum pressures of 11 - >100 psi and rise times of 1 - 5 milliseconds.
- (e) Normal smelt, under 100%  $\text{CO}_2$  and 15%  $\text{CO}_2$  - 85% He atmosphere, in four tests, did not explode with the number of water injections that would have been expected to produce explosions. In 100%  $\text{CO}_2$  the  $\text{Na}_2\text{S}$  content of the smelt was markedly lowered (to 5.7 - 8.07%). In 15%  $\text{CO}_2$  - 85% He the  $\text{Na}_2\text{S}$  concentrations had been reduced to 16.5% and 19.1%.
- (f) A 30%  $\text{Na}_2\text{S}$  smelt containing 5.7% NaCl exploded at 1600°F in a helium atmosphere, as well as in a  $\text{CO}_2$  atmosphere when the  $\text{CO}_2$  atmosphere had been present for 7 minutes, upon the first addition of water.
- (g) The identical smelt as in (f), when held under a  $\text{CO}_2$

atmosphere during the entire run did not explode, in duplicate tests, with two successive water additions. The smelt analysis after these runs showed 22.4% and 24.8%  $\text{Na}_2\text{S}$ .

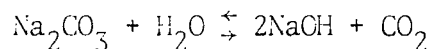
- (h) In two tests, smelt with 5% added carbon did not explode at 1800°F when four 2-cc portions of water were injected. When the temperature was lowered to 1600F, the smelt exploded upon the addition of one 2-cc portion. In one case a 60 psi pressure peak was observed, in the second a milder explosion (11 psi) occurred.
  - (i) When water was added to the smelt charge containing 5% sodium hydroxide, pressure excursions were noted while heating the sample to test temperature. In one test the excursion was sufficient to eject the smelt from its crucible. In a second test the smelt exploded at the first water injection.
  - (j) Addition of  $\text{Na}_2\text{O}$  to smelt apparently did not increase its reactivity.
  - (k) No correlation could be made between explosibility and hydrogen yields.
  - (l) When explosions took place in an air atmosphere, the pressure wave gave the appearance of a smelt-water reaction.
  - (m) No correlation could be made between sodium sulfate content and explosibility.
- (2) Tests aimed at determining the role of elemental sodium in the

explosion mechanism showed that only small amounts of elemental sodium (.03 - .11%) were retained in smelt at 1700 - 2000°F.

5. A second test to determine furnace conditions during shut down was successfully carried out.
4. A report and user's guide to the computer program for the calculation of chemical equilibria by the Free Energy Minimization Technique was completed and is issued as an Appendix to this Progress Report.

### CONCLUSIONS

1. Under the proper conditions, an explosive reaction, not associated with combustion, takes place between molten smelt and liquid water. The mechanism of this reaction is not understood, but appears to involve the rapid release of water vapor.
2. Sodium hydroxide plays a significant role in the smelt-water physical type reaction. At 1600°F normal smelts do not explode until a critical amount of hydroxide has formed from the reaction



- At 1800°, in the absence of carbon or other competing reactions, sodium hydroxide forms more readily and smelt may explode with the addition of lesser amounts of water than at 1600°F.
3. The presence of sodium chloride in smelt tends to increase the probability of a smelt water physical type explosion. There is some evidence, although not conclusive, that the role of sodium chloride in sensitizing smelt may be the result of its reaction with water to form sodium hydroxide.

4. The role of sodium hydroxide in the smelt-water physical type explosive reaction is not yet understood.
5. To date no self-sustaining exothermic chemical reactions contributing to smelt water explosions have been identified.
6. Hydrogen gas is released in substantial quantities whenever water comes in contact with smelt whether or not an explosion takes place. It is concluded that the formation of hydrogen may be a significant factor in causing a combustion gas-air explosion if present in sufficient quantities and an ignition source is present. It is further concluded that the generation of hydrogen is not a factor in the physical type smelt-water reaction.
7. The formation of elemental sodium and its subsequent reaction with water is probably not a significant factor in the smelt-water explosive reaction.
8. Smelt and water will not explode in an atmosphere sufficiently high in  $\text{CO}_2$ . The predominant effect of a  $\text{CO}_2$  atmosphere is to effect a reduction of smelt sulfidity. Although it would be expected that a  $\text{CO}_2$  atmosphere would also tend to keep the hydroxide concentration at negligible levels, confirming experimental evidence was not conclusive.
9. A carbon-smelt mixture reacts with water at  $1800^\circ\text{F}$  to yield gas compositions characteristic of a combined water-gas and smelt-water reaction. There is some evidence that the water-gas

reaction tends to inhibit the smelt water explosion at this temperature. At 1600°F the carbon apparently had little influence on the smelt-water physical type reaction.

#### INVESTIGATION OF THE FORMATION OF ELEMENTAL SODIUM

The question of whether elemental sodium exists in smelt and plays a part in the explosion mechanism has been raised many times. It has been shown from the B&W computer studies reported in Progress Report No. 3, March 5, 1965 (1) that elemental sodium vapor can exist in the highly reducing atmosphere of the smelt bed. In view of its boiling point (1616°F), the possibility that the elemental sodium would be retained in the molten smelt remained to be investigated experimentally. These experiments are described below.

#### Apparatus

The tests were carried out in capsules fabricated from stainless type 304 and illustrated in Figure 1. The capsule consisted of two parts, a lower part 11" long of 1" schedule 40 stainless type 304 pipe, (wall thickness .133"). The top, 4" long was 1.25" stainless type 304, but with .035" wall. A thermocouple was inserted through a Conax fitting in the top. Tubing, 3/8" O.D. of stainless 304 material was welded to the top of the capsule and was attached to a Nupro 10 psi check valve and a side fitting to the argon supply. The inner graphite crucible was 5" long, 1/2" I.D., 7/8" O.D.

#### Procedure

A synthetic smelt sample containing 30% Na<sub>2</sub>S was prepared by heating the calculated amount of Na<sub>2</sub>S·5H<sub>2</sub>O, Technical Grade, and Na<sub>2</sub>CO<sub>3</sub>, C.P., in a graphite crucible in a muffle furnace to 2000°F for 15 minutes. This smelt

sample was mixed with sugar charcoal in the proportions 3 pts smelt: 1 pt charcoal (by weight). A second mixture of 6 pts smelt: 1 pt charcoal was also prepared. The smelt-charcoal charge was loaded into the graphite crucible, the crucible placed in the lower stainless steel capsule and the capsule top with its tubing and check valve welded to the base. The capsule was inserted in a vertical tube furnace and the temperature of the furnace raised to test temperature, usually in 60 - 90 minutes. The capsule was held at test temperature for one hour, the argon pressure valve opened, quickly removed from the furnace and quenched in a water bath. After cooling, the argon valve was closed and the entire apparatus removed to a large dry box previously evacuated to 10 microns pressure and then filled to one atmosphere with nuclear grade argon. The capsule was cut open and the lowest 1/3 of the graphite crucible, holding the reacted smelt, was cut and removed from the bulk of the reaction mixture. This lower portion was placed in a 500 ml Erlenmeyer flask, fitted with a side-arm stopcock and a 500 ml dropping funnel sealed in the top. After sealing the stopcock, the flask was removed from the dry box and 200 - 300 ml of water added to the dropping funnel. A measured amount of water, 100 - 150 ml, was added to the Erlenmeyer flask, the flask was agitated to insure good contact with the smelt and a gas sample was removed via the side-arm and analyzed for hydrogen content. The water solution remaining was analyzed for total sodium by flame photometry. From the effective volume of the flask and the hydrogen analysis the moles of hydrogen were calculated. Assuming that one mole of hydrogen formed from one mole of elemental sodium, the amount of elemental sodium formed could be calculated.

A blank run of the dry box procedure using freshly prepared metallic sodium was carried out and resulted in an 80% recovery of elemental sodium (from the hydrogen analysis).

Tests were carried out at two temperatures, 1750°F and 2000°F.

## RESULTS

The results of these tests are tabulated below:

Test No.	Temp. °F	Smelt:Carbon	Percent Elemental Sodium in Smelt
1	1700	6:1	<.05%
2	1750	3:1	.03
3	2000	6:1	.15
4	2000	3:1	.11

## SMELT-WATER (LIQUID) EXPERIMENTS

### Apparatus

The experimental apparatus used in the work reported during this period was similar to that described in B&W Progress Report No. 6, September 15, 1965, (2) but with some modifications. An illustrative diagram of the present apparatus is shown in Figure 2. The major modifications from the previous apparatus were (a) addition of a water-cooled water injection system, (b) relocation of the thermocouple entry to the vessel, and (c) the addition of an oscilloscope and camera for recording pressure traces. The water injection system (Figure 3) consisted of a 7/8" O.D. stainless steel casing in which was inserted a 1/8" O.D. tube for the cooling water inlet extending to the bottom end of the casing. The cooling water exit was simply a 1/8" stub at the top of the casing. Initially, a 3/8" tubing, whose purpose was to hold a pressure transducer was inserted concentrically with the casing and extended to the bottom. As such a transducer arrangement

was not satisfactory, the ends of this tubing were welded shut and the system used as simply a water-injection system. The water injector was a 1/8" O.D. tubing, connected at the top with a Luerloc fitting and valve for attaching a hypodermic syringe. The volume of the water injection tube was 3.4 ml, and this volume was taken into account when water was added to the system. All of the tubes were seal-welded to the top and bottom of the casing. When fully inserted the tip of the water injection was 1/2" from the top of the molten smelt. A swage-lock fitting allowed the injection apparatus to be raised or lowered at will and a fiducial mark allowed the position of the tip of the water injector to be reproduced. A Tektronix 545A oscilloscope, equipped with a Polaroid camera and a Tektronix C-12 camera attachment was used to record the pressure traces; a Kistler 601A quartz pressure transducer and a Kistler model 566 charge amplifier were used to generate the oscilloscope pulse. A Honeywell galvanometer amplifier and Visicorder were also used to record the pressure peaks.

The stainless steel crucibles were given a hard chrome plate in an effort to reduce the smelt attack.

## PROCEDURE

### Smelt Preparation

Synthetic smelts containing a range of sulfidities (25 - 35%) were prepared in 1 kilogram batches by heating the calculated quantities  $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ , Technical Grade, and  $\text{Na}_2\text{CO}_3$ , C.P., contained in a graphite crucible, in a muffle furnace to 2000°F and holding the charge at this temperature for 15 minutes. The charges were cooled in the furnace

atmosphere, samples taken for analysis, and stored in polyethylene bags in a desiccator. In the case of the sodium chloride tests, this same general procedure was followed. In tests involving other additive materials, i.e. NaOH, Na<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub>, these other compounds were added to the previously prepared and fused smelt just prior to charging the reaction vessel.

The analyses of the prepared smelts are tabulated in Table I.

#### Test Procedure

For the most part the procedure followed was similar to that described in B&W Progress Report No. 6, September 15, 1965 (2). Cooling water temperature was held constant at 100°F to prevent undue condensation of water on the injection system. (Condensation, however, did take place.) The injection system initially was raised so that its tip was flush with the inside top of the pressure vessel. The smelt charge was placed in the reactor and heated to 800°F in a vacuum ( $\approx$  1. mm Hg absolute). The test atmosphere was bled in to 1 atmosphere pressure and the heating continued to test temperature. After sampling, and analyzing the gas, the vessel was again evacuated, the test atmosphere admitted to 1 atmosphere pressure, the water-injection tube lowered to its position and water injected. In an effort to eliminate the manner in which the water came into contact with the molten smelt as a variable the injection procedure was carried out in each case as reproducibly as possible. In general, 2 ml portions of room temperature water, with the cooling water at 100°F, were injected. The oscilloscope and Visicorder traces were observed, and the gas in the vessel analyzed. If no explosion took place, the water in the injection tube was expelled, the vessel evacuated, a fresh test atmosphere admitted and the injection was

repeated. When sharp explosions occurred, as indicated by the Visicorder, or oscilloscope, a sharp ping was audible and the pressure gauge on the top of the vessel indicated 11 - >100 psig (the pressure gauge was calibrated for 100 psig, in one case the maximum pressure was an estimated 120 psig).

## RESULTS

Thirty two experiments involving smelt-water reactions were carried out during this period. The results of thirty-one tests are summarized in numerical order in Table II. Table III, IV, and V are summaries of results, taken from Table I, combined such that certain experiments can be more readily compared.

Although it was attempted to record oscillographic and Visicorder pressure responses in every experiment, occasionally the pressure transducer failed to respond during the experiment. As a result the pressures indicated are those obtained from the pressure gauge (or manometer where applicable). As noted above when an explosion took place, generally, there was no doubt concerning its occurrence, and is indicated in the tables by an \*.

In tables of results the analysis of the gas generated by heating the smelt charge is shown as the first analysis, corresponding to zero water addition. It should be kept in mind that this atmosphere, after analysis, was replaced with pure test atmosphere prior to each water injection. When CO<sub>2</sub> was used it was noted that some of the CO<sub>2</sub> reacted with the smelt to form CO.

Gas analyses are reported as analyzed on a dry basis; the remainder of the gas consisted of helium (or air). As it would be expected that

some water vapor would condense on the water-cooled injection probe, it was not possible to convert percent composition to percent conversion from water. However the gas analyses from all of these current runs can be compared in order to assess the effects of variables.

#### Chemical Analyses - Uncertainties

Although chemical analyses were carried out on all smelt samples before and after water additions it should be kept in mind that the smelt analysis procedure is inherently not capable of high accuracy. While carbonate, sulfide, and sulfate can be determined satisfactorily, the accurate determination of other forms of sulfur, and in particular, hydroxide is particularly difficult. Furthermore, obtaining a representative sample of smelt in some cases was a problem. Although every effort was made to carry out a careful analysis of a representative sample, these limitations on the accuracy of the analysis should be kept in mind.

#### NaCl-KCl Experiments

In an effort to determine the characteristics of what might be considered to be "physical" type reaction of a molten salt with water, two experiments were carried out using an equi-molar molten mixture of NaCl and KCl. These compounds form a eutectic melting at approximately 1250°F and the experiments were carried out at 1350°F. In each test mild explosions were indicated upon the injection of 1-cc of liquid water. A satisfactory visicorder tracing was obtained in but one experiment and showed a maximum pressure of 8 - 10 psi with a very erratic pressure-time relationship. An analysis for hydroxide was carried out by a conventional titrimetric procedure and no hydroxide was detected.

## DISCUSSION AND SIGNIFICANCE OF RESULTS

### Explosion Characteristics

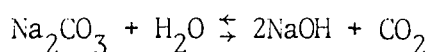
In B&W Progress Report No. 6, September 15, 1965 (2) it was reported that relatively slow pressure rise times were observed when liquid water was injected through a hypodermic needle inserted beneath the smelt. In the experiments reported in this progress report, when explosions are reported, for the most part, there was no doubt that an explosive reaction had taken place. Pressure rise times of 1 - 5 milliseconds were recorded on the oscilloscope as well as the Visicorder, the pressure gauge quickly hit a maximum pressure and fell back to an equilibrium value, a sharp ping was heard, and, upon opening the vessel the smelt was completely thrown out of the crucible and covered the walls and top of the pressure vessel. Figure 4 shows a typical pressure tracing on a contracted time scale and Figure 5 shows the first 25 milliseconds as recorded by the Visicorder. It will be noted that the pressure initially rises quickly to its peak pressure and falls at a somewhat lower rate. The pressure decay reaches a maximum negative pressure and finally, after a longer time period, rises more slowly to a maximum positive pressure and then falls off to its equilibrium pressure. The exact shape of the pressure wave after its initial rise is probably a function of the size and shape of the pressure vessel.

### Significance of Multiple Injections

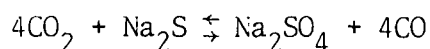
The results of experiments carried out on the as-prepared smelt materials are summarized in Table III and show several significant features. In the first place, at the lower temperatures, 1500° and 1600°F, none of these samples exploded upon the first injection of water. As a matter

of fact three out of four (Nos. 2, 15, and 20) samples exploded only after multiple injections and the fourth test (No. 3) was terminated before the explosion took place in order to analyze the smelt in a presumably sensitized condition. At the higher temperature investigated (1800°) two of four runs exploded; one (Run 16) upon the addition of one 2-cc portion of water after a single 1-cc portion had not exploded, the other (Run 21) upon the first 2-cc addition. A third (Run 18) did not explode, but forced the smelt from the crucible at the first injection. In Run 19, no explosion took place even after six water additions.

It had been previously noted (2) that there appeared to be an inverse correlation between smelt reactivity with water and the production of CO and CO<sub>2</sub>. Furthermore, it was observed that CO and CO<sub>2</sub> production decreased with increasing additions of water. The CO and CO<sub>2</sub> amounts were also found to depend upon the sodium hydroxide content of the smelt, i.e., the lower the hydroxide content of the smelt the higher the CO and CO<sub>2</sub> concentrations found in the gas after the injection of water. As a result it was proposed that the following reaction takes place in a smelt-water system.



A further reaction of CO<sub>2</sub> can take place in the smelt to give CO:



Thus the total (CO + CO<sub>2</sub>) can be used as an indication of the reaction of water with sodium carbonate.

The results of the current series of experiments can be interpreted on the same basis. In every case, except Run 19 (discussed

below), the sodium hydroxide content of the smelt increased to 1.1 - 4.4%. Furthermore, although not so straight-forward, the CO and CO<sub>2</sub> contents of the gas tended to decrease with the number of water injections, and always fell to only low concentrations after an explosion had taken place. Run No. 20 showed this behavior very clearly; Runs 2, 15 and 16 show this behavior also.

The smelt in Run No. 19 did not explode as expected, but continued to generate significant quantities of CO and CO<sub>2</sub> even after six injections of water. Upon analysis of the smelt it was found that very low hydroxide (0.2%) was present and this correlated with the higher quantities of CO and CO<sub>2</sub> found. It will be noted that the hydroxide found after the experiment was concluded was less than that present in the original smelt charge (0.7%). It therefore seems reasonable to postulate that in this particular case the hydroxide, originally present in the smelt and as generated from the smelt-water reaction, reacted with the crucible material (the crucible had lost its chrome plating during previous runs) and therefore was not available to suppress the formation of CO<sub>2</sub>.

This evidence and reasoning from the known chemical principles outlined above led to the conclusion that the significance of the required multiple injections of water for an explosion to take place (particularly at 1500 - 1600°F) involved the production of a critical amount of sodium hydroxide.

That more water injections were required at 1500 and 1600° than at 1800° can be explained on the basis that at the higher temperature, (1) the equilibrium constant for the sodium carbonate-water reaction is more

favorable, ( $2.0 \times 10^{-3}$  at  $1800^{\circ}\text{F}$  vs.  $4.8 \times 10^{-4}$  at  $1600^{\circ}\text{F}$ ) and (2) the reaction rate increases with temperature. Hence the required amount of sodium hydroxide tends to be generated at a faster rate. Further, confirming evidence that sodium hydroxide formation is a critical factor in the explosion mechanism is discussed below.

#### Effect of Sodium Hydroxide

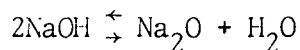
If sodium hydroxide is a reaction product of smelt and water contributing to explosions, then the addition of sodium hydroxide to smelt should render the smelt explosive upon the first addition of water. A summary of such experiments, using the same smelt sample as the base material is shown in Table IV. It is significant to note that four (Nos. 4, 9, 12, 14) out of five experiments, at  $1600^{\circ}\text{F}$ , produced explosions upon the first water injection. In addition Run No. 13, with water added, exploded apparently from condensed water dropping into the smelt (see further below). As this behavior is in marked contrast to the behavior of the smelt with no added hydroxide, it was concluded that sodium hydroxide plays an important role in the smelt-water explosion and tended to confirm that its formation in smelt was an important chemical reaction in the explosion mechanism.

Except for the smelts containing added water the sodium hydroxide found in the smelts after the explosion was somewhat less than that added, and it is postulated that under a helium atmosphere some NaOH volatilized from the melt during heating.

#### Effect of $\text{Na}_2\text{O}$ -NaOH Additions

That sodium hydroxide might play an important role in the explosion mechanism was suggested in a previous Progress Report (3). One mechanism

proposed was that possibly sodium hydroxide might exist in equilibrium with Na<sub>2</sub>O in the melt,



and that the reaction would proceed to the left upon the addition of water. As the Na<sub>2</sub>O-H<sub>2</sub>O reaction is exothermic (44.7 Kcal/mol) it might be expected to be a contributing factor to the smelt-water explosion. Since conventional chemical analysis does not distinguish between NaOH and Na<sub>2</sub>O, whether this reaction takes place and is significant cannot be established through analysis. Therefore tests 10 and 11 were carried out in which 3% Na<sub>2</sub>O and 3% NaOH were added to the smelt and its reactivity tested by water injection. In neither case was an explosion observed, and it was tentatively concluded that the Na<sub>2</sub>O-water reaction per se was not a significant factor in the smelt explosion mechanism. This view is substantiated by the humidification experiments discussed in the next section.

#### Humidification Tests

If an exothermic hydration reaction were occurring and if it were contributing to explosive reactions it would be expected that a smelt saturated with water would be less explosive. In Runs No. 13 and 14, 3-cc of water was added to the smelt charge while cold, and the charge heated under the atmosphere generated by the water in helium. During Run 13, while the charge was being heated, and prior to any water injection, some reaction took place that forced the mercury out of the manometer used to monitor pressure while bringing the smelt to test temperature. (When explosions are expected the manometer is valved off.) The temperature, as indicated by the thermocouple fell to 530°F

and did not rise again and indicated that the smelt had been expelled from the crucible. As a result the test was stopped before injecting any water, and examination of the vessel indeed confirmed that a mild explosion had taken place. During Run 14 a similar reaction took place; a sharp pressure excursion in the pressure gauge was noted but there was no attendant lowering of the smelt temperature. This latter smelt exploded at the first injection of water.

These experiments were the only ones exhibiting this phenomenon and is suspected that the pressure excursions in both runs were due to drops of water condensing on the injection tube and falling into the smelt.

It was concluded that the humidification of the smelt did not reduce its explosibility; indeed, if it were certain that condensing drops of water had caused the observed pressure excursions it would be concluded that the humidification tended to sensitize the smelt.

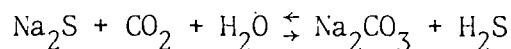
It will be noted that in each of these runs relatively high hydroxide levels were found and it appeared that water vapor over-pressure tended to keep the sodium hydroxide dissolved in the smelt.

As it would be expected that  $\text{Na}_2\text{O}$  could not form under these conditions, the explosive reaction taking place could not be attributed to the  $\text{Na}_2\text{O}$ -water reaction, or indeed any other simple hydration reaction requiring up to approximately one atmosphere of water vapor pressure.

