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THERMOCHEMICAL WATER-SPLITTING CYCLE, BENCH SCALE INVESTIGATIONS AND PROCESS ENGINEERING

ANNUAL REPORT
FOR THE PERIOD FEBRUARY THROUGH DECEMBER 31, 1977

WORK DONE BY:

G. B. BURNS
G. CAPRIOGLIO
J. D. de GRAAF
K. H. Mc CORKLE
J. H. NORMAN
T. OHNO
R. SHARP
P. W. TRESTER
G. B. WEBB

REPORT WRITTEN BY:

G. CAPRIOGLIO
J. D. de GRAAF
K. H. Mc CORKLE
J. H. NORMAN
T. OHNO
J. L. RUSSELL
G. C. WEBB

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ABSTRACT

This document is an annual progress report of DOE-sponsored process development work on the General Atomic sulfur-iodine thermochemical water-splitting cycle. The work consists of laboratory bench-scale investigations and process engineering design studies.

A bench scale system, consisting of three subunits, has been planned to study the cycle under continuous flow conditions. The design of subunit I, which models the main solution reaction and product separation, and subunit II, which models the concentration and decomposition of sulfuric acid, is presented and discussed. Progress on the construction and operation of subunit I is described.

The process engineering addresses the flowsheet design of a large-scale production process consisting of four chemical sections (I through IV) and one helium heat supply section (V). The completed designs for sections I (main solution reaction) and II (sulfuric acid-water separation and sulfuric acid decomposition) are given along with a partial design for section IV (hydrogen iodide decomposition and hydrogen recovery), which is not yet complete. The appendix contains a description of the process simulator computer code that is being used to aid the process design.

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1. INTRODUCTION

Thermochemical water splitting potentially provides a nonfossil, renewable source of hydrogen. It characteristically requires high-temperature heat input to achieve the necessary conditions for the chemical reactions to take place and appears to be compatible with heat characteristics projected for three important heat sources: the gas-cooled fission and fusion reactors and systems for concentrating solar energy.

General Atomic (GA) is working on the development of all three of these heat sources and in October 1972 began investigating thermochemical water splitting. General Atomic has discovered a promising cycle (called the sulfur-iodine cycle) that requires no solids handling, and is cooperating with the U.S. Department of Energy (DOE) and the Gas Research Institute (GRI) to develop the thermochemical water-splitting process to the point where it can be demonstrated as a commercially feasible source of hydrogen. In this effort there have been other participants, including the American Gas Association (whose sponsorship has been assumed by GRI), Northeast Utilities Service Company, Southern California Edison Company, and the University of California Los Alamos Scientific Laboratory.

The abbreviated chemical description of the sulfur-iodine cycle is

$$2H_2O + xI_2 + SO_2 \rightarrow H_2SO_4(sol) + 2HI_x(sol) \qquad (1)$$

$$H_2SO_4(sol) \rightarrow H_2O + SO_2 + 1/2\ O_2 \qquad (2)$$

$$2HI_x(sol) \rightarrow H_2 + xI_2 \qquad (3)$$

where the x in the reactions represents the average of several polyiodides formed in the initial solution reaction. Although the cycle can be represented by the three previous reactions, several processing steps are necessary to accomplish these reactions.

In February 1977 DOE (then ERDA) began sponsoring process engineering design studies and laboratory bench-scale investigations under contract No. EY-76-C-03-0167, Project Agreement 63. The general objective of the bench-scale work is to obtain better insight into the actual processing steps and their interaction by conducting key continuous flow reaction and separation steps that had previously been done on a batch basis. Bench-scale investigations will also give information on the handling of fluids involved, on the operational behavior of key pieces of equipment, and on the effects of incomplete physical separations and possible side reactions. Process engineering efforts will show what energy efficiency can be obtained, will give guidance to further chemical investigations, and will become a basis for realistic cost estimates.

This document is a progress report on the DOE-sponsored work for the period February 1, 1977 through December 31, 1977. The report contains three sections and an appendix. Section 2 describes the bench-scale investigations and Section 3 presents the process engineering. The appendix contains a description of the process simulator computer code that is being used to aid the process design.

2. BENCH-SCALE INVESTIGATIONS

After extensive studies of the chemistry of the sulfur-iodine cycle described by Reactions 1-3, a bench-scale system was planned to study the cycle under continuous operation conditions. This section describes the status of the design and construction of the system, which consists of three subunits corresponding to the three basic reactions of the cycle.

Subunit I (HI-H_2SO_4 production and separation) supplies I_2, H_2O, and SO_2 to a reactor where these ingredients are mixed and equilibrated, forming two liquid product phases which are later separated. Included in Subunit I is the removal of unreacted SO_2 from the HI_x(sol) phase.

Subunit II (H_2SO_4 concentration and decomposition) concentrates and purifies H_2SO_4(sol) by removal of iodine-containing species, H_2O, and dissolved SO_2. This is followed by vaporization and decomposition of H_2SO_4 to equilibrium concentrations at ∿1100K. The products of the decomposition are separated from unreacted acid and they themselves separated, providing SO_2 and H_2O for recycle and product O_2. The O_2 is later cleaned up before discharge.

Subunit III (HI concentration and decomposition) separates I_2 and H_2O from the HI_x phase by first contacting the degassed HI_x(sol) with H_3PO_4(sol) followed by a column distillation of HI out of the H_3PO_4(sol). The H_3PO_4(sol) is reconcentrated for recycle by boiling out H_2O. The formed HI is decomposed to H_2 and I_2 at near equilibrium conditions. The product H_2 and I_2 and the unreacted HI are separated for recycle or discharge, as in the case of H_2, after appropriate clean up.

Section I has been partially constructed and is undergoing checkout-testing. Section II has been designed, and the writing of purchase specifications is in progress. Design of Section III has been initiated.

2.1. DESIGN AND PROCUREMENT

2.1.1. Subunit I, HI-H_2SO_4 Production and Separation

Figure 2-1 is the detailed flowsheet, as originally developed, for Subunit I, the HI-H_2SO_4 production and separation system. Construction details of the actual equipment may differ, however, from those shown on Fig. 2-1 for reasons explained later in the report. Usually the modifications with respect to the original design and specifications do not make an explicit, visible difference in the schematic representation on Fig. 2-1. Most changes are of geometrical layout of the equipment, of the thermal insulation, and of the heat supply temperature controls. For sake of visual clarity on Fig. 2-1 only some of the insulation and the heating of portions of the system were explicitly indicated, as such. Additional insulation and heat tracing are also necessary for process lines and equipment in which I_2(s) might precipitate and cause plugging. The parts of the system most liable to I_2(s) precipitation are associated with the I_2 feed-melting tanks (V-1A and V-1B). All valving, flowmetering equipment, and lines between V-1A,B and the main reactor (R-1) need to be heated and insulated.

Those parts of the system after R-1 which carry "heavy phase" flow are also subject to I_2(s) precipitation, but to a lesser extent than the I_2 feed system. The equipment items involving heavy phase flow (R-2, P-2, FC-5, FI-4, and FC-6) and their associated process flow lines require either heating or insulation, depending on the startup-run-shutdown operating procedures which are being developed. The heavy phase flow after H-4 (the line heater upstream of R-3) might not require insulation or heating, depending on how this portion of the system (R-3, FI-8, FC-8, V-4, and FC-10) is operated.

Other parts of the system do not carry enough I_2 to require heating and insulation to prevent I_2(s) precipitation unless the system is in an abnormal operating state. It is, however, appropriate to allow for abnormal operating states for the pressure relief valves other than PRV-1

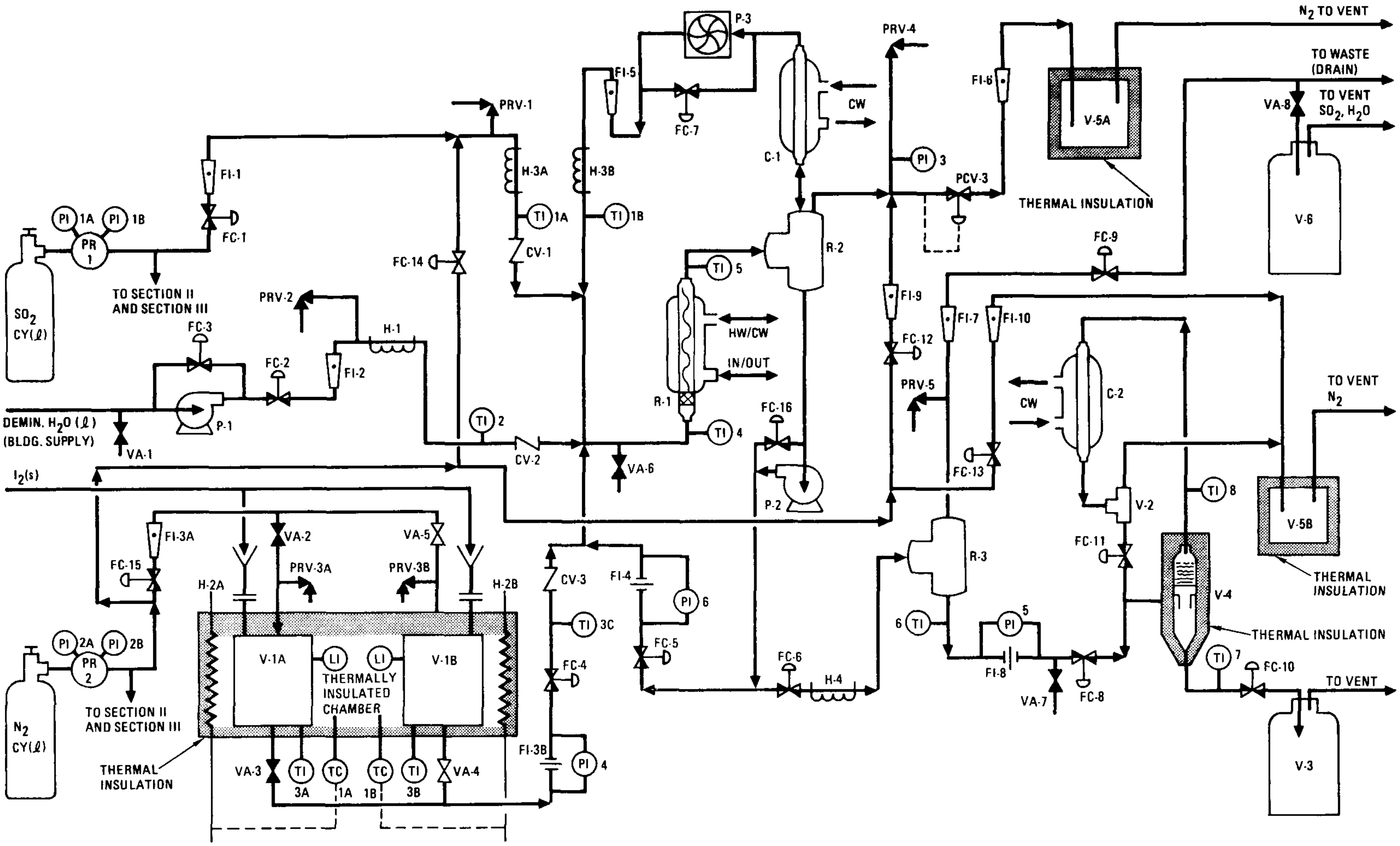

Fig. 2-1. Original flowsheet of Subunit I, bench-scale HI-H_2SO_4 production and separation

and PRV-2. These relief valves are protected from I_2 by check valves CV-1 and CV-2, but all the other pressure relief valves could be exposed to $I_2(\ell)$ or to heavy phase during abnormal operation. Even under normal operating conditions it is possible for slow vapor deposition of $I_2(s)$ to occur in PRV-3A, PRV-3B, and PRV-4 if they are not heated. The assurance of safe, correct functioning of the pressure relief valves, other than PRV-1 and PRV-2, requires that they and their access lines be heated.

Portions of the system for which equipment is still on order or undergoing assembly are the SO_2 recycle associated with P-3, the offgas cold traps V-5A and V-5B, and the lower phase outgassing system associated with V-4.

Table 2-1 is a list of the specific items shown in Fig. 2-1. All heating elements are external to the equipment containing the process materials. Temperature instrumentation refers to thermocouples in glass or teflon thermowells, or which are in contact with the exterior of the process equipment. The LI (liquid level indication) functions for V-1A and V-1B require no special instrumentation since they are glass vessels in an insulated enclosure with windows which permit visual observation.

The equipment has been sized for the following feed rates:

		Feed Rate		
Feed Material	Mol/min	10^{-6} m^3/s	g/s	lb/hr
H_2O	0.516	0.157	0.155	1.23
SO_2	0.127	50.5*	0.135	1.07
I_2	0.229	0.245	0.969	7.69

The foregoing feed rates correspond to about 1.7 x 10^{-5} m^3/s (1 liter/min) of $H_2(g)$ at STP* from the overall process if all sections were functioning, but the actual capacity of many equipment items is greater than

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*Gas flow at 289 K and 1.013 x 10^5 Pa.

TABLE 2-1

EQUIPMENT LIST FOR THE HI-H_2SO_4 PRODUCTION AND SEPARATION BENCH-SCALE SYSTEM (SUBUNIT I)

Equipment Number	Equipment Name	Material of Construction	Normal Process Materials Exposure†	Design Operating Conditions	
				Temperature, K	Pressure Pa, Absolute
C-1	Reactor Offgas Condenser	Glass	SO_2, H_2O, (I_2, H_2SO_4, HI)	390	$3.1x10^5$
C-2	Lower Phase Offgas Condenser	Glass	SO_2, H_2O, (I_2, H_2SO_4, HI)	390	6000-600
CV-1	SO_2 Feed Check Valve	Teflon	SO_2 (H_2O), (I_2, H_2SO_4, HI)	390	$3.1x10^5$
CV-2	H_2O Feed Check Valve	Teflon	H_2O (SO_2), (I_2, H_2SO_4, HI)	390	$3.1x10^5$
CV-3	I_2 Feed Check Valve	Teflon	I_2 (HI, H_2O, SO_2, H_2SO_4)	390	$3.1x10^5$
FC-1	SO_2 Feed Valve	316 Stainless Steel*	SO_2	Ambient	$3.1x10^5$
FC-2	H_2O Feed Throttle Valve	316 Stainless Steel*	H_2O	Ambient	$3.1x10^5$
FC-3	H_2O Feed Bypass Valve	316 Stainless Steel*	H_2O	Ambient	$3.1x10^5$
FC-4	I_2 Feed Valve	Teflon	I_2	390	$3.1x10^5$
FC-5	Lower Phase Recycle Flow Valve	Teflon	HI, I_2, H_2O, SO_2, (H_2SO_4)	390	$3.1x10^5$
FC-6	Lower Phase Output Flow Valve	Teflon	HI, I_2, H_2O, SO_2, (H_2SO_4)	390	$3.1x10^5$
FC-7	Reactor Offgas Pump Bypass Valve	Teflon	SO_2, H_2O	315	$3.1x10^5$
FC-8	Lower Phase Degassing Feed Valve	Teflon	HI, I_2, H_2O, SO_2 (H_2SO_4)	390	$3.1x10^5$
FC-9	Upper Phase Output Flow Valve	Teflon	H_2SO_4, H_2O, SO_2 (I_2, HI)	390	$3.1x10^5$
FC-10	Degassed Lower Phase Flow Valve	Teflon	HI, I_2, H_2O (SO_2, H_2SO_4)	390	Ambient
FC-11	Lower Phase Offgas Condensate Valve	Teflon	SO_2, I_2 (H_2O, HI, H_2SO_4)	373	Ambient
FC-12	Reactor Offgas N_2 Purge Valve	316 Stainless Steel*	N_2, SO_2 (H_2O)	Ambient	$3.1x10^5$
FC-13	Lower Phase Offgas N_2 Purge Valve	316 Stainless Steel*	N_2, SO_2 (H_2O)	Ambient	$3.1x10^5$
FC-14	SO_2 Feed N_2 Purge Valve	316 Stainless Steel*	N_2, SO_2	Ambient	$3.1x10^5$
FC-15	N_2 Feed Valve	316 Stainless Steel*	N_2	Ambient	$3.1x10^5$
FC-16	Lower Phase Pump Bypass Valve	Teflon	HI, I_2, H_2O, SO_2, (H_2SO_4)	390	$3.1x10^5$
FI-1	SO_2 Feed Rotameter	316 Stainless Steel (SS) and Glass	SO_2, (N_2)	Ambient	$3.1x10^5$
FI-2	H_2O Feed Rotameter	316 SS and glass	H_2O	Ambient	$3.1x10^5$
FI-3A	N_2 for I_2 Feed Rotameter	316 SS and glass	N_2	Ambient	$3.1x10^5$
FI-3B	I_2 Feed ΔP Orifice	Teflon	I_2	390	$3.1x10^5$
FI-4	Lower Phase Recycle ΔP Orifice	Teflon	HI, I_2, H_2O, SO_2, (H_2SO_4)	390	$3.1x10^5$
FI-5	SO_2 Recycle Rotameter	316 SS and glass	SO_2, H_2O	315	$3.1x10^5$

†Substances present in low concentration are shown parenthetically.

*or 303 Stainless Steel.

TABLE 2-1 (continued)

Equipment Number	Equipment Name	Material of Construction	Normal Process Materials Exposure†	Design Operating Conditions	
				Temperature, K	Pressure, Pa, Absolute
FI-6	Waste SO_2 Offgas Rotameter	316 SS and Glass	SO_2, H_2O (I_2, H_2SO_4, HI)	390	Ambient
FI-7	Upper Phase Flow Rotameter	316 SS and Glass	H_2SO_4, H_2O, SO_2 (HI, I_2)	390	3.1×10^5
FI-8	Lower Phase Output ΔP Orifice	Teflon	HI, I_2, H_2O, SO_2, (H_2SO_4)	390	3.1×10^5
FI-9	Reactor Offgas N_2 Purge Rotameter	316 SS and Glass	N_2, SO_2, H_2O (I_2, HI, H_2SO_4)	Ambient	3.1×10^5
FI-10	Lower Phase Offgas N_2 Purge Rotameter	316 SS and Glass	N_2, SO_2, H_2O	Ambient	Ambient
H-1	H_2O Feed Line Heater	Fiberglass-Electric Wire	None	>390	Ambient
H-2A	I_2 Feed Tank "A" Heater	Metallic Strap	None	>390	Ambient
H-2B	I_2 Feed Tank "B" Heater	Metallic Strap	None	>390	Ambient
H-3A	SO_2 Feed Line Heater	Fiberglass-Electric Wire	None	>390	Ambient
H-3B	SO_2 Recycle Line Heater	Fiberglass-Electric Wire	None	>390	Ambient
H-4	Liquid Phase Line Heater	Fiberglass-Electric Wire	None	>390	Ambient
P-1	H_2O Feed Pump	Stainless Steel	H_2O	Ambient	3.1×10^5
P-2	Lower Phase Recycle Pump	Teflon	HI, I_2, H_2O, SO_2, (H_2SO_4)	390	3.1×10^5
P-3	SO_2 Recycle Pump	Teflon-Hypalon	SO_2, H_2O	315	3.1×10^5
PI-1A	SO_2 Tank Pressure Gauge	Stainless Steel	SO_2	Ambient	Cylinder Pressure ($\sim 7 \times 10^5$)
PI-1B	SO_2 Feed Pressure Gauge	Stainless Steel	SO_2	Ambient	3.1×10^5
PI-2A	N_2 Tank Pressure Gauge	Stainless Steel	N_2	Ambient	Cylinder Pressure ($\leq 165 \times 10^5$)
PI-2B	N_2 Feed Pressure Gauge	Stainless Steel	N_2	Ambient	3.1×10^5
PI-3	Main Reactor Pressure Gauge	Stainless Steel**	SO_2, H_2O, (I_2, H_2SO_4, HI)	390	3.1×10^5
PI-4	I_2 Feed Flow ΔP Manometer	Glass††	I_2	390	3.1×10^5
PI-5	Lower Phase Product Flow ΔP Manometer	Glass††	HI, I_2, H_2O, SO_2, (H_2SO_4)	390	3.1×10^5
PI-6	Lower Phase Recycle Flow ΔP Manometer	Glass††	HI, I_2, H_2O, SO_2, (H_2SO_4)	390	3.1×10^5
PR-1	SO_2 Feed Gas Pressure Regulator	Stainless Steel	SO_2	Ambient	Cylinder Pressure ($\sim 7 \times 10^5$)
PR-2	N_2 Feed Gas Pressure Regulator	Stainless Steel	N_2	Ambient	Cylinder Pressure ($\leq 165 \times 10^5$)

†Substances present in low concentration are shown parenthetically.

**Protected by a Teflon diaphragm.

††Special manometers, fabricated at GA.