#### Effect of $\text{CO}_2$ Atmosphere (100% and 15%)

In order to further test the hypothesis that the sodium hydroxide concentration in the smelt was an important and possibly critical parameter in the explosion mechanism, tests were carried out in a  $\text{CO}_2$  atmosphere. It

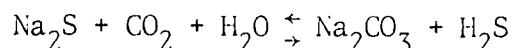
would be expected that the CO<sub>2</sub> would react with any sodium hydroxide formed, prevent sufficient amounts of sodium hydroxide from forming, and inhibit the explosive reactivity. In addition, such experiments would provide an indication of the importance of the following exothermic reaction referred to in an earlier Progress Report (4).



Two sets of experiments were carried out, one set in 100% CO<sub>2</sub> (which ultimately became CO + CO<sub>2</sub>), a second set in 15% CO<sub>2</sub> - 85% He.

The tests carried out in 100% CO<sub>2</sub> (Runs 22 and 23, Table V) did not explode upon the addition of six and eight 2-cc portions of water. In Run No. 23 an additional nine 2-cc portions were added under a helium atmosphere after the first sets of eight portions had been added under a CO<sub>2</sub> atmosphere in order to attempt to explode the smelt, but without success. The analysis of the smelt after the explosion showed a large reduction in the sodium sulfide content and it is concluded that these tests showed that the major effect of CO<sub>2</sub> was to lower the sulfidity such that the smelt became non-explosive.

As the following reaction must have taken place



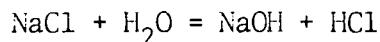
and as no explosion took place, it is concluded that probably this reaction plays little part in effecting explosions of smelt and water.

As the analysis of the smelt samples after the experiments in a 100% CO<sub>2</sub> atmosphere showed very low sulfidity, two additional tests (Runs 29 and 30) were carried out in an atmosphere of 15% CO<sub>2</sub> - 85% He, with the amount of added water corresponding to that required for explosions

in an inert atmosphere. One test carried out at 1600° and a second at 1800°. Anticipating the use of a combustion gas atmosphere as a possible remedial measure, this composition of CO<sub>2</sub> would closely approximate what might be achieved from oil or gas burners. No explosions were observed after six 2-cc additions of water at 1600° nor after three 2-cc additions of 1800°, criteria that would have expected to result in explosions in an inert atmosphere. It will be noted that the sulfidity in these cases was also reduced somewhat, and may have been below the explosive limit.

#### Effect of Sodium Chloride

That sodium hydroxide contributes to smelt explosions has been shown by the work described previously in this report. It might be postulated that the role of sodium hydroxide is similar to that of sodium chloride, also known to increase the explosive character of smelt possibly by altering the physical characteristics of the smelt. An alternative explanation of the effect of sodium chloride might be that it also reacts at these temperatures to form sodium hydroxide,



and that the hydroxide, formed by the reaction, is the compound affecting the smelt reactivity.

Although at first glance such a reaction might appear unlikely, there is evidence that it can take place. Mellor (5) for example cites eleven patents relating to the production of sodium hydroxide from a reaction of sodium chloride with super-heated steam. Mellor also quotes Emich (6) who carried out qualitative tests of the sodium chloride-water

reaction. Emich dropped water on sodium chloride "heated to bright redness" and quickly transferred the water to a beaker and observed an acid reaction of the water to litmus. The remaining salt, when dissolved in water, showed a basic reaction, attributed to the presence of sodium hydroxide.

More recent work done in Japan by Hamamoto (7) also is pertinent. Hamamoto found that a mixture of sodium chloride and phosphate rock, treated with steam at 800°C (1472°F) produced soluble sodium, aluminum, and calcium phosphates and postulated that the mechanism involved a reaction of sodium chloride with water vapor to form NaOH which in turn reacted with the phosphate rock.

A test of the hypothesis that the effect of sodium chloride is dependent upon its hydrolysis to hydroxide was carried out in Run Nos. 24, 25, 31 and 32 (Table V). It was first confirmed in Run No. 24 that sodium chloride indeed sensitized the smelt such that it exploded upon the first injection of water. It will be noted that the analysis after the explosion showed an increase of hydroxide and decrease of chloride. In two subsequent experiments (Nos. 25 and 31), carried out with the same batch of smelt but in a CO<sub>2</sub> atmosphere, no explosion occurred with two injections of water. It will be noted that the smelt analysis after these tests showed Na<sub>2</sub>S contents of 24.8% and 22.4%, levels which would be expected to explode in the presence of NaCl.

One additional experiment (No. 32) was carried out in which the smelt-sodium chloride melt was taken to test temperature in a helium atmosphere, then the atmosphere changed CO<sub>2</sub> prior to the injection of water. The purpose of this test was to determine whether a short exposure to CO<sub>2</sub> would be sufficient to inhibit the explosion. As an explosion occurred

at the first injection, it appeared that there was apparently insufficient time available for the  $\text{CO}_2$  to react with the hydroxide present initially in the smelt as well as that apparently temporarily formed from sodium chloride. This test, however emphasized that the smelt was indeed sensitive and ready to explode at the first addition of water. Hydroxide was not found in the smelt after this run. As the smelt is distributed uniformly over the inside of the vessel after an explosion, any hydroxide would be expected to react with the  $\text{CO}_2$  atmosphere and not be detected.

The importance of these experiments with sodium chloride should be emphasized. In these cases, there appears to be little doubt that the smelt was initially explosive to one addition of water. Furthermore in the  $\text{CO}_2$  atmosphere, present for a sufficient time, no explosions occurred and the smelt analysis after the run showed sufficient sulfidity to have been explosive. If the sodium chloride itself, by its effect on the physical properties of the smelt, were contributing to the explosion, the presence of  $\text{CO}_2$  should have made no difference in its reactivity. On the other hand, if the sodium chloride were a precursor of sodium hydroxide the  $\text{CO}_2$  atmosphere would have been expected to have inhibited the explosion.

It is recognized that it is difficult to prove a hypothesis that depends upon the absence of an explosion and time did not permit carrying out additional experiments with sodium chloride. Nevertheless there appear to be strong indications that the effect of sodium chloride in smelt explosions lies in its conversion in the melt to sodium hydroxide.

### Effect of Carbon

Experiments described in Progress Report No. 5, June 6, 1965 (3) showed that under quasi-equilibrium conditions smelt contained in a graphite crucible yielded a higher conversion of water to hydrogen and CO than smelt contained in stainless steel crucibles. As it appeared that carbon affected the smelt-water vapor reaction it was therefore of importance to determine whether carbon affected the smelt-liquid water reaction.

It was first established in Run No. 26 that carbon in the form of sugar charcoal reacted with water at 1650 - 1840°F to give significant yields of hydrogen and carbon oxides. In duplicate runs (Nos. 27 and 28), 5% carbon was added to smelt and four 2-cc portions of water injected at 1800°F. As no explosion took place under these conditions, the temperature was lowered to 1600°F for additional injections. At 1600°F explosions took place at the first injection of water, one significantly greater than the other.

The gas analysis from the reaction at 1800°F shows an increased hydrogen, CO and CO<sub>2</sub> over previous runs containing no carbon and it was concluded that the water reacted with both carbon and smelt. At 1600° the carbon-water reaction apparently was not significant. It is suggested that at the higher temperature the kinetics of the water-carbon reaction are sufficiently favorable to inhibit the formation of the required amount of sodium hydroxide. On the contrary, at the lower temperature the carbon-water reaction is relatively slower than the smelt-water reaction and an explosion can therefore take place.

### Effect of Sodium Sulfate

The effect of sodium sulfate is not so clear-cut as the effect of hydroxide. The analysis of samples after the individual experiment had been completed ranged from .01% for Run No. 4 to 3.8%, and no correlation could be made between sulfate content and degree of explosibility. In one run (No. 6) added sodium sulfate apparently increased the sensitivity of the smelt and an explosion resulted after the second injection of water. It could be speculated that there is an interaction of hydroxide and sulfate, but time did not permit an investigation of such effects. There is some evidence that at 1600° higher sulfate contents resulted in lower yields of hydrogen. At 1800°, in the limited number of tests, sulfate apparently affected the hydrogen yields to a very limited extent.

### Effect of Air Atmosphere

Two tests were carried out in an air atmosphere in an attempt to distinguish between a smelt-water explosion and a hydrogen-air explosion. In both cases, Runs 8 and 9, there was but one fast pressure rise, apparently due to the smelt-water reaction, and the pressure trace did not show any separate explosions. It was noted, however, that when air was introduced into the reaction vessel at one atmosphere and 1600°F that the pressure gradually fell apparently due to the burning of hydrogen as it evolved from the smelt, prior to water additions.

### Significance of Hydrogen Formation

It has been pointed out in previous reports (3, 4) that hydrogen is a major product of the smelt-water reaction. It has been found as a product when no smelt-water explosion takes place, as well as a product

after explosions take place. It is therefore concluded that whenever smelt and water co-exist, whether or not an explosion takes place, hydrogen will be generated and is therefore a potential hazard from the point of view of a fuel-air explosion.

However, ~~in view of the fact that hydrogen is found whether explosions take place or not,~~ leads to the conclusion that the generation of hydrogen by smelt and water plays relatively minor, if indeed any, role in the smelt-water explosion.

#### Effect of Ammonium Carbonate (20% Solution)

One test, in which a solution of ammonium carbonate (20%) in water was injected into smelt in order to assess its possible effectiveness as a quenching agent in preventing explosions was carried out. In this test (No. 17), the second 2-cc injection produced the most rapid and intense explosion of any in the series. No other experiments of this type were carried out.

#### Explosive Mechanism and Role of Hydroxide

At present the mechanism producing physical type explosions has not been delineated. A large number of chemical reactions of smelt and water have been examined; it appears that the predominate conventional chemical reactions involve the production of hydrogen and carbon oxides. It has been pointed out above that hydrogen forms whether or not an explosion takes place and it would appear that this behavior would rule out hydrogen production as a factor. When carbon oxides are produced in large quantities, the explosive behavior is in general diminished; hence their production can be ruled out as a causative factor.

By elimination, it appears that the explosion mechanism involves the rapid release of superheated water vapor. Therefore an additional property of smelt, its strong tendency to combine with water, should be considered as a possible contributing factor in the smelt-water explosion mechanism. While it is well-known that room-temperature smelt absorbs water readily, it was somewhat surprising that experimental work described in Progress Report No. 5, June 6, 1965 showed the smelt at 1600°F and under a partial water vapor pressure of 30 mm Hg absorbed approximately .5 gm of water per 100 gms of smelt. While the mechanism of this absorption is not as yet known the water must be held as molecular water by some reasonably strong bonding mechanism. Furthermore, some evidence was found that the smelt tended to release water when the water vapor pressure was removed or the temperature raised.

A great deal of fundamental information concerning this hydration reaction is not known. If, for example more knowledge were available concerning the quantitative effect of pressure (it would be expected that higher water vapor pressures would increase the amount taken up by the smelt) and temperature, a firmer basis for advancing or rejecting an explosion mechanism involving this reaction could possibly be made.

At the present time it is suggested that the explosion mechanism consists of molecular water being taken up locally by smelt and then subsequently being released as water vapor. The driving force for the water going into the smelt would be a combination of the high equivalent water vapor pressure and the locally lower smelt temperature. Once the water vapor pressure were removed, the bulk smelt temperature would furnish the energy for the rapid release of superheated steam.

If no hydroxide is present, there must be a stronger driving force for the carbonate-water reaction than for the smelt-water absorption. Thus it would seem that the role of sodium hydroxide is that of suppressing the carbonate-water reaction so that the hydration can take place.

#### Proposed Remedial Measures

Although the exact role of sodium hydroxide in the explosion mechanism is not understood, its presence is required for the smelt to be explosive. Therefore, such a criterion can be used as a unifying concept for measures aimed at preventing explosions. For example, it has been found by the Combustion Engineering team (8, 9) that concentrated ammonium sulfate and ammonium bicarbonate solutions do not explode when injected into molten smelts. The effect of ammonium sulfate was explained on the basis that sodium hydroxide reacted with ammonium sulfate to release ammonia and prevent smelt encapsulation. Ammonium bicarbonate might be expected to behave similarly. On the other hand it was found in one test described in this current report (Run No. 17) that ammonium carbonate did not inhibit the explosion. It would be expected that ammonium carbonate would release as much vapor as ammonium sulfate and have the same effect if vapor production were the ruling criterion. An alternate explanation might be that sodium hydroxide is either prevented from forming or removed by reaction with sulfate and bicarbonate and hence no explosion takes place. In the case of ammonium carbonate no such inhibiting reaction takes place.

Based upon the experiments in a CO<sub>2</sub> atmosphere described above, it is proposed that any oxidizing combustion gas atmosphere (possibly from gas or oil burners) in continuous contact with the smelt during an emergency shut-down would inhibit a smelt-water explosion. Carrying this idea even further, it would seem that an increased amount of primary air in the furnace during an emergency would also minimize the explosion hazard. It is recognized that further tests, probably on a prototype scale, are required to substantiate such procedures.

#### RECOVERY UNIT SHUTDOWN TESTS

A second recovery unit shutdown test was carried out September 4, 1965 at the Thilmany Pulp and Paper Company Kraft Recovery unit, Kaukauna Wisconsin. The purpose of this test was to obtain further confirmation of furnace conditions existing when a recovery unit is shutdown while maintaining an air-rich furnace atmosphere.

#### Test Program

The Thilmany Pulp and Paper Company has a B&W 390 ton/day recovery unit (see Figure 6 - PR-63). This unit was equipped with a guillotine-type shut-off damper located in the primary air duct of the furnace.

A test was planned and executed on September 4.

Objective. The objective of the test was to obtain further confirmation on the rate of temperature depression in the bed and throughout the unit plus the variations in gas analysis during a shutdown.

Sequence of Events. Data on the Thilmany Recovery Unit was obtained prior to, during, and following the below sequence of events:

1. All auxiliary fuel to be secured and the unit operating at normal mill rates.

2. Shut off black liquor flow to furnace.
3. Open tertiary air dampers wide.
4. Shut off primary air by closing louvre dampers.
5. Maintain total air flow equivalent to that which existed prior to closing primary louvre air dampers.
6. Close emergency trip dampers in primary duct. Maintain same total air flow.
7. Readjust furnace draft to 0.20" - 0.30" of water.

Test Data. The following data were obtained:

(1) Bed Temperature\*

A thermocouple was inserted through the primary air port on the right side of the unit. The thermocouple was connected to an L&N Visicorder. Temperature of the smelt is shown on Figure 7 - TC No. 4.

A thermocouple was also located in the char on the left hand side of the unit through a secondary air port. This thermocouple is shown with respect to time as TC No. 1<sup>1</sup> on Figure 7.

(2) Gas Temperature - Primary Air Ports

Another thermocouple was placed through a primary air port on the right side of the unit. This thermocouple was maintained in the gas zone. The temperature with respect to time is shown as TC No. 3 on Figure 7.

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\*All temperatures reported herein are bare thermocouple readings.

1. Too short to measure char - actually were measuring gas temperature.

A second thermocouple was located through the secondary air port on the left side of the unit. This is shown as TC No. 2 on Figure 7.

(3) Gas Temperature - Furnace Outlet

A thermocouple supported by a water-cooled probe was located at the furnace outlet behind the furnace screen tubes. This couple was connected to an L&N Visicorder. Its specific location is shown on Figure 6. The change in temperature of TC No. 6 with respect to time is shown on Figure 7.

(4) Gas Temperature - Boiler Outlet

TC No. 5 was located at the boiler outlet. This TC was again connected to a Visicorder and is shown plotted on Figure 7. Its specific location at the boiler outlet is shown on Figure 6.

(5) Gas Analysis

Boiler Outlet.  $O_2$  at the boiler outlet was obtained by a Bailey Gas Analyzer. This instrument was calibrated prior to the test.

Furnace. The location at which gas samples were obtained at the furnace outlet is shown on Figure 6.

$H_2S-CO-CO_2-H_2-N_2$  was determined at the furnace outlet by means of a gas chromatograph. Simultaneous gas samples were recorded in gas sampling bottles for subsequent complete analysis in the laboratory on a Perkin-Elmer Gas Chromatograph, Table VI.

(6) Miscellaneous

- a. Smelt samples from the smelt spout were taken as the shutdown test proceeded.
- b. Panel Board Data - To obtain a complete record of other critical conditions such as temperatures, pressures, and flows, 35 mm pictures were taken of the entire panel board at approximately 5 second intervals.
- c. Motion Pictures - In order to obtain a photographic history of bed conditions and smelt spout conditions, color motion pictures were obtained as the test proceeded.

Preliminary Results

- (1) Smelt and gas temperatures in the primary zone dropped off at equivalent rates (see Figure 7) to those observed during the D. M. Bare tests.
- (2) The furnace outlet temperature was approximately equivalent to the boiler outlet temperature within 15 minutes from the start of the shutdown test.
- (3) Gas analyses at the furnace outlet indicated essentially no combustibles during the entire shutdown (see Table VI).
- (4) The smelt analyses indicated a decrease in per cent reduction and a rise in sulfidity (see Table VII). The sulfate level of smelt as the shutdown proceeded revealed approximately a 5-fold increase. The indicated rise in sulfidity during the Thilmany tests is contrary to that data obtained at D. M. Bare where a decrease in sulfidity was noted.

- (5) Smelt continuing to run freely from both smelt spouts of the recovery unit. A very minimum of smelt spout rodding was required for one hours duration following the shutdown test. No auxiliary fuel was used during the entire shutdown and subsequent start up of the unit revealed that a normal start up condition existed.
- (6) As the shutdown proceeded, gas evolution was noted from the char bed. The appearance was similar to a multi-series of gas torches that would, in a random fashion, be ignited.
- (7) The entire shutdown, as per previous experience at D. M. Bare, was a smooth one -- no erratic changes which could be classified as hazardous were discernible.

#### FUTURE WORK PLANNED

As the experimental work on this project has terminated, our future work will consist of the preparation and submission of a final summary report.

#### EXPENDITURES

Expenditures to March 1, 1966 are as follows:

Labor plus Overhead	\$140,128
Material	18,486
Total Expenditures	<u>\$158,614</u>

Submitted by: \_\_\_\_\_  
C. H. Anderson  
Research Specialist

CHA/djl

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- (4) Progress Report No. 2 of The Babcock & Wilcox Company, September 1, 1964.

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- (5) Mellor, J. W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry" Vol. II, p. 497, Longmans (1946).
- (6) Emich, F., Ber., 40, 1482 (1907). Cited in Mellor, *ibid.*, p. 553.
- (7) Hamamoto, M., J. Sci. Soil Manure, Japan, 25, 72 (1954). C.A., 49, 1289.
- (8) Progress Report No. 3 of Combustion Engineering, Inc., November 6, 1965.
- (9) Progress Report No. 5 of Combustion Engineering, Inc., June 5, 1965.

TABLE I  
ANALYSIS OF SMELT PREPARATIONS

<u>Nominal</u>	<u>Analysis</u>				
	$\text{Na}_2\text{S}$	$\text{Na}_2\text{CO}_3$	$\text{Na}_2\text{SO}_4$	NaOH	NaCl
25% $\text{Na}_2\text{S}$	25.0%	71.5%	.17%	.6%	--
30% $\text{Na}_2\text{S}$	28.3	68.9	.03	1.6	--
30% $\text{Na}_2\text{S}$ , 5% NaCl	30.7	61.7	--	.9	5.7
35% $\text{Na}_2\text{S}$	39.7	56.9	.17	0.7	--

TABLE II

## SUMMARY OF RESULTS OF SMELT-WATER REACTION EXPERIMENTS

RUN NO.	CHARGE	ATMOSPHERE	TEMP. °F	H <sub>2</sub> O cc	Pressure psig		Gas Analysis (Dry Basis)			Smelt Analysis After Run			Remarks
					Max.	Final	H <sub>2</sub>	CO	CO <sub>2</sub>	Na <sub>2</sub> S	Na <sub>2</sub> SO <sub>4</sub>	NaOH	
2	35% Na <sub>2</sub> S	He	1600	0	0		9.4%	.39%	<.1%				
			1590	1	5.	-	2.3	<.1	<.1				
			1590	1	6.	-	1.9	<.1	<.1				
			1620	2	9.	-	11.4	.13	1.75				
			1750	2	8.	-	11.0	.31	2.65				
			1700	2	9.	-	7.5	<.1	1.40				
			1600	2	55.*	3.8	8.8	<.1	<.1	36.0%	2.75%	1.5%	
3	35% Na <sub>2</sub> S	He	1600	0	0		13.3	0.5	1.5				Stopped Water Injections to Check Composition Prior to Explosion.
				1	6.	3.5	5.4	<.1	.42				
				1	6.	3.5	10.0	.17	1.0				
				1	7.	4.1	4.0	<.1	<.1				
				2	8.	4.5	6.4	<.1	<.1				
				2	7.	4.1	5.5	<.1	<.1	38.5	1.28	1.5	
4	35% Na <sub>2</sub> S +5% NaOH	He	1600	0		4.8	.48	<.1					
				2	60.*	5.5	11.3	<.1	<.1	37.9	.01	2.7	
5	35% Na <sub>2</sub> S +5% NaOH	He	1580	0		7.6	.4	.33					
			1600	2	15.	8.7	11.9	<.1	<.1				
			1600	2	10.	5.1	17.0	<.1	<.1	38.1	.67	2.1	
6	35% Na <sub>2</sub> S +5% Na <sub>2</sub> SO <sub>4</sub>	He	1600	0		3.4	.1	.88					
			1640	2	10	5.7	4.8	<.1	.22				
			1620	2	60.*	4.2	7.5	.12	.23	36.1	3.37	.6	
7	35% Na <sub>2</sub> S +5% NaOH +5% Na <sub>2</sub> SO <sub>4</sub>	He	1580	0		.29	<.1	.14					
			1595	2	15.*	4.9	9.9	<.1	<.1	32.7	4.00	4.5	
8	35% Na <sub>2</sub> S +5% NaOH +5% Na <sub>2</sub> SO <sub>4</sub>	Air	1600	0		3.1	<.1	.5					
				2	20.*	4.5	5.3	<.1	<.1	34.5	5.5	2.6	Could not distinguish hydrogen-air reaction from smelt-water reaction.
9	35% Na <sub>2</sub> S +5% NaOH	Air	1600	0		14.8	.62	.21					
				2	21.*	3.2	7.0	<.1	<.1	36.7	2.1	2.4	Could not distinguish hydrogen-air reaction from smelt-water reaction.
10	35% Na <sub>2</sub> S +3% Na <sub>2</sub> O +3% NaOH	He	1590	0		10.0	.12	.29					
			1475	2	-	-	6.6	<.1	<.1	36.2	.04	4.5	No explosion. Furnace failure.

TABLE II (Continued)

RUN NO.	CHARGE	ATMOSPHERE	TEMP. °F	H <sub>2</sub> O cc	Pressure psig		Gas Analysis (Dry Basis)			Smelt Analysis After Run			Remarks
					Max.	Final	H <sub>2</sub>	CO	CO <sub>2</sub>	Na <sub>2</sub> S	Na <sub>2</sub> SO <sub>4</sub>	NaOH	
11	35% Na <sub>2</sub> S + 3% Na <sub>2</sub> O + 3% NaOH	He	1600	0			12.0%	.37%	.22%				
				2	11.	6.5	14.3	<.1	.21				
				2	10.	5.5	12.2	<.1	<.1				
				2	6.	6.0	14.0	<.1	<.1				
				2	6.	5.5	12.3	<.1	<.1	33.6%	3.41%	4.7%	
12	35% Na <sub>2</sub> S + 5% NaOH	He	1600	0			8.0	.22	.61				
				2	60.*	5.3	15.0	.11	<.1	39.0	0.19	2.8	Smelt was heated in He plus its atmosphere generated by the smelt.
13	35% Na <sub>2</sub> S + 5% NaOH + 3 cc H <sub>2</sub> O	He + H <sub>2</sub> O	1550	0			26.	<.1	<.1				
			1560	0		40.	<.1	.19	33.4	3.80	5.7	Manometer blew out while heating. Smelt blown out of crucible. Suspect water drops condensed and dropped in smelt.	
14	35% Na <sub>2</sub> S + 5% NaOH + 3% cc H <sub>2</sub> O	He + H <sub>2</sub> O	1600	0			11.8	<.1	<.1				
				2	27.*	3.2	15.8	<.1	<.1				Pressure excursion to 25# before adding water.
15	35% Na <sub>2</sub> S	He	1500	0			5.4	<.1	.54				
				1	4.1	2.2	4.1	<.1	.82				
				2	11.9	5.7	11.9	<.1	.89				
				2	9.1	4.7	9.1	<.1	.61				
				2	12.1	4.4	12.1	<.1	.72				
				2	44.*	2.4	7.7	<.1	<.1	37.6	3.80	1.3	
16	35% Na <sub>2</sub> S	He	1800	0			15.0	11.6	4.2				
				1	7.	2.8	9.2	2.3	3.8				
				2	96.*	3.3	17.0	2.5	<.1	37.9	.30	1.1	
17	30% Na <sub>2</sub> S	He	1560	0			8.8	1.7	1.0				
			1600	2	16	12.	19.8	.52	.79				
			1600	2	120.*est	4.8	17.2	.11	<.1	33.6	.39	.6	20% Ammonium Carbonate solution injected. Gave fastest rise time (less than 1 millisec) and highest pressure of any experiment.
18	35% Na <sub>2</sub> S	He	1800	2	22.	20.	22.0	2.2	6.2				
				2	25.	20.	18.8	1.2	6.4	37.7	3.76	4.4	Apparently a blurb at first injection. Smelt found on shoulder of crucible.
19	35% Na <sub>2</sub> S	He	1800	1	9.	8.5	17.0	1.5	7.7				
				2	14.	12.7	24.2	1.2	5.2				
				2	14.5	14.0	25.2	.72	4.8				
				2	14.5	13.2	24.9	.76	3.8				
				2	15.0	15.0	27.0	.56	3.0				
				2	18.0	9.8	23.6	.28	3.5	28.1	.22	.2	No explosion. Possible reaction of NaOH with crucible.

TABLE II (Continued)

RUN NO.	CHARGE	ATMOSPHERE	TEMP °F	H <sub>2</sub> O cc	Pressure psig		Gas Analysis (Dry Basis)			Smelt Analysis After Run			Remarks
					Max.	Final	H <sub>2</sub>	CO	CO <sub>2</sub>	Na <sub>2</sub> S	Na <sub>2</sub> SO <sub>4</sub>	NaOH	
20	25% Na <sub>2</sub> S	He	1600	0			13.0%	3.4%	3.3%				
				2	19.	12.7	16.8	.22	8.2				
				2	17.	9.5	18.0	.42	5.8				
				2	19.	12.7	16.0	<.1	.31				
				2	55.*	6.5	10.8	<.1	<.1	21.8%	.88%	2.1%	
21	25% Na <sub>2</sub> S	He	1810	0			14.1	8.7	7.5				
				2	57.*	7.7	20.9	.58	<.1	21.8	.07	1.1	
22	30% Na <sub>2</sub> S	CO <sub>2</sub>	1600	2 6 2-cc inj.	17.	16.5	21.6	4.3	72.0	5.7	.97	.6	Some H <sub>2</sub> S formed. No explosion. CO <sub>3</sub> <sup>=</sup> increased to 83.4.
23	30% Na <sub>2</sub> S	CO <sub>2</sub>	1700	0			10.1	52.5	38.0				
				8 2-cc inj.			21.1	8.2	70.5				
		He	1600	9 2-cc inj.				22.5	<.1	1.5 (Last Inj.)	8.07	2.17	3.3
24	30% Na <sub>2</sub> S + 5.7% NaCl	He	1600	0			2.1	2.0	6.4				
				2	22.*	5.0	10.3	.25	<.1	32.7	.43	1.3	Final chloride conc. 4.13%.
25	30% Na <sub>2</sub> S + 5.7% NaCl	CO <sub>2</sub>	1600	0			6.1	30.	64.				
				2	18	8.8	20.0	13.	51.				
				2	10	8.0	19.5	10.	65.	24.8	2.10	.8	No explosion. Final chloride conc. 4.13%
26	26.5 gms Sugar Charcoal	He	1650	0			1.3	2.1	.21				
				1	17.	17.	22.8	12.3	9.5				
				1	22.	22.	23.8	23.1	4.8				
				0			2.9	1.2	<.1				
				1	23.	23.	25.1	28.0	3.9				
27	30% Na <sub>2</sub> S + 5% Carbon	He	1780	0			27.0	38.	3.2				
				2	24.	25.	30.1	13.	6.0				
				2	21.	25.	31.	6.6	7.8				
				2	12.	13.	23.	1.8	6.6				
				2	11.	12.	19.5	.6	5.7				
				2	66.*	16.	21.7	<.1	<.1	24.9	2.08	1.0	
28	30% Na <sub>2</sub> S + 5% Carbon	He	1720	0			14.8	37.0	0.1				
				2	20.	21.	28.4	6.6	5.6				
				2	21.	21.5	22.0	.76	8.0				
				2	22.	21.	26.0	.81	3.9				
				2	15.	16.	22.1	.90	8.1				
				2	11.*	12.	23.1	<.1	<.1	22.8	2.8	1.1	Mild explosion at 1600°. 15 millisecc rise time. Smelt blown out of crucible.

TABLE II (Continued)

RUN NO.	CHARGE	ATMOSPHERE	TEMP. °F	H <sub>2</sub> O cc	Pressure psig		Gas Analysis (Dry Basis)			Smelt Analysis After Run			Remarks
					Max.	Final	H <sub>2</sub>	CO	CO <sub>2</sub>	Na <sub>2</sub> S	Na <sub>2</sub> SO <sub>4</sub>	NaOH	
29	30% Na <sub>2</sub> S	15% CO <sub>2</sub> + 85% He <sup>2</sup>	1600	0			20.0%	2.3%	3.8%				
			1600	2	21.	13.	14.0	.98	6.6				
			1600	2	23	14.	17.0	.51	9.2				
			1600	2	11.	10.	13.8	.46	7.7				
			1600	2	21.	13.	17.9	.29	3.5				
			1600	2	22.	12.5	17.2	.32	6.2	16.5%	5.0%	3.5%	No explosion.
30	30% Na <sub>2</sub> S	15% CO <sub>2</sub> + 85% He <sup>2</sup>	1800	0			.8	7.5	4.3				
			1800	2	21.	15.	16.0	2.5	14.0				
			1800	2	10.	12.	15.3	1.1	11.5				
			1800	2	12.	12.	22.0	1.1	11.0	19.1	3.45	4.4	No explosion.
31	30% Na <sub>2</sub> S + 5.7% NaCl	CO <sub>2</sub>	1500	0			18.0	77.	4.8				
			1600	2	19.	13.	24.8	22.	52.				
			1600	2	23.	23.	19.0	16.	65.	22.4	2.55	neg.	Final chloride conc.= 4.1%.
32	30% Na <sub>2</sub> S + 5.7% NaCl	He then CO <sub>2</sub> for 7 min.	1500	0			5.5	9.8	1.4 (Helium Atmos.)				
			1610	2	25.*	4.	30.2	19.	36.	26.1	1.21	neg.	Final chloride conc.= 4.8%.

TABLE III

## RESULTS OF SMELT-WATER REACTION EXPERIMENTS USING AS-PREPARED SMELT

RUN NO.	CHARGE	ATMOSPHERE	TEMP. °F	H <sub>2</sub> O cc	Pressure psig		Gas Analysis (Dry Basis)			Smelt Analysis After Run			Remarks	
					Max.	Final	H <sub>2</sub>	CO	CO <sub>2</sub>	Na <sub>2</sub> S	Na <sub>2</sub> SO <sub>4</sub>	NaOH		
15	35% Na <sub>2</sub> S	He	1500	0			5.4	<.1	.54					
				1	4.1	2.2	4.1	<.1	.82					
				2	11.9	5.7	11.9	<.1	.89					
				2	9.1	4.7	9.1	<.1	.61					
				2	12.1	4.4	12.1	<.1	.72					
				2	44.*	2.4	7.7	<.1	<.1	37.6	3.80	1.3		
2	35% Na <sub>2</sub> S	He	1600	0	0		9.4%	.39%	<.1%					
				1590	1	5.	-	2.3	<.1	<.1				
				1590	1	6.	-	1.9	<.1	<.1				
				1620	2	9.	-	11.4	.13	1.75				
				1750	2	8.	-	11.0	.31	2.65				
				1700	2	9.	-	7.5	<.1	1.40				
				1600	2	55.*	3.8	8.8	<.1	<.1	36.0%	2.75%	1.5%	
3	35% Na <sub>2</sub> S	He	1600	0	0		13.3	0.5	1.5					
				1	6.	3.5	5.4	<.1	.42					
				1	6.	3.5	10.0	.17	1.0					
				1	7.	4.1	4.0	<.1	<.1					
				2	8.	4.5	6.4	<.1	<.1					
				2	7.	4.1	5.5	<.1	<.1	38.5	1.28	1.5		
20	25% Na <sub>2</sub> S	He	1600	0			13.0%	3.4%	3.3%					
				2	19.	12.7	16.8	.22	8.2					
				2	17.	9.5	18.0	.42	5.8					
				2	19.	12.7	16.0	<.1	.31					
				2	55.*	6.5	10.8	<.1	<.1	21.8%	.88%	2.1%		
16	35% Na <sub>2</sub> S	He	1800	0			15.0	11.6	4.2					
				1	7.	2.8	9.2	2.3	3.8					
				2	96.*	3.3	17.0	2.5	<.1	37.9	.30	1.1		
18	35% Na <sub>2</sub> S	He	1800	2	22.	20.	22.0	2.2	6.2					
				2	25.	20.	18.8	1.2	6.4	37.7	3.76	4.4		Apparently a blurb at first injection. Smelt found on shoulder of crucible.
19	35% Na <sub>2</sub> S	He	1800	1	9.	8.5	17.0	1.5	7.7					
				2	14.	12.7	24.2	1.2	5.2					
				2	14.5	14.0	25.2	.72	4.8					
				2	14.5	13.2	24.9	.76	3.8					
				2	15.0	15.0	27.0	.56	3.0					
				2	18.0	9.8	23.6	.28	3.5	28.1	.22	.2		
21	25% Na <sub>2</sub> S	He	1810	0			14.1	8.7	7.5					
				2	57.*	7.7	20.9	.58	<.1	21.8	.07	1.1		

TABLE IV

## EFFECT OF SODIUM HYDROXIDE ADDITIONS TO SMELT

RUN NO.	CHARGE	ATMOSPHERE	TEMP. °F	H <sub>2</sub> O cc	Pressure psig		Gas Analysis (Dry Basis)			Smelt Analysis After Run			Remarks	
					Max.	Final	H <sub>2</sub>	CO	CO <sub>2</sub>	Na <sub>2</sub> S	Na <sub>2</sub> SO <sub>4</sub>	NaOH		
4	35% Na <sub>2</sub> S + 5% NaOH	He	1600	0 2			4.8 11.3	.48 <.1	<.1 <.1	37.9	.01	2.7		
5	35% Na <sub>2</sub> S + 5% NaOH	He	1680 1600 1600	0 2 2		15. 10.	8.7 5.1	7.6 11.9 17.0	.4 <.1 <.1	<.1 <.1 <.1	38.1	.67	2.1	
9	35% Na <sub>2</sub> S + 5% NaOH	Air	1600	0 2		21.*	3.2	14.8 7.0	.62 <.1	.21 <.1	36.7	2.1	2.4	Could not distinguish hydrogen-air reaction from smelt-water reaction.
12	35% Na <sub>2</sub> S + 5% NaOH	He	1600	0 2		60.*	5.3	8.0 15.0	.22 .11	.61 <.1	39.0	0.19	2.8	Smelt was heated in He plus its atmosphere generated by the smelt
13	35% Na <sub>2</sub> S + 5% NaOH + 3 cc H <sub>2</sub> O	He + H <sub>2</sub> O	1550 1560	0 0				26. 40.	<.1 <.1	<.1 .19	33.4	3.80	5.7	Manometer blew out while heating. Smelt blown out of crucible. Suspect water drops condensed and dropped in smelt.
14	35% Na <sub>2</sub> S + 5% NaOH + 3% cc H <sub>2</sub> O	He + H <sub>2</sub> O	1600	0 2		27.*	3.2	11.8 15.8	<.1 <.1	<.1 <.1	35.0	.73	4.0	Pressure excursion to 25# before adding water.

TABLE V

EFFECT OF CO<sub>2</sub> ATMOSPHERE AND SODIUM CHLORIDE ADDITIONS

RUN NO.	CHARGE	ATMOSPHERE	TEMP. °F	H <sub>2</sub> O cc	Pressure psig		Gas Analysis (Dry Basis)			Smelt Analysis After Run			Remarks
					Max.	Final	H <sub>2</sub>	CO	CO <sub>2</sub>	Na <sub>2</sub> S	Na <sub>2</sub> SO <sub>4</sub>	NaOH	
22	30% Na <sub>2</sub> S	CO <sub>2</sub>	1600	7 6 2-cc inj.	17.	16.5	21.6	4.3	72.0	5.7	.97	.6	Some H <sub>2</sub> S formed. No explosion. CO <sub>2</sub> increased to 83.4.
23	30% Na <sub>2</sub> S	CO <sub>2</sub>	1700	0 8 2-cc inj.			10.1 21.1	52.5 8.2	38.0 70.5				No explosion
		He	1600	9 2-cc inj.			22.5	<.1	(Last Inj.) 1.5 (Last Inj.)	8.07	2.17	3.3	
29	30% Na <sub>2</sub> S + 85% He <sup>2</sup>	15% CO <sub>2</sub> + 85% He <sup>2</sup>	1600	0			20.0%	2.3%	3.8%				No explosion.
			1600	2	21.	13.	14.0	.98	6.6				
			1600	2	23	14.	17.0	.51	9.2				
			1600	2	11.	10.	13.8	.46	7.7				
			1600	2	21.	13.	17.9	.29	3.5				
			1600	2	22.	12.5	17.2	.32	6.2	16.5%	5.0%	3.5%	
30	30% Na <sub>2</sub> S + 85% He <sup>2</sup>	15% CO <sub>2</sub> + 85% He <sup>2</sup>	1800	0			.8	7.5	4.3				No explosion.
			1800	2	21.	15.	16.0	2.5	14.0				
			1800	2	10.	12.	15.3	1.1	11.5				
			1800	2	12.	12.	22.0	1.1	11.0	19.1	3.45	4.4	
24	30% Na <sub>2</sub> S + 5.7% NaCl	He	1600	0			2.1	2.0	6.4				Final chloride conc. 4.13%.
				2	22.5	5.0	10.3	.25	<.1	32.7	.43	1.3	
32	30% Na <sub>2</sub> S + 5.7% NaCl	He then CO <sub>2</sub> for 7 min.	1500	0			5.5	9.8	1.4 (Helium Atmos.)				Final chloride conc.= 4.8%.
			1610	2	25.5	4.	30.2	19.	36.	26.1	1.21	neg.	
25	30% Na <sub>2</sub> S + 5.7% NaCl	CO <sub>2</sub>	1600	0			6.1	30.	64.				No explosion. Final chloride conc. 4.13%
			1610	2	18	8.8	20.0	13.	51.				
			1600	2	10	8.0	19.5	10.	65.	24.8	2.10	.8	
31	30% Na <sub>2</sub> S + 5.7% NaCl	CO <sub>2</sub>	1500	0			18.0	77.	4.8				Final chloride conc.= 4.1%.
			1600	2	19.	13.	24.8	22.	52.				
			1600	2	23.	23.	19.0	16.	65.	22.4	2.55	neg.	

TABLE VI  
GAS ANALYSIS AT FURNACE OUTLET

Time	Field Analysis		Laboratory Analysis Gas Collector Bottles					
	% O <sub>2</sub>	% Combustible	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub>
2108	0.9	0.7						
2135	2.8	N.D.						
2142	2.4	N.D.						
2145	2.5	N.D.						
2152	3.4	N.D.						
2155			78.1	13.7	7.0	N.D.	N.D.	<.1
2159	14.9	N.D.						
2203			78.0	17.9	1.8	N.D.	N.D.	<.1
2205	15.3	N.D.						
2210	15.5	N.D.						
2211			79.7	18.7	1.0	N.D.	N.D.	<.1
2219	15.7	N.D.						
2219			79.8	19.1	0.8	N.D.	N.D.	<.1
2225	15.5	N.D.						
2225			78.7	19.4	0.6	N.D.	N.D.	<.1
2230	16.1	N.D.						
2231			77.8	19.5	0.5	N.D.	N.D.	<.1
2235	16.1	N.D.						
2240	16.1	N.D.						

TABLE VII  
ANALYSIS OF SMELT SAMPLES

	<u>Before</u>	<u>During</u>	<u>At End of Test</u>
Na <sub>2</sub> CO <sub>3</sub> %	68.9	67.1	62.5
Na <sub>2</sub> S	22.6	24.0	26.1
NaHS	2.5	2.1	1.6
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1.8	2.3	2.2
Na <sub>2</sub> SO <sub>3</sub>	0.5	0.6	1.2
Na <sub>2</sub> SO <sub>4</sub>	<u>1.3</u>	<u>1.1</u>	<u>5.6</u>
	97.6	97.2	99.2
Sulfidity	32.4	34.1	37.2
Reduction (Total)	90.5	89.0	82.5
(Mill)	97.0	97.5	89.6

where

$$\text{Sulfidity} = \frac{(\text{Na}_2 \text{ S}/78) + (\text{NaHS}/56)(1/2)}{(\text{Na}_2 \text{ S}/78) + (\text{NaHS}/56)(1/2) + (\text{Na}_2\text{CO}_3/106)} \times 100 \text{ based on Na}_2\text{O}$$

$$\text{Reduction} = \frac{(\text{Na}_2 \text{ S}/78) + (\text{NaHS}/56) \cdot 100}{(\text{Na}_2 \text{ S}/78 + (\text{NaHS}/56) + (\text{Na}_2\text{SO}_4/142) + (\text{Na}_2\text{SO}_3/126) + 2(\text{Na}_2\text{S}_2\text{O}_3/158)}$$

Reduction is based on sulfur.

$$\text{Mill Reduction} = (\text{Na}_2 \text{ S}/78) / [(\text{Na}_2 \text{ S}/78) + (\text{Na}_2\text{SO}_4/142)]$$