TABLE 2-1 (continued)

Equipment Number	Equipment Name	Material of Construction	Normal Process Materials Exposure†	Design Operating Conditions	
				Temperature K	Pressure Pa, Absolute
PRV-1	SO_2 Feed Overpressure Relief Valve	316 Stainless Steel*	SO_2, N_2	Ambient	3.1×10^5
PRV-2	H_2O Feed Overpressure Relief Valve	316 Stainless Steel*	H_2O	Ambient	3.1×10^5
PRV-3A	I_2 Feed Tank "A" Overpressure Relief Valve	316 Stainless Steel*	I_2	390	3.1×10^5
PRV-3B	I_2 Feed Tank "B" Overpressure Relief Valve	316 Stainless Steel*	I_2	390	3.1×10^5
PRV-4	Reactor Overpressure Relief Valve	316 Stainless Steel*	SO_2, H_2O (I_2, H_2SO_4, HI)	390	3.1×10^5
R-1	Main Reactor	Glass (Teflon-coated Mixer)	H_2O, SO_2, I_2, H_2SO_4, HI	390	3.1×10^5
R-2	Gas-Liquid Phase Separator	Glass	H_2O, SO_2, I_2, H_2SO_4, HI	390	3.1×10^5
R-3	Liquid-Liquid Phase Separator	Glass	H_2O, SO_2, I_2, H_2SO_4, HI	390	3.1×10^5
TC-1A	I_2 Melting Heater, V-1A	--	None	390	--
TC-1B	I_2 Melting Heater, V-1B	--	None	390	--
TC-2+	PRV-3A, 3B Heater	--	None	390	--
TC-3+	I_2 Feed Line Heater	--	None	390	--
TC-4+	I_2 Feed Manometer (FI-3B, PI-4) Heater	--	None	390	--
TC-5+	R-2, R-3 Enclosure Heater	--	None	390	--
TC-6+	R-2 Offgas (PRV-4, PI-3) Heater	--	None	390	--
TC-7+	Heavy Phase Output Manometer (FI-8, PI-5) Heater	--	None	390	--
TI-1A	SO_2 Feed Temperature	--	None	390	--
TI-1B	Recycle SO_2 Temperature	--	None	390	--
TI-2	H_2O Feed Temperature	--	None	390	--
TI-3A	I_2 Melter "A" Temperature	--	None	390	--
TI-3B	I_2 Melter "B" Temperature	--	None	390	--
TI-3C	I_2 Feed Temperature	--	None	390	--
TI-4	Main Reactor Inlet Temperature	--	None	∿390	--
TI-5	Main Reactor Outlet Temperature	--	None	∿390	--
TI-6	Heavy Phase Degassing Feed Temperature	--	None	∿400	--
TI-7	Heavy Phase Product Temperature	--	None	∿390	--
TI-8	Heavy Phase Offgas Temperature	--	None	∿390	--

†Substances present in low concentration are shown parenthetically.

*or 303 Stainless Steel.

+Not shown on Figure 2-1.

TABLE 2-1 (continued)

Equipment Number	Equipment Name	Material of Construction	Normal Process Materials Exposure†	Design Operating Conditions	
				Temperature, K	Pressure Pa, Absolute
V-1A	I_2 Feed-Melting Tank "A"	Glass	I_2	390	$3.1\text{x}10^5$
V-1B	I_2 Feed-Melting Tank "B"	Glass	I_2	390	$3.1\text{x}10^5$
V-2	Lower Phase Offgas Condensate Separator	Glass	SO_2, H_2O, I_2, HI, H_2SO_4	373	6000-600
V-3	Lower Phase Storage Carboy	Glass	HI, I_2, H_2O, (SO_2, H_2SO_4)	<390	6000-600
V-4	Lower Phase SO_2 Disengagement Chamber	Glass	HI, I_2, H_2O, SO_2 (H_2SO_4)	<390	6000-600
V-5A	Vent Offgas Cold Trap	Glass	N_2 (SO_2)	77	Ambient
V-5B	Lower Phase SO_2 Offgas Cold Trap	Glass	N_2 (SO_2)	77	6000-600
V-6	Upper Phase Storage Carboy	Polypropylene	H_2SO_4, H_2O, SO_2 (I_2HI)	<390	Ambient
VA-1	H_2O Feed Pump Drain Valve	Stainless Steel	H_2O	Ambient	Bldg. Dist. H_2O Press. ($\sim 1.4\text{x}10^4$)
VA-2	I_2 Feed-Melt Tank "A" N_2 Valve	Teflon	N_2, I_2	390	$3.1\text{x}10^5$
VA-3	I_2 Feed-Melt Tank "A" Outlet Valve	Teflon	I_2	390	$3.1\text{x}10^5$
VA-4	I_2 Feed-Melt Tank "B" Outlet Valve	Teflon	I_2	390	$3.1\text{x}10^5$
VA-5	I_2 Feed-Melt Tank "B" N_2 Valve	Teflon	N_2, I_2	390	$3.1\text{x}10^5$
VA-6	Main Reactor Drain Valve	Teflon	H_2O, SO_2, I_2, HI, H_2SO_4	390	$3.1\text{x}10^5$
VA-7	Liquid-Liquid Separator Drain Valve	Teflon	HI, I_2, H_2O, SO_2 (H_2SO_4)	390	$3.1\text{x}10^5$
VA-8	Upper Phase Storage Inlet Valve	Teflon	H_2SO_4, H_2O, SO_2 (I_2, HI)	<390	Ambient

†Substances present in low concentration are shown parenthetically.

the nominal design values. The heavy phase recycle pump, P-2, has a maximum delivery rate of 1.08×10^{-5} m^3/s, corresponding to a recycle ratio of about 20 at the design input rate to the system. The SO_2 recycle pump, P-3, has a maximum delivery rate of about 6×10^{-5} m^3/s, which is a recycle ratio of about 1 for SO_2 when main reactor, R-1, is operated at 1.013×10^5 Pa (1 atm). The SO_2 recycle ratio is proportional to the pressure in R-1.

One of the main reasons for overcapacity of specific equipment items is the difficulty in finding very low flow pumps, flowmeters, flow controllers, and such, which are standard articles of commerce rather than expensive custom fabrication or special-order items with long and uncertain delivery times. It was not possible to avoid, entirely, all custom fabrication and expensive, long delivery time items, but sometimes they could be avoided by accepting larger-than-design equipment items.

The corrosive reaction products and I_2 contact only glass or teflon throughout the system; those parts not subjected to such highly corrosive materials are made of stainless steel. Process flow lines between equipment items are 6.35 mm and 9.53 mm O.D. teflon tubing connected by teflon nut-ferrule tube fittings. Glass-to-teflon connections were also made by teflon tube fittings. The glass equipment items are generally commercial pipe connected by standard commercial clamps and flanges, the principal exceptions being C-1, C-2, and R-1. These three items are laboratory glassware condensers. Figures 2-2, -3, -4, -5, -6, and -7 are assembly drawings for typical equipment and show associated valves and fittings. The physical layout of the actual equipment shown in Figures 2-2 through 2-7 was later adapted to convenience of construction and to the dimensions of the laboratory hood space for the equipment. The device at the inlet of R-1 indicated on Figure 2-4 is a Koch Co. patented in-line passive fluid mixer which subdivides the stream and then recombines it in a mesh of interchanging flow channels.

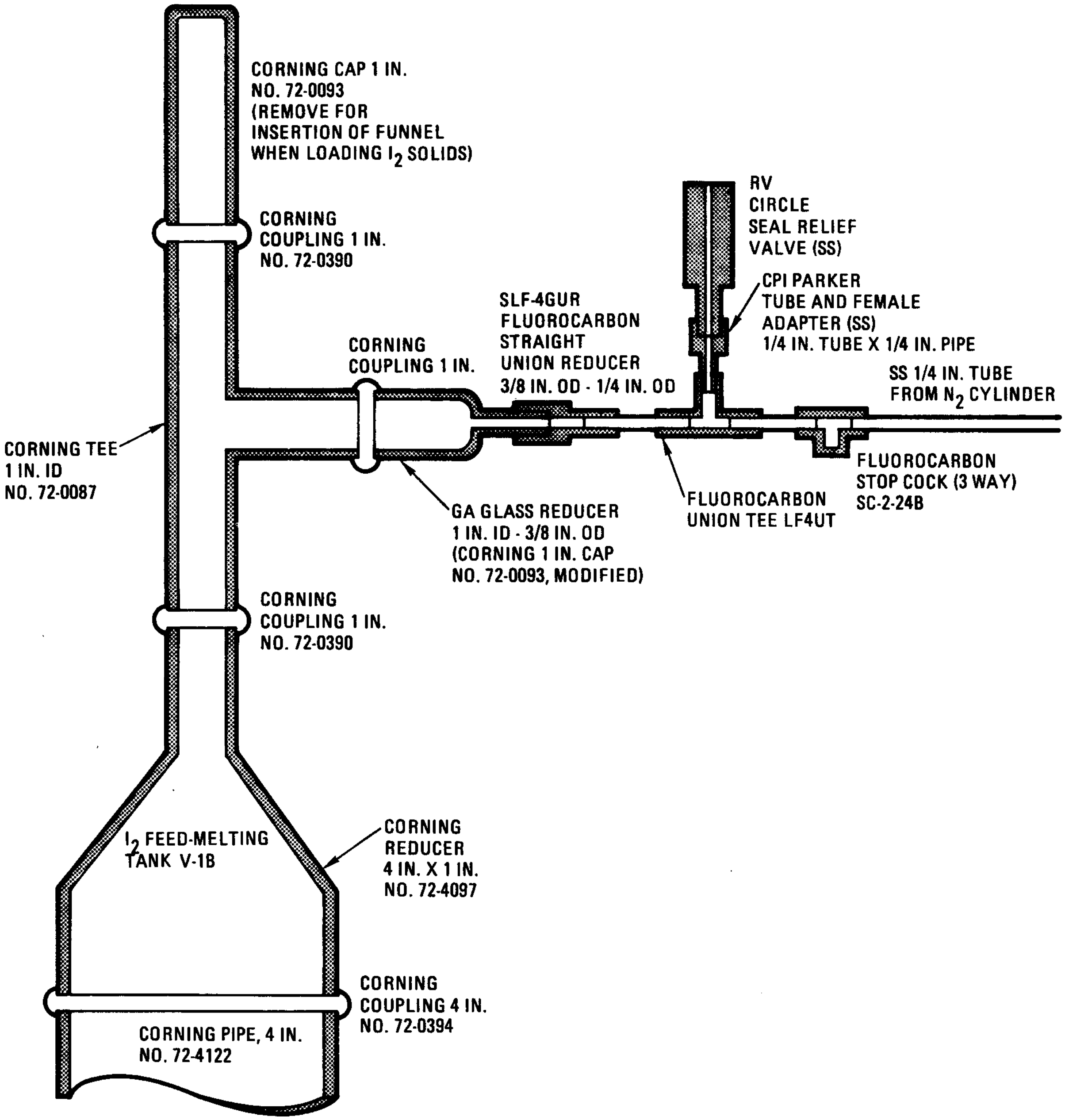

Fig. 2-2. I_2 feed-melting tank V-1B inlet assembly

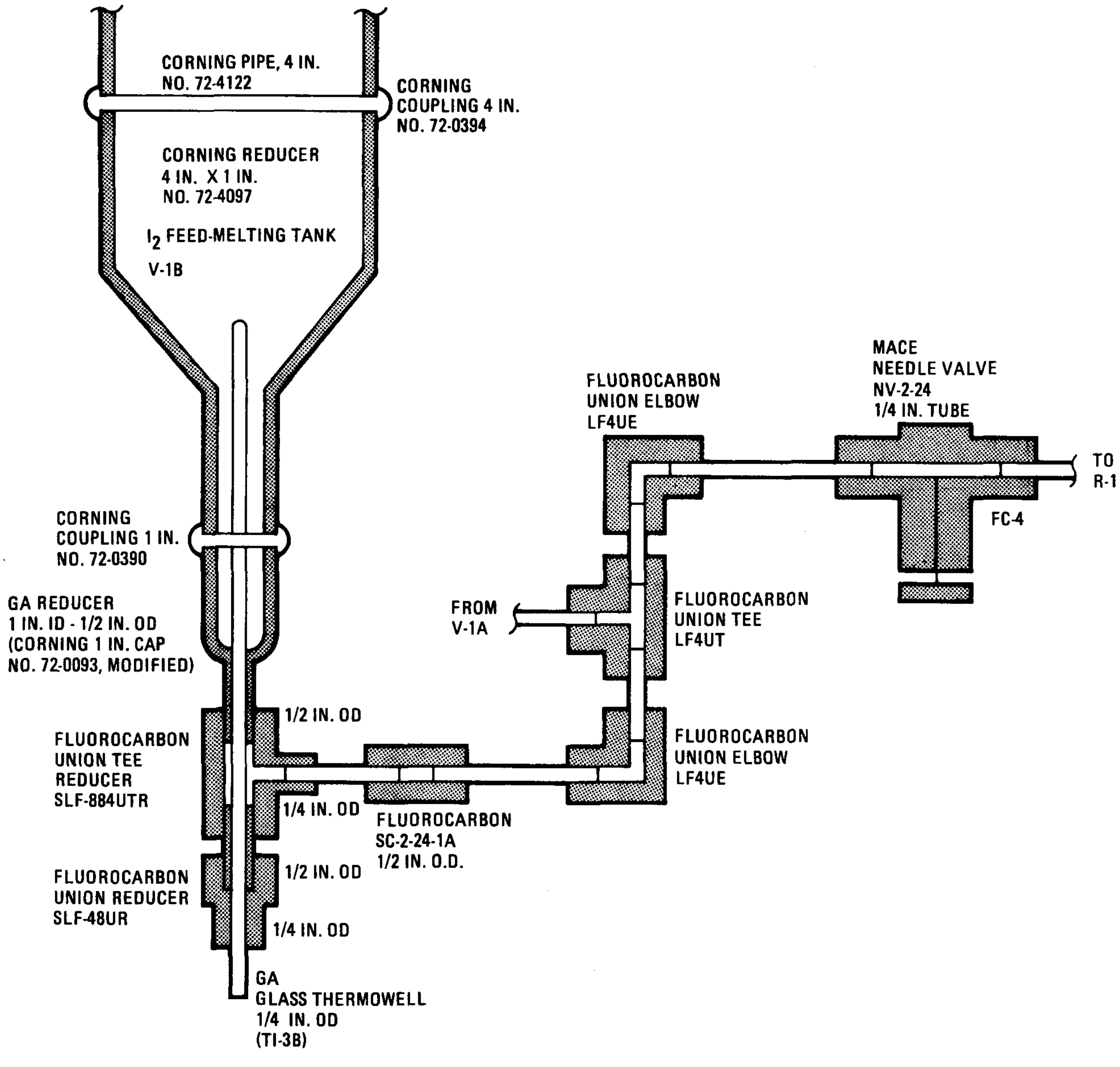

Fig. 2-3. I_2 feed-melting tank V-1B outlet assembly

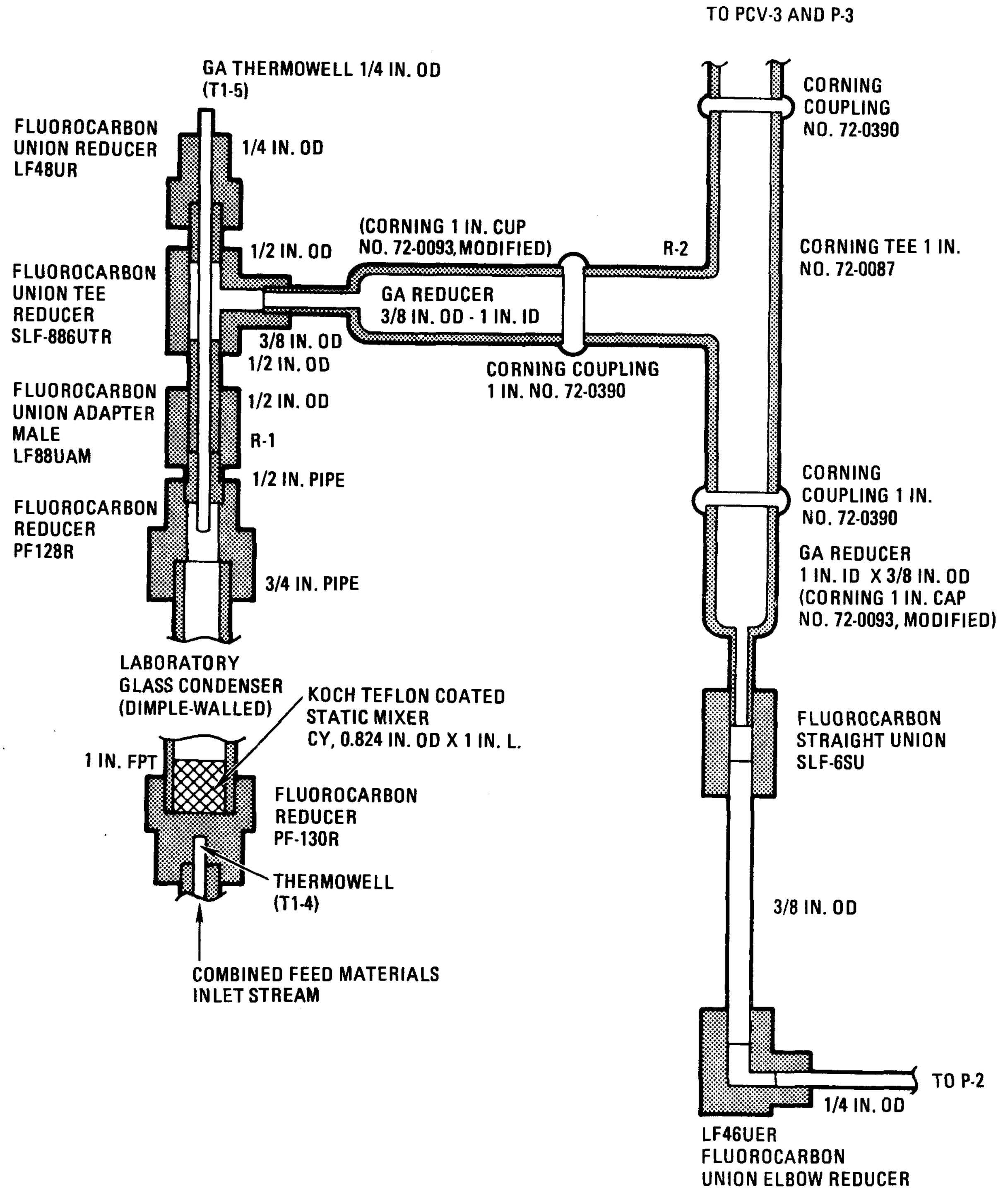

Fig. 2-4. Main reactor R-1 assembly and gas-liquid phase separator R-2 lower assembly