# CAPSULE FOR SODIUM TEST

FIGURE 1

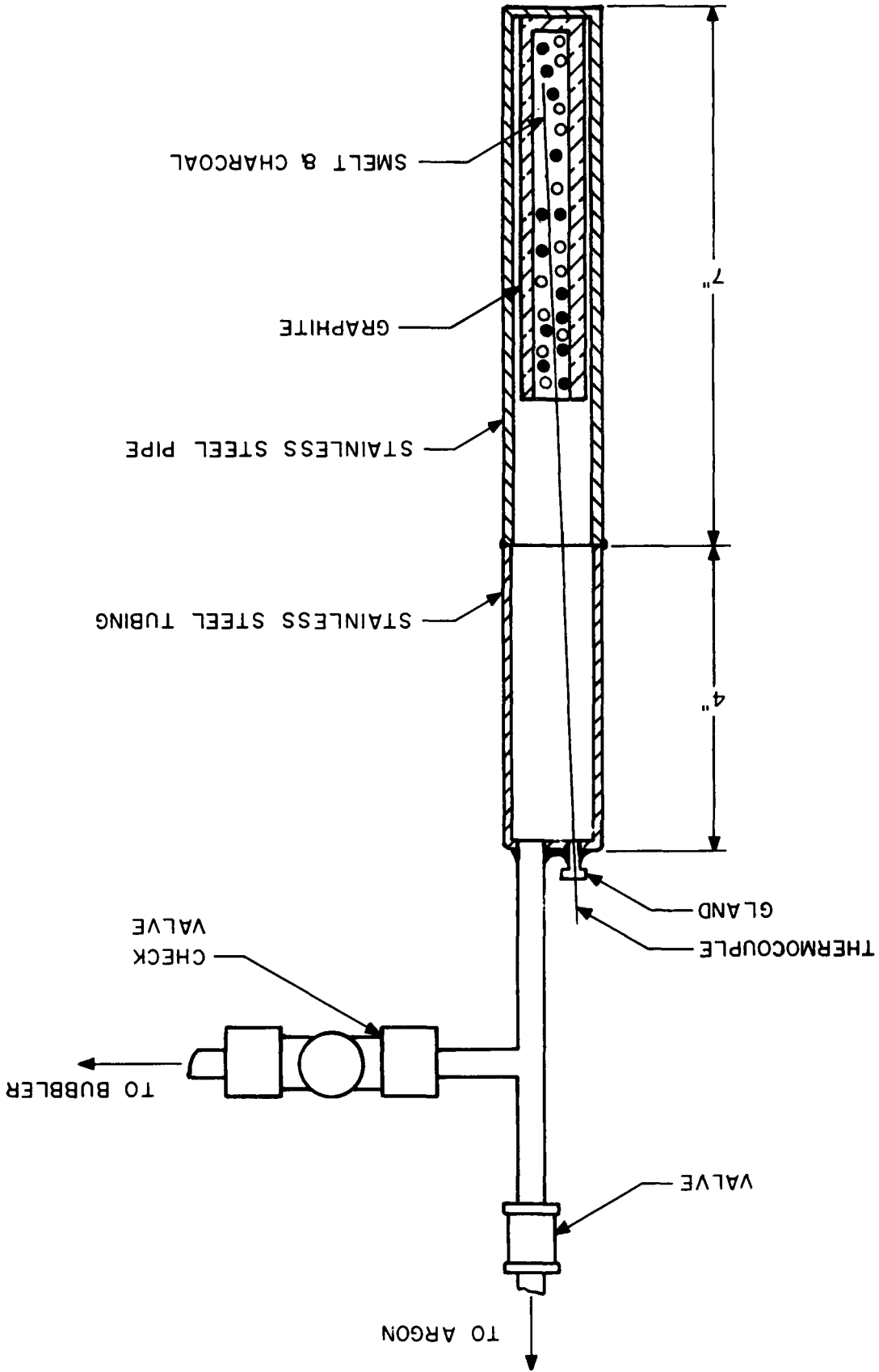
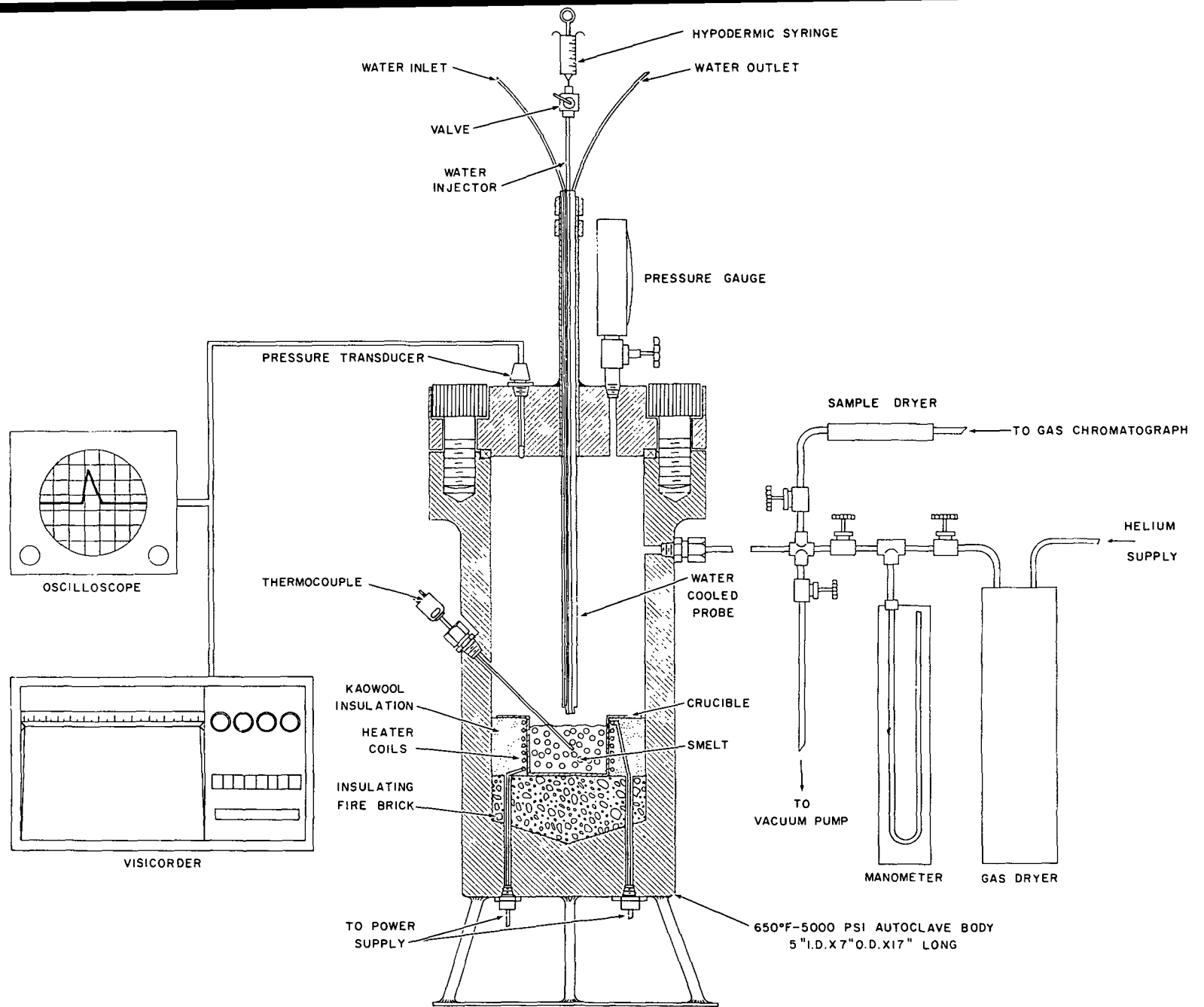
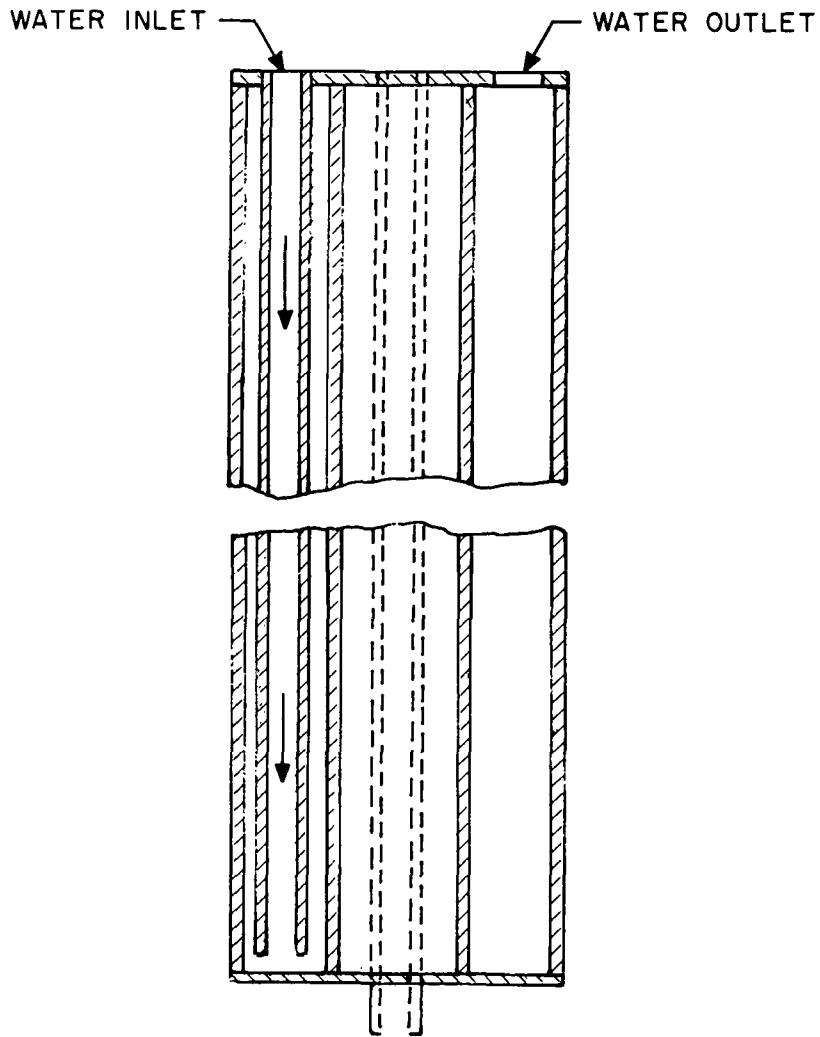
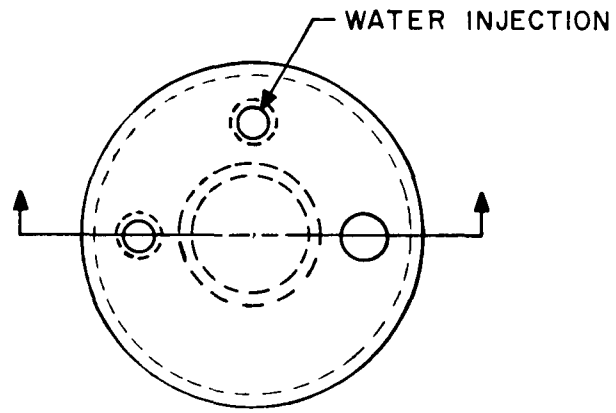


FIGURE 2

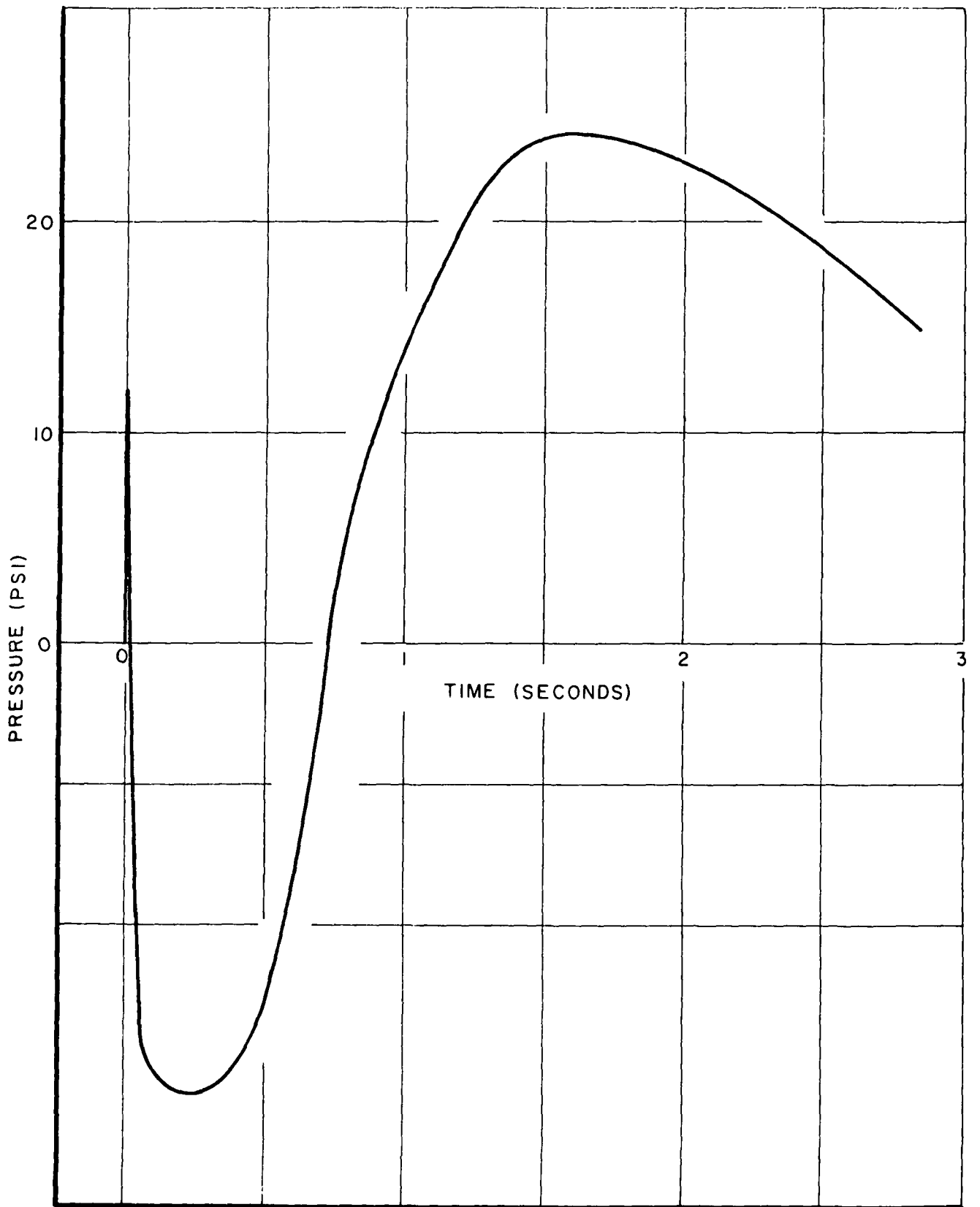


SCHEMATIC DRAWING OF EXPLOSION APPARATUS



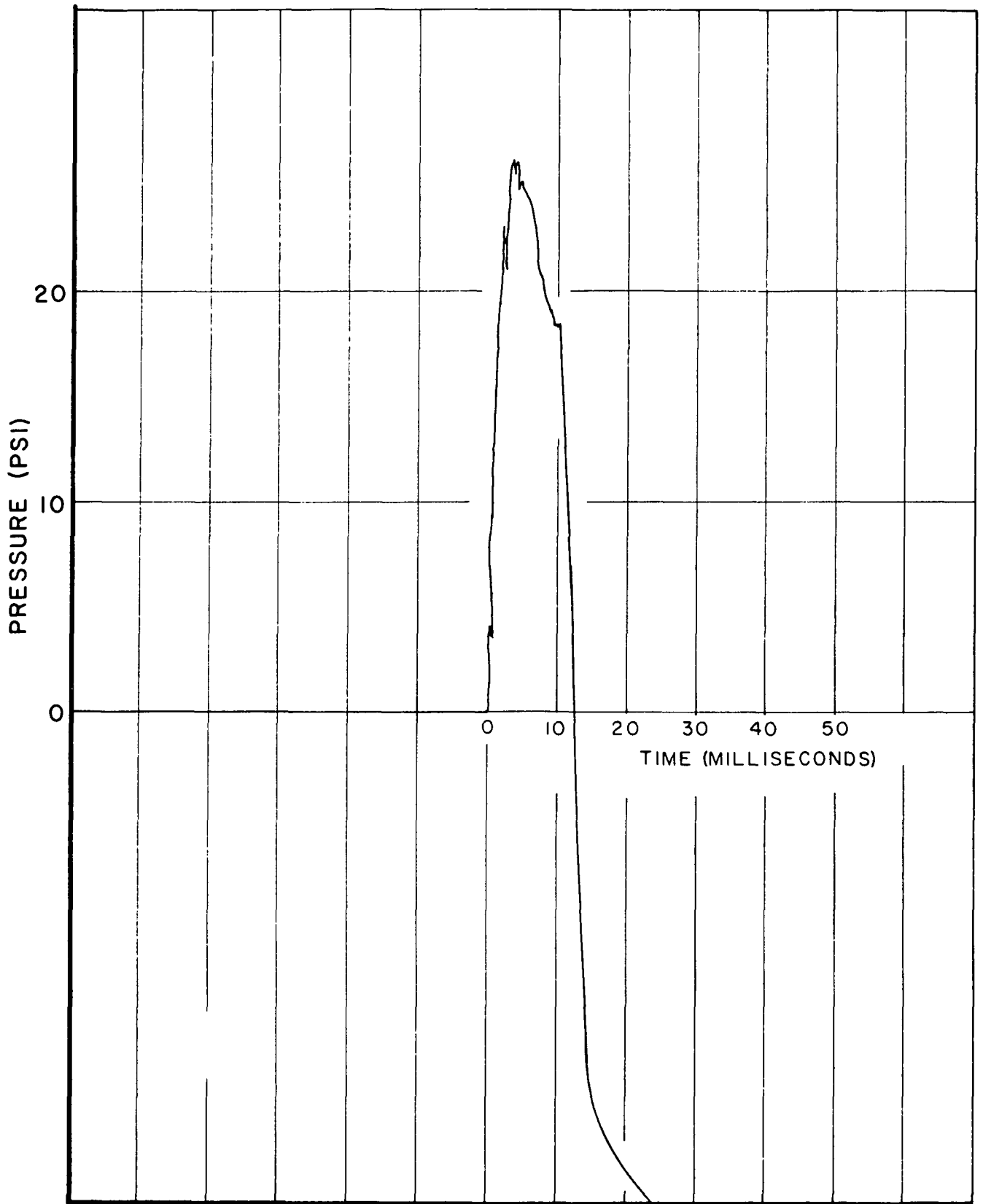
WATER INJECTION SYSTEM

FIGURE 3



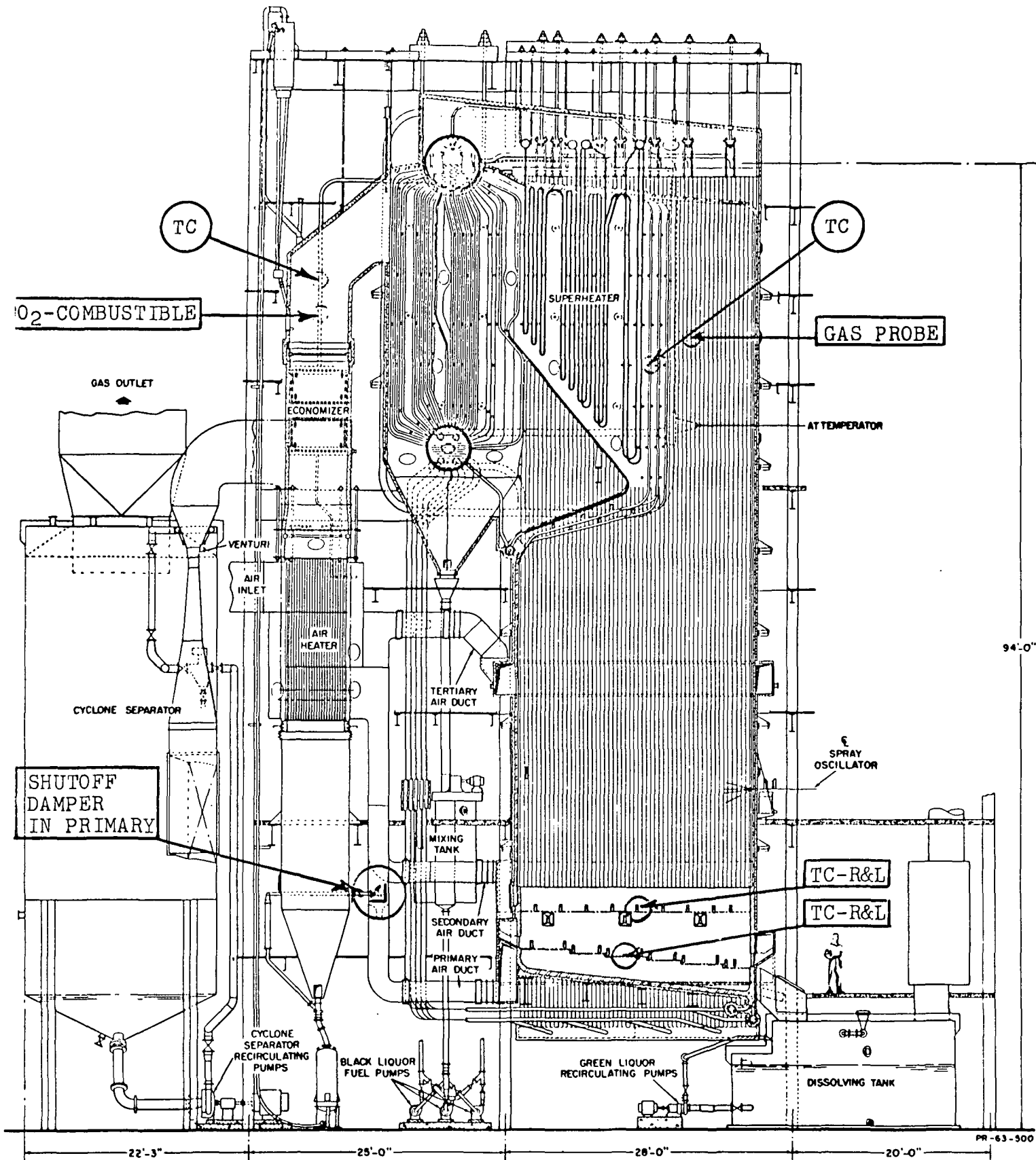
TYPICAL EXPLOSION PRESSURE-TIME  
TIME RELATIONSHIP

FIGURE 4



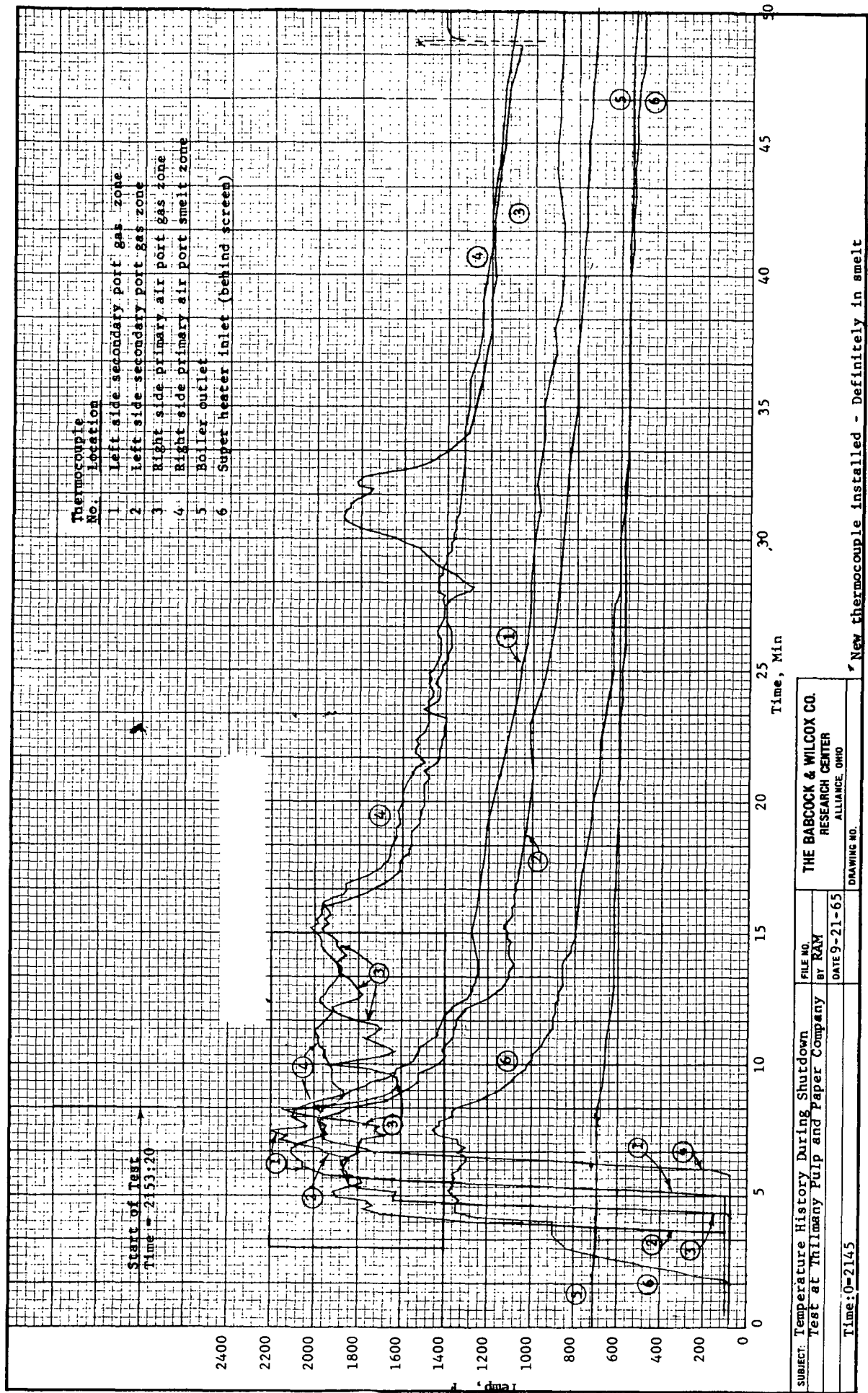
PRESSURE - TIME RELATIONSHIP  
RUN NO. 20