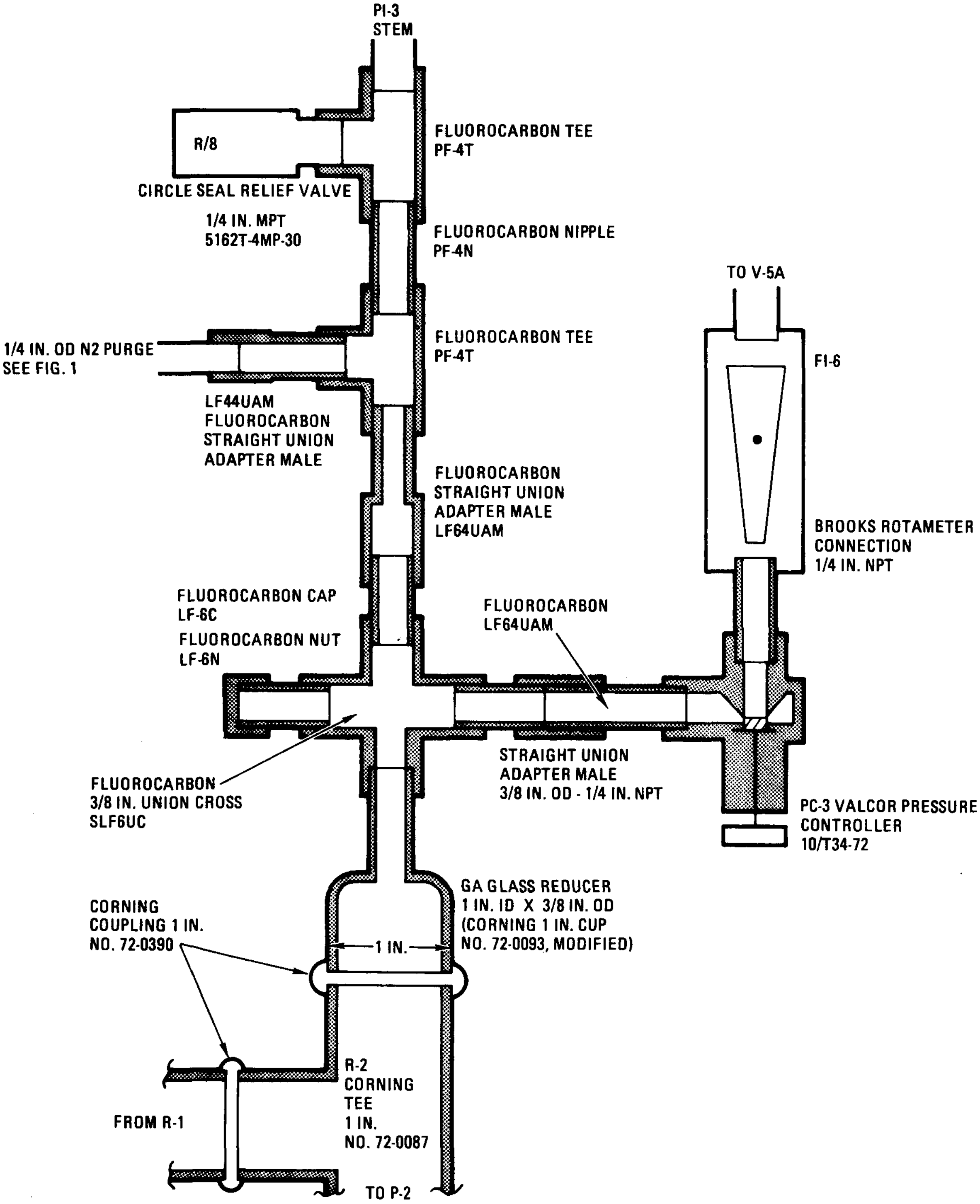

Fig. 2-5. Gas-liquid phase separator R-2 upper assembly

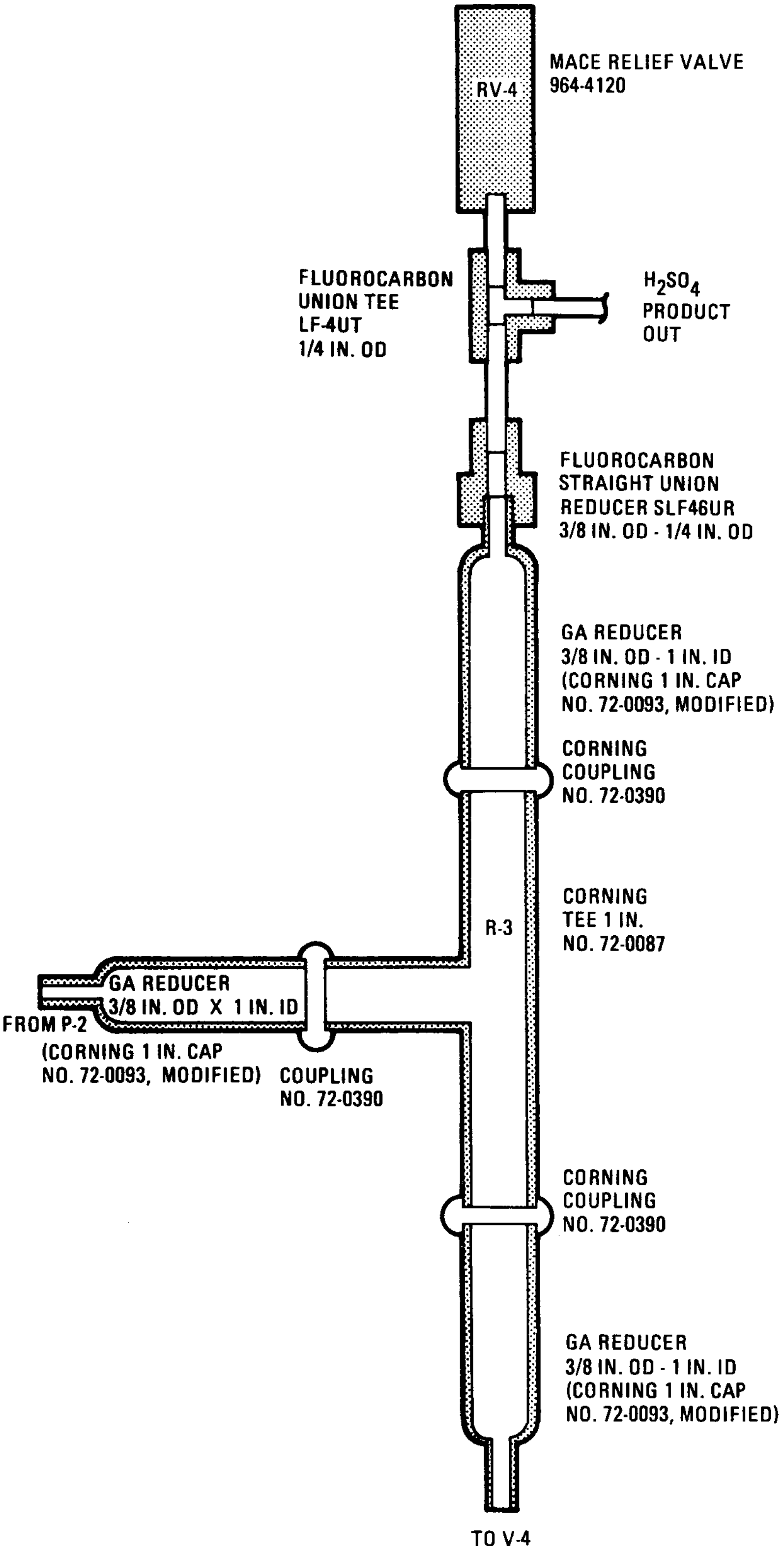

Fig. 2-6. Liquid-liquid phase separator R-3

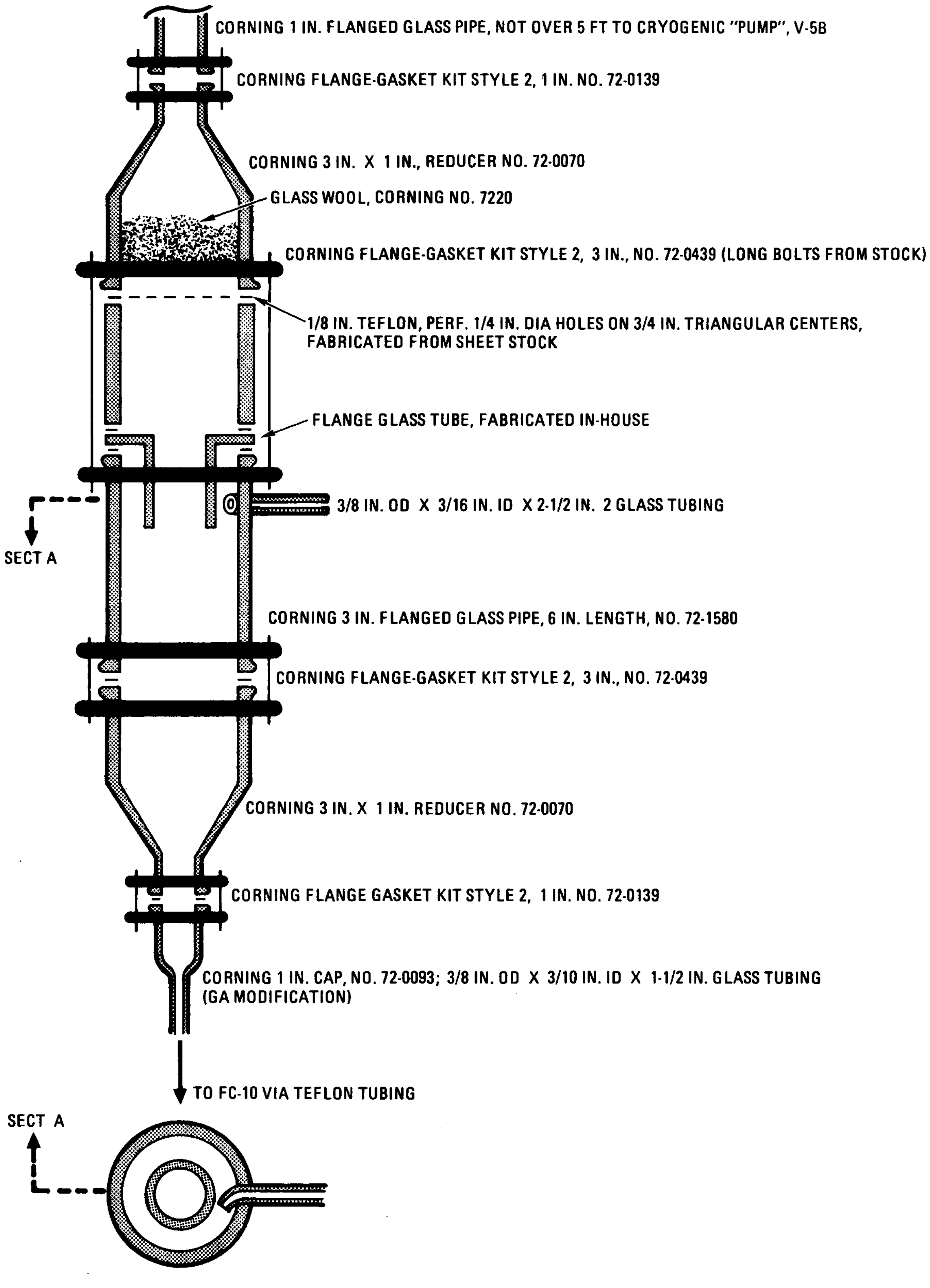

Fig. 2-7. Lower phase SO_2 offgas disengagement chamber V-4

2.1.2. Subunit II, H_2SO_4 Concentration and Decomposition

The initial flowsheet design for the H_2SO_4 concentration and decomposition section is shown in Fig. 2-8. The heating and insulation indicated on the figure are all that are needed, with the possible exception of the offgas lines from V-2 to PRV-2. Downstream of PCV-1 there should be enough SO_2 and H_2O present together to dissolve $I_2(s)$ if offgas condensate were to form. There should be little I_2 anywhere in Subunit II at any time, and it is probable that small amounts of I_2 would steam-distill through the offgas system with little difficulty. Heating may be needed, however, to ensure that PRV-2, in a dead-ended tee-off, does not collect I_2 solids.

The corrosion problems in Subunit II should be less severe than in Subunit I since HI and I_2 are present only in low concentrations or are absent. The main process streams after V-2, the I_2 removal column, should contain no HI or I_2 under normal operating conditions, but as a contingency in the event of abnormal operating conditions the downstream materials are generally specified to be resistant to HI and I_2. The principal exception is the end pieces of the pulsation snubbers PS-1 and 2, which are 316 stainless steel. Table 2-2 lists the specific equipment items shown on Fig. 2-8, along with materials of construction and operating conditions.

All heating elements are external to the equipment containing the process materials. Temperature instrumentation refers to thermocouples in glass, quartz, or teflon thermowells, or which are in contact with the exterior of the process equipment. The LI (liquid level indication) functions for V-1A and B, V-3, V-4, V-6, and V-7 require no special instrumentation. They are glass vessels, either bare or in insulated enclosures windows, which permit visual observation.

The nominal design feed rate for the system is slightly, but not significantly, greater than that for Subunit I. The nominal feed rate of $0.102 \times 10^{-6}\ m^3/s$ (0.006 liter/min) corresponds to about $2 \times 10^{-5}\ m^3/s$

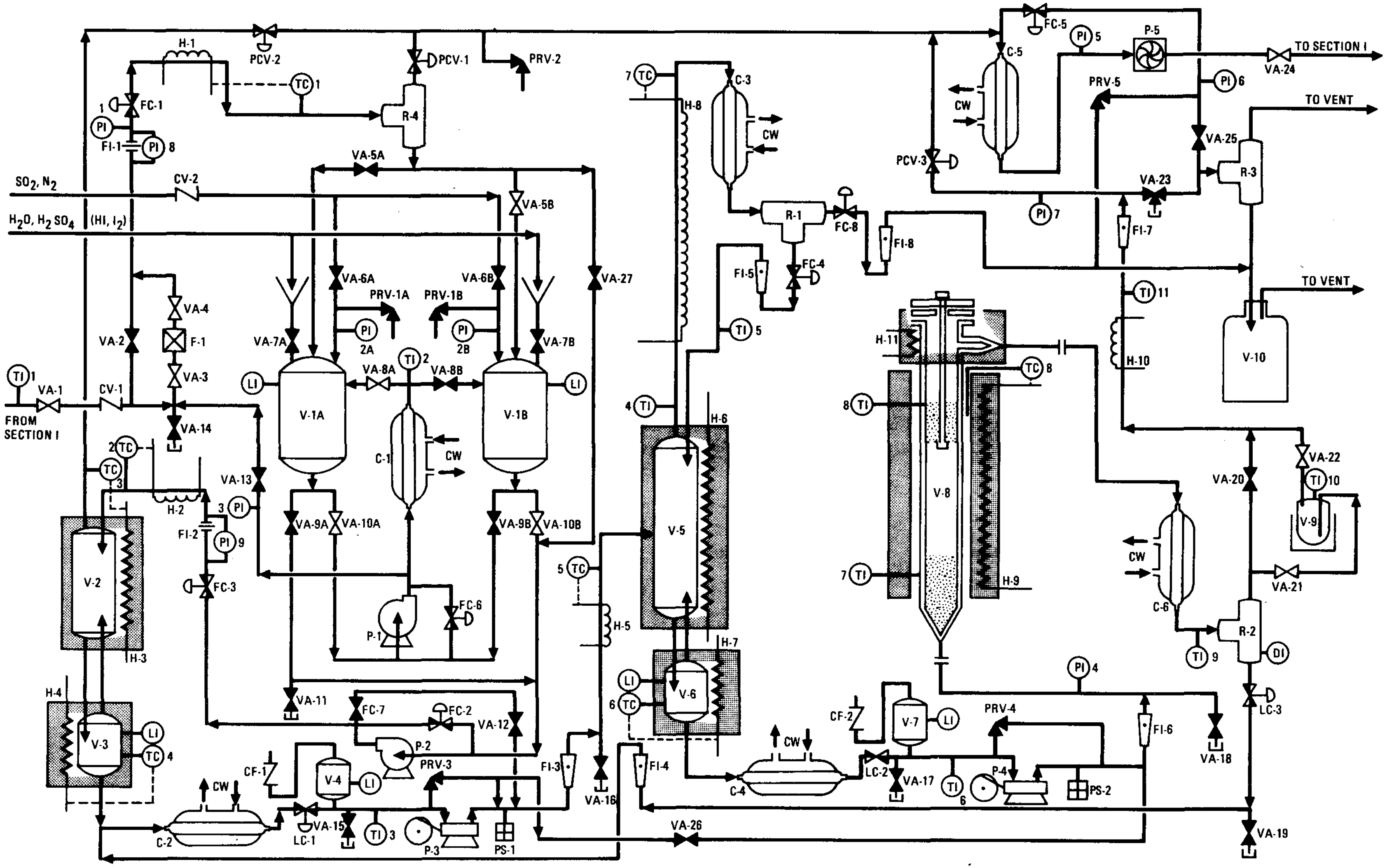

Fig. 2-8. Original flowsheet of Subunit II, bench-scale H_2SO_4 concentration and decomposition

TABLE 2-2
EQUIPMENT LIST FOR THE H_2SO_4 CONCENTRATION AND DECOMPOSITION BENCH-SCALE SYSTEM (SUBUNIT II)

Equipment Number	Equipment Name	Material of Construction	Normal Process Materials Exposure[(a)]	Normal Operating Conditions	
				Temperature, K	Pressure, 10^5 Pa Absolute
C-1	Feed Makeup Cooler	Glass	H_2SO_4, H_2O, SO_2 (HI, I_2)	<425	3.1
C-2	Dilute Acid Cooler	Glass	H_2SO_4, H_2O	Ambient	Ambient
C-3	Still Reflux Condenser	Glass	H_2O (H_2SO_4)	373	Ambient
C-4	Concentrated Acid Cooler	Glass	H_2SO_4, H_2O, SO_2, O_2	625	Ambient
C-5	Offgas Cooler	Glass	H_2O, SO_2, O_2 (HI, I_2, H_2SO_4)	<425	Slightly below Ambient
C-6	Recycle Acid Condenser	Glass	SO_2, H_2SO_4, H_2O, SO_2, O_2	<800	Ambient
CF-1	Dilute H_2SO_4 Float Valve	Glass	H_2SO_4, H_2O	315	Ambient
CF-2	Concentrated H_2SO_4 Float Valve	Glass	H_2SO_4, H_2O	315	Ambient
CV-1	Feed Inlet Check Valve	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	<390	3.1
CV-2	SO_2 Makeup Check Valve	Stainless Steel	SO_2 (H_2O, H_2SO_4)	Ambient	Ambient
F-1	Feed Filter	Teflon	H_2SO_4, H_2O (HI, I_2, SO_2)	<390	<3.1
FC-1	Feed Inlet Control Valve	Glass-Teflon	H_2SO_4, H_2O (HI, I_2, SO_2)	<390	<3.1
FC-2	P-2 Bypass Loop Control Valve	Glass-Teflon	H_2SO_4, H_2O (HI, I_2, SO_2)	<425	Ambient
FC-3	I_2 Removal Column Feed Control Valve	Glass-Teflon	H_2SO_4, H_2O (HI, I_2)	<425	Ambient
FC-4	Still Reflux Control Valve	Stainless Steel	H_2O (H_2SO_4)	373	Ambient
FC-5	P-5 Bypass Loop Control Valve	Glass-Teflon	H_2O, SO_2, O_2 (HI, I_2, H_2SO_4)	315	3.1
FC-6	P-1 Bypass Loop Control Valve	Glass-Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	<425	Ambient
FC-7	Makeup-to-Still Feed Control Valve	Glass-Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	<425	Ambient
FC-8	Excess Still H_2O Control Valve	Glass-Teflon	H_2O (H_2SO_4)	373	Ambient
FI-1	Feed Inlet Orifice	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	<390	3.1
FI-2	I_2 Column Feed Orifice	Teflon	H_2SO_4, H_2O, (HI, I_2)	<425	Ambient
FI-3	Still Feed Rotameter	Glass-Kynar	H_2SO_4, H_2O	315	Ambient
FI-4	Still Recycle Feed Rotameter	Glass-Kynar	H_2SO_4, H_2O	<400	Ambient
FI-5	Still Reflux Rotameter	Glass-Kynar	H_2O (H_2SO_4)	373	Ambient
FI-6	SO_3 Decomposer Feed Rotameter	Glass-Kynar	H_2SO_4, H_2O	315	Ambient
FI-7	O_2 Gases Rotameter	Glass-Kynar	H_2O, SO_2, O_2, (H_2SO_4)	(b)	Ambient
FI-8	Excess Still H_2O Rotameter	Glass-Kynar	H_2O (H_2SO_4)	370	Ambient

TABLE 2-2 (continued)

Equipment Number	Equipment Name	Material of Construction	Normal Process Materials Exposure(a)	Normal Operating Conditions Temperature, K	 Pressure, 10^5 Pa Absolute
H-1	SO_2 Removal Feed Heater	--(c)	--(c)	430	1.01
H-2	I_2 Removal Feed Heater	--	--	<430	>1.01
H-3	I_2 Removal Column Heater	--	--	<430	>1.01
H-4	I_2 Removal Reboiler Heater	--	--	<430	>1.01
H-5	Still Feed Heater	--	--	<440	Ambient
H-6	Still Column Heater	--	--	(d)	Ambient
H-7	Still Reboiler Heater	--	--	605	Ambient
H-8	Reflux Prevention Heater	--	--	375	Ambient
H-9	SO_3 Decomposition Furnace	--	--	<1200	>1.01
H-10	O_2 Gases Reheater	--	--	(e)	>1.01
H-11	SO_3 Decomposer Exit Heater	--	--	(e)	>1.01
LC-1	I_2 Removal Reboiler Level Control Valve	Stainless Steel	H_2SO_4, H_2O	<430	>1.01
LC-2	H_2SO_4 Still Reboiler Level Control Valve	Stainless Steel	H_2SO_4, H_2O	605	Ambient
LC-3	R-3 Liquid Level Control Valve	Stainless Steel	H_2SO_4, H_2O	<440	(f)
P-1	Feed Makeup and Transfer Pump	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	<425	3.1
P-2	I_2 Removal Feed Supply Pump	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	<390	3.1
P-3	Still Feed Metering Pump	Ceramic-Teflon	H_2SO_4, H_2O	315	Ambient
P-4	Decomposer Feed Metering Pump	Ceramic-Teflon	H_2SO_4, H_2O	315	Ambient
P-5	Offgas Transfer Pump	Ryton-Hypalon	H_2O, SO_2, O_2 (HI, I_2, H_2SO_4)	315	3.1
PCV-1	SO_2 Flash Pressure Control Valve	Glass-Teflon	H_2O, SO_2 (HI, I_2, H_2SO_4)	<425	3.1
PCV-2	I_2 Removal Offgas Pressure Control Valve	Glass-Teflon	H_2O, (HI, I_2)	<430	$\sim$Ambient
PCV-3	O_2 Gases Pressure Control Valve	Stainless Steel	H_2O, SO_2, O_2 (H_2SO_4)	<430	$\sim$Ambient
PI-1	Upstream SO_2 Flash Pressure Gauge	Stainless Steel(g)	H_2SO_4, H_2O, SO_2 (HI, I_2)	<390	3.1
PI-2A	Makeup Vessel V-1A Pressure Gauge	Stainless Steel(g)	SO_2, H_2O (H_2SO_4)	<390	3.1
PI-2B	Makeup Vessel V-1B Pressure Gauge	Stainless Steel	SO_2, H_2O (H_2SO_4)	<390	3.1
PI-3	Makeup Feed Pressure Gauge	Stainless Steel	H_2SO_4, H_2O (HI, I_2)	<390	3.1
PI-4	SO_3 Decomposer Supply Pressure Gauge	Stainless Steel	H_2SO_4, H_2O	315	$\sim$1.01
PI-5	Offgas Pressure Gauge	Stainless Steel	H_2O, SO_2, O_2 (HI, I_2, H_2SO_4)	315	$\sim$1.01
PI-6	Offgas Pump Discharge Pressure Gauge	Stainless Steel	H_2O, SO_2, O_2 (HI, I_2, H_2SO_4)	315	3.1
PI-7	O_2 Gases Flowmeter Pressure Gauge	Stainless Steel	H_2O, SO_2, O_2 (H_2SO_4)	<430	$\sim$Ambient
PI-8	Feed Orifice Manometer	Glass	H_2SO_4, H_2O, SO_2 (HI, I_2)	390	3.1
PI-9	I_2 Column Orifice Manometer	Glass	H_2SO_4, H_2O, SO_2 (HI, I_2)	<425	Ambient