FIGURE 5



390 TON RECOVERY UNIT FOR  
 THILMANY PULP & PAPER COMPANY  
 KAUKAUNA, WISCONSIN  
 B & W CONTRACT NO. PR-63

FIGURE 6



SUBJECT: Temperature History During Shutdown  
Test at Millman Pulp and Paper Company

FILE NO.  
BY RAY

DATE 9-21-65

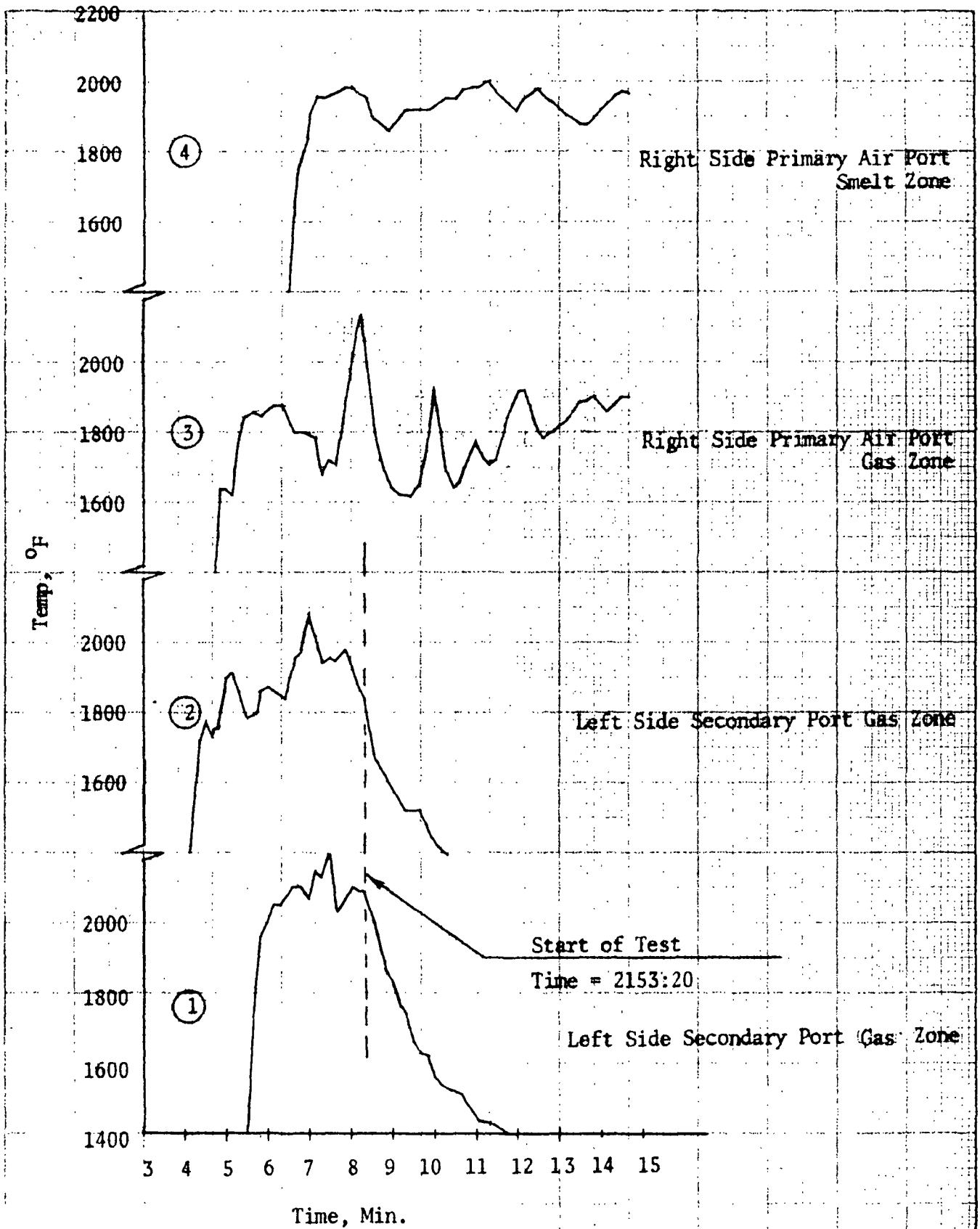
THE BABCOCK & WILCOX CO.  
RESEARCH CENTER  
ALLIANCE, OHIO

DRAWING NO.

Time: 0-2145

✓ New thermocouple installed - Definitely in smelt

FIGURE 7



Expanded Temperature History at  
 Start of Shutdown Test  
 Thilmany Pulp and Paper Company

By RAM  
 Date 9-22-65

THE BABCOCK & WILCOX CO.  
 RESEARCH CENTER  
 ALLIANCE, OHIO

FIGURE 8

APPENDIX I  
COMPUTER PROGRAM  
FOR THE  
CALCULATION OF CHEMICAL EQUILIBRIUM  
BY THE  
FREE ENERGY MINIMIZATION METHOD

## TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	iB
MATHEMATICAL DERIVATION	iB
COMPUTER PROGRAM	viiiB
SAMPLE INPUT	xB
SAMPLE OUTPUT	xixB
FLOWCHARTS	xxivB
PROGRAM LISTING	xxxixB
BIBLIOGRAPHY	lvB

CALCULATION OF CHEMICAL EQUILIBRIUM  
BY THE FREE ENERGY MINIMIZATION METHOD

INTRODUCTION

The determination of equilibrium composition for a chemical system of many constituents is generally difficult because the equations to be solved are not simultaneously linear. Since a direct solution to the equations is usually not feasible, some iterative technique must be used.

In order to solve many of the complex equilibrium composition problems arising from Kraft Recovery Boilers, an iterative technique by Oliver, Stephanou, and Baier was selected and a computer program was written. This method is based on the fact that chemical equilibrium occurs in mixtures whose total free energy (Gibb's function) is a minimum and thus is applicable to most chemical systems.

In the following derivation it is assumed (1) that gases are ideal and (2) that condensed phases are immiscible.

MATHEMATICAL DERIVATION

The total free energy of a mixture of  $n$  gaseous and  $p$  condensed chemical species can be expressed as:

$$F(X) = \sum_{i=1}^n f_i^g + \sum_{h=1}^p f_h^c \quad (1)$$

The free energy contributed by a gaseous species is given by the expression:

$$f_i^g = x_i^g (c_i^g + \ln (x_i^g / \bar{x})) \quad (2)$$

where

$$c_i^g = (F/RT)_i^g + \ln P \quad (3)$$

and

P is the total pressure in atmosphere,  $(F/RT)_i^g$  is the molal standard free energy function for the  $i^{\text{th}}$  gaseous species,  $x_i^g$  is the mole number for the  $i^{\text{th}}$  gaseous species,

and

$$\bar{x} = \sum_{i=1}^n x_i^g .$$

For a condensed species the effects of pressure and mixing are excluded so that the free energy expression becomes:

$$f_h^c = x_h^c \cdot c_h^c \quad (4)$$

where

$$c_h^c = (F/RT)_h^c \quad (5)$$

and

$(F/RT)_h^c$  is the molal standard free energy function for the  $h^{\text{th}}$  condensed species,  $x_h^c$  is the mole number for the  $h^{\text{th}}$  condensed species.

In the free energy expressions (3) and (5),  $(F/RT)_i$  is defined in the following manner:

$$(F/RT)_i = \frac{1}{R} \left( \frac{F - H_{298}}{T} \right)_i + \frac{\Delta H_{298}^f}{RT} \quad (6)$$

where

R is the universal gas constant, T is the temperature in °K,

$\Delta H_{298}^f$  is the standard enthalpy of formation at 298°K,

$\left( \frac{F - H_{298}}{T} \right)_i$  is the free energy function (thermodynamic tables)

for the  $i^{\text{th}}$  species.

Determination of the equilibrium composition requires finding a non-negative set of mole numbers  $X = (x_1^g, x_2^g, \dots, x_n^g, x_1^c, x_2^c, \dots, x_p^c)$  which will minimize the total free energy  $F(x)$  of the system. However, this set of mole numbers must also satisfy mass-balance considerations so that:

$$\sum_{i=1}^n a_{ij} x_i^g + \sum_{h=1}^p a_{hj}^c x_h^c = b_j, \quad j=1, 2, \dots, m \quad (7)$$

where

$m$  is the number of elements,  $b_j$  is the total number of atomic weights of the  $j^{\text{th}}$  element,  $a_{ij}$  is the number of atoms of the  $j^{\text{th}}$  element in the  $i^{\text{th}}$  species.

Let  $Y^g = (y_1^g, y_2^g, \dots, y_n^g)$  be an initial guess for the mole numbers of the gaseous species  $(x_1^g, x_2^g, \dots, x_n^g)$ . Let  $Y^c = (y_1^c, y_2^c, \dots, y_p^c)$  be an initial guess for the mole numbers of the solid species  $(x_1^c, x_2^c, \dots, x_p^c)$ . And let  $Y = (Y^g, Y^c)$ .

Now choose  $Y$  such that it satisfies the mass balance constraints and also such that it is a positive set. The free energy for this mixture is:

$$F(Y) = \sum_{i=1}^n y_i^g (c_i^g + \ln(y_i^g/\bar{y})) + \sum_{h=1}^p c_h^c y_h^c \quad (8)$$

where

$$\bar{y} = \sum_{i=1}^n y_i^g$$

An expression  $Q(x)$  is obtained as an approximation for  $F(x)$ , the minimum free energy, by using a Taylor's expansion about the initial guess  $Y$ . Using this expansion technique, and substituting in values of the partial derivative  $\partial F/\partial x_i^g$  and  $\partial F/\partial x_h^c$  the following expression can be obtained.

$$Q(x) = F(Y) + \sum_{i=1}^n (c_i^g + \ln(y_i^g/\bar{y}))\Delta_i^g + \sum_{h=1}^p c_h^c \Delta_h^c + \frac{1}{2} \sum_{i=1}^n y_i^g \left( \frac{\Delta_i^g}{y_i^g} - \frac{\Delta'}{\bar{y}} \right) \quad (9)$$

where

$$\Delta_i^g = x_i^g - y_i^g, \Delta_h^c = x_h^c - y_h^c, \Delta' = \bar{x} - \bar{y}.$$

In order to find a better approximation to the desired solution,  $Q(x)$  is minimized subject to the mass-balance constraints of equation (7). First, however, it is necessary to define a function  $G(x)$  as follows:

$$G(x) = Q(x) + \sum_{j=1}^m \pi_j (b_j - \sum_{i=1}^n a_{ij}^g x_i^g - \sum_{h=1}^p a_{hj}^c x_h^c) \quad (10)$$

where the  $\pi_j$ 's are Lagrange multipliers. Then setting

$$\partial G(x)/\partial x_i^g = \partial G(x)/\partial x_h^c = 0$$

the change in free energy with a change in the moles of the gaseous species becomes

$$\partial G(x)/\partial x_i^g = (c_i^g + \ln(y_i^g/\bar{y})) + (x_i^g/y_i^g - \bar{x}/\bar{y} - \sum_{j=1}^m \pi_j a_{ij}^g) = 0 \quad (11)$$

and the change in free energy with a change in the moles of the condensed species is

$$\partial G(x)/\partial x_h^c = c_h^c - \sum_{j=1}^m \pi_j a_{hj}^c = 0 \quad (12)$$

Solving equation (11) for  $x_i^g$  and summing over  $i$  gives

$$x_i^g = -y_i^g(c_i^g + \ln(y_i^g/\bar{y})) + y_i^g(\bar{x}/\bar{y}) + \sum_{j=1}^m \pi_j a_{ij}^g y_i^g \quad (13)$$

and then

$$\sum_{j=1}^m \pi_j \sum_{i=1}^n a_{ij}^g y_i^g = \sum_{i=1}^n y_i^g(c_i^g + \ln(y_i^g/\bar{y})) \quad (14)$$

Now let

$$r_{jk} = r_{kj} = \sum_{i=1}^n (a_{ij}^g a_{ik}^g) y_i^g, \quad j, k = 1, 2, \dots, m \quad (15)$$

The substitution of equation (13) into equation (7) gives  $m$  equations which together with equations (12) and (14) give  $m + p + 1$  linear equations in the unknowns  $\pi_1, \pi_2, \dots, \pi_m$  and  $x_1^c, x_2^c, \dots, x_p^c$  and  $\bar{x}/\bar{y}$  as follows:

$$\alpha_1(\bar{x}/\bar{y}) + a_{11}^c x_1^c + a_{21}^c x_2^c + \dots + a_{p1}^c x_p^c + r_{11}\pi_1$$

$$+ r_{12}\pi_2 + \dots + r_{1m}\pi_m = b_1 + \sum_i a_{i1}^g f_i^g$$

$$\alpha_2(\bar{x}/\bar{y}) + a_{12}^c x_1^c + a_{22}^c x_2^c + \dots + a_{p2}^c x_p^c + r_{21}\pi_1$$

$$+ r_{22}\pi_2 + \dots + r_{2m}\pi_m = b_2 + \sum_i a_{i2}^g f_i^g$$

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$$\alpha_m(\bar{x}/\bar{y}) + a_{1m}^c x_1^c + a_{2m}^c x_2^c + \dots + a_{pm}^c x_p^c + r_{m1}\pi_1$$

$$+ r_{m2}\pi_2 + \dots + r_{mm}\pi_m = b_m + \sum_i a_{im}^g f_i^g$$

$$\alpha_1\pi_1 + \alpha_2\pi_2 + \dots + \alpha_m\pi_m = \sum_i f_i^g$$

$$a_{11}^c \pi_1 + a_{12}^c \pi_2 + \dots + a_{1m}^c \pi_m = c_1^c$$

$$a_{21}^c \pi_1 + a_{22}^c \pi_2 + \dots + a_{2m}^c \pi_m = c_2^c$$

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$$a_{m1}^c \pi_1 + a_{m2}^c \pi_2 + \dots + a_{pm}^c \pi_m = c_p^c$$

where

$$\alpha_j = \sum_{i=1}^m a_{ij}^g y_i^g \quad (16)$$

The solution to this set of equations gives the new approximation to the condensed species  $x_h^c$  directly. To find the new values of the gaseous species  $x_i^g$ , it is necessary to substitute the  $\alpha_j$ ,  $\bar{x}/\bar{y}$ , and  $y_i^g$  values into equation 13. In this way a new set of  $x_i^g$  and  $x_h^c$  values are found which represent a new approximation to the desired result. In addition, values of trace gaseous species omitted from the system are computed by the formula

$$x_i^g = \bar{x} \exp(-c_i^g + \sum_{j=1}^m \pi_j a_{ij}^g) \quad (17)$$

where

$$1.0 \times 10^{-5} \geq x_i^g \geq 1.0 \times 10^{-90}$$

and the species are then added to the system. The procedure is repeated, using the  $x_i$  values that are found as answers from the last calculation as new  $y_i$  values, until the differences between subsequent iterations are less than  $1.0 \times 10^{-5}$ .

It is possible that the computed part of new mole numbers  $x_i^g$  and  $x_h^c$  will include some negative numbers. If so, the computed values of mole numbers cannot be used directly in the next approximation since zero or negative

mole numbers are not permitted. Instead, the new set is taken to be an indication of the direction of desired travel and  $x$  is allowed to proceed in this direction only so far as it remains a positive set.

This is done by choosing a value of  $\lambda$  so that

$$y_i' = y_i + \lambda(x_i - y_i) \quad (18)$$

is not zero or negative. The method for selecting  $\lambda$  is to compute for each species where  $(x_i - y_i)$  is negative a value of  $\lambda'$  such that  $y_i'$  is zero

$$\lambda' = -y_i / (x_i - y_i) ,$$

select the smallest value of  $\lambda_1'$ , and then set  $\lambda = 0.99\lambda'$  so that all  $y_i$  are positive. The same value of  $\lambda$  is used in adjusting all the mole numbers to maintain mass-balance in the resulting set.

In each iteration after the set of mole numbers has been adjusted to a positive set, a test is used to determine whether or not omitted condensed species should be added to the system. If the following relationship, for the  $H^{\text{th}}$  condensed species, holds

$$\left| \left( (F/RT)_H - \sum_{j=1}^m \pi_j a_{hj}^c \right) / (F/RT)_H \right| \geq 1.0 \times 10^{-3} \quad (19)$$

then the species is added to the system with a value of  $1.0 \times 10^{-8}$ .

In order to minimize matrix system difficulties, any species (gaseous or condensed) which is less than  $1.0 \times 10^{-8}$  is thrown out of the calculation and omitted from the system by simply setting it to zero.

After converging to a solution for the initial temperature, the algorithm is repeated for eight successive temperatures ( $T_{i+1} = T_i + 100$ ) with the final values from one temperature being used as a first approximation to the values at the next temperature.

#### COMPUTER PROGRAM

The application of this method to a chemical system requires that certain thermodynamic data be supplied for each species. This data includes the standard enthalpy of formation at 298°K  $\{\Delta H_{298}^f\}$  and values of the free energy function  $\{(F - H_{298})/T\}$ .

Each set of data should be punched on cards in the following manner. The first card in the set is a header card with the words "FREE ENERGY DATA FOR" in columns 1-20 and the formula name of the species in columns 22-31. The next  $n$  cards ( $9 \leq n \leq 20$ ) each contains a temperature in columns 1-4, the value of  $\{-(F - H_{298})/T\}$  at that temperature in columns 5-12 and the value of  $\{\Delta H_{298}^f\}$  in columns 13-20. The temperatures should be in ascending order with increments of 100°K. The last card in each set should be a blank card.

In order for the computer program to sense the end of the thermodynamic data, a flag is placed at the end of the data. This flag consists of a header card with a dummy species name and one temperature card with a negative temperature. After this flag has been sensed, the values of  $F/RT$  from equation 6 are printed out.

The next set of cards contain the data for the actual problem. The first card in the set has the number of elements in columns 1-2, the number

of gaseous species in columns 3-4, the number of condensed species in columns 5-6, the initial temperature in columns 7-10, the pressure in atmospheres in columns 11-14 and % total air in columns 15-17.

The computer program will accept up to 10 elements and up to 40 chemical species. These species can be either gaseous or condensed; however, if there are only  $m$  elements in the system, there cannot be more than  $m-1$  condensed species. Otherwise, the matrix will be singular.

The second card contains the  $b_j$  values which are the amounts in lb-atoms of each element in the system and the third card contains the atomic weights of the corresponding elements. The data on both of these cards is punched in columns 1-6, 7-12, ..., 55-60.

The next  $n$  cards ( $n \leq 40$ ) each contain the formula name of a species in columns 1-10, an initial guess in lb-moles in columns 11-16, and the  $a_{ij}$  values or the number of atoms of the corresponding elements in columns 17-22, 23-28, ..., 71-76.

The gaseous species must be listed first and the condensed species last. Caution must be taken to insure that the sequence of species is the same for both the thermodynamic data and the problem data.

Any problem which does not converge in 50 iterations is marked on the printout by an asterisk.

Successive sets of problem data can be run without reloading the thermodynamic data as long as the chemical system remains the same. If, however, the system changes, then both the program and the thermodynamic data must be reloaded.