TABLE 2-2 (continued)

Equipment Number	Equipment Name	Material of Construction	Normal Process Materials Exposure(a)	Normal Operating Conditions	
				Temperature, K	Pressure, 10^5 Pa Absolute
PRV-1A	Makeup Tank "A" Pressure Relief Valve	Teflon	H_2O, SO_2 (H_2SO_4)	<425	3.1
PRV-1B	Makeup Tank "B" Pressure Relief Valve	Teflon	H_2O, SO_2 (H_2SO_4)	<425	3.1
PRV-2	Offgas System Pressure Relief Valve	Teflon	H_2O, (HI, I_2)	430	1.01
PRV-3	P-3 Discharge Pressure Relief Valve	Stainless Steel	H_2SO_4, H_2O	315	Ambient
PRV-4	P-4 Discharge Pressure Relief Valve	Stainless Steel	H_2SO_4, H_2O	315	1.01
PRV-5	P-5 Discharge Pressure Relief Valve	Teflon	H_2O, SO_2, O_2 (HI, I_2, H_2SO_4)	315	3.1
PS-1	Dil. H_2SO_4 Feed Pulse Snubber	Teflon & Stainless Steel	H_2SO_4, H_2O	315	Ambient
PS-2	Con. H_2SO_4 Feed Pulse Snubber	Teflon & Stainless Steel	H_2SO_4, H_2O	315	Ambient
R-1	Still Reflux Overflow Chamber	Glass	H_2O (H_2SO_4)	373	Ambient
R-2	O_2 Gases - Recycle Acid Phase Separator	Glass	H_2SO_4, H_2O, SO_2, O_2	<430	1.01
R-3	Waste Offgas Phase Separator	Glass	H_2O, SO_2, O_2 (HI, I_2, H_2SO_4)	<435	Ambient
R-4	SO_2 Gas-Feed Liquid Phase Separator	Glass	H_2SO_4, H_2O, SO_2 (HI, I_2)	<425	1.01
TC-1	SO_2 Degasser Feed Heater Control	--	None	<425	--
TC-2	HI-I_2 Vaporizer Feed Heater Control	--	None	<430	--
TC-3	HI-I_2 Vaporizer Heater Control	--	None	<430	--
TC-4	H_2-I_2 Vaporization Reboiler Control	--	None	<430	--
TC-5	Still Feed Heater Control	--	None	<440	--
TC-6	Still Reboiler Heater Control	--	None	605	--
TC-7	Still Vapor Line Heater Control	--	None	375	--
TC-8	Furnace Temperature Control	--	None	<1200	--
TI-1	Feed Temperature	--	None	<390	--
TI-2	Makeup Feed Temperature	--	None	<425	--
TI-3	Dil. H_2SO_4 Pump Feed Temperature	--	None	315	--
TI-4	Still Overhead Vapor Temperature	--	None	374	--
TI-5	Still Reflux Temperature	--	None	373	--
TI-6	Con. H_2SO_4 Pump Feed Temperature	--	None	315	--
TI-7	Furnace Inlet Temperature	--	None	315	--
TI-8	Decomposition Catalyst Temperature	--	None	<1200	--
TI-9	Acid Phase Separator Feed Temperature	--	None	<440	--
TI-10	Caustic Scrubber Temperature	--	None	<800	--
TI-11	Offgas Rotameter Feed Temperature	--	None	(b)	--

TABLE 2-2 (continued)

Equipment Number	Equipment Name	Material of Construction	Normal Process Materials Exposure(a)	Normal Operating Conditions	
				Temperature, K	Pressure, 10^5 Pa Absolute
V-1A	Feed Makeup - Storage Tank "A"	Glass	H_2SO_4, H_2O, SO_2 (HI, I_2)	≤ 425	3.1
V-1B	Feed Makeup - Storage Tank "B"	Glass	H_2SO_4, H_2O, SO_2 (HI, I_2)	≤ 425	3.1
V-2	HI-I_2 Vaporization Vessel	Glass	H_2SO_4, H_2O (HI, I_2)	430	1.01
V-3	HI-I_2 Vaporization Reboiler	Glass	H_2SO_4, H_2O	430	1.01
V-4	Dilute H_2SO_4 Surge Tank	Glass	H_2SO_4, H_2O	315	Ambient
V-5	H_2SO_4 Still Column	Glass	H_2SO_4, H_2O	374-600	Ambient
V-6	H_2SO_4 Still Reboiler	Glass	H_2SO_4, H_2O	605	Ambient
V-7	Concentrated H_2SO_4 Surge Tank	Glass	H_2SO_4, H_2O	315	Ambient
V-8	SO_3 Decomposition Vessel	Quartz	H_2SO_4, H_2O, SO_3,SO_2, O_2	1200	1.01
V-9	Static-Liquid Caustic Scrubber	Glass	NaOH,(h)H_2O,Na_2SO_3,O_2 (Na_2SO_4)	~ 320	1.01
V-10	Wastewater Storage Vessel	Polypropylene	H_2O (SO_2, HI, I_2, H_2SO_4)	<374	Ambient
VA-1	Feed Shutoff Valve	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	≤ 390	3.1
VA-2	Feed Filter Bypass Valve	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	≤ 390	3.1
VA-3	Feed Filter Inlet Valve	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	≤ 390	3.1
VA-4	Feed Filter Outlet Valve	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	≤ 390	3.1
VA-5A	Feed Inlet Valve to V-1A	Teflon	H_2SO_4, H_2O, (HI, I_2)	≤ 425	3.1
VA-5B	Feed Inlet Valve to V-1B	Teflon	H_2SO_4, H_2O, (HI, I_2)	≤ 425	3.1
VA-6A	SO_2 Inlet Valve to V-1A	Stainless Steel	H_2SO_4, H_2O, SO_2	≤ 425	3.1
VA-6B	SO_2 Inlet Valve to V-1B	Stainless Steel	H_2SO_4, H_2O, SO_2	≤ 425	3.1
VA-7A	Funnel Inlet Valve to V-1A	Stainless Steel	H_2SO_4, H_2O, SO_2	≤ 425	3.1
VA-7B	Funnel Inlet Valve to V-1B	Stainless Steel	H_2SO_4, H_2O, SO_2	≤ 425	3.1
VA-8A	Mixing-Cooling Return Valve to V-1A	Teflon	H_2SO_4, H_2O, SO_2	≤ 425	3.1
VA-8B	Mixing Cooling Return Valve to V-1B	Teflon	H_2SO_4, H_2O, SO_2	≤ 425	3.1
VA-9A	I_2 Removal Feed Valve from V-1A	Teflon	H_2SO_4, H_2O, SO_2	≤ 425	3.1
VA-9B	Mixing-Cooling Exit Valve from V-1B	Teflon	H_2SO_4, H_2O, SO_2	≤ 425	3.1
VA-10A	I_2 Removal Feed Valve from V-1A	Teflon	H_2SO_4, H_2O, SO_2	≤ 425	3.1
VA-10B	Mixing-Cooling Exit Valve from V-1B	Teflon	H_2SO_4, H_2O, SO_2	≤ 425	3.1
VA-11	Feed-Makeup System Drain Valve	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	≤ 425	3.1
VA-12	Makeup-to-Still Shutoff Valve	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	315	1.01
VA-13	Feed Recycle Valve	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	≤ 390	3.1
VA-14	SO_2 Removal System Drain Valve	Teflon	H_2SO_4, H_2O, SO_2 (HI, I_2)	≤ 390	3.1
VA-15	I_2 Removal System Drain Valve	Stainless Steel	H_2SO_4, H_2O	315	1.01
VA-16	Still Feed System Drain Valve	Stainless Steel	H_2SO_4, H_2O	<440	Ambient
VA-17	Still Drain Valve	Stainless Steel	H_2SO_4, H_2O	315	Ambient
VA-18	SO_3 Decomposer Drain Valve	Stainless Steel	H_2SO_4, H_2O	<800	1.01

TABLE 2-2 (continued)

Equipment Number	Equipment Name	Material of Construction	Normal Process Materials Exposure(a)	Normal Operating Conditions Temperature, K	Normal Operating Conditions Pressure, 10^5 Pa Absolute
VA-19	Recycle Acid System Drain Valve	Stainless Steel	H_2SO_4, H_2O	<440	1.01
VA-20	Caustic Scrubber Bypass Valve	Stainless Steel	H_2O, SO_2, O_2 (H_2SO_4)	<440	1.01
VA-21	Caustic Scrubber Inlet Valve	Stainless Steel	H_2O, SO_2, O_2 (H_2SO_4)	<440	1.01
VA-22	Caustic Scrubber Outlet Valve	Stainless Steel	H_2O, O_2 (NaOH)(h)	~320	1.01
VA-23	Offgas Pump Bypass Valve	Teflon	H_2O, O_2, SO_2 (HI, I_2, H_2SO_4)	315	3.1
VA-24	Offgas Output to System I Shutoff Valve	Teflon	H_2O, O_2, SO_2 (HI, I_2, H_2SO_4)	315	3.1
VA-25	Offgas Vent Shutoff Valve	Teflon	H_2O, O_2, SO_2 (HI, I_2, H_2SO_4)	315	3.1
VA-26	Makeup-to-Decomposer Shutoff Valve	Teflon	H_2SO_4, H_2O (HI, I_2)	315	1.01
VA-27	Feed Makeup Bypass Valve	Teflon	H_2SO_4, H_2O (HI, I_2)	425	Ambient

NOTES

(a) Constituents present in small amounts or low concentrations are shown parenthetically.

(b) Temperature is set, empirically, to exceed the condensation temperature of all constituents in the stream.

(c) Heating elements do not come in direct contact with process materials.

(d) Temperature is variable along the column, and will be set, empirically to adjust the internal column reflux.

(e) Temperature is empirically adjusted to exceed the dewpoint of the gas composition which is flowing.

(f) Pressure is adjusted via PCV-3 to give net head pressure for flow > 1.01 x 10^5 Pa.

(g) The gauges are protected from the process materials by a teflon diaphragm.

(h) Any of a large variety of alkaline solutions could be used, as convenient.

(1.2 liter/min) of product $H_2(g)$ at STP. The nominal design flowrates of the individual chemical species are:

Feed Material	Feed Rate Mol/min	g/s	lb/hr
H_2SO_4	0.052	0.085	0.676
H_2O	0.286	0.086	0.681
SO_2	0.001	0.001	0.009
HI*	0.001	0.002	0.018

"Light Phase" from Subunit I enters Subunit II through valves VA-1 and CV-1, and it then passes through filter F-1 which protects the small orifice of FI-1 from adventitious crud in the light phase. If the light phase feed is pressurized and hot it will flash in the flow control valve FC-1, and SO_2-H_2O vapor will disengage from the liquid in R-4. If the feed is cool and not pressurized it is necessary to heat it with H-1 sufficiently to boil off dissolved SO_2. The SO_2 and water vapor are pumped out of R-4 under a slight vacuum which is provided by P-5 and which is controlled by PCV-1.

The SO_2-free feed is collected in either V-1A or V-1B, from which it is then metered into V-2, the I_2 removal column. In V-2 the solution is trickled down through raschig ring packing against an upflow of water vapor provided by boilup from V-3. The water vapor strips elemental I_2 from the liquid and promotes the back-reaction of HI with H_2SO_4 to produce I_2, SO_2 and H_2O. I_2, SO_2, and water vapor leave V-2 under a slight vacuum provided by P-5 and controlled by PRV-2.

The solution leaving the bottom of V-3 is pure aqueous H_2SO_4, now somewhat more concentrated than the original light phase. The H_2SO_4 solution is then cooled in C-2 and collected in a surge tank, V-4, from which it is metered into the H_2SO_4 concentration still (V-5 and V-6). The feed is cooled in C-2 in order to protect stainless steel in PS-1 from corrosion and Kynar in FI-3 from heat softening.

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*Iodine is present as both HI and I_2 but the relative proportion is variable and undefined.

V-5 is a packed column of raschig rings in which H_2O is removed from the H_2SO_4. Substantially pure H_2O vapor leaves the top of the column and is totally condensed in C-3. The condensate is divided in R-1 into a condensate reflux stream which is metered through FI-5 back into the top of V-5. Excess overflow is metered to waste through FI-8.

The concentrated H_2SO_4 leaving the still reboiler, V-6, is cooled in C-4 in order to protect the teflon parts of P-4, the stainless steel parts of PS-2, and the Kynar parts of FI-6. The cooled, concentrated H_2SO_4 is collected in surge tank V-7 and then metered into V-8, the H_2SO_4 decomposition chamber.

In the lower end of V-8 the concentrated H_2SO_4 is vaporized from a bed of porous porcelain fragments which extends from the cool exterior portion of the vertical quartz tube into the heating zone of the furnace. The mixture of H_2O, SO_3 and H_2SO_4 vapor is then heated in an unpacked midsection of the tube to a selected decomposition temperature, whereupon it is permitted to contact a bed of catalyst material which is suspended in the upper portion of the heated zone of the furnace. The partially decomposed vapors are disengaged from the catalyst in a section of the quartz tube which extends from the top of the furnace and which is thermally guarded by a heater, H-11, to the extent needed to prevent recondensation of unreacted H_2SO_4.

The vapor effluent from V-8 is then partially condensed in C-6 to a temperature so adjusted that virtually all the H_2SO_4 condenses as a solution, but virtually none of the SO_2 dissolves in the solution. The acid condensate is then disengaged from the remaining H_2O-SO_2-O_2 gas-vapor in R-2 and is metered through FI-4 into the feed stream to the H_2SO_4 distillation column V-5. The oxygen-containing vapor may then either be crudely "analyzed" by running it through a caustic scrub in V-9 prior to metering the residual gas to waste through VA-23, or the total gas may be recycled to Subunit I, without removal of SO_2, through VA-20, PCR-3, C-5, P-5, and VA-24. The function of H-10 is to eliminate condensation in the low-flow gas rotameter FI-7, thus permitting accurate flowrate metering.

The foregoing system is designed to provide some operational conservatism and flexibility, and to separate its functional steps. The ease of procurement of parts and the ease of construction of the system could be made greater by reducing the operational conservatism and flexibility, but any compromise that is drawn among various conflicting objectives and the practical limitations which exist will necessarily be in a judgmental gray area. As designed, this system has about two dozen or so manual controls which are likely to be difficult, because of the typically low flowrates and high surface-to-volume ratios. The manual control of this system will be extremely demanding of operator attention when it is all running in continuous flow, even with the degree of conservatism and flexibility in the design. If the practical operability of the system is to be maintained in a simpler system it will be necessary to reduce its flexibility and to combine operations which are now separated.

2.1.3. Subunit III, HI Separation and Decomposition

Design of the HI separation and decomposition system, Subunit III of the overall bench-scale system, has been initiated but is in an incomplete, preliminary stage. The design of the heavy phase feed metering, storage, and synthetic heavy phase makeup system is being modeled on the I_2 melting and feed system of Subunit I. The liability to plugging of the feed system of Subunit III is less than that of the Subunit I I_2 feed system, but still exists.

2.2. CONSTRUCTION AND OPERATION

2.2.1. Subunit I Construction Criteria

2.2.1.1. Reactant Supply. The main solution reaction will be carried out under a pressure of up to 250 kPa and at a temperature at least up to the melting point of I_2. It is necessary that the reactants be supplied with enough pressure to drive them into the reaction vessel. It is also required in a continuous reaction that these reactants be metered into the reactor. The reactants, SO_2 and H_2O, are metered with flow control valves and their flowrate measured using conventional rotameters. The sources are cylinder SO_2 and a N_2-pressurized H_2O reservoir. The H_2O reservoir has sufficient capacity to supply the system for several hours, and is easily replenished directly from a distilled water line. The cylinder of SO_2 has a capacity of several days. The reactant I_2 is melted and delivered as a liquid. Metering of I_2 is accomplished by using a Teflon flow control valve and measuring the flowrate by manometrically observing the pressure drop across an in-line orifice. Two alternate I_2 supplies have at least two hours capacity each. While one supply is being used the other supply is loaded, melted and pressurized with N_2.

2.2.1.2. Reactor. The reactor is intended to provide adequate mixing and residence time of the reactants in controlled temperature conditions. The reactor consists of an internally finned tube which alters fluid flow directions a number of times. This flow is driven by an excess gaseous SO_2 flow. The liquid residence time is long compared to the gas residence time, that is, many seconds compared to fractions of a second. The reactants are supplied to the reactor by a train injection system where the SO_2 enters at the bottom of the train and both H_2O and filtered $I_2(\ell)$ are sequentially injected into the flowing SO_2 through 0.25 mm diameter orifices. The injecting of these reactants should tend to provide better metering and mixing characteristics. Provision for recycling the SO_2 driving gas will be added to the system later. However, in initial tests the excess SO_2 will be vented from the system. The reactor is jacketed for temperature control.

2.2.1.3. Gas-Liquid Separator. After discharge from the reactor, the reaction mixture flows to a thermostated chamber which serves as a gas-liquid disentrainment system. The pressure in the system is controlled by a relief valve which vents unreacted SO_2 thus holding the pressure constant in the reactor. The two liquid phases which have been disentrained from the SO_2 by the action of gravity on the system are discharged from the bottom of the separator.

2.2.1.4. Liquid-Liquid Separator. This system, which is very similar in design to the gas-liquid separator, provides separation of the H_2SO_4(sol) phase from the heavier HI_x(sol) phase. The controls for the liquid level in the gas separator and the liquid-liquid interface level in the gravity-operated liquid separator are the exit flow control valves of the liquid-liquid separator. When the system is in balance the rates of delivery of each liquid phase from the gas separator matches their individual production rates and, of course, the exit rates from the liquid-liquid separator. For the purpose of matching these flows, there are flow control valves and flow metering devices in the exit lines. The H_2SO_4(sol) is monitored by a rotameter and the HI_x(sol) is monitored by a differential manometer which measures pressure drop across an orifice identical to that in the I_2 supply.

2.2.1.5. Materials of Construction. Glass and Teflon have been selected as materials of construction to provide corrosion resistance to the product HI_x(sol) and H_2SO_4(sol). For the I_2 supply and the phase separators commercial Pyrex pipe with Teflon (TFE) gaskets are used. For connections, valves, and some of the tubing Teflon has also been utilized. For the reactor and manometers Pyrex units, as constructed at GA, have been employed. Teflon check valves have been used to protect gas and water supply lines, which are made of stainless steel.

2.2.1.6. Vacuum Flask SO_2 Degasser. The HI_x lower phase of the liquid-liquid separator is saturated with unreacted SO_2. It is essential to remove the SO_2 from this phase to avoid the possibility of formation of H_2S and sulfur by reaction with the product HI during the various treatments of the lower phase. A vacuum flask degasser for removal of the SO_2 is being constructed. The liquid to be flashed is entered tangentially at moderate velocities into a flash drum which has a demister to remove spray carried by the vaporized SO_2. The SO_2 evaporates from a thin film of HI_x(sol) on the walls of the drum. After degassing the liquid collects in the bottom of the drum and is pumped from there to the next unit.

2.2.1.7. Flow Diagram. Figure 2-9 shows the as-built flow diagram for Subunit I and Figs. 2-10, 2-11 and 2-12 are photographs showing Subunit I

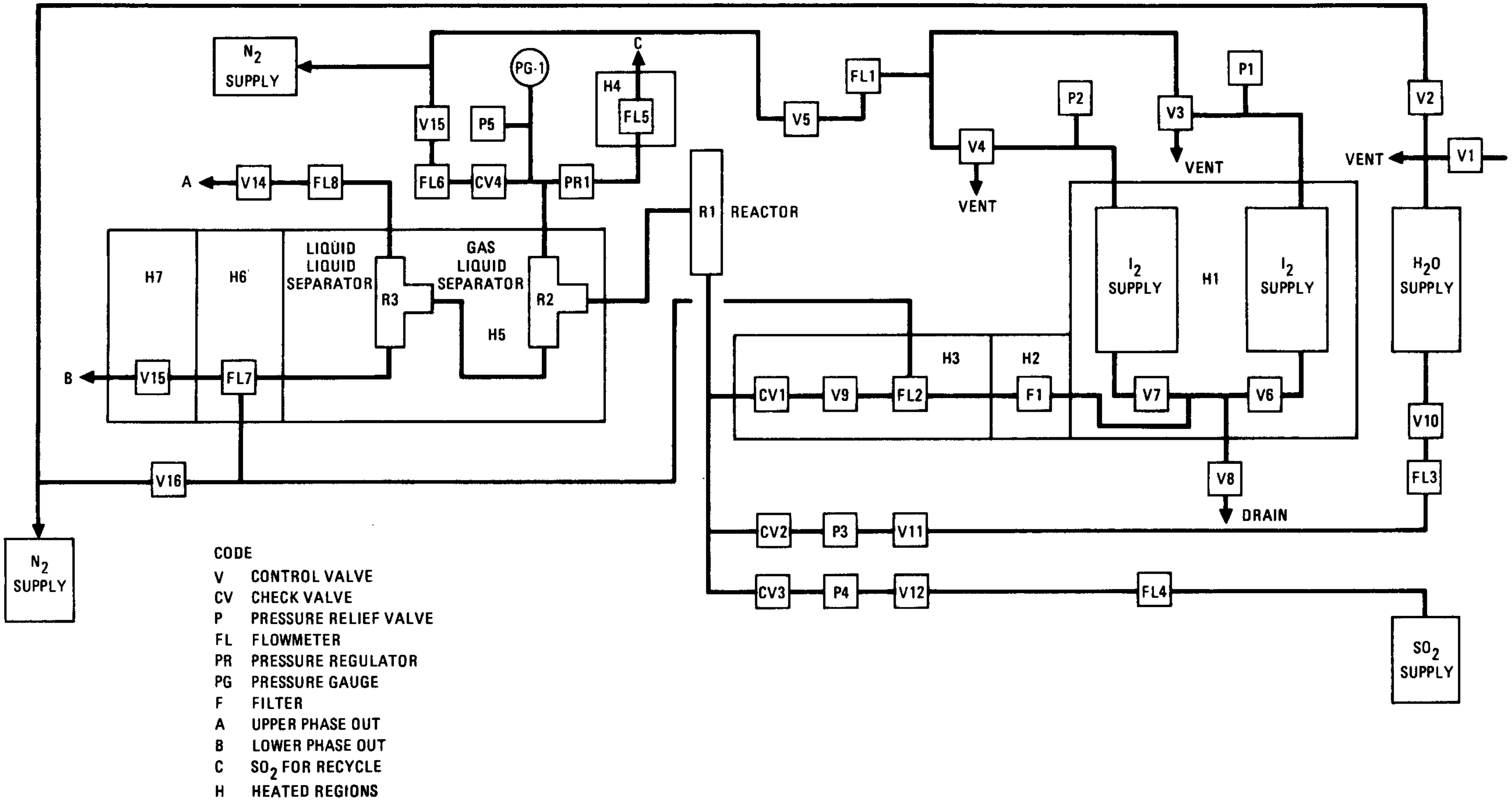

Fig. 2-9. Subunit I as-built flow diagram

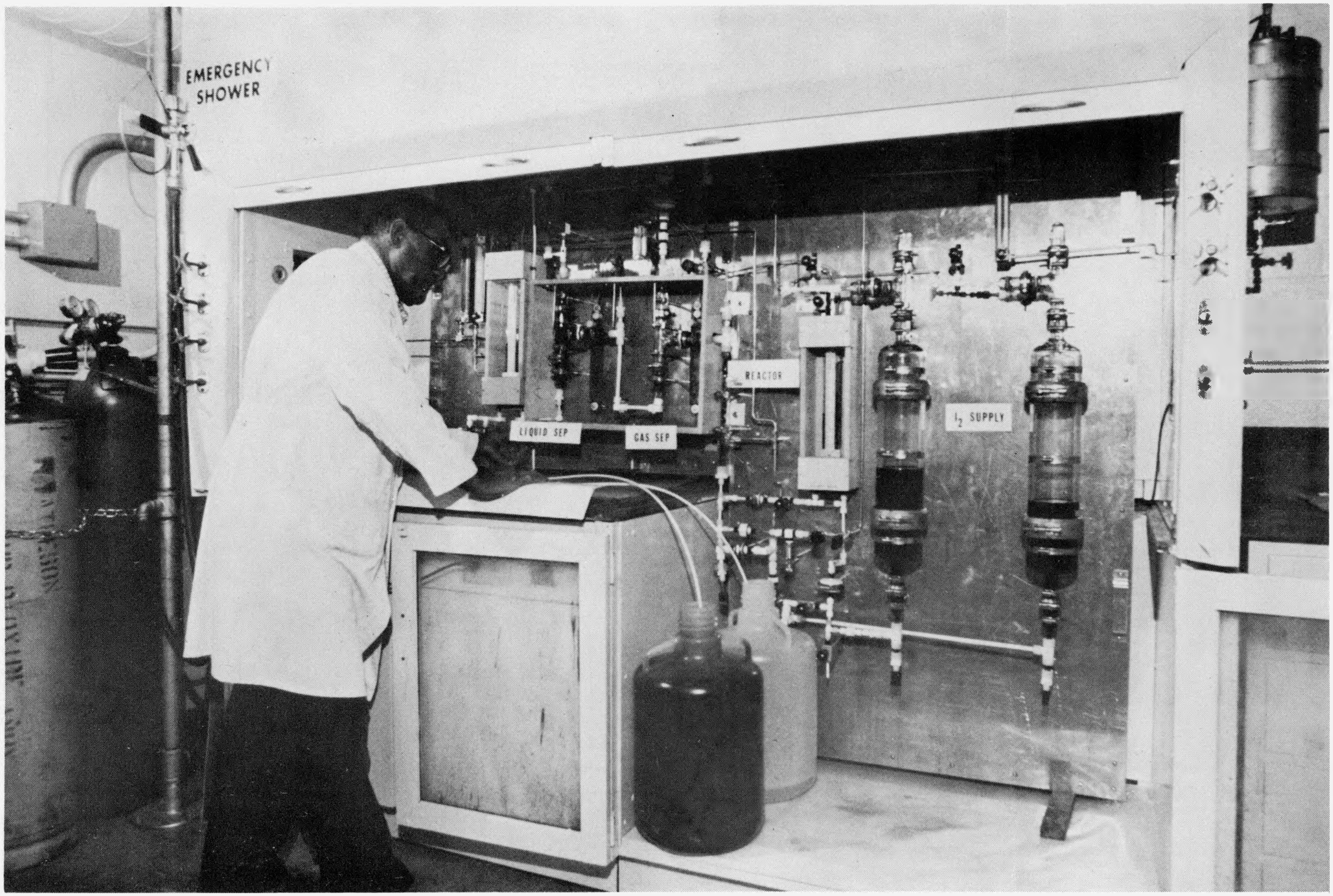

Fig. 2-10. Subunit I during cold flow testing

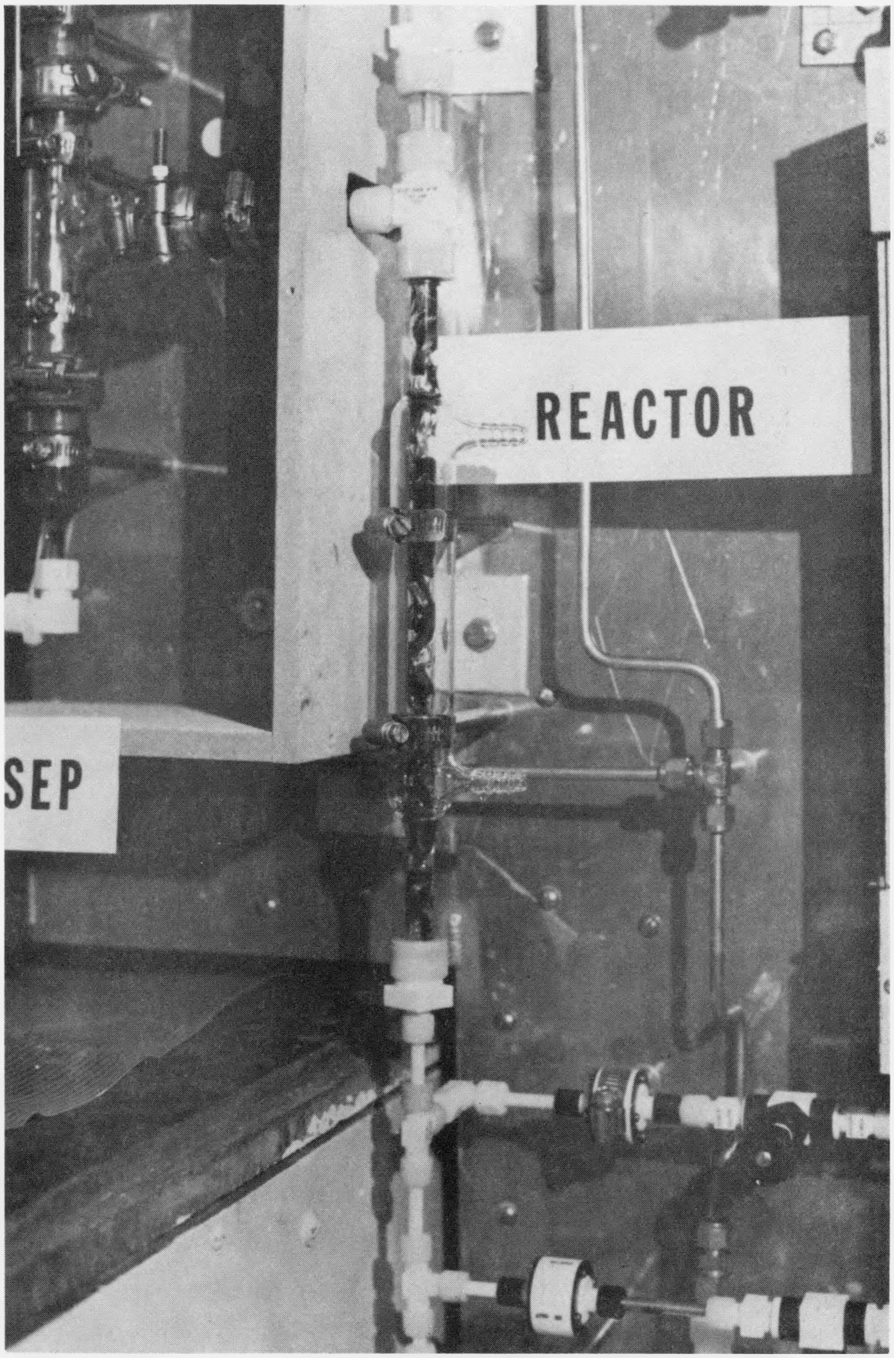

Fig. 2-11. Subunit I, reactor during cold flow testing

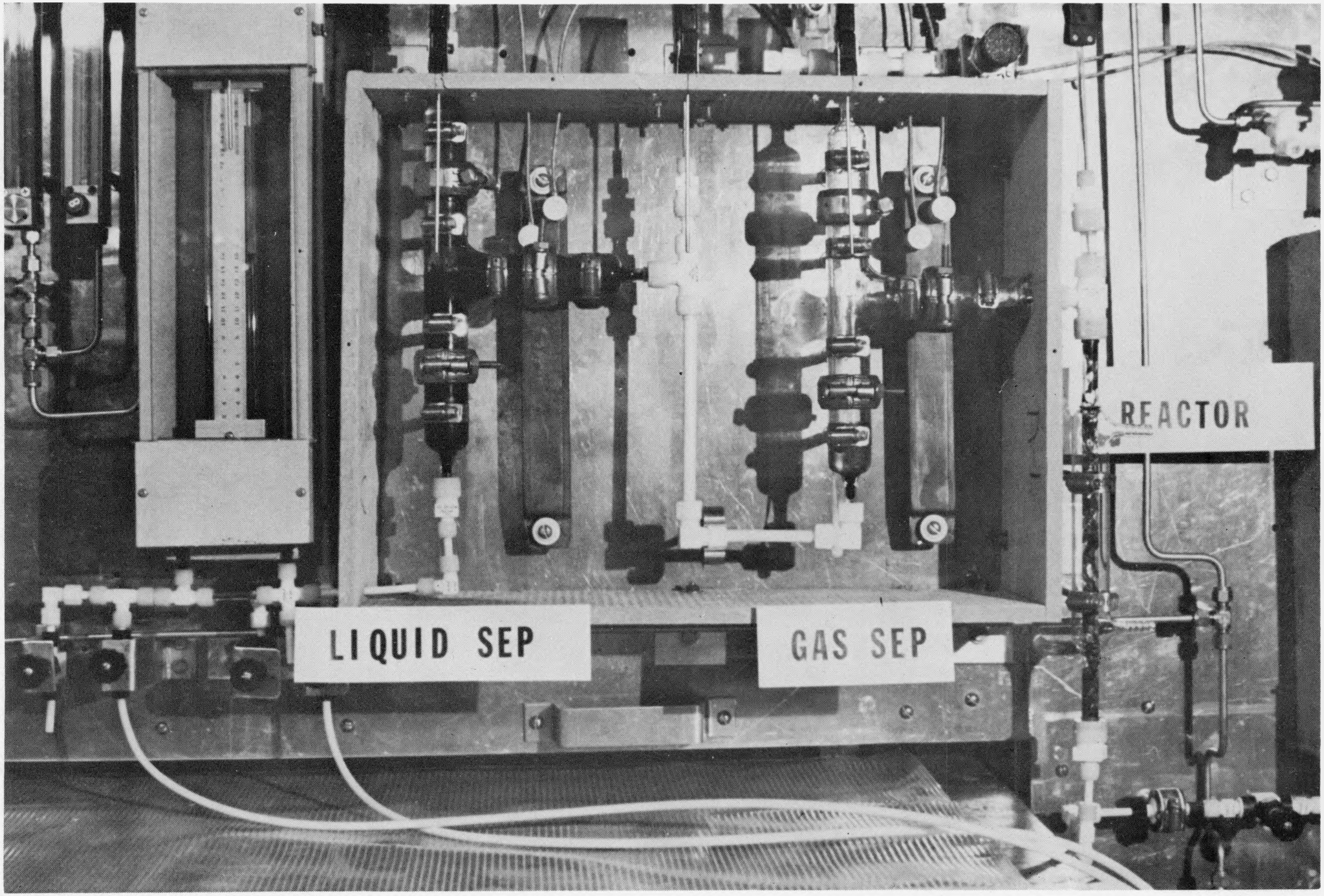

Fig. 2-12. Subunit I, phase separators during cold flow testing

during cold flow testing. As is apparent from the flow diagram and photographs, the subunit as built differs from the original flowsheet (Fig. 2-1) on a few points. Most of the differences are due to three major construction considerations.

1. Space — While a separate laboratory is being readied for assembly of the entire bench-scale system, Subunit I is temporarily housed in a chemistry fume hood with limited space.

2. Time — Modifications to the original flowsheet were made to avoid delays caused by long lead time items, e.g. liquid movement is being accomplished by N_2 overpressure instead of with pumps.

3. Visibility — In order to visually observe as much as possible of the various components, thermally insulated chambers with windows, instead of jacket heaters, have been used more extensively than planned.

A detailed description follows on how the system as built differs from the original flowsheet.

H_2O system

a. Pump P-1 has been replaced by a pressurized N_2 system (space saver).

b. Heater H-1 has been deleted as such. The H_2O supply line is adjacent to the I_2 supply ovens and receives adequate heat.

SO_2 system

a. Heater H-3A has been deleted because the SO_2 temperature was found adequate for the reaction.

b. The SO_2 recycle unit has not yet been assembled, thus excess SO_2 is being vented into the fume hood.

c. The SO_2 cryogenic trap V-5A has also not been assembled. Its size will depend on measurements of total SO_2 flow and I_2 content.

I_2 supply system

a. Extra heaters were added to the I_2 supply chamber to achieve a more uniform temperature distribution.

b. A filter was added to the I_2 supply line to avoid the necessity of using extra-pure I_2.

c. The entire I_2 supply system, up to the point of injection into the reactor, was placed in a thermally insulated, heated chamber to prevent freezing.

Reactor and separators

a. The recycle system from R-2 (liquid-gas separator) to R-1 (main reactor) which includes pump P-2, has not yet been built: its need and use will be evaluated during operation.

b. R-2 and R-3 (liquid-liquid separators) have been placed in a heated chamber with windows to maintain the required temperature and permit visual observation of the separator behavior. Heater H-4, between R-2 and R-3, could therefore be omitted.

2.2.2. Construction of Subunit I

2.2.2.1. Mounting Systems. The subunit has been constructed as a single unit and each component has been mounted on a large aluminum mounting board designed to fit in a hood as shown in Fig. 2-10. The back of this board has been stiffened through the use of aluminum angle iron outlining and crossing the back of the board. Thus, using care, the unit can be moved. It is held in place in the hood by connections to the hood walls. The unit will be moved later for system integration purposes.

Stainless steel adjustable clamps mounted on standoffs on the aluminum board are generally used to hold the Pyrex units. Valves are also mounted on standoffs. Much of the Teflon piping is free standing.

2.2.2.2. Temperature Control. Since I_2 and the product HI_x are solids at room temperature (hydrous HI_x will precipitate I_2 as temperature is reduced) forced air ovens are built around the units. The I_2 supply vessels are in a partly isolated oven such that one side of the oven may be supplied with more heat than the other. This is useful because of the need to heat and melt the I_2 in one supply vessel while the other is operating at a fixed temperature. Four separate 1 kW heaters are used. Control is accomplished using a thermocouple located near the surface of each heater. The signal from the thermocouple is input to a Barber-Coleman Model 1254 Controller which controls the duration of the power cycle to the heater. The I_2 temperatures are sensed by thermocouples located internally within the lower part of the supply vessels. The I_2 supply oven also contains flow shutoff valves, the I_2 filter, and the appropriate transfer lines.

The I_2 manometer and the delivery and control lines are each located in a separate, temperature-controlled oven. The differential manometer utilizes liquid I_2 as the manometric fluid. Temperatures above the melting point of I_2 are also necessary to keep $I_2(\ell)$ flowing to the reactor.

The reactor is designed to accept gaseous SO_2, liquid H_2O, and liquid I_2. This mixture reacts exothermically, raising the average temperature. During operation it will be necessary to either heat or cool the reactor. For this reason the reactor has been designed with a jacket so that a temperature-controlled fluid from a thermostated source may be pumped through the jacket. This will establish the main solution reaction temperature, which is measured in the exit stream from the reactor.

The separator oven is expected to be operated at this main solution reaction temperature. It is controlled by two 500 watt heaters in parallel and controlled using a single thermocouple. There are two additional temperature readouts within the forced air oven that encloses the two separators. Additionally, a thermocouple, which senses the temperature of the products themselves going from the gas separator to the liquid separator, is installed within the Teflon line.

Temperature control is accomplished in the SO_2 exit line to assure operation of the flow meter and avoid plugging the exit line.

Two temperature-controlled ovens have been built around the HI_x(sol) exit differential manometer and the exit lines, including the flow control and sampling valves. No temperature control has been installed around the H_2SO_4(sol) exit system.

2.2.3. Preliminary and Operational Testing of Subunit I

2.2.3.1. Cold Testing of the Engineering Characteristics of the System. After assuring integrity by pressure leak testing, an attempt to understand the flow characteristics of the constructed unit was made. In the cold flow tests, CH_3-CCl_3 with a little dissolved I_2 was used to simulate molten I_2 and N_2 was used in place of SO_2. During the tests the behavior of the differential manometers and the flow control valves, and the reactor flow and separator characteristics, were all observed. After initial tests some changes were made to the reactor fin system to provide better mixing properties which were verified in later tests. Instability of Teflon control valves was found to be a problem and seems to indicate that the operation of the reactor will depend on continuous visual monitoring and flow control. In fact, steady state operation of the reaction is best assured by achieving and maintaining stable levels in the gas-liquid and liquid-liquid interfaces in the two separators. This, coupled with constant inlet flow of H_2O and I_2 should allow attainment of steady state. It was also noted that a considerable excess of SO_2 was needed to drive the liquids through the reactor fin system. Thus, a recycle system for gaseous SO_2 now has a higher priority than before these tests.

2.2.3.2. Hot Testing of the Ovens. The thermal characteristics of the ovens built around the components have been tested. The first test revealed the temperature gradients in the ovens to be too large. Since these first tests forced air circulation and additional insulation have been added to the ovens to provide sufficient temperature uniformity.

2.2.4. Subunit II Construction Criteria

The overall criteria for Subunit II, H_2SO_4 concentration and decomposition, are:

1. The unit shall reproduce the individual process operating steps of the large-plant conceptual flowsheet.
2. The process operating steps shall occur at the temperatures used for the large-plant conceptual flowsheet.
3. The bench-scale equipment shall be designed and instrumented to facilitate the gathering of performance data useful for guiding scaleup and detailed design of pilot-plant-scale equipment.

Limitations of time and resources make it unfeasible to meet all the foregoing criteria strictly, and some of their particular aspects are conflicting. The strictness which the particular processing steps of the large-plant conceptual flowsheet are reproduced in the bench-scale system has been somewhat relaxed to facilitate the taking of data on the behavior of the materials as they undergo processing; for example, the SO_2, HI, and I_2 are removed from the H_2SO_4 solution in a single step of the large-plant conceptual flowsheet, but the removals are done in two steps in the bench-scale design.

In the current design of Subunit II the main departure from criterion 1) is that the H_2SO_4 concentration is done in distillation column instead of a series of flash chambers. Criterion 2) departs from the large-plant conceptual flowsheet in that the H_2SO_4 concentration is at constant ambient pressure instead of in a sequence of pressure stages, and that the H_2SO_4 decomposition occurs at ambient pressure instead of 8.6×10^5 to 5.2×10^5 Pa, absolute. The main departures from criterion 3) are that energy conservation and thermodynamic efficiency are ignored and that automatic process control has been avoided, with the exception of a few temperature controls.

A simplified schematic illustration of the current design of Subunit II is given in Fig. 2-13. A more detailed flowsheet is given in Fig. 2-8.

The functional subsystems of Subunit II are defined for convenience in later discussion to be:

1. the feed system
2. the SO_2 removal system
3. the $HI-I_2$ removal system
4. the H_2SO_4 concentration system
5. the H_2SO_4 decomposition system
6. the offgas system.

2.2.4.1. Feed System. The feed system shall provide flow metering of the "light phase" liquid effluent from Subunit I at a rate of 1×10^{-7} m^3/s. The light phase flow from Subunit II is assumed to be 50 wt% H_2SO_4 aqueous solution at an absolute pressure from ambient to 3.1×10^5 Pa and at a temperature from ambient to 390 K. Variable amounts of SO_2, HI, and I_2 on the order of 0.5 to 1.5 wt% each are dissolved in the solution, with some of the I_2 possibly occurring as a solid phase.