SAMPLE INPUT

T °K

 $-(F - H_{298})/T$  $\Delta H_f 298^\circ$ 

FREE E				ENERGY				DATA				FOR CO							
		9	0	0		5	0	.	3	1	4		-	2	6	.	4	1	7
1	0	0	0		5	0	.	8	4	5		-	2	6	.	4	1	7	
1	1	0	0		5	1	.	3	5	1		-	2	6	.	4	1	7	
1	2	0	0		5	1	.	8	3	4		-	2	6	.	4	1	7	
1	3	0	0		5	2	.	2	9	5		-	2	6	.	4	1	7	
1	4	0	0		5	2	.	7	3	6		-	2	6	.	4	1	7	
1	5	0	0		5	3	.	1	5	8		-	2	6	.	4	1	7	
1	6	0	0		5	3	.	5	6	2		-	2	6	.	4	1	7	
1	7	0	0		5	3	.	9	5	0		-	2	6	.	4	1	7	
					b	l	a	n	k		c	a	r	d					
FREE E				ENERGY				DATA				FOR CO 2							
		9	0	0		5	5	.	5	4	6		-	9	4	.	0	5	4
1	0	0	0		5	6	.	3	5	9		-	9	4	.	0	5	4	
1	1	0	0		5	7	.	1	4	3		-	9	4	.	0	5	4	
1	2	0	0		5	7	.	8	9	6		-	9	4	.	0	5	4	
1	3	0	0		5	8	.	6	2	0		-	9	4	.	0	5	4	
1	4	0	0		5	9	.	3	1	5		-	9	4	.	0	5	4	
1	5	0	0		5	9	.	9	8	4		-	9	4	.	0	5	4	
1	6	0	0		6	0	.	6	2	7		-	9	4	.	0	5	4	
1	7	0	0		6	1	.	2	4	6		-	9	4	.	0	5	4	
					b	l	a	n	k		c	a	r	d					
FREE E				ENERGY				DATA				FOR H 2							
		9	0	0		3	4	.	2	5	0			0	.	0			
1	0	0	0		3	4	.	7	5	8			0	.	0				
1	1	0	0		3	5	.	2	4	0			0	.	0				
1	2	0	0		3	5	.	6	9	6			0	.	0				
1	3	0	0		3	6	.	1	3	0			0	.	0				
1	4	0	0		3	6	.	5	4	3			0	.	0				
1	5	0	0		3	6	.	9	3	7			0	.	0				
1	6	0	0		3	7	.	3	1	4			0	.	0				
1	7	0	0		3	7	.	6	7	5			0	.	0				
					b	l	a	n	k		c	a	r	d					

T °K

 $-(F - H_{298})/T$  $\Delta H_f 298^\circ$ 

FREE				ENERGY				DATA				FOR				H 2 O						
				9	0	0		4	8	.	7	4	9		-	5	7	.	7	9	8	
1	0	0	0	4	9	.	3	8	2		-	5	7	.	7	9	8					
1	1	0	0	4	9	.	9	9	1		-	5	7	.	7	9	8					
1	2	0	0	5	0	.	5	7	4		-	5	7	.	7	9	8					
1	3	0	0	5	1	.	1	3	5		-	5	7	.	7	9	8					
1	4	0	0	5	1	.	6	7	5		-	5	7	.	7	9	8					
1	5	0	0	5	2	.	1	9	5		-	5	7	.	7	9	8					
1	6	0	0	5	2	.	6	9	7		-	5	7	.	7	9	8					
1	7	0	0	5	3	.	1	8	2		-	5	7	.	7	9	8					
				b l a n k				c a r d														
FREE				ENERGY				DATA				FOR				C H 4						
				9	0	0		4	9	.	0	9	8		-	1	7	.	8	9	5	
1	0	0	0	5	0	.	0	1	6		-	1	7	.	8	9	5					
1	1	0	0	5	0	.	9	2	2		-	1	7	.	8	9	5					
1	2	0	0	5	1	.	8	1	4		-	1	7	.	8	9	5					
1	3	0	0	5	2	.	6	9	0		-	1	7	.	8	9	5					
1	4	0	0	5	3	.	5	4	8		-	1	7	.	8	9	5					
1	5	0	0	5	4	.	3	8	7		-	1	7	.	8	9	5					
1	6	0	0	5	5	.	2	0	8		-	1	7	.	8	9	5					
1	7	0	0	5	6	.	0	1	0		-	1	7	.	8	9	5					
				b l a n k				c a r d														
FREE				ENERGY				DATA				FOR				N 2						
				9	0	0		4	8	.	8	5	3		0	.	0					
1	0	0	0	4	9	.	3	7	8		0	.	0									
1	1	0	0	4	9	.	8	7	9		0	.	0									
1	2	0	0	5	0	.	3	5	7		0	.	0									
1	3	0	0	5	0	.	8	1	3		0	.	0									
1	4	0	0	5	1	.	2	4	8		0	.	0									
1	5	0	0	5	1	.	6	6	5		0	.	0									
1	6	0	0	5	2	.	0	6	5		0	.	0									
1	7	0	0	5	2	.	4	4	8		0	.	0									
				b l a n k				c a r d														

T °K

 $-(F - H_{298})/T$  $\Delta H_f 298^\circ$ 

FREEE				ENERGY				DATA				FOR O2										
				9	0	0		5	2	.	2	0	9			0	.	0				
				1	0	0		5	2	.	7	6	5			0	.	0				
				1	1	0		5	3	.	2	9	5			0	.	0				
				1	2	0		5	3	.	8	0	1			0	.	0				
				1	3	0		5	4	.	2	8	3			0	.	0				
				1	4	0		5	4	.	7	4	4			0	.	0				
				1	5	0		5	5	.	1	8	5			0	.	0				
				1	6	0		5	5	.	6	0	8			0	.	0				
				1	7	0		5	6	.	0	1	3			0	.	0				
								b	l	a	n	k			c	a	r	d				
FREEE				ENERGY				DATA				FOR H2S										
				9	0	0		5	2	.	9	7	4			-	4	.	8	1	5	
				1	0	0		5	3	.	6	5	4			-	4	.	8	1	5	
				1	1	0		5	4	.	3	1	1			-	4	.	8	1	5	
				1	2	0		5	4	.	9	4	4			-	4	.	8	1	5	
				1	3	0		5	5	.	5	5	3			-	4	.	8	1	5	
				1	4	0		5	6	.	1	4	1			-	4	.	8	1	5	
				1	5	0		5	6	.	7	0	8			-	4	.	8	1	5	
				1	6	0		5	7	.	2	5	5			-	4	.	8	1	5	
				1	7	0		5	7	.	7	8	4			-	4	.	8	1	5	
								b	l	a	n	k			c	a	r	d				
FREEE				ENERGY				DATA				FOR SO2										
				9	0	0		6	3	.	9	8	5			-	7	0	.	9	4	7
				1	0	0		6	4	.	8	2	5			-	7	0	.	9	4	7
				1	1	0		6	5	.	6	3	1			-	7	0	.	9	4	7
				1	2	0		6	6	.	4	0	2			-	7	0	.	9	4	7
				1	3	0		6	7	.	1	4	1			-	7	0	.	9	4	7
				1	4	0		6	7	.	8	4	7			-	7	0	.	9	4	7
				1	5	0		6	8	.	5	2	4			-	7	0	.	9	4	7
				1	6	0		6	9	.	1	6	4			-	7	0	.	9	4	7
				1	7	0		6	9	.	7	9	7			-	7	0	.	9	4	7
								b	l	a	n	k			c	a	r	d				

T °K

 $-(F - H_{298})/T$  $\Delta H_f 298^\circ$ 

FREE E				ENERGY				DATA				FOR				SO					
				9	0	0		5	6	.	3	7	6				0	.	5	1	9
1	0	0	0					5	6	.	9	5	8				0	.	5	1	9
1	1	0	0					5	7	.	5	1	1				0	.	5	1	9
1	2	0	0					5	8	.	0	3	9				0	.	5	1	9
1	3	0	0					5	8	.	5	4	1				0	.	5	1	9
1	4	0	0					5	9	.	0	2	0				0	.	5	1	9
1	5	0	0					5	9	.	4	7	6				0	.	5	1	9
1	6	0	0					5	9	.	9	1	3				0	.	5	1	9
1	7	0	0					6	0	.	3	3	1				0	.	5	1	9
								b l a n k				c a r d									
FREE E				ENERGY				DATA				FOR				COS					
				9	0	0		6	0	.	2	3	9		-	3	3	.	0	8	0
1	0	0	0					6	1	.	1	1	7		-	3	3	.	0	8	0
1	1	0	0					6	1	.	9	6	0		-	3	3	.	0	8	0
1	2	0	0					6	2	.	7	6	7		-	3	3	.	0	8	0
1	3	0	0					6	3	.	5	4	0		-	3	3	.	0	8	0
1	4	0	0					6	4	.	2	8	0		-	3	3	.	0	8	0
1	5	0	0					6	4	.	9	9	0		-	3	3	.	0	8	0
1	6	0	0					6	5	.	6	7	1		-	3	3	.	0	8	0
1	7	0	0					6	6	.	3	2	5		-	3	3	.	0	8	0
								b l a n k				c a r d									
FREE E				ENERGY				DATA				FOR				CS 2					
				9	0	0		6	2	.	1	0	6		2	7	.	9	8	0	
1	0	0	0					6	3	.	0	3	5		2	7	.	9	8	0	
1	1	0	0					6	3	.	9	2	3		2	7	.	9	8	0	
1	2	0	0					6	4	.	7	7	0		2	7	.	9	8	0	
1	3	0	0					6	5	.	5	7	9		2	7	.	9	8	0	
1	4	0	0					6	6	.	3	5	1		2	7	.	9	8	0	
1	5	0	0					6	7	.	0	8	9		2	7	.	9	8	0	
1	6	0	0					6	7	.	7	9	6		2	7	.	9	8	0	
1	7	0	0					6	8	.	4	7	3		2	7	.	9	8	0	
								b l a n k				c a r d									

T °K

 $-(F - H_{298})/T$  $\Delta H_f 298^\circ$ 

F	R	E	E	E	N	E	R	G	Y	D	A	T	A	F	O	R	S	2						
---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--

				9	0	0		5	8	.	0	9	9				3	0	.	8	4	0		
--	--	--	--	---	---	---	--	---	---	---	---	---	---	--	--	--	---	---	---	---	---	---	--	--

1	0	0	0	5	8	.	7	1	2								3	0	.	8	4	0		
---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	---	---	---	---	---	---	--	--

1	1	0	0	5	9	.	2	9	4								3	0	.	8	4	0		
---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	---	---	---	---	---	---	--	--

1	2	0	0	5	9	.	8	4	6								3	0	.	8	4	0		
---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	---	---	---	---	---	---	--	--

1	3	0	0	6	0	.	3	7	1								3	0	.	8	4	0		
---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	---	---	---	---	---	---	--	--

1	4	0	0	6	0	.	8	7	0								3	0	.	8	4	0		
---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	---	---	---	---	---	---	--	--

1	5	0	0	6	1	.	3	4	4								3	0	.	8	4	0		
---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	---	---	---	---	---	---	--	--

1	6	0	0	6	1	.	7	9	7								3	0	.	8	4	0		
---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	---	---	---	---	---	---	--	--

1	7	0	0	6	2	.	2	3	0								3	0	.	8	4	0		
---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	---	---	---	---	---	---	--	--

				b	l	a	n	k	c	a	r	d											
--	--	--	--	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	--	--	--	--

F	R	E	E	E	N	E	R	G	Y	D	A	T	A	F	O	R	N	A	2						
---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--

				9	0	0		5	8	.	9	5	0				3	2	.	8	7	0		
--	--	--	--	---	---	---	--	---	---	---	---	---	---	--	--	--	---	---	---	---	---	---	--	--

1	0	0	0	5	9	.	6	1	1								3	2	.	8	7	0		
---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	---	---	---	---	---	---	--	--

1	1	0	0	6	0	.	2	3	7								3	2	.	8	7	0		
---	---	---	---	---	---	---	---	---	---	--	--	--	--	--	--	--	---	---	---	---	---	---	--	--

1	2	0	0	6	0	.	8	2	9								3	2	.	8	7	0		
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1	3	0	0	6	1	.	3	9	1								3	2	.	8	7	0		
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1	4	0	0	6	1	.	9	2	4								3	2	.	8	7	0		
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1	5	0	0	6	2	.	4	3	2								3	2	.	8	7	0		
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1	6	0	0	6	2	.	9	1	5								3	2	.	8	7	0		
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1	7	0	0	6	3	.	3	7	7								3	2	.	8	7	0		
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				b	l	a	n	k	c	a	r	d											
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F	R	E	E	E	N	E	R	G	Y	D	A	T	A	F	O	R	N	A	H						
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				9	0	0		4	8	.	3	8	0				2	9	.	7	0	0		
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1	0	0	0	4	8	.	9	6	7								2	9	.	7	0	0		
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1	1	0	0	4	9	.	5	2	8								2	9	.	7	0	0		
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1	2	0	0	5	0	.	0	6	2								2	9	.	7	0	0		
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1	3	0	0	5	0	.	5	7	2								2	9	.	7	0	0		
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1	4	0	0	5	1	.	0	5	8								2	9	.	7	0	0		
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1	5	0	0	5	1	.	5	2	2								2	9	.	7	0	0		
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1	6	0	0	5	1	.	9	6	6								2	9	.	7	0	0		
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1	7	0	0	5	2	.	3	9	2								2	9	.	7	0	0		
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				b	l	a	n	k	c	a	r	d											
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T °K

 $-(F - H_{298})/T$  $\Delta H_f 298^\circ$ 

F	R	E	E	E	N	E	R	G	Y	D	A	T	A	F	O	R	N	A	O	H						
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	9	0	0		6	1	.	3	5	0				-	5	5	.	4	4	0			
1	0	0	0		6	2	.	1	2	3				-	5	5	.	4	4	0			
1	1	0	0		6	2	.	8	6	2				-	5	5	.	4	4	0			
1	2	0	0		6	3	.	5	6	7				-	5	5	.	4	4	0			
1	3	0	0		6	4	.	2	4	1				-	5	5	.	4	4	0			
1	4	0	0		6	4	.	8	8	6				-	5	5	.	4	4	0			
1	5	0	0		6	5	.	5	0	3				-	5	5	.	4	4	0			
1	6	0	0		6	6	.	0	9	5				-	5	5	.	4	4	0			
1	7	0	0		6	6	.	6	6	4				-	5	5	.	4	4	0			

b l a n k c a r d

F	R	E	E	E	N	E	R	G	Y	D	A	T	A	F	O	R	C	(	S	)						
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	9	0	0			2	.	7	3	6					0	.	0						
1	0	0	0			3	.	0	2	0					0	.	0						
1	1	0	0			3	.	3	0	0					0	.	0						
1	2	0	0			3	.	5	7	3					0	.	0						
1	3	0	0			3	.	8	3	9					0	.	0						
1	4	0	0			4	.	0	9	8					0	.	0						
1	5	0	0			4	.	3	4	8					0	.	0						
1	6	0	0			4	.	5	9	1					0	.	0						
1	7	0	0			4	.	8	2	7					0	.	0						

b l a n k c a r d

F	R	E	E	E	N	E	R	G	Y	D	A	T	A	F	O	R	N	A	2	C	O	3	(	C	)						
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	9	0	0		4	7	.	0	5	9				-	2	7	0	.	3	0	0			
1	0	0	0		4	9	.	8	3	0				-	2	7	0	.	3	0	0			
1	1	0	0		5	2	.	5	0	2				-	2	7	0	.	3	0	0			
1	2	0	0		5	5	.	0	8	0				-	2	7	0	.	3	0	0			
1	3	0	0		5	7	.	5	7	0				-	2	7	0	.	3	0	0			
1	4	0	0		6	0	.	2	9	0				-	2	7	0	.	3	0	0			
1	5	0	0		6	2	.	7	3	0				-	2	7	0	.	3	0	0			
1	6	0	0		6	5	.	1	6	0				-	2	7	0	.	3	0	0			
1	7	0	0		6	7	.	3	4	0				-	2	7	0	.	3	0	0			

b l a n k c a r d





**SAMPLE OUTPUT**

EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

TEMPERATURE	900.	1000.	1100.	1200.	1300.	1400.	1500.
SPECIES	VALUES OF ( F/RT )						
CO	-40.0897	-38.8798	-37.9260	-37.1619	-36.5418	-36.0333	-35.6126
CO2	-80.5407	-75.6909	-71.7827	-68.5761	-65.9064	-63.6556	-61.7385
H2	-17.2353	-17.4909	-17.7335	-17.9630	-18.1814	-18.3892	-18.5875
H2O	-56.8483	-53.9352	-51.5975	-49.6875	-48.1054	-46.7790	-45.6557
CH4	-34.7128	-34.1742	-33.8115	-33.5782	-33.4417	-33.3787	-33.3721
N2	-24.5838	-24.8480	-25.1001	-25.3407	-25.5701	-25.7891	-25.9989
O2	-26.2726	-26.5524	-26.8191	-27.0738	-27.3163	-27.5483	-27.7702
H2S	-29.3498	-29.4228	-29.5331	-29.6681	-29.8193	-29.9820	-30.1520
SO2	-71.8675	-68.3233	-65.4832	-63.1665	-61.2498	-59.6434	-58.2840
SO	-28.0794	-28.4013	-28.7033	-28.9888	-29.2581	-29.5135	-29.7554
COS	-48.8097	-47.4019	-46.3128	-45.4578	-44.7797	-44.2374	-43.8020
CS2	-15.6084	-17.6404	-19.3673	-20.8602	-22.1698	-23.3320	-24.3738
S2	-11.9929	-14.0258	-15.7295	-17.1830	-18.4420	-19.5458	-20.5233
NA2	-11.2861	-13.4566	-15.2754	-16.8264	-18.1695	-19.3465	-20.3898
NAH	-7.7395	-9.6956	-11.3366	-12.7375	-13.9522	-15.0180	-15.9632
NAOH	-61.8710	-59.1601	-56.9958	-55.2370	-53.7878	-52.5795	-51.5615
C(S)	-1.3768	-1.5197	-1.6606	-1.7980	-1.9319	-2.0622	-2.1880
NA2CO3(C)	-174.8150	-161.0960	-150.0751	-141.0678	-133.6016	-127.4967	-122.2474
NA2S(C)	-65.5478	-61.1614	-57.6842	-54.8108	-52.4693	-50.5485	-49.0791
NA2SO4(C)	-213.1413	-196.1906	-182.5469	-171.4565	-162.3347	-154.6483	-148.1012

EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

TEMPERATURE	1600.	1700.
SPECIES	VALUES OF ( F/RT )	
CO	-35.2620	-34.9685
CO2	-60.0900	-58.6614
H2	-18.7772	-18.9588
H2O	-44.6964	-43.8712
CH4	-33.4100	-33.4825
N2	-26.2002	-26.3929
O2	-27.9831	-28.1869
H2S	-30.3263	-30.5034
SO2	-57.1185	-56.1245
SO	-29.9862	-30.2062
COS	-43.4511	-43.1682
CS2	-25.3163	-26.1746
S2	-21.3979	-22.1864
NA2	-21.3221	-22.1627
NAH	-16.8093	-17.5732
NAOH	-50.6970	-49.9576
C(S)	-2.3103	-2.4290
NA2CO3(C)	-117.8027	-113.8990
NA2S(C)	-47.8814	-46.8765
NA2SO4(C)	-142.4687	-137.5853

EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

	PRESSURE: 1.00 ATMOS.			PER CENT TOTAL AIR: 60.0					
TEMPERATURE	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)	1700 K (2601 F)
SPECIES( GASEOUS )	LB MOLS / 100 LBS OF FEED								
CO	0.357E 00	0.546E 00	0.563E 00	0.578E 00	0.604E 00	0.663E 00	0.730E 00	0.736E 00	0.744E 00
CO2	0.244E 00	0.161E 00	0.148E 00	0.136E 00	0.130E 00	0.137E 00	0.153E 00	0.147E 00	0.139E 00
H2	0.291E 00	0.328E 00	0.315E 00	0.300E 00	0.274E 00	0.215E 00	0.148E 00	0.142E 00	0.135E 00
H2O	0.859E-01	0.672E-01	0.834E-01	0.961E-01	0.103E 00	0.957E-01	0.798E-01	0.845E-01	0.857E-01
CH4	0.916E-02	0.116E-02	0.722E-04	0.697E-05	0.878E-06	0.102E-06	0.109E-07	0.291E-08	0.922E-09
N2	0.199E 01	0.199E 01	0.199E 01	0.199E 01	0.199E 01	0.199E 01	0.199E 01	0.199E 01	0.199E 01
O2	0.261E-23	0.978E-21	0.371E-18	0.510E-16	0.330E-14	0.131E-12	0.354E-11	0.533E-10	0.553E-09
H2S	0.432E-02	0.268E-02	0.926E-03	0.406E-03	0.199E-03	0.120E-03	0.150E-03	0.798E-03	0.267E-02
SO2	0.134E-10	0.727E-10	0.507E-09	0.269E-08	0.115E-07	0.590E-07	0.608E-06	0.130E-04	0.143E-03
SO	0.700E-12	0.109E-10	0.104E-09	0.723E-09	0.389E-08	0.232E-07	0.262E-06	0.649E-05	0.829E-04
COS	0.178E-03	0.147E-03	0.545E-04	0.259E-04	0.146E-04	0.125E-04	0.254E-04	0.144E-03	0.517E-03
CS2	0.298E-07	0.308E-07	0.459E-08	0.112E-08	0.374E-09	0.259E-09	0.946E-09	0.315E-07	0.429E-06
S2	0.318E-08	0.110E-07	0.102E-07	0.113E-07	0.132E-07	0.270E-07	0.257E-06	0.197E-04	0.543E-03
NA2	0.180E-16	0.110E-12	0.537E-10	0.887E-08	0.624E-06	0.178E-04	0.124E-03	0.186E-03	0.291E-03
NAH	0.337E-11	0.589E-09	0.234E-07	0.489E-06	0.606E-05	0.417E-04	0.126E-03	0.201E-03	0.317E-03
NAOH	0.201E-05	0.545E-04	0.822E-03	0.751E-02	0.459E-01	0.179E 00	0.344E 00	0.345E 00	0.352E 00
TOTAL	0.298E 01	0.310E 01	0.310E 01	0.311E 01	0.315E 01	0.328E 01	0.345E 01	0.345E 01	0.345E 01
SPECIES( CONDENSED )	LB MOLS / 100 LBS OF FEED								
C(S)	0.963E-01	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99
NA2CO3(C)	0.176E 00	0.175E 00	0.173E 00	0.169E 00	0.149E 00	0.828E-01	0.000E-99	0.000E-99	0.000E-99
NA2S(C)	0.000E-99	0.168E-02	0.352E-02	0.407E-02	0.429E-02	0.437E-02	0.432E-02	0.350E-02	0.000E-99
NA2SO4(C)	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99
TOTAL	0.273E 00	0.176E 00	0.176E 00	0.173E 00	0.154E 00	0.872E-01	0.432E-02	0.350E-02	0.000E-99

EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQDOR

PRESSURE: 1.00 ATMOS.

PER CENT TOTAL AIR: 60.0

TEMPERATURE	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)	1700 K (2601 F)
SPECIES( GASEOUS )									
	VOLUME PERCENT								
CO	0.120E 02	0.176E 02	0.181E 02	0.186E 02	0.192E 02	0.202E 02	0.212E 02	0.214E 02	0.216E 02
CO2	0.817E 01	0.521E 01	0.476E 01	0.438E 01	0.412E 01	0.418E 01	0.445E 01	0.427E 01	0.403E 01
H2	0.977E 01	0.106E 02	0.102E 02	0.964E 01	0.871E 01	0.655E 01	0.430E 01	0.412E 01	0.393E 01
H2O	0.288E 01	0.217E 01	0.269E 01	0.309E 01	0.327E 01	0.292E 01	0.232E 01	0.245E 01	0.248E 01
CH4	0.307E 00	0.376E-01	0.233E-02	0.224E-03	0.279E-04	0.312E-05	0.315E-06	0.845E-07	0.267E-07
N2	0.667E 02	0.643E 02	0.642E 02	0.640E 02	0.632E 02	0.607E 02	0.578E 02	0.577E 02	0.577E 02
O2	0.874E-22	0.316E-19	0.120E-16	0.164E-14	0.105E-12	0.400E-11	0.103E-09	0.155E-08	0.160E-07
H2S	0.145E 00	0.864E-01	0.299E-01	0.131E-01	0.632E-02	0.367E-02	0.437E-02	0.232E-01	0.774E-01
SO2	0.450E-09	0.235E-08	0.164E-07	0.867E-07	0.367E-06	0.180E-05	0.176E-04	0.377E-03	0.416E-02
SO	0.235E-10	0.354E-09	0.335E-08	0.232E-07	0.124E-06	0.708E-06	0.759E-05	0.188E-03	0.240E-02
COS	0.596E-02	0.475E-02	0.176E-02	0.833E-03	0.465E-03	0.382E-03	0.737E-03	0.417E-02	0.150E-01
CS2	0.100E-05	0.995E-06	0.148E-06	0.361E-07	0.119E-07	0.789E-08	0.275E-07	0.913E-06	0.124E-04
S2	0.107E-06	0.356E-06	0.330E-06	0.362E-06	0.419E-06	0.823E-06	0.747E-05	0.573E-03	0.157E-01
NA2	0.604E-15	0.357E-11	0.173E-08	0.285E-06	0.198E-04	0.544E-03	0.359E-02	0.539E-02	0.845E-02
NAH	0.113E-09	0.190E-07	0.756E-06	0.157E-04	0.193E-03	0.127E-02	0.366E-02	0.583E-02	0.918E-02
NAOH	0.673E-04	0.176E-02	0.265E-01	0.241E 00	0.146E 01	0.545E 01	0.998E 01	0.100E 02	0.102E 02
SPECIES( CONDENSED )									
	LBS / 100 LBS OF FEED								
C(S)	0.116E 01	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99
NA2CO3(C)	0.187E 02	0.185E 02	0.183E 02	0.179E 02	0.158E 02	0.878E 01	0.000E-99	0.000E-99	0.000E-99
NA2S(C)	0.000E-99	0.131E 00	0.275E 00	0.317E 00	0.335E 00	0.341E 00	0.337E 00	0.273E 00	0.000E-99
NA2SO4(C)	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99	0.000E-99
TOTAL	0.199E 02	0.187E 02	0.186E 02	0.182E 02	0.162E 02	0.912E 01	0.337E 00	0.273E 00	0.000E-99

EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

PRESSURE: 1.00 ATMOS.