The feed system shall also provide the capability for makeup of synthetic feed solutions in batches of 3×10^{-3} m^3 each and with a makeup

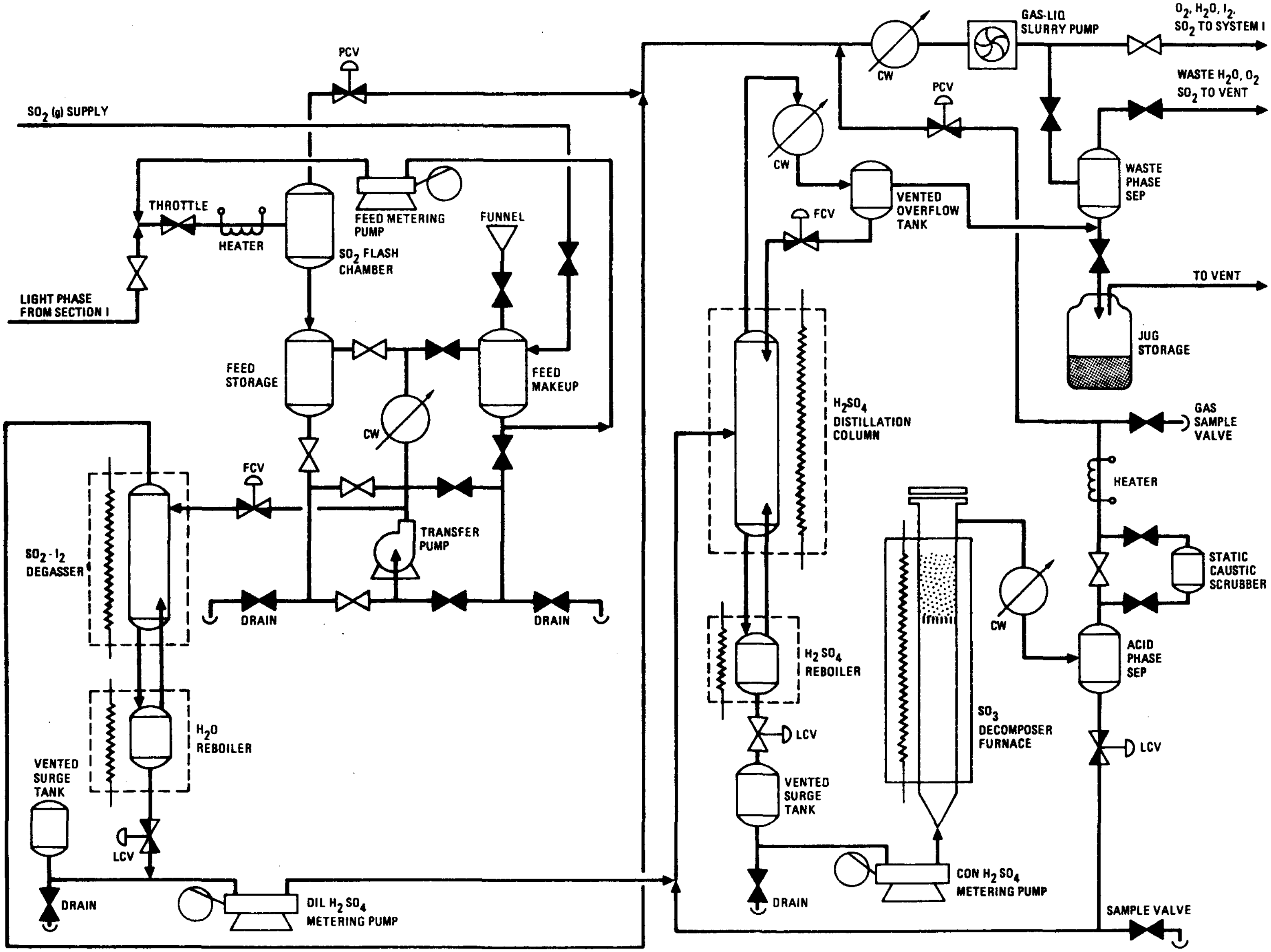

Fig. 2-13. Bench-scale Subunit H_2SO_4 concentration and decomposition (simplified)

time not exceeding 30 minutes. The synthetic feed solution compositions are:

Feed	Weight Percents H_2SO_4	H_2O	HI	I_2	SO_2
SO_2 Removal System Feed	49.0	48.7	1.2	0.8	0.3
$HI-I_2$ Removal System Feed	53.0	48.7	1.2	0.8	0
H_2SO_4 Concentration System Feed	60.0	40.0	0	0	0
H_2SO_4 Decomposition System Feed	98.0	2.0	0	0	0

Capability for delivering these feeds to the inlets of the respective subsystem of Subunit II shall be provided.

2.2.4.2. <u>SO_2 Removal System</u>. The SO_2 removal system shall provide flow control at a rate of 1×10^{-7} m^3/s for light phase supplied at an absolute pressure of 3.1×10^5 Pa by throttling to approximately ambient pressure. Provision for heating the light phase to its normal boiling point and for separating residual liquid from gases evolved following depressurization and heating shall be made.

2.2.4.3. <u>$HI-I_2$ Removal System</u>. The $HI-I_2$ removal system shall provide flow metering and control at a rate of 1×10^{-7} m^3/s for input SO_2-free light phase at its normal boiling point. Heating capability for the input shall be provided to ensure that its temperature is that of the subsequent $HI-I_2$ removal operation.

Removal of I_2 shall be effected by countercurrent contact of the input liquid against heated water vapor at temperatures and for times adequate to vaporize substantially all the I_2 from the liquid. The heated water vapor shall be generated from the liquid effluent of the countercurrent contacting operation. The countercurrent contact time and temperature shall also effect the substantially complete conversion of any HI present to I_2 and SO_2 by back-reaction with H_2SO_4.

2.2.4.4. $\underline{H_2SO_4}$ Concentration System. The H_2SO_4 concentration system shall cool the effluent of the HI-I_2 removal system from its normal boiling point to 315 K. The effluent is assumed to be 60 wt% H_2SO_4 aqueous solution flowing at a rate of 9×10^{-8} m^3/s. After cooling, the acid solution shall be metered at a controlled flowrate of 9×10^{-8} m^3/s into a fractionation still from which 98 wt% H_2SO_4 solution and H_2O vapor substantially free of H_2SO_4 shall be produced in separate streams.

The system shall be capable of storing 3×10^{-3} m^3 of cooled effluent from the HI-I_2 removal step, and of reheating the cooled effluent to temperatures up to its normal boiling point.

2.2.4.5. $\underline{H_2SO_4}$ Decomposition System. The H_2SO_4 decomposition system shall cool the 98 wt% H_2SO_4 effluent of the H_2SO_4 concentration system from its normal boiling point to 315 K, at a flowrate of 8×10^{-8} m^3/s. After cooling, the acid shall be metered at a controlled flowrate of 4×10^{-8} m^3/s into a vertical-tube decomposition chamber where vaporization of the liquid occurs and then catalytic decomposition of the vapor occurs to within 98% of composition change associated with the decomposition stoichiometry. The system shall provide nominally isothermal decomposition temperatures from 800 K to 1300 K at ambient pressure for varying catalyst bed volumes having empty-tube nominal slug flow contact times of up to 10 sec.

The system shall provide controllable cooling of the effluent from the decomposition chamber such that undecomposed H_2SO_4 solution may be condensed at a temperature effecting a virtually complete partitioning between H_2SO_4 and SO_3 versus SO_2 and O_2. The H_2SO_4 solution and the uncondensed gases shall then be separated, and the solution metered at a flowrate of 4×10^{-8} m^3/s into the still feed stream of the H_2SO_4 concentration system.

2.2.4.6. Offgas System. The offgas system shall collect gas and vapor from the SO_2 removal step, the HI-I_2 removal system, and the H_2SO_4 decomposition system through control valves which permit regulating the pressure differential between the offgas system and the other subsections of the overall unit. The pressure on the offgas pump suction side of the system shall be adjustable from 5×10^4 to 1×10^5 Pa, absolute. The maximum gas flowrate at operating temperature and pressure at the offgas pump suction shall be 6×10^{-5} m^3/s. Capability of condensing H_2O vapor at 315 K shall be provided at the offgas pump suction to maintain the total gas plus condensate volumetric flowrate below 6×10^{-5} m^3/s against discharge pressures of up to 3.1×10^5 Pa, absolute with suction pressures as low as 5×10^4 Pa, absolute. The system shall have the options of discharging to the feed inlet SO_2 stream of Subunit I or to a gaseous waste vent.

For the gaseous effluent of the H_2SO_4 decomposition system the offgas system shall provide means of removing substantially all SO_2 from the O_2 in a form amenable to subsequent quantitative chemical analysis, and shall provide flowmetering capability of the SO_2-free gaseous effluent, or of the whole gaseous effluent of the H_2SO_4 decomposition system when the SO_2 removal capability is bypassed.

2.2.4.7. Materials of Construction. The materials of construction of Subunit II which contact the process materials are glass, quartz, an alumina ceramic, Teflon, Polypropylene, Kynar, Hypalon, and 316 stainless steel. The foregoing selection of materials is conditioned by the commercial availability of the various equipment components at reasonable cost and with reasonable delivery times. Glass and teflon have been preferred unless some specific consideration supervened. Quartz is used for the H_2SO_4 decomposition chamber to withstand temperatures up to 1300 K and the strong thermal gradients which will exist in the chamber. The metering pumps which seem most suited to the precise-flow feed service for the H_2SO_4 concentration still and the H_2SO_4 decomposer are commercially supplied with alumina ceramic plungers. The rotameters commercially available in the very low flow rate ranges required have Kynar end-fitting pieces. The offgas pump capable of withstanding the corrosive action of HI and I_2 for gas-liquid-solid flow is available with a variety of plastic body-elastomeric impeller combinations, of which a Teflon body and a Hypalon impeller seem likely to be most resistant to chemical attack. The pressure snubbers, which are incorporated with the intent of ensuring accurate instantaneous flow measurements of the H_2SO_4 concentration and H_2SO_4 decomposition feeds, are commercially available with 316 stainless steel end fittings. The feed makeup and transfer pump wetted parts are Ryton. The cooling of some streams is an adaptation to the limits on the service conditions of those materials other than glass, teflon, and quartz instead of adhering to strict modeling of the large-plant conceptual flowsheet.

2.2.5. Construction of Subunit II

Construction of Subunit II has not been initiated yet. Some equipment items have been procured or are on order, but most parts are still in the process of being specified in detail and ordered. Items which have been procured or are on order are V-8 and its furnace, P-3, P-5, and some temperature and electric power control instruments.

2.2.5.1. Mounting System. The mounting system will in general be similar to that for Subunit I. Its detailed specification in particular instances will be done after the specification and ordering of the main equipment items is substantially completed.

2.2.5.2. Thermal Supplies and Controls. Equipment-on-loan is being collected wherever possible, and the ordering of items for service to which loaned equipment cannot be adapted will be done after collection and checkout of loan items is completed.

3. PROCESS ENGINEERING

3.1. INITIAL CONSIDERATIONS

In the process of screening thermochemical water-splitting cycles, short-cut calculations, for example on theoretical thermodynamic efficiencies, have their place in revealing potentially attractive cycles. But once screening has been done and a potential cycle is discovered, a complete process engineering flowsheet is the only basis for a good evaluation of that cycle. Such a flowsheet will reveal how the phase separations and the heat exchanges required to perform the cycle's chemistry have their effect on the actual performance of that cycle.

The GA sulfur-iodine cycle, which is purely thermochemical, can be described by chemical reactions (1) through (3). Separation of the H_2SO_4 and HI_x formed in the initial solution reaction takes place under gravity, as the acids are almost completely immiscible. The upper phase contains almost all of the H_2SO_4, and the lower phase contains almost all of the HI_x. It takes, however, several process engineering steps to perform the chemistry described by the reactions. The following list of transformations, for example, is a more realistic description of the cycle.

$$H_2O\ (1) + SO_2\ (g) + xI_2\ (1) \rightarrow H_2SO_4\ (sol) + 2HI_x\ (sol) \tag{4}$$

$$H_2SO_4\ (sol) \rightarrow H_2SO_4\ (1) \tag{5}$$

$$H_2SO_4\ (1) \rightarrow H_2SO_4\ (g) \tag{6}$$

$$H_2SO_4\ (g) \rightarrow H_2O\ (g) + SO_3\ (g) \tag{7}$$

$$SO_3\ (g) \rightarrow SO_2\ (g) + 1/2\ O_2\ (g) \tag{8}$$

$$2HI_x\ (sol) \xrightarrow{H_3PO_4} 2HI\ (g) + (x-1)I_2\ (l) \qquad (9)$$

$$2HI\ (g) \rightarrow H_2\ (g) + I_2\ (g) \qquad (10)$$

$$I_2\ (g) \rightarrow I_2\ (l) \qquad (11)$$

From an engineering viewpoint, a major advantage of the GA thermochemical water-splitting process is that the system is virtually an all-fluid process. Potentially some solid I_2 must be handled, but I_2 melts at the relatively low temperature of 387 K, and if its handling as a solid is inconvenient, it can be liquefied. The chemical complexity of the system is moderate. Three primary chemical reactions and the separation steps permit good flexibility in fitting the process to varying thermal matching requirements while not leading to overwhelmingly complex reactions and separation steps.

The first process engineering evaluation of a new process often begins before the needed data are fully available. The initial flowsheet defines the energy-sensitive process areas and contributes to guiding the subsequent laboratory data acquisition. It is, therefore, appropriate to bridge data gaps somewhat optimistically rather than discard the process by making overly conservative assumptions. On this basis, in 1975 a potentially attainable thermal efficiency* was estimated to be 52% [Ref. 3-1]. Then strengthened by this result, the design of a complete process engineering flowsheet was started, which resulted in a 41% efficiency [Ref. 3-2]. For this process design, however, data gaps no longer needed to be bridged with optimistic assumptions, but actual data on reaction yields and physical separations could be used, which then had become available from laboratory experiments. Where data were still missing, realistic engineering estimates were made.

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*Thermal efficiency is defined as the ratio of the higher heating value of the H_2 produced to thermal output of the nuclear reactor.

Although this first complete process engineering flowsheet reflects a greater chemical knowledge and engineering understanding than the initial evaluation, it is still an interim result and needs to be further modified. The most efficient meshing of energy flow patterns is determined by a trial and error process requiring several overall system iterations. Moreover, continued efforts in the laboratory on the chemistry of the cycle [Ref. 3-3] have developed improved yield data and alternate processing methods whose effects should be investigated. Therefore, under DOE sponsorship, the design of a new flowsheet was initiated. Several constraints and subobjectives guide this process engineering design effort:

1. The design reference heat source is a process heat HTGR, producing 1256 K helium at the core outlet. The inlet temperature associated with this outlet temperature specification, for proper temperature distribution in the core, is 772 K.

2. The heat content of the helium circulating through the core of the process heat HTGR is transferred to the water-splitting process through an intermediate helium heat-transfer loop. This assures isolation of the water-splitting process from radioactive contamination that potentially could be caused by leaks in heat exchangers containing the reactor core primary helium.

3. The various transfer pump and gas compressor power demands of the process are supplied by turbomachinery in the intermediate helium heat-transfer loop, rather than under the more severe temperature service and more difficult radioactive contamination maintenance conditions of the primary helium.

4. Since a high thermodynamic efficiency is sought, the process heat demand vs. temperature function and the helium heat delivery vs. temperature function must be matched to avoid large thermodynamic irreversibilities associated with too-large values of heat transfer ΔT.

5. Heat available from within the water-splitting process must be reused whenever it is at a temperature greatly different from that of cooling water or cooling air; the tendency is to be more capital-intensive with respect to energy reuse and efficient transfer of energy than has been justifiable, historically, in industrial chemical processes when energy was relatively cheap.

6. Many of the thermochemical data needed to optimize the design are being obtained but will not all be available at the time it is necessary to specify the base process flowsheet design. Best estimates will be made in portions of the design, necessitating flowsheet review and modification later, as data become available.

Due to the aforementioned continued laboratory efforts the flowsheet under current development will differ significantly from the previous one. The following summarizes the major changes:

1. The main solution reaction (4) where the SO_2, H_2O and I_2 are reacted to form the two acids, will be operated at approximately 368 K with an increased amount of I_2. This is based on optimization studies on this reaction using as a measure the heat required for the recovery of unreacted reactants. As a result of this higher operating temperature, refrigeration is no longer required and the yield of the reaction is increased by approximately 20 percent.

2. By experiment, it has been shown that O_2 in the main solution reaction (4) can pass as an inert substance. Therefore, the SO_2-O_2 product stream from the SO_3 decomposition reaction (8) can be sent directly into the main solution reaction, thus obviating the need of a separate SO_2-O_2 separation step.

3. For the separation of HI and I_2 from the aqueous HI_x phase, H_3PO_4 appears to be more attractive than the LiI which was used

previously: I_2 can be separated as a liquid and the actual boiling of the H_2O can occur at relatively low temperatures from H_3PO_4. This should improve the heat economy while material cost associated with this evaporation step should be less as well.

4. For the concentration of the aqueous H_2SO_4, the distillation step is replaced by a multi-stage flash evaporation with the object of improving the thermal matchup.

5. The thermal decomposition of H_2SO_4 will be performed at higher pressures, with a considerable allowance for pressure drop (i.e. process pressure varies from 850 to 200 kPa). This will have a negative effect on the thermal efficiency of the cycle since the yield per pass decreases with increasing pressure. It is, however, expected that the efficiency loss will be offset by a reduction in capital cost of the decomposer/heat exchanger which will be reduced in size because of increased heat transfer coefficients and decreased volume of the gas processed.

6. Good catalysts for the decomposition of the HI have been found at GA making it possible to choose an optimum temperature for the decomposition reaction. This temperature will now be governed by the overall heat supply and demand situation instead of HI decomposition kinetics.

For design, the process engineering flowsheet has been divided into 5 major sections, the functions of which are described below:

Section I (Main Solution Reaction): This section produces the acids H_2SO_4 and HI_x from H_2O, SO_2 and I_2. The SO_2 that is fed to this section contains all the O_2 generated by the decomposition of the H_2SO_4. The O_2 product is taken from this section.

Section II (H_2SO_4-H_2O Separation and H_2SO_4 Decomposition): This section concentrates and decomposes H_2SO_4 received from Section I.

Section III (HI-H_2O Separation and Recovery): This section removes the very small amount of unreacted SO_2 from lower phase product (HI_xsol) and then separates it into HI, I_2, and H_2O using H_3PO_4.

Section IV (HI Decomposition and H_2 Recovery): This section decomposes HI into H_2 and I_2 and separates products. The H_2 product is taken from this section.

Section V (Helium Heat and Power Supply): This section combines the helium-related parts of the process including the process power generation and the process heat supply stream.

In Fig. 3-1 a block diagram is given which shows the molal flows between the four chemical sections per mole of the H_2 produced. Sections I and II are completed and Section IV is approximately halfway finished. The following subsections of this report provide the details of the process engineering design. In order to possibly expedite the process engineering effort and to be able to do some optimization, the possibility of using process engineering computer codes was investigated. A design code package from the ChemShare Corporation has been selected and implemented. A justification for this decision and an example of an initial application is given in the Appendix.

3.2. SECTION I (MAIN SOLUTION REACTION)

This section produces mutually insoluble liquid phases which separate the H_2SO_4 from the HI-I_2 in the reaction:

$$(2H_2O + \text{excess}) + (SO_2 + \text{excess}) + [(x + 1)I_2] \rightarrow H_2SO_4 \text{ (light solution)} + [2\ HI \cdot x/2\ I_2] \text{ (heavy solution)} \qquad (12)$$

Since the SO_2 recycled from Section II contains all the O_2 from the decomposition of the H_2SO_4 in Section II the foregoing reaction is specified to occur in countercurrent scrubbing towers.

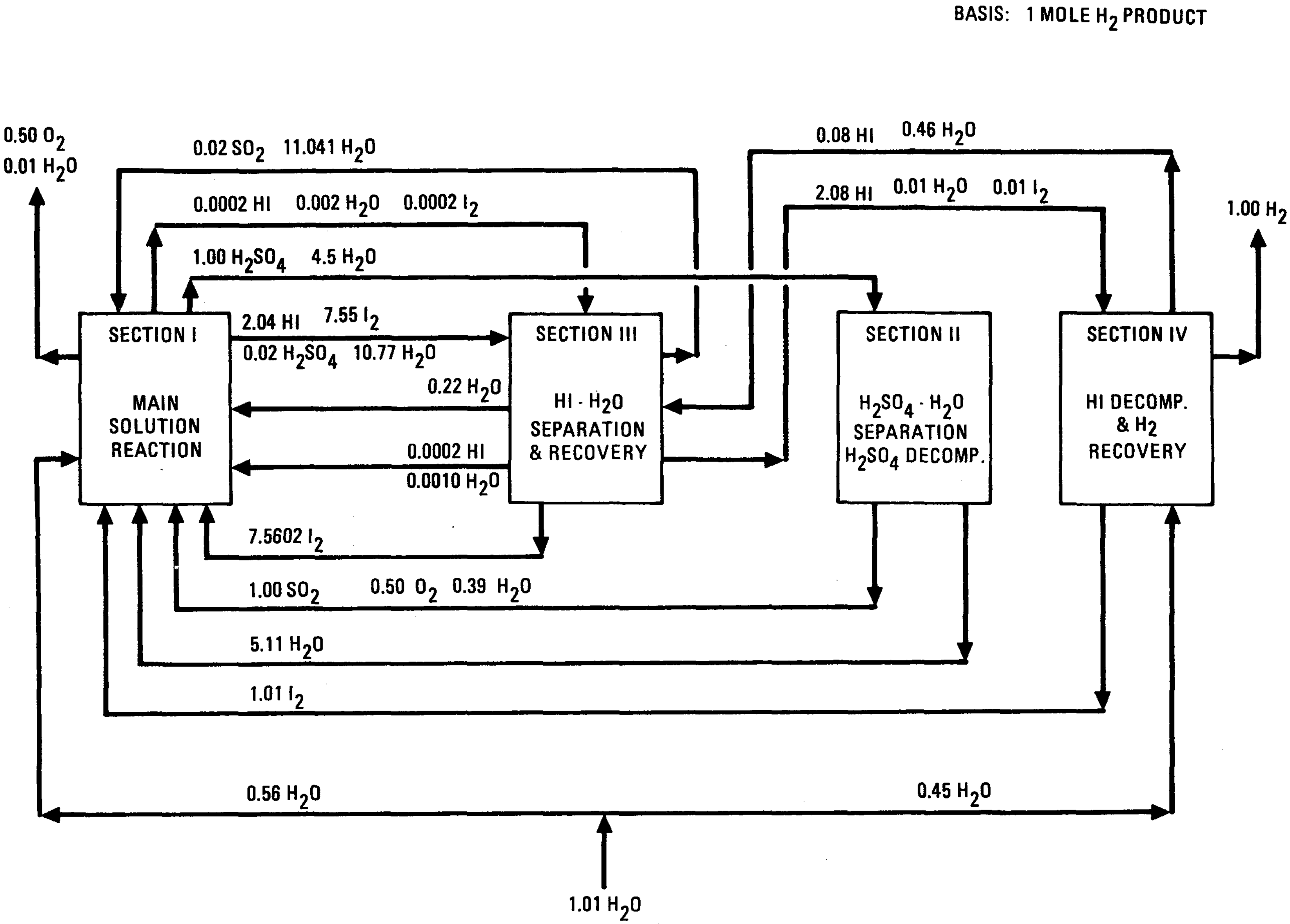

Fig. 3-1. Block diagram of process engineering flowsheet

The gaseous SO_2-O_2 input from Section II becomes an O_2-I_2 gaseous output in which the I_2 residual is low and is relatively easier to remove from the final effluent O_2 product stream in an energy-efficient physical separation operation than is SO_2.

Figure 3-2 is a diagram of the current conceptual flowsheet for Section I. Iodine, H_2O, and SO_2 are collected from the other sections and are introduced such that the I_2 and most of the H_2O act as countercurrent scrub stages against the input SO_2-O_2 stream. The temperature of the SO_2 removal column is set somewhat higher than the main solution reaction column to ensure that $I_2(s)$ will not freeze out in the equipment. Most of the reaction and SO_2 removal is expected to occur in the main solution reaction column, with the SO_2 removal column performing a final polishing operation.

The H_2SO_4-HI liquid phases leave the bottom of the main solution reaction column and are partially concentrated by a throttle-flash from 180 kPa to ambient pressure. The gaseous portion of the flash mixture is separated from the liquid and is recycled directly to the main solution reaction column. The immiscible solutions are then separated by gravity.

The evaporation step for the H_2SO_4 light phase is to remove the corrosive residuals of HI and I_2 before the stream goes to Section II. The amount of water boilup associated with the back-reaction of HI and H_2SO_4 and the volatilization of elemental I_2 is probably conservative (i.e., the separation might be shown later, by laboratory data, to require less boilup). The evaporation step for the HI-I_2 heavy phase is to remove thoroughly the SO_2 residual under conditions sufficiently mild that reaction between SO_2 and HI does not occur.

The O_2 offgas from the SO_2 removal column is cooled first with water and then by adiabatic expansion, to condense out most of the I_2. Virtually all remaining traces of I_2 are removed by scrubbing with a dilute solution of HI which forms HI_3 complex in solution.

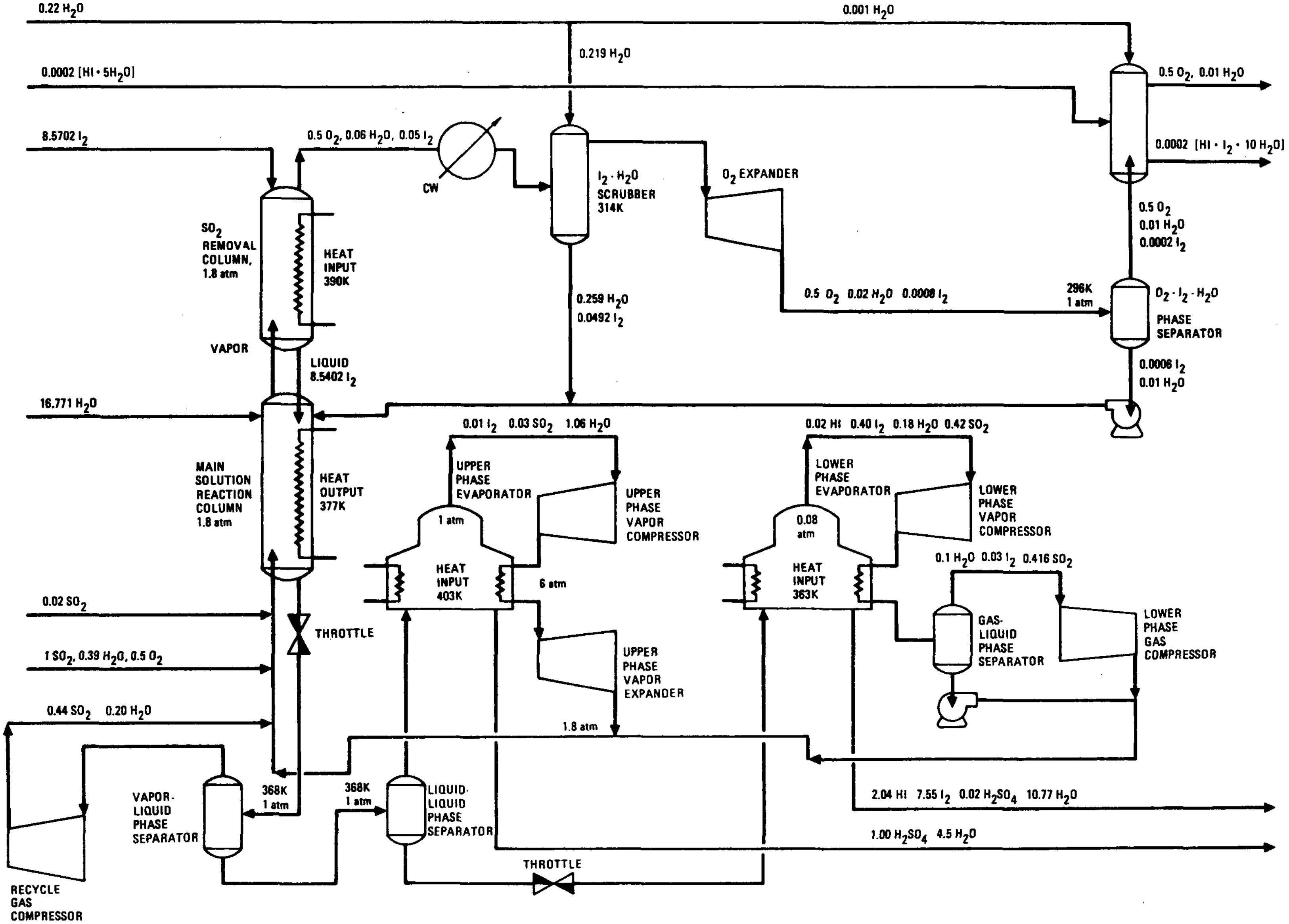

Fig. 3-2. Section I, main solution reaction (H_2SO_4-HI production and separation, and O_2 removal)

The design of the system was made relatively work-intensive to avoid a high external heat demand. The heat demands in Section I are at temperatures among the lowest in the entire process. Supply of heat directly from secondary helium would require extensive decompression/recompression of the secondary helium to make a thermally efficient matchup. Further, the option of possibly using a low-temperature bottoming power cycle on the large amount of reject heat from the main solution reaction column at 377 K has not been foreclosed by designing for lower heat-higher power demand.

The net external work requirement is 33 kJ/mol H_2SO_4, and the external heat requirement is 14 kJ/mol. The appropriateness of the particular flowsheeting alternatives and assumptions made here will be subject to checking after all other sections have been designed and the energy flow integrated in order to make the secondary helium loop design. Details of specific process pressure-temperature conditions are given in Table 3-1. Table 3-2 gives the energy load and more detail of input/output conditions for each equipment item involving energy transfer. Table 3-3 shows net energy transfers in a partially summarized form.

3.3. SECTION II (H_2SO_4-H_2O SEPARATION AND H_2SO_4 DECOMPOSITION)

In Section II aqueous H_2SO_4 is concentrated to 98 wt% and decomposed according to reactions (2) through (9). The endothermic heat required for the decomposition as well as the heats necessary to concentrate and vaporize the H_2SO_4 are the major heat requirements of the sulfur-iodine cycle. They not only have a dominating effect on the thermal efficiency of the cycle, but are also a major factor in the capital cost of the chemical plant. Considering this and bearing in mind the results of the previous flow sheeting efforts [Ref. 3-4], the following guidelines were established for the design of Section II:

1. For an efficient thermal matchup with the nonisothermal heat sources (helium), isothermal heat loads should be avoided as much as possible.

TABLE 3-1
SECTION I PROCESS CONDITIONS

Equipment Name		Temp., K	Pressure, kPa
Final Scrubber (Product)		314	101
Phase Separator		296	101
Phase Separator-Scrubber		314	184
Liquid-Liquid Phase Separator		368	101
Gas-Liquid Phase Separator		368	101
Upper Phase Sulfur Dioxide Stripper		403	101
Lower Phase Sulfur Dioxide Stripper		363	0.80
Main Reactor-Oxygen Scrubber, Upper Section		390	184
Main Reactor-Oxygen Scrubber, Lower Section		377	184
Heat Exchanger, HE-1	Maximum	390	184
	Minimum	303	
Heat Exchanger, HE-2	Maximum	657	590
	Minimum	403	
Heat Exchanger, HE-3	Maximum	467	101
	Minimum	363	

TABLE 3-2
SECTION I ENERGY TRANSFERS SUMMARY

Heat Transfer Equipment Name	Hot Side		Cold Side		Heat* Transfer kJ
	Inlet Temp. K	Outlet Temp. K	Inlet Temp. K	Outlet Temp. K	
Main Reactor-O_2 Scrubber, Upper Section	>390	>390	390	390	1.6
Main Reactor-O_2 Scrubber, Lower Section	377	377	303	303	264
Upper Phase SO_2 Strip. Auxiliary Heat	>403	>403	403	403	10.2
Upper Phase SO_2 Strip. HE-2	657	425	403	403	31.7
Lower Phase SO_2 Strip. Auxiliary Heat	>363	>363	363	363	4.1
Lower Phase SO_2 Strip. HE-3	467	386	363	363	30.7
Oxygen Cooler, HE-1	390	314	303	303	7.5

Power Machinery Name	Inlet Press Pa	Outlet Press Pa	Inlet Temp. K	Outlet Temp. K	Power* kJ
Expander Number 1	$1.84x10^5$	$1.01x10^5$	314	296	0.61
Expander Number 2	$5.9 x10^5$	$1.84x10^5$	425	391	1.25
Compressor Number 1	$1.01x10^5$	$1.84x10^5$	368	427	1.54
Compressor Number 2	$1.01x10^5$	$5.9 x10^5$	403	657	10.00
Compressor Number 3	800	$1.01x10^5$	363	467	22.00
Compressor Number 4L (Liquid)	$1.01x10^5$	$1.84x10^5$	386	426	1.22
Compressor Number 4G (Gas)	$1.01x10^5$	$1.84x10^5$	386	387	0.02

*Per Mol H_2SO_4 Output

TABLE 3-3
SECTION I NET ENERGY TRANSFERS

Power	kJ/mol H_2SO_4	kcal/mol H_2SO_4
Gross Compressors Load	34.78	8.31
Expanders Power Recovery	- 1.86	- 0.44
Net External Power Demand	32.92	7.87

Sensible Heat Transfers	kJ/mol	kcal/mol
Upper Phase SO_2 Strip Aux Heat	-10.2	- 2.44
Lower Phase SO_2 Strip Aux Heat	- 4.1	- 0.98
Main Reactor-O_2 Scrub Upper Sect.	1.6	0.38
Main Reactor-O_2 Scrub Lower Sect.	264.0	63.10
O_2 Cooler, HE-1	7.5	1.80
Net External Heat Output	258.8	61.86

2. The decomposition of the H_2SO_4 and SO_3 should be done at higher pressures and with larger pressure drops than in the previous flowsheet. Although this will adversely affect the thermodynamic equilibria of both reactions (7) and (8) and therefore increase the recycle and associated heatloads, it is felt that more can be gained from the decrease in the capital cost of the decomposers, since they will considerably decrease in size due to increased heat transfer coefficients and decreased gas volumes.

3. To make the most efficient use of heats possibly available from other sections, only heat loads should be calculated and thermal matchup should be done after all other sections are finished.

It is expected that several iterations will have to be carried out before a reasonable optimum can be obtained. Modeling on a computer with process simulators may be of help.

Figure 3-3 is the flowsheet of Section II; Table 3-4 gives the stream-point data; heatloads for heating are given in Table 3-5; and, heat loads for cooling are given in Table 3-6.

In order to solve the complex mass balance of the series of flash evaporation stages in a reasonable amount of time some simplifying assumptions were made. The result may therefore deviate somewhat from the exact solution, however, this deviation is expected to be of the same order as what can be expected from the inaccuracy of the basic property data. Simulation by computer (see Appendix) will make an exact solution possible, and it is planned for next year to check the results, and correct them if necessary, to make them more consistent with the overall mass balance. To comply with guideline 1) the concentration of the H_2SO_4 is performed in a series of six flash evaporators consisting of a flash heater, e.g. E-3, a flash drum, e.g. V-1, a condensor, e.g. E-2, and a separator, e.g. V-12.

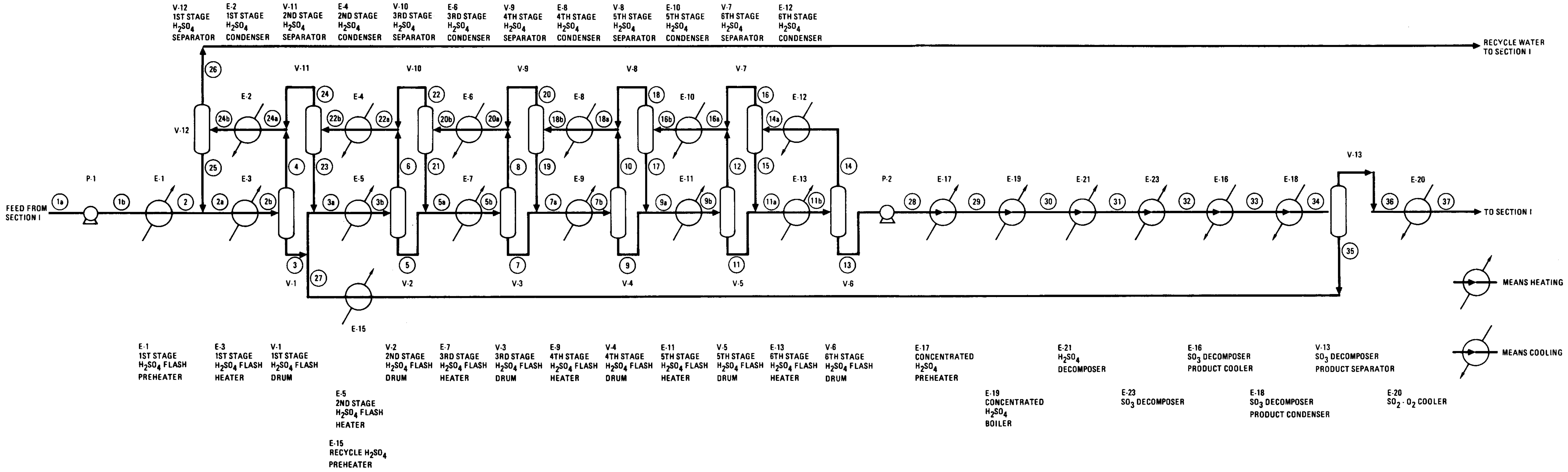

Fig. 3-3. Section II, H_2SO_4-H_2O separation and H_2SO_4 decomposition

TABLE 3-4
STREAMPOINT DATA FOR SECTION II

Stream No.	1a	1b	2	2a	2b	3	3a	3b	4
Flow, Mol/Mol H_2									
H_2O	4.5000	4.5000	4.5000	4.5045	4.5045	2.1185	2.9014	2.9014	2.3860
H_2SO_4	1.0000	1.0000	1.0000	1.0011	1.0011	1.0006	1.3704	1.3704	0.0005
SO_3	-	-	-	-	-	-	-	-	-
SO_2	-	-	-	-	-	-	-	-	-
O_2	-	-	-	-	-	-	-	-	-
Total	5.5000	5.5000	5.5000	5.5056	5.5056	3.1191	4.2718	4.2718	2.3865
Phase	L	L	L	L	V/L	L	L	V/L	V
Pressure, kPa	100	200	→	→	→	→	→	→	→
Temperature, K	403	425	→	→	470	→	→	502	470

TABLE 3-4 (continued)

Stream No.	5	5a	5b	6	7	7a	7b	8
Flow, Mol/Mol H_2								
H_2O	1.8606	1.9046	1.9047	1.0408	1.2274	1.3017	1.3037	0.6773
H_2SO_4	1.3674	1.3997	1.3996	0.0030	1.3853	1.4691	1.4671	0.0143
SO_3	-	-	0.0001	-	-	-	0.0020	0.0001
SO_2	-	-	-	-	-	-	-	-
O_2	-	-	-	-	-	-	-	-
Total	3.2280	3.3043	3.3044	1.0438	2.6127	2.7708	2.7728	0.6917
Phase	L	L	V/L	V	L	L	V/L	V
Pressure, kPa	200	→	→	→	→	→	→	→
Temperature, K	502	→	536	502	536	→	573	536

TABLE 3-4 (continued)

Stream No.	9	9a	9b	10	11	11a	11b	12
Flow, Mol/Mol H_2								
H_2O	0.7294	0.8333	0.8650	0.5743	0.3004	0.3309	0.3972	0.5646
H_2SO_4	1.4159	1.6175	1.5858	0.0512	1.4172	1.5611	1.4948	0.1686
SO_3	-	-	0.0317	0.0020	-	-	0.0663	0.0317
SO_2	-	-	-	-	-	-		-
O_2	-	-	-	-	-	-		-
Total	2.1453	2.4508	2.4825	0.6275	1.7176	1.8920	1.9583	0.7649
Phase	L	L	V/L	V		L	V/L	V
Pressure, kPa	200	→	→	→	→	→	→	→
Temperature, K	573	→	613	573	613	→	634	613

TABLE 3-4 (continued)

Stream No.	13	14	14a	15	16	16a	16b	17	18
Flow, Mol/Mol H_2									
H_2O	0.1548	0.2424	0.1847	0.0305	0.1543	0.7189	0.6805	0.1039	0.5766
H_2SO_4	1.3625	0.1323	0.1899	0.1439	0.0460	0.2146	0.2530	0.2016	0.0514
SO_3	-	0.0663	0.0087	-	0.0087	0.0404	0.0020	-	0.0020
SO_2	-	-		-	-	-	-	-	-
O_2	-	-		-	-	-	-	-	-
Total	1.5173	0.4410	0.3833	0.1744	0.2090	0.9739	0.9355	0.3055	0.6300
Phase	L	V	V/L	L	V	V	V/L	L	V
Pressure, kPa	200	→	→	→	→	→	→	→	→
Temperature, K	634	→	613	→	→	→	573	→	→

TABLE 3-4 (continued)

Stream No.	18a	18b	19	20	20a	20b	21	22
Flow, Mol/Mol H_2								
H_2O	1.1509	1.1471	0.0743	1.0728	1.7501	1.7498	0.0440	1.7058
H_2SO_4	0.1026	0.1064	0.0838	0.0226	0.0369	0.0372	0.0323	0.0049
SO_3	0.0040	0.0002	-	0.0002	0.0003	-	-	-
SO_2	-	-	-	-	-	-	-	-
O_2	-	-	-	-	-	-	-	-
Total	1.2575	1.2537	0.1581	1.0956	1.7873	1.7870	0.0763	1.7107
Phase	V	V/L	L	V	V	V/L	L	V
Pressure, kPa	200	→	→	→	→	→	→	→
Temperature, K	573	536	→	→	→	602	→	→

TABLE 3-4 (continued)

Stream No.	22a	22b	23	24	24a	24b	25	26
Flow, Mol/Mol H_2								
H_2O	2.7466	2.7466	0.0155	2.7311	5.1171	5.1171	0.0045	5.1126
H_2SO_4	0.0079	0.0079	0.0073	0.0006	0.0011	0.0011	0.0011	T
SO_3	-	-	-	-	-	-	-	-
SO_2	-	-	-	-	-	-	-	-
O_2	-	-	-	-	-	-	-	-
Total	2.7545	2.7545	0.0228	2.7317	5.1182	5.1182	0.0056	5.1126
Phase	V	V/L	L	V	V	V/L	L	V
Pressure, kPa	200	→	→	→	→	→	→	→
Temperature, K	502	470	→	→	→	425	→	→