PER CENT TOTAL AIR: 60.0

TEMPERATURE	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)	1700 K (2601 F)
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SPECIES( GASEOUS )

VOLUME PERCENT

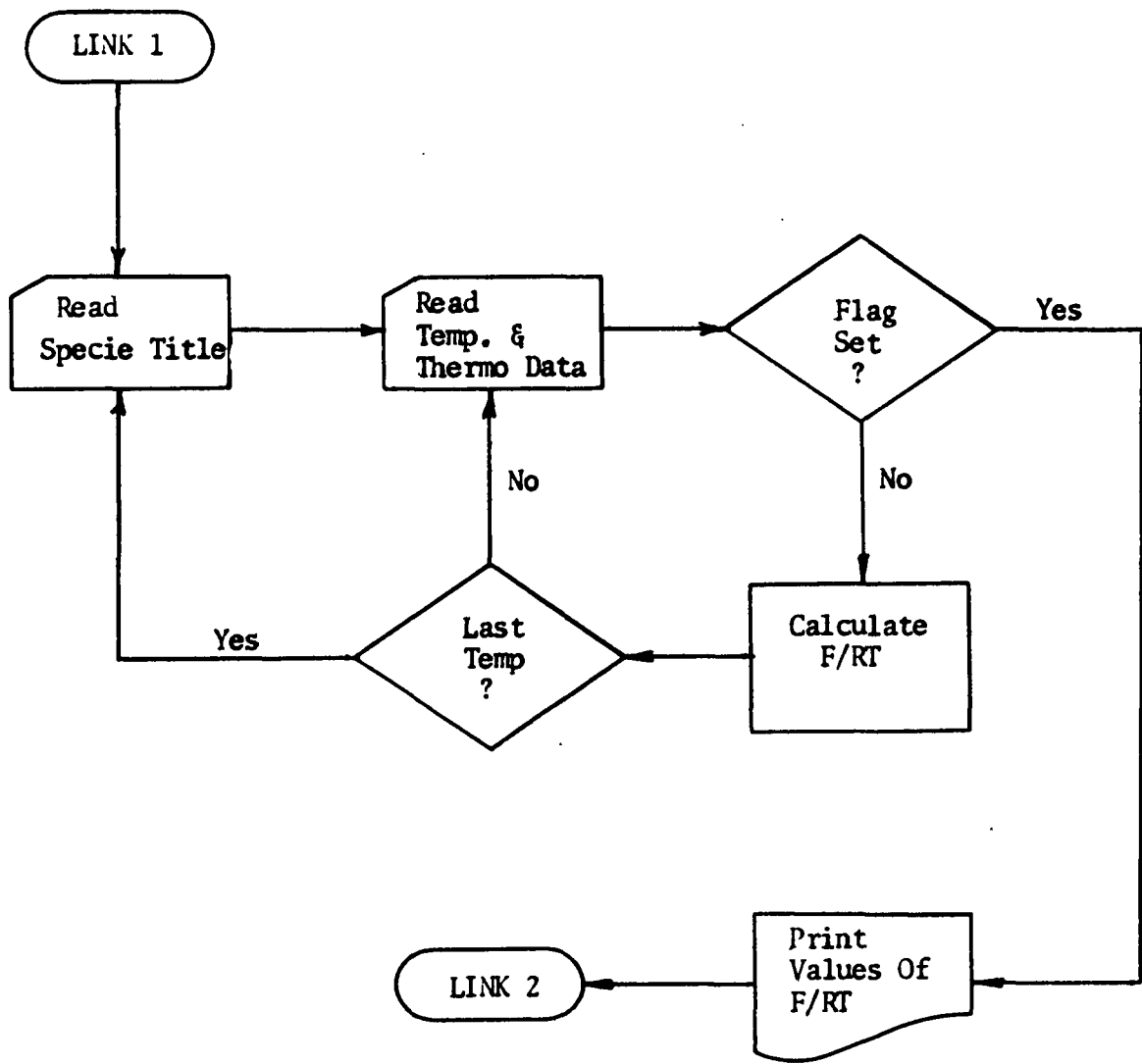
CO	11.984	17.621	18.143	18.606	19.196	20.219	21.181	21.352	21.552
CO2	8.167	5.212	4.765	4.376	4.121	4.181	4.448	4.268	4.025
H2	9.774	10.588	10.164	9.642	8.706	6.551	4.297	4.118	3.926
H2O	2.881	2.170	2.689	3.093	3.270	2.918	2.315	2.451	2.482
CH4	.307	.038	.002	.000	.000	.000	.000	.000	.000
N2	66.736	64.279	64.179	64.027	63.241	60.679	57.762	57.747	57.677
H2S	.145	.086	.030	.013	.006	.004	.004	.023	.077
COS	.006	.005	.002	.001	.000	.000	.001	.004	.015
S2	.000	.000	.000	.000	.000	.000	.000	.001	.016
NAOH	.000	.002	.027	.241	1.458	5.446	9.984	10.024	10.205

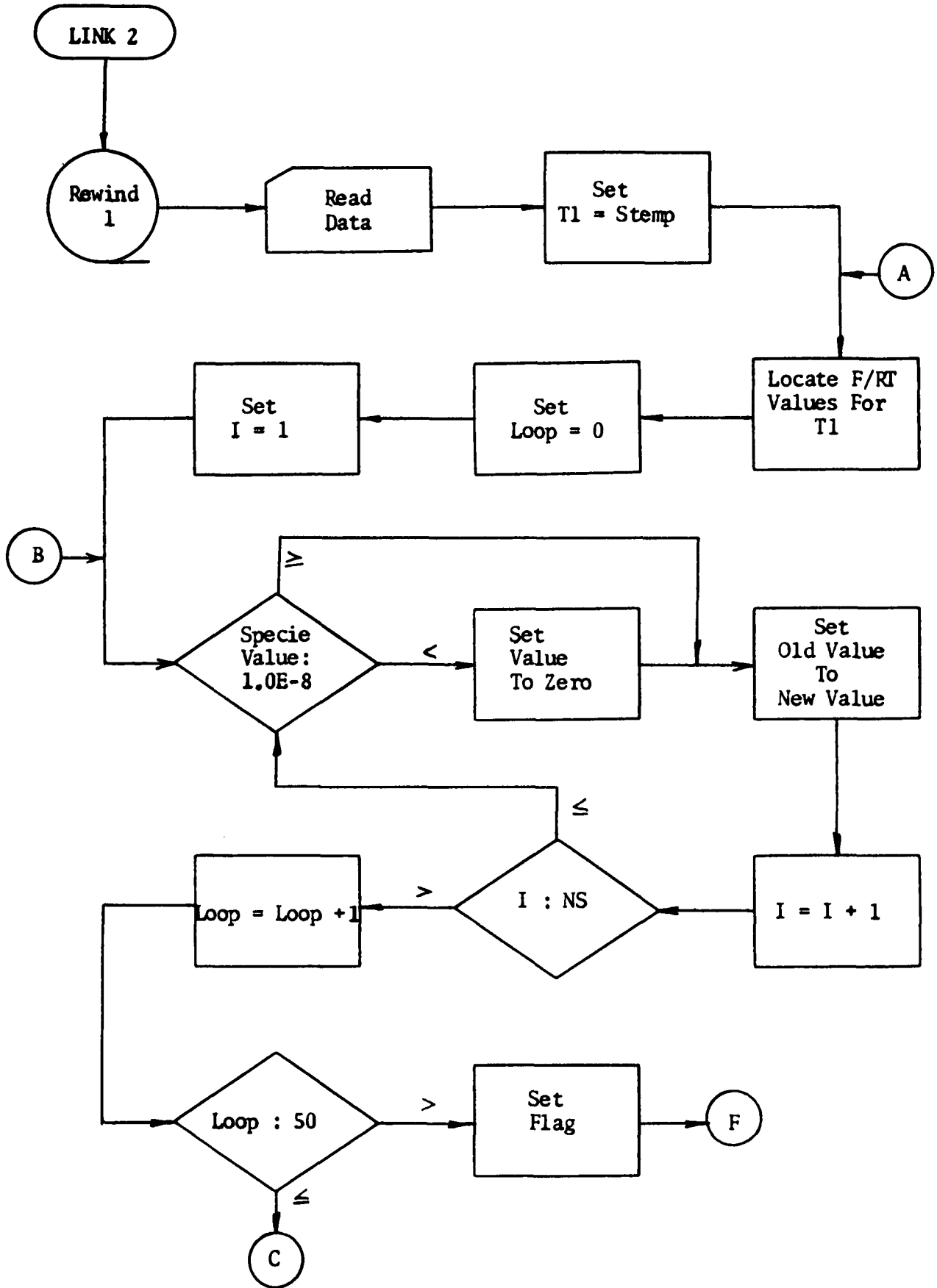
SPECIES( CONDENSED )

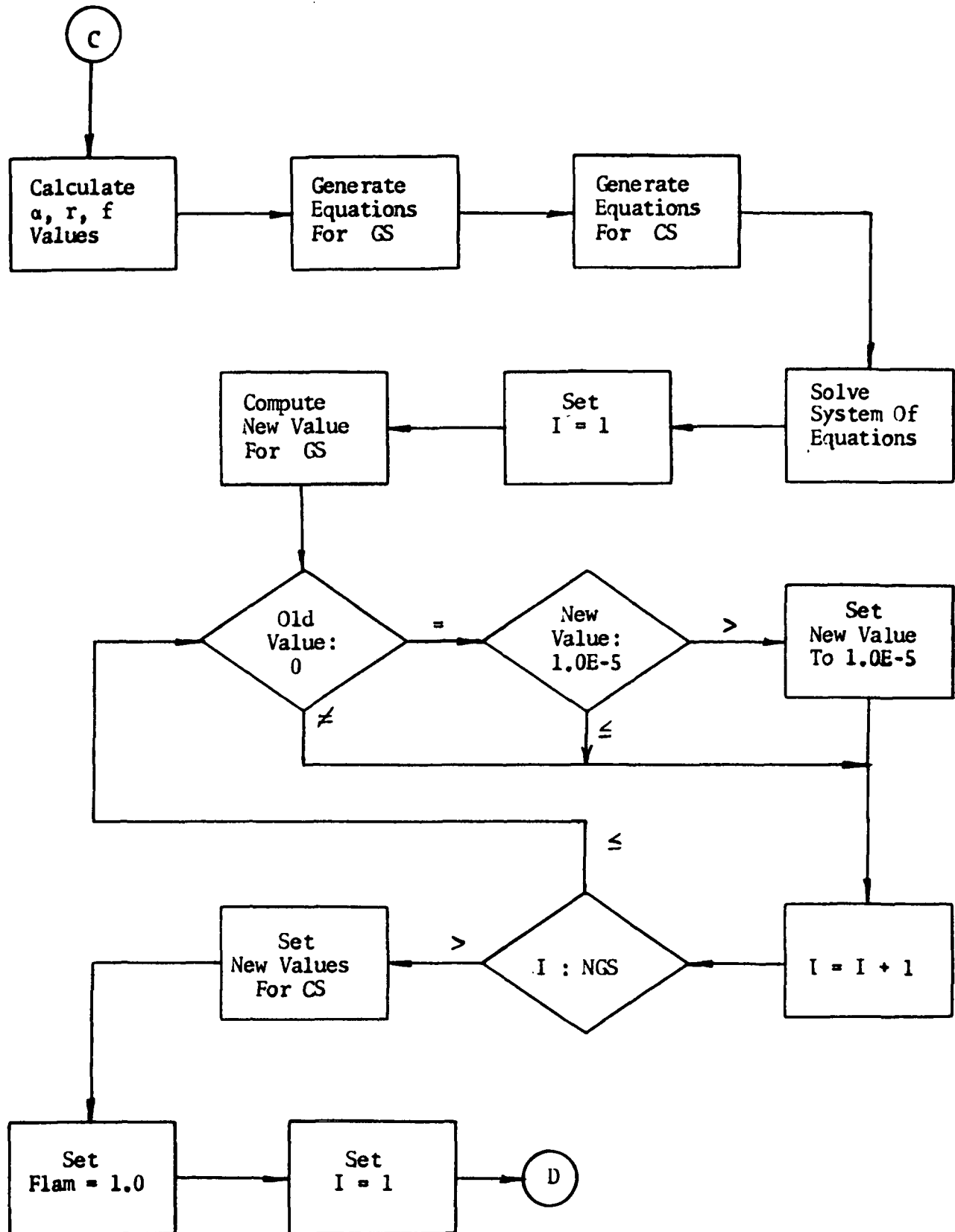
LBS / 100 LBS OF FEED

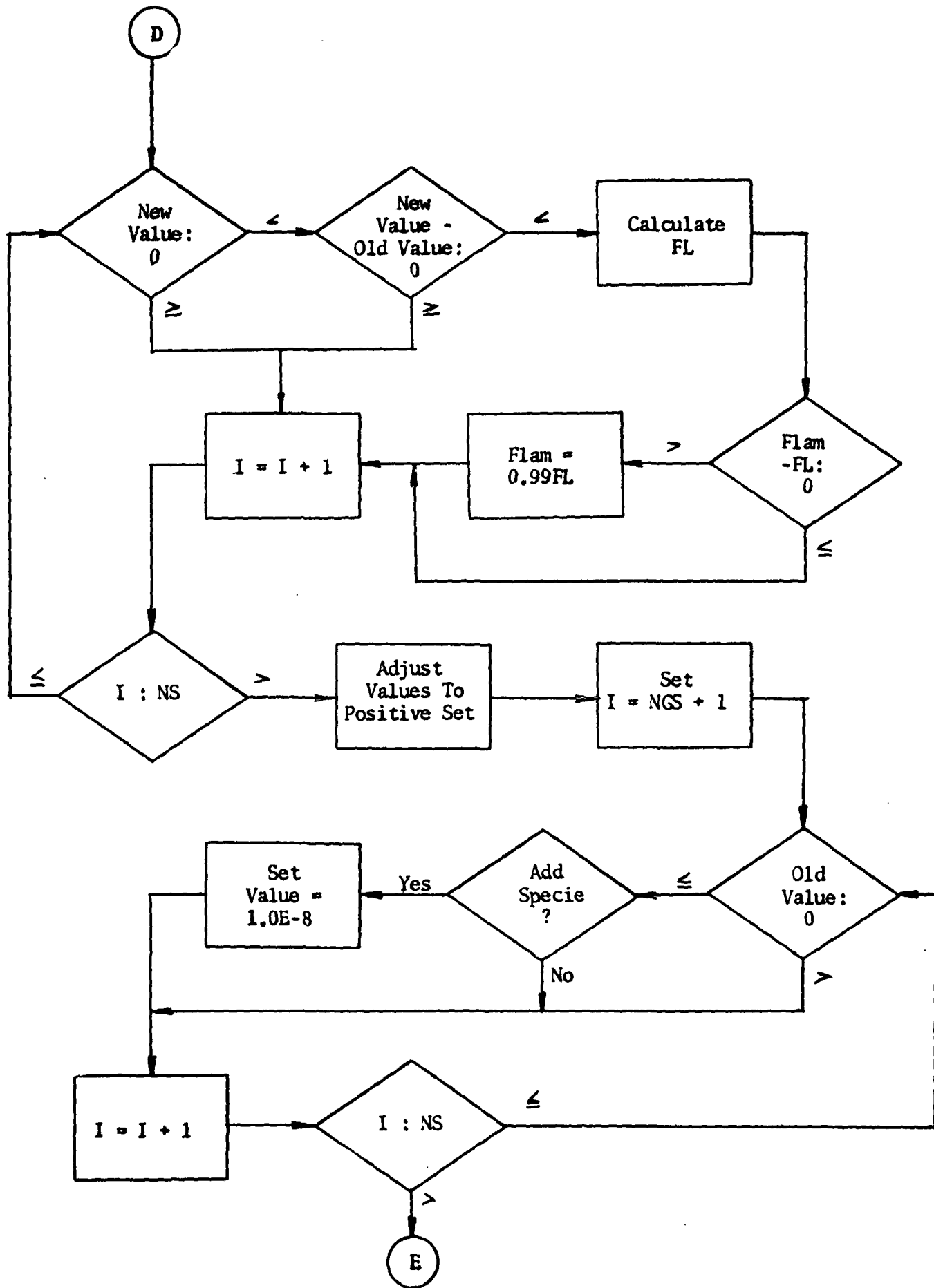
C(S)	1.1564	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
NA2CO3(C)	18.7096	18.5291	18.2927	17.8807	15.8234	8.7762	.0000	.0000	.0000
NA2S(C)	.0000	.1309	.2750	.3175	.3346	.3409	.3375	.2732	.0000
TOTAL	19.8660	18.6600	18.5677	18.1981	16.1579	9.1171	.3375	.2732	.0000

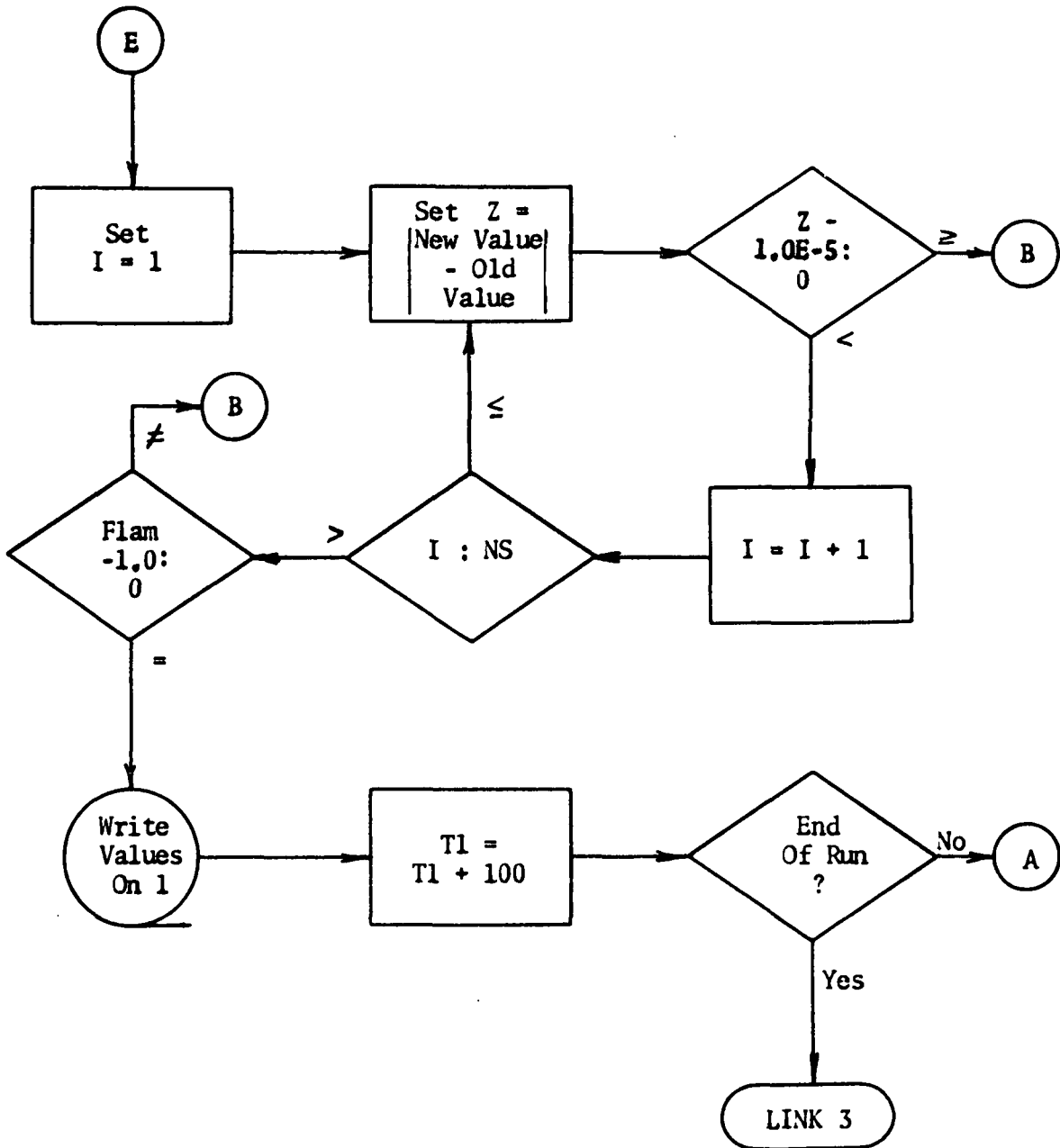
**FLOWCHARTS**

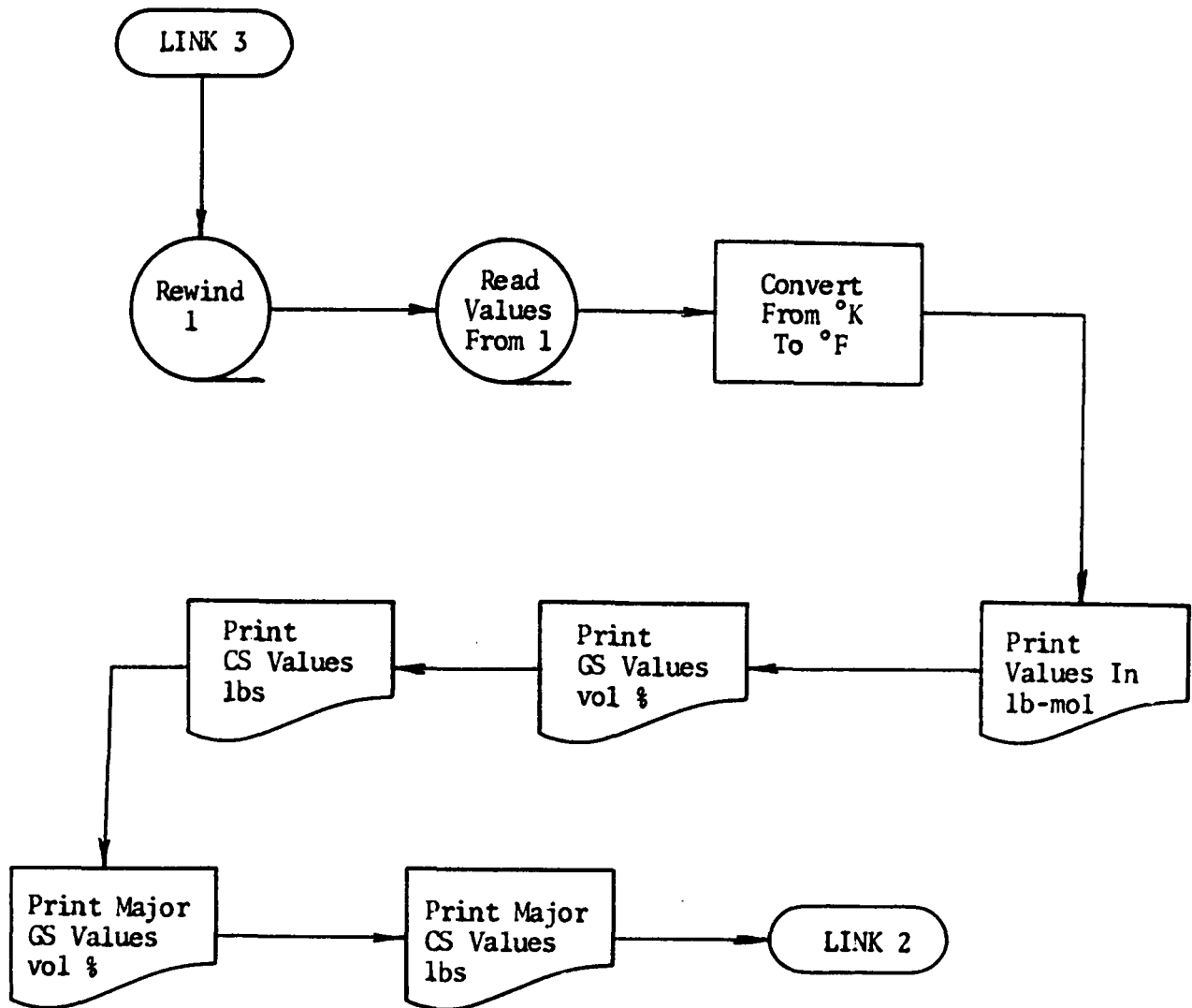












**PROGRAM LISTING**

```

C      CHEMICAL EQUILIBRIUM BY FREE ENERGY MINIMIZATION METHOD

C      LINK 1 - CALCULATION OF THERMODYNAMIC CONSTANT ( F/RT )
          DIMENSION TEMP( 20), FRT( 40, 20), THERM1( 20), THERM2( 20),
1          TITLE( 40)
          COMMON TEMP, FRT

C
C      READ THERMODYNAMIC DATA AND CALCULATE ( F/RT ) FOR EACH SPECIE
C
          NS = 1
          50 NT = 1
          100 READ 101, TITLE(NS)
          101 FORMAT( A31 )
          120 READ 121, TEMP1,      THERM1(NT), THERM2(NT)
          121 FORMAT( F4.0, 2F8.4 )
          IF ( TEMP1      ) 400, 200, 130
          130 TEMP(NT) = TEMP1
          NT = NT + 1
          GO TO 120
          200 NT = NT - 1
          DO 230 I = 1, NT

```

```

230 FRT( NS, I) = - THERM1(I) / 1.9872 + THERM2(I) / ( 1.9872 *
      1      TEMP(I) ) * 1000.0
      NS = NS + 1
430 NTEMP = NT
      GO TO 50
C
C      PRINT OUT VALUES OF TEMPERATURE AND ( F/RT ) FOR EACH SPECIE
C
400 NS = NS - 1
      NT1 = 1
      NT4 = 7
450 PRINT 451
451 FORMAT( 1H1, 19X, 38HEQUILIBRIUM COMPOSITION OF COMBUSTION ,
      1      25HPRODUCTS OF BLACK LIQUOR )
      IF ( NTEMP = NT4 ) 460, 480, 480
460 NT4 = NTEMP
480 PRINT 481, ( TEMP(I), I = NT1, NT4 )
481 FORMAT( // 1H0, 11HTEMPERATURE, 7( 5X, F5.0, 3X ) )
      PRINT 501
501 FORMAT( 1H0, 8H SPECIES, 38X, 18HVALUES OF ( F/RT ) / )
      LINE = 32

```

```
DO 510 I = 1, NS
LINE = LINE + 1
IF ( LINE ) 1000, 1000, 510
1000 LINE = 32
PRINT 451
PRINT 481, ( TEMP(I), I = NT1, NT4 )
PRINT 501
510 PRINT 511, TITLE(I), ( FRT( I, II), II = NT1, NT4 )
511 FORMAT( 1H , A10, 7( 3X, F9.4, 1X ) )
NT1 = NT4 + 1
NT4 = NT4 + 7
IF ( NTEMP - NT1 ) 600, 450, 450
600 CALL CHAIN( 2, 3 )
END
```

C CHEMICAL EQUILIBRIUM BY FREE ENERGY MINIMIZATION METHOD

C LINK 2 - FREE ENERGY CALCULATIONS

DIMENSION TEMP( 20), FRT( 40, 20), B( 10), AW( 10), TITLE( 40),

1 A( 40, 10), Y( 40), F( 40), ALPHA( 10),

2 R( 10, 10), Y1( 40), X( 21, 22), NONCON( 9)

COMMON TEMP, FRT, TITLE, AW, A, NONCON

COMMON NE, NGS, NCS, NS, STEMP, P, AIR

100 REWIND 1

READ 121, NE, NGS, NCS, STEMP, P, AIR

121 FORMAT( 3I2, F4.0, F4.2, F3.0 )

READ 141, ( B(I), I = 1, NE )

READ 142, ( AW(I), I = 1, NE )

141 FORMAT( 10F6.4 )

142 FORMAT( 10F6.3 )

NS = NGS + NCS

DO 150 I = 1, NS

150 READ 151, TITLE(I), Y(I), ( A(I,II), II = 1, NE )

151 FORMAT( A10, F6.4, 10( 4X, F2.0 ) )

T1 = STEMP

ITEMP = 1

200 IF ( TEMP(ITEMP) - T1 ) 210, 250, 220

210 ITEMP = ITEMP + 1

GO TO 200

220 PAUSE 9669

C

C FIND SOLUTION FOR EACH TEMPERATURE

C

250 NGS1 = NGS + 1

NE1 = NE + 1

DO 1100 IT = 1, 9

LOOP = 0

NONCON(IT) = 0

260 DO 270 I = 1, NS

IF ( Y(I) - 1.0E-8 ) 265, 270, 270

265 Y(I) = 0.0

270 Y1(I) = Y(I)

LOOP = LOOP + 1

IF ( LOOP - 50 ) 280, 280, 275

275 NONCON(IT) = 1

GO TO 1080

280 N = NE1

```
      IF ( NS - NGS1 ) 350, 300, 300
300 DO 340 I = NGS1, NS
      IF ( Y(I) ) 320, 340, 320
320 N = N + 1
340 CONTINUE
350 N1 = N + 1
      DO 370 I = 1, N
      DO 370 J = 1, N1
370 X(I,J) = 0.0
```

C

C FIND VALUES OF ALPHA, R, AND F

C

```
      IF ( SENSE SWITCH 1 ) 390, 400
390 PRINT, ( Y(I), I = 1, NS )
400 YBAR = 0.0
      DO 420 I = 1, NGS
420 YBAR = YBAR + Y(I)
      DO 440 I = 1, NGS
440 F(I) = Y(I) * ( FRT(I,ITEMP) + LOGF( P ) + LOGF( Y(I)/YBAR ) )
      DO 480 J = 1, NE
      ALPHA(J) = 0.0
```

```

DO 460 K = 1, NE
R(J,K) = 0.0
DO 460 I = 1, NGS
460 R(J,K) = R(J,K) + A(I,J) * A(I,K) * Y(I)
DO 480 I = 1, NGS
480 ALPHA(J) = ALPHA(J) + A(I,J) * Y(I)

```

C

C SET UP THE SYSTEM OF EQUATIONS

C

C

C EQUATIONS FOR GASEOUS SPECIES

C

```

DO 550 I = 1, NE
X(I,N1) = B(I)
X(I,1) = ALPHA(I)
II = N - NE + I
X(NE1,II) = ALPHA(I)
DO 530 J = 1, NE
JJ = N - NE + J
530 X(I,JJ) = R(I,J)
DO 550 J = 1, NGS

```

```
550 X(I,N1) = X(I,N1) + A(J,I) * F(J)
```

```
DO 570 I = 1, NGS
```

```
570 X(NE1,N1) = X(NE1,N1) + F(I)
```

```
IF ( NS - NGS1 ) 680, 600, 600
```

```
C
```

```
C EQUATIONS FOR CONDENSED SPECIES
```

```
C
```

```
600 NC = 0
```

```
DO 650 I = NGS1, NS
```

```
IF ( Y(I) ) 620, 650, 620
```

```
620 NC = NC + 1
```

```
NN = NE1 + NC
```

```
X(NN,N1) = FRT(I,ITEMP)
```

```
DO 640 J = 1, NE
```

```
NJ = N - NE + J
```

```
X(J,NC+1) = A(I,J)
```

```
640 X(NN,NJ) = A(I,J)
```

```
650 CONTINUE
```

```
C
```

```
C SOLVE THE SYSTEM OF EQUATIONS
```

```
C
```

```
680 IF ( SENSE SWITCH 2 ) 685, 690
685 PRINT, ( ( X(I,J), J = 1, N1 ), I = 1, N )
690 CALL GPIVOT( N, X )
```

C

C COMPUTE NEW VALUES

C

```
DO 780 I = 1, NGS
SUM = 0.0
DO 700 J = 1, NE
NN = N - NE + J
700 SUM = SUM + X(NN,N1) * A(I,J)
IF ( Y1(I) ) 720, 750, 720
720 Y(I) = Y1(I) * ( - FRT(I,ITEMP) - LOGF( P ) - LOGF( Y1(I)/YBAR )
1 + X(1,N1) + SUM )
GO TO 780
750 Y(I) = YBAR * EXPF( - FRT(I,ITEMP) + SUM )
IF ( Y(I) - 1.0E-5 ) 770, 770, 760
760 Y(I) = 1.0E-5
GO TO 780
770 IF ( Y(I) - 1.0E-90 ) 775, 780, 780
775 Y(I) = 1.0E-90
```

780 CONTINUE

IF ( NS - NGS1 ) 850, 800, 800

800 NC = 1

DO 840 I = NGS1, NS

IF ( Y1(I) ) 820, 840, 820

820 NC = NC + 1

Y(I) = X(NC, N1)

840 CONTINUE

C

C ADJUST NEW VALUES TO A POSITIVE SET

C

850 FLAM = 1.0

DO 900 I = 1, NS

IF ( Y(I) ) 855, 900, 900

855 IF ( Y(I) - Y1(I) ) 860, 900, 900

860 FL = - Y1(I) / ( Y(I) - Y1(I) )

IF ( FLAM - FL ) 900, 900, 880

880 FLAM = 0.99 \* FL

900 CONTINUE

IF ( SENSE SWITCH 3 ) 905, 910

905 PRINT, FLAM

```
      PRINT, ( Y(I), I = 1, NS )
910 DO 920 I = 1, NS
920 Y(I) = Y1(I) + FLAM * (Y(I) - Y1(I))
      IF ( NS - NGS1 ) 1050, 950, 950
950 DO 1000 I = NGS1, NS
      IF ( Y1(I) ) 955, 955, 1000
955 SUM = 0.0
      DO 960 J = 1, NE
      NN = N - NE + J
960 SUM = SUM + X(NN,N1) * A(I,J)
      DIF = FRT(I,ITEMP) - SUM
      IF ( DIF ) 980, 1000, 1000
980 IF ( ABSF( DIF / FRT(I,ITEMP) ) - 1.0E-3 ) 1000, 990, 990
990 Y(I) = 1.0E-8
1000 CONTINUE
C
C      CHECK FOR CONVERGENCE
C
1050 DO 1070 I = 1, NS
      IF ( ABSF( Y(I) - Y1(I) ) - 1.0E-5 ) 1070, 260, 260
1070 CONTINUE
```

```

      IF ( FLAM - 1.0 ) 260, 1080, 260
1080 WRITE TAPE 1, ( Y(I), I = 1, NS )
      T1 = T1 + 100.0
      ITEMP = ITEMP + 1
1100 CONTINUE
      CALL CHAIN( 3, 3 )
      END

```

```

SUBROUTINE GPIVOT( N, A )

```

```

  DIMENSION A(21,22)

```

```

C
C
C

```

```

  N1=N+1

```

```

4 DO 8 I=1,N

```

```

  I1=I+1

```

```

  IF ( I-N ) 40,45,45

```

```

40 Q=ABSF(A(I,I))

```

```

  MAX=0

```

```

  DO 42 J=I1,N

```

```

  P=ABSF(A(J,I))

```

```

  IF ( Q-P ) 41,42,42

```

```

GPIVOT

```

```

GPIVOT

```

```

GPIVOT

```

```

GPIVOT

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GPIVOT

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```

GPIVOT

```

41 Q=P	GPIVOT
MAX=J	GPIVOT
42 CONTINUE	GPIVOT
IF (MAX) 45,45,43	GPIVOT
43 DO 44 K=I,N1	GPIVOT
B=A(I,K)	GPIVOT
A(I,K)=A(MAX,K)	GPIVOT
44 A(MAX,K)=B	GPIVOT
45 Z=A(I,I)	GPIVOT
DO 5 J=I1,N1	GPIVOT
5 A(I,J)=A(I,J)/Z	GPIVOT
IF (I-N) 6,8,6	GPIVOT
6 DO 7 K=I1,N	GPIVOT
DO 7 J=I1,N1	GPIVOT
7 A(K,J)=A(K,J)-A(K,I)*A(I,J)	GPIVOT
8 CONTINUE	GPIVOT
N2=N-1	GPIVOT
DO 9 K=1,N2	GPIVOT
I=N-K	GPIVOT
I1=I+1	GPIVOT
DO 9 J=I1,N	GPIVOT

9 A(I,N1)=A(I,N1)-A(I,J)\*A(J,N1)

GPIVOT

RETURN

GPIVOT

END

GPIVOT

```
DIMENSION TEMP( 20), FRT( 40, 20), TITLE( 40), AW( 10),  
1      A( 40, 10), Y( 40, 9), ITEMP( 9), JTEMP( 9), TOTC( 9)  
2      , NONCON( 9)
```

```
COMMON TEMP, FRT, TITLE, AW, A, NONCON  
COMMON NE, NGS, NCS, NS, STEMP, P, AIR
```

```
C  
C  
C
```

```
REWIND 1
```

```
DO 120 I = 1, 9
```

```
120 READ TAPE 1, ( Y(II,I), II = 1, NS )
```

```
NGS1 = NGS + 1
```

```
C  
C  
C
```

```
CONVERT TEMPERATURES FROM ABSOLUTE TO FARENHEIT
```

```
DO 160 I = 1, 9
```

```
ITEMP(I) = STEMP + FLOATF( I-1 ) * 100.0
```

```
160 JTEMP(I) = 1.8 * ( FLOATF( ITEMP(I) ) - 273.0 ) + 32.5
```

```
C  
C  
C
```

```
PRINT ALL SPECIES IN LB MOLLS / 100 LBS OF FEED
```

```

        ASSIGN 2240 TO NN
        ASSIGN 2300 TO NNN
        GO TO 200

2300 ASSIGN 2350 TO NNN
        DO 2320 I = 1, 9
2320 TOTC(I) = 0.0
        DO 2350 I = 1, NGS
        DO 2340 II = 1, 9
2340 TOTC(II) = TOTC(II) + Y(I,II)
        PRINT 321, TITLE(I), ( Y(I,II), II = 1, 9 )
        LINE = LINE - 1
        IF ( LINE ) 200, 200, 2350

2350 CONTINUE
        PRINT 431, TOTC
        ASSIGN 2260 TO NN
        ASSIGN 2450 TO NNN
        IF ( NS - NGS1 ) 130, 2400, 2400

2400 LINE = LINE - 5
        PRINT 2261
        DO 2420 I = 1, 9
2420 TOTC(I) = 0.0

```

```
2430 DO 2450 I = NGS1, NS
      DO 2440 II = 1, 9
2440 TOTC(II) = TOTC(II) + Y(I,II)
      PRINT 321, TITLE(I), ( Y(I,II), II = 1, 9 )
      LINE = LINE + 1
      IF ( LINE ) 200, 200, 2450
```

```
2450 CONTINUE
```

```
      PRINT 431, TOTC
```

```
130 DO 150 I = 1, 9
```

```
      TPRES = 0.0
```

```
      DO 140 II = 1, NGS
```

```
140 TPRES = TPRES + Y(II,I)
```

```
      DO 150 II = 1, NGS
```

```
150 Y(II,I) = Y(II,I) / TPRES * 100.0
```

```
      ASSIGN 240 TO NN
```

```
      ASSIGN 300 TO NNN
```

```
C
```

```
C      PRINT ALL GASEOUS SPECIES IN VOLUME PERCENT
```

```
C
```

```
200 PRINT 201, P, AIR
```

```
201 FORMAT( 1H1, 29X, 38HEQUILIBRIUM COMPOSITION OF COMBUSTION ,
```

```

1          24HPRODUCTS OF BLACK LIQUOR // 1H0, 20X, 12HPRESSURE:
2          , F6.2, 8H ATMOS. , 27X, 22HPER CENT TOTAL AIR: ,
3          F6.1 )

PRINT 221, ITEMP, JTEMP

221 FORMAT( 1H0, 12HTEMPERATURE , 9( 3X, 14, 5H K ) / 1H ,
1          12X, 9( 3H (, 14, 5H F) ) )

LINE = 46

GO TO NN, ( 240, 260, 2240, 2260 )

240 PRINT 241

241 FORMAT( 1H0, 18HSPECIES( GASEOUS ), 47X, 14HVOLUME PERCENT / )

GO TO 250

2240 PRINT 2241

2241 FORMAT( 1H0, 18HSPECIES( GASEOUS ) , 41X,
1          25HLB MOLS / 100 LBS OF FEED / )

250 SENSE LIGHT 4

DO 1150 I = 1, 9

IF ( NONCON(I) ) 1150, 1150, 1000

1000 IF ( SENSE LIGHT 4 ) 1010, 1020

1010 PRINT 1011

1011 FORMAT( 1H0 )

1020 GO TO ( 1030, 1040, 1050, 1060, 1070, 1080, 1090, 1100, 1110 ), I

```

```
1030 PRINT 1031
1031 FORMAT( 1H+, 18X, 1H* )
      GO TO 1150
1040 PRINT 1041
1041 FORMAT( 1H+, 30X, 1H* )
      GO TO 1150
1050 PRINT 1051
1051 FORMAT( 1H+, 42X, 1H* )
      GO TO 1150
1060 PRINT 1061
1061 FORMAT( 1H+, 54X, 1H* )
      GO TO 1150
1070 PRINT 1071
1071 FORMAT( 1H+, 66X, 1H* )
      GO TO 1150
1080 PRINT 1081
1081 FORMAT( 1H+, 78X, 1H* )
      GO TO 1150
1090 PRINT 1091
1091 FORMAT( 1H+, 90X, 1H* )
      GO TO 1150
```

```

1100 PRINT 1101
1101 FORMAT( 1H+, 102X, 1H* )
      GO TO 1150
1110 PRINT 1111
1111 FORMAT( 1H+, 114X, 1H* )
1150 CONTINUE
      GO TO 280
260 PRINT 261
261 FORMAT( 1H0, 20HSPECIES( CONDENSED ), 40X, 21HLBS / 100 LBS OF FEE
      1D / )
      GO TO 280
2260 PRINT 2261
2261 FORMAT( 1H0, 20HSPECIES( CONDENSED ) , 39X,
      1          25HLB MOLS / 100 LBS OF FEED / )
280 GO TO NNN, ( 300, 340, 400, 500, 550, 600, 650, 2300, 2350, 2450 )
300 ASSIGN 340 TO NNN
      DO 340 I = 1, NGS
      PRINT 321, TITLE(I), ( Y(I,II), II = 1, 9 )
321 FORMAT( 1H , A10, 2X, 9( 1X, E10.3, 1X ) )
      LINE = LINE + 1
      IF ( LINE ) 200, 200, 340

```

340 CONTINUE

ASSIGN 260 TO NN

ASSIGN 400 TO NNN

C

C PRINT ALL CONDENSED SPECIES IN LB / 100 LBS OF FEED

C

LINE = LINE - 4

PRINT 261

IF ( NS - NGS1 ) 450, 360, 360

360 DO 400 I = NGS1, NS

FMOLE = 0.0

DO 380 II = 1, NE

380 FMOLE = FMOLE + AW(II) \* A(I,II)

DO 390 II = 1, 9

390 Y(I,II) = Y(I,II) \* FMOLE

PRINT 321, TITLE(I), ( Y(I,II), II = 1, 9 )

LINE = LINE - 1

IF ( LINE ) 200, 200, 400

400 CONTINUE

DO 420 I = 1, 9

TOTC(I) = 0.0

\* Y(I,II)

FORMAT

FORMAT( 1H , 5X, 5HTOTAL, 2X, 9( 1X, E10.3, 1X ) )

C PRINT MAJOR SPECIES ONLY

C

450 ASSIGN 500 TO NNN

ASSIGN 240 TO NN

GO TO 200

500 ASSIGN 550 TO NNN

DO 550 I = 1, NGS

DO 520 II = 1, 9

IF ( Y(I,II) = 0.01 ) 520, 540, 540

520 CONTINUE

GO TO 550

540 PRINT 541, TITLE(I), ( Y(I,II), II = 1, 9 )

541 FORMAT( 1H , A10, 2X, 9( 3X, F6.3, 3X ) )

LINE = LINE + 1

IF ( LINE ) 200, 200, 550

550 CONTINUE

-111B-

```
ASSIGN 260 TO NN
ASSIGN 600 TO NNN
IF ( NS = NGS1 ) 700, 600, 600
600 ASSIGN 650 TO NNN
PRINT 261
LINE = LINE + 4
DO 650 I = NGS1, NS
DO 620 II = 1, 9
IF ( Y(I,II) = 0.001 ) 620, 640, 640
620 CONTINUE
GO TO 650
640 PRINT 641, TITLE(I), ( Y(I,II), II = 1, 9 )
641 FORMAT( 1H , A10, 2X, 9( 3X, F7.4, 2X ) )
LINE = LINE + 1
IF ( LINE ) 200, 200, 650
650 CONTINUE
PRINT 661, TOTC
661 FORMAT( 1H , 5X, 5HTOTAL, 2X, 9( 2X, F8.4, 2X ) )
700 CALL CHAIN( 2, 3 )
END
```

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