TABLE 3-4 (continued)

Stream No.	27	28	29	30	31	32	33	34
Flow, Mol/Mol H_2								
H_2O	0.7674	0.1548	→	0.6895	1.3205	1.5168	1.1679	1.1548
H_2SO_4	0.3625	1.3625	→	0.8278	0.1968	0.0005	0.3489	0.3625
SO_3	-	-	-	0.5347	1.1657	0.3620	0.0136	-
SO_2	-	-	-	-	-	1.0000	→	→
O_2	-	-	-	-	-	0.5000	→	→
Total	1.1299	1.5173		2.0520	2.6830	3.3793	3.0304	3.0173
Phase	L	L	L	V	V	V	V	V/L
Pressure, kPa	200	860	→	→	780	520	240	200
Temperature, K	470	635	686	→	800	1144	579	418

TABLE 3-4 (continued)

Stream No.	35	36	37	38	39	40	41	42
Flow, Mol/Mol H_2								
H_2O	0.7674	0.3874	→					
H_2SO_4	0.3625	T	→					
SO_3	-	-	→					
SO_2	-	1.0000	→					
O_2	-	0.5000	→					
Total	1.1299	1.8874	→					
Phase	L	V	V					
Pressure, kPa	200	→	185					
Temperature, K	418	→	368					

TABLE 3-5
HALF HEAT EXCHANGER (COLD SIDE) HEATING DUTIES FOR SECTION II

Item No.	Duty, kJ/mol H_2	Temperature, K		Stream No.	
		In	Out	In	Out
E-1	11.013	403	425	1b	2
E-3	123.457	425	470	2a	2b
E-5	98.819	470	502	3a	3b
E-7	49.508	502	536	5a	5b
E-9	49.215	536	573	7a	7b
E-11	59.944	573	613	9a	9b
E-13	34.334	613	634	11a	11b
E-15	6.103	418	470	35	27
E-17	13.558	635	686	28	29
E-19	132.663	686	686	29	30
E-21	81.702	686	800	30	31
E-23	173.108	800	1144	31	32

TABLE 3-6
HALF HEAT EXCHANGER (HOT SIDE) COOLING DUTIES FOR SECTION II

Item No.	Duty, kJ/mol H_2	Temperature, K		Stream No.	
		In	Out	In	Out
E-2	8.690	470	425	24a	24b
E-4	4.525	502	470	22a	22b
E-6	6.999	536	502	20a	20b
E-8	11.997	573	536	18a	18b
E-10	24.199	613	573	16a	16b
E-12	16.355	634	613	14	14a
E-16	123.818	1144	579	32	33
E-18	93.515	579	418	33	34
E-20	3.579	418	368	36	37

In each case the conditions are chosen such that the compositions, temperatures and pressures of streams to be mixed are equal. The conditions for vessels V-1 through V-6 are chosen with the object of minimizing recycle and regenerative heat exchange, and to arrive at a net heat demand that has an acceptable enthalpy-temperature relationship. The desired enthalpy-temperature relationship depends on the particular heat source relationship. Since the overall net heat demand of the process will be dominated by this section the internal heat matchup will be determined after the other sections are finished. Then the total net heat and power demand of the process can be determined and an efficient matchup with the nuclear heat source attempted. At that time, in order to obtain a better matchup, conditions chosen for various processing steps in Section II may have to be reconsidered and possibly some modifications made.

The 98 wt% H_2SO_4 which leaves the flash drum, V-6, of the last concentration stage is brought to 860 kPa by P-2, heated to the boiling point in E-17, and vaporized in E-19 at 686 K. The acid vapor, which by then already is partly decomposed according to reaction (7), is heated to 1144 K in E-21 and E-23. It is assumed that in E-23 a catalyst will be present, and that as a consequence the SO_3 decomposition reaction [Reaction (8)] will go essentially to equilibrium. It should be noted, however, that because of the elevated pressure at this point, 520 kPa, the equilibrium of Reactions (7) and (8) is shifted to the left, and as a result of this even the H_2SO_4 is not completely decomposed. The reaction products, after being disengaged from the catalyst, are cooled to 418 K in E-16 and E-18 and the undecomposed SO_3 is separated in V-13 as a 72 wt% H_2SO_4 recycle stream. The top product from V-13, str. 36, contains all the SO_2 and O_2 and most of the H_2O. This stream is recycled to Section I.

3.4. SECTION IV (HI DECOMPOSITION AND H_2 RECOVERY)

In Section IV anhydrous HI vapor is thermally decomposed according to Reaction (10), and the reaction products are separated. In the previous flowsheet [Ref. 3-4] HI was decomposed to H_2 and I_2 at high temperature in two decomposers in series. The stream from the first decomposer was cooled and most of the I_2 condensed out. The remaining gas stream was fed to the second decomposer and the H_2 was recovered from the stream from this decomposer by cooling and condensing out I_2 and HI, followed by a water wash. Recent considerations of this process have led to the following conclusions:

1. In cooling the streams from the decomposers, all the I_2 does not condense out before HI begins to condense. Based on ideal solutions for the system H_2-HI-I_2, if a stream from a decomposer is cooled enough to condense out essentially all of the I_2, then a significant fraction of the HI is also condensed. This means that it is necessary to separate an HI-I_2 mixture.

2. A second decomposer does not improve the process. The energy requirement is essentially proportional to the amount of HI decomposed, and the same net amount of HI is decomposed whether one or two decomposers are used. Also, as a result of item 1, cooling to condense out I_2 after the first decomposer also condenses out a large fraction of HI. Thus the feed to the second decomposer is more deficient in HI than in the previous flowsheet and conversion in this decomposer is much less.

Laboratory investigations on HI decomposition have been directed towards gas-phase decomposition at low temperatures with a catalyst and towards decomposition under conditions that produce liquid I_2 in order to increase conversion. Gas-phase decomposition with a catalyst have shown satisfactory results (essentially equilibrium in a reasonable time) at temperatures as low as about 520 K. Conversion at this temperature, however, is about 16% compared to about 24% at 900 K, the condition of the previous flowsheet. Experiments on decomposition under conditions that produce liquid I_2 have not yet progressed far enough to give results useful for process engineering.

Based on the above considerations, work has begun on two conceptual schemes for HI decomposition and H_2 recovery. These are:

Scheme A: This scheme is illustrated by Fig. 3-4. HI is fed to a decomposer and the outlet stream consisting of H_2, HI and I_2 is distilled to give essentially pure I_2 as a bottom and a H_2-HI mixture as overhead. The I_2 is recycled to Section I. The H_2-HI overhead is then cooled down in several steps to about 273 K to condense out most of the HI which is recycled to the decomposer. The uncondensed phase consisting of the H_2 product plus some HI is water washed to remove the HI. The dilute water solution is recycled to the HI separation and recovery section.

Scheme B: This scheme is shown in Fig. 3-5. It differs from Scheme A only in some of the separation steps. The effluent stream from the decomposer is cooled down to condense out practically all of the I_2. A significant amount of HI is also condensed. The HI-I_2 liquid phase is distilled to give I_2 as a bottoms and HI as an overhead. The H_2-HI gas phase is subjected to cooling and water washing steps as in Scheme A. Condensed HI and the HI overhead of the distillation step are recycled to the decomposer. I_2 and the water solution of HI are recycled as in Scheme A.

It is planned that both schemes be investigated to determine which is best for separating the H_2-HI-I_2 effluent from the decomposer. It is also planned that decomposition of HI at two temperature levels, about 550 K with a catalyst and a higher temperature without a catalyst, be considered. The latter temperature depends upon quenching the decomposer effluent fast enough to prevent any significant back reaction. It is necessary to integrate this process engineering work with work on other sections from an energy exchange point of view in order to optimize the energy requirements of the overall water-splitting process.

The separation steps for the H_2-HI-I_2 effluent from the decomposer will at present be based on ideal solution theory because of lack of

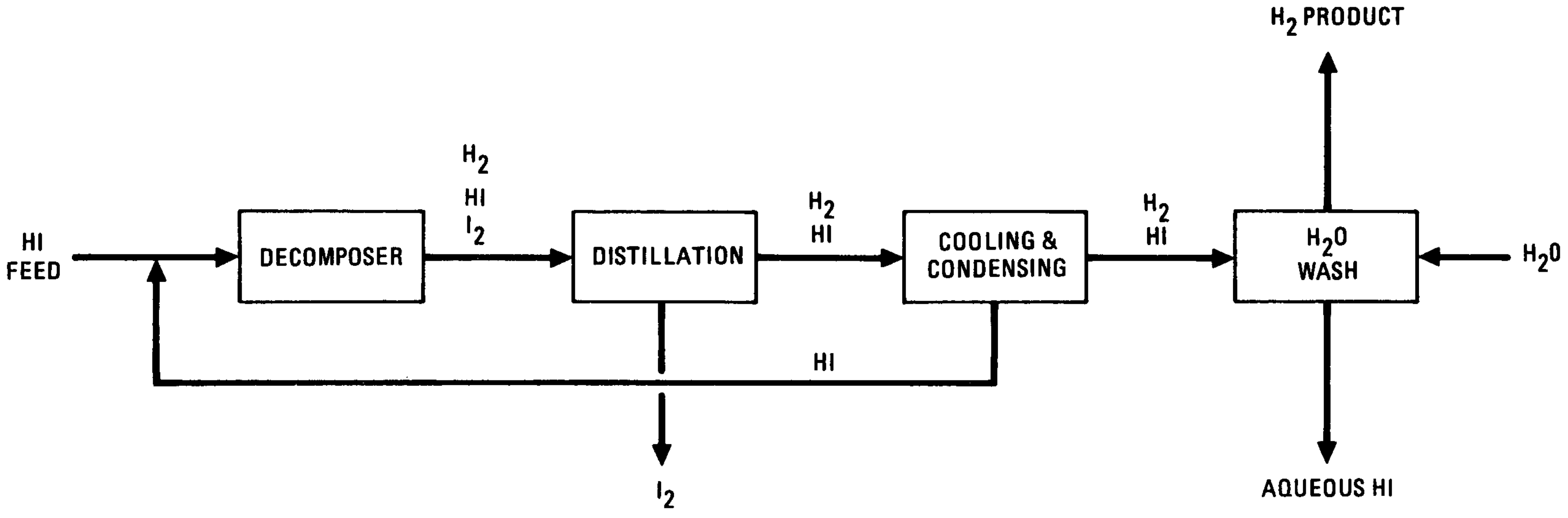

Fig. 3-4. Scheme A for HI decomposition and H_2 recovery

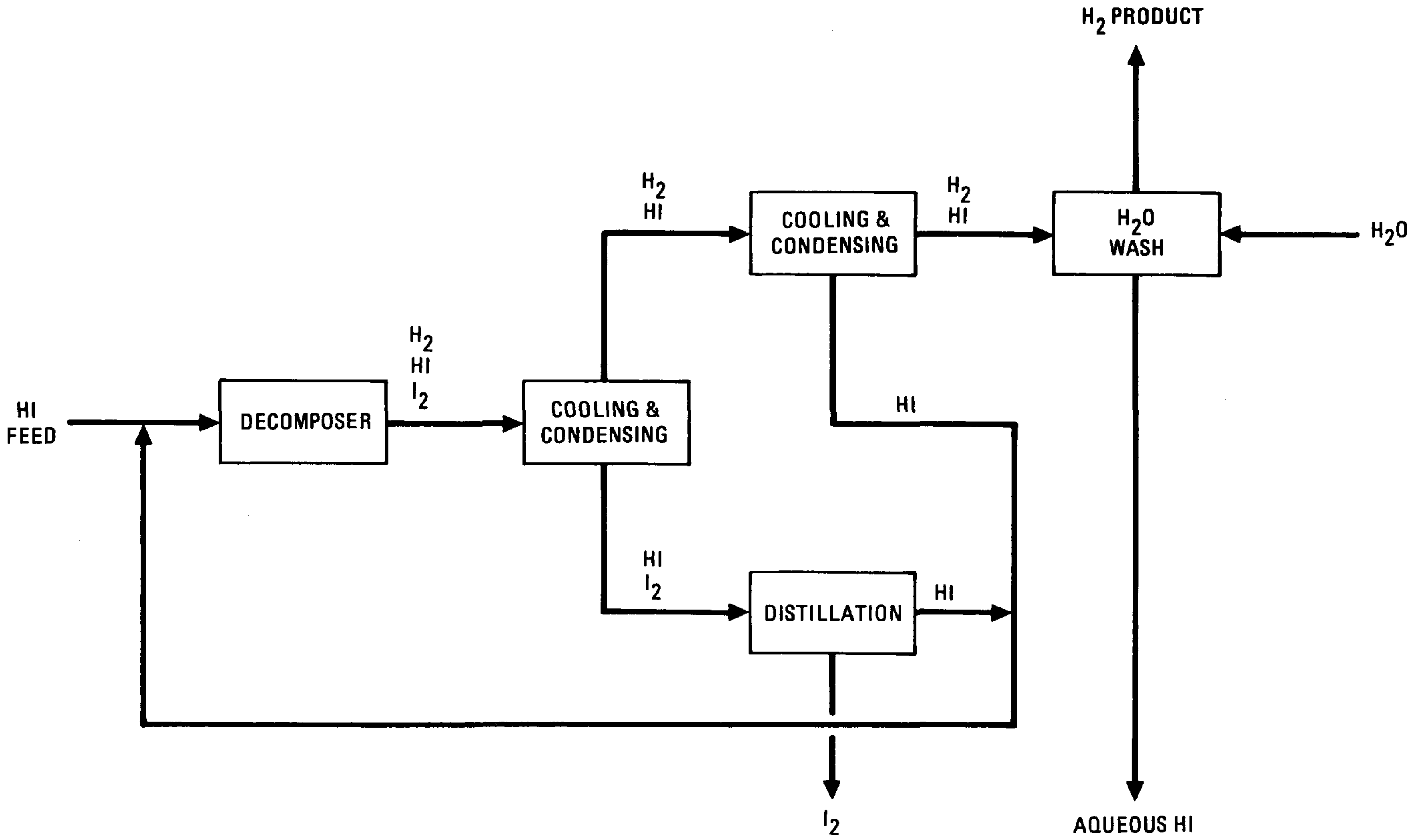

Fig. 3-5. Scheme B for HI decomposition and H_2 recovery

information on vapor-liquid equilibria. Laboratory experiments on vapor-liquid equilibria are planned. Appropriate revisions of the flowsheet will need to be made when equilibria data are available.

The HI decomposition and H_2 recovery section is being modeled with the ChemShare computer package for process simulation and design. The computer can then be used for parametric studies and for making changes as new data become available.

REFERENCES

3-1 Russell, J. L., et al., "Production of Hydrogen from Water," General Atomic Company Report GA-A13302, January 1975.

3-2 Schuster, J. R. and Russell, J. L., "Thermochemical Water-Splitting at General Atomic," Eighth Synthetic Pipeline Gas Symposium Proceedings, Chicago, Illinois, October 1976.

3-3 Schuster, J. R., et al., "Status of Thermochemical Water-Splitting at General Atomic," Ninth Synthetic Pipeline Gas Symposium Proceedings, Des Plaines, Illinois, October 31 - November 2, 1977.

3-4 HTGR Thermochemical Water-Splitting for Hydrogen Production, Annual Report for the period January 1, 1976 through December 31, 1976, General Atomic Company Report GA-A14265, April 1977.

APPENDIX A

PROCESS SIMULATOR COMPUTER CODE

A.1. GENERAL

The evaluation of thermochemical water-splitting cycles in general and of process alternatives in one cycle in particular are difficult and time consuming. The ultimate analysis should be based on a complete process engineering design which is based on experimentally proven results and which is optimized in such a way to result in the lowest possible price for the hydrogen product. For the process engineer this means trying to strike a balance between two usually counteracting characteristics of the chemical plant: (1) its thermal efficiency which represents the cost of energy, and, (2) its capital costs.

Such efforts may require many process design iterations. However, time and funding are limited, and therefore major iterations are not always possible. Because of this it was decided to obtain a computer code that could be used to aid in process engineering design, and an investigation was initiated on the availability of computer codes for use in process engineering design work for thermochemical water splitting and process heat. It soon became apparent that due to the general nature of the process engineering designs only the so-called process simulator codes would be of any value.

A.2. SURVEY

In the search for process simulator codes, computer codes available from GA's owners (Gulf and Royal Dutch Shell) were among those considered. Table A.1 gives a list of codes which eventually emerged for evaluation. From these the package from the ChemShare Corporation was chosen because

TABLE A.1
LIST OF CODES INVESTIGATED

	Name	Company
1.	DESIGN/DISTILL/CHEMTRAN/REFINE	ChemShare Corp.
2.	SSI/100	Simulation Sciences Inc.
3.	Pacer-245	Digital Systems Corp.
4.	Flowtran	Monsanto
5.	Proslator	Nippon-Univac
6.	PDA	Phillips Petroleum Co.
7.	PDS	General Electric
8.	Heat Exchange Network Simulator	Elshout & Assoc.

it is the most comprehensive, complete, and versatile package with good service backing, and it can be operated at a reasonable cost. The most important features are:

1. To model a flowsheet modules are used which describe a particular unit operation, e.g., pump, heat exchanger, distillation tower, chemical reactor, and process controller.
2. The user has the option of generating his own modules, such as, for example, to describe a peculiar, possibly proprietary, operating step.
3. The system has a very extensive intrinsic property data bank. The user has the option of choosing from several types of enthalpy and phase equilibria calculation techniques.
4. There is an option which enables the user to correlate his own property data, in a preprocessing run, in such a way that the data is transformed in a format that can directly be accessed by the process simulator.*

A.3. EXAMPLE OF APPLICATION

The ChemShare code should be considered a process engineering tool for the chemical engineer, and the results obtained with it will be an integral part of an engineering design. However, since this is a rather novel tool an example describing the first application in water-splitting will be given. The first application at GA of DESIGN actually was for a process heat project in the design of a synthetic natural gas-aromatics-sour water separation system. The results obtained with the code were very satisfactory, and the code was relatively easy to use.

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*Further information can be obtained from The ChemShare Corporation, 2500 Transco Tower, Houston, Texas 77056.

The first water-splitting application was on the H_2SO_4 concentration step in Section II. Even though this section was almost completed, it was felt that modeling would be attractive since in this section the largest amount of process heat is exchanged. As a first step, a part of the flowsheet consisting of a heat exchanger (E11 in the heating mode) and the subsequent separator vessel (V5) were modeled. For this system it was necessary to create a so-called chemical data file with a preprocessor run in DISTILL, because H_2SO_4 and heat of mixing for the system H_2SO_4-H_2O is not contained in the data bank.

Since H_2SO_4 at higher temperatures is partly decomposed into H_2O and SO_3, in effect three components in the gas phase are in phase equilibrium with two components in the liquid phase, and this condition cannot be described with the use of ordinary K values. Therefore the DESIGN model of the flowsheet was modified as shown in Fig. A.1. It is assumed that H_2SO_4 does not decompose in the vapor phase in exchanger E11 (named E1 in DESIGN) and therefore SO_3 does not exist in vessel V5 (named V1 in DESIGN), and the hypothetical reactor R1 is introduced to do the partial decomposition of the H_2SO_4. The phase equilibrium in V1 can then be described by defining apparent mole fractions as follows:

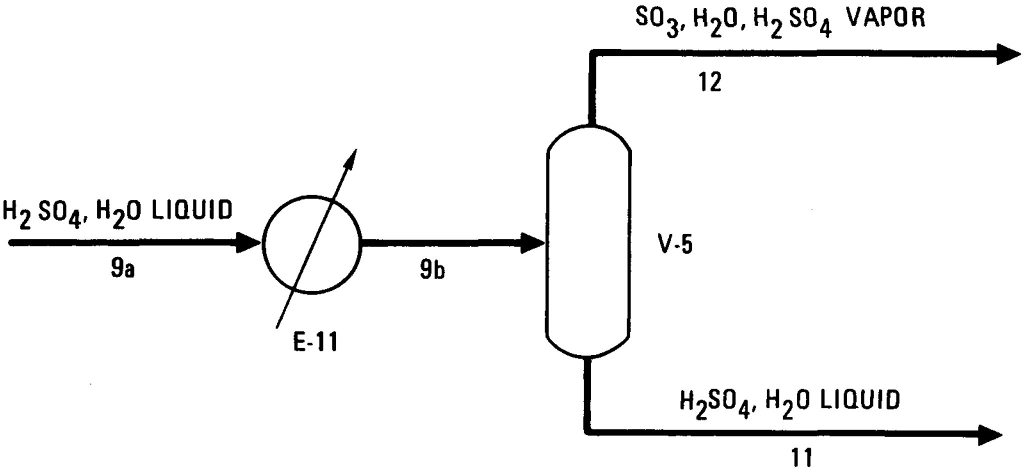
$$y^a_{H_2SO_4} = \frac{p^a_{H_2SO_4}}{p^a_T} = \frac{p_{H_2SO_4} + p_{SO_3}}{p_{H_2SO_4} + p_{H_2O}}$$

$$y^a_{H_2O} = \frac{p^a_{H_2O}}{p^a_T} = \frac{p_{H_2O} - p_{SO_3}}{p_{H_2SO_4} + p_{H_2O}}$$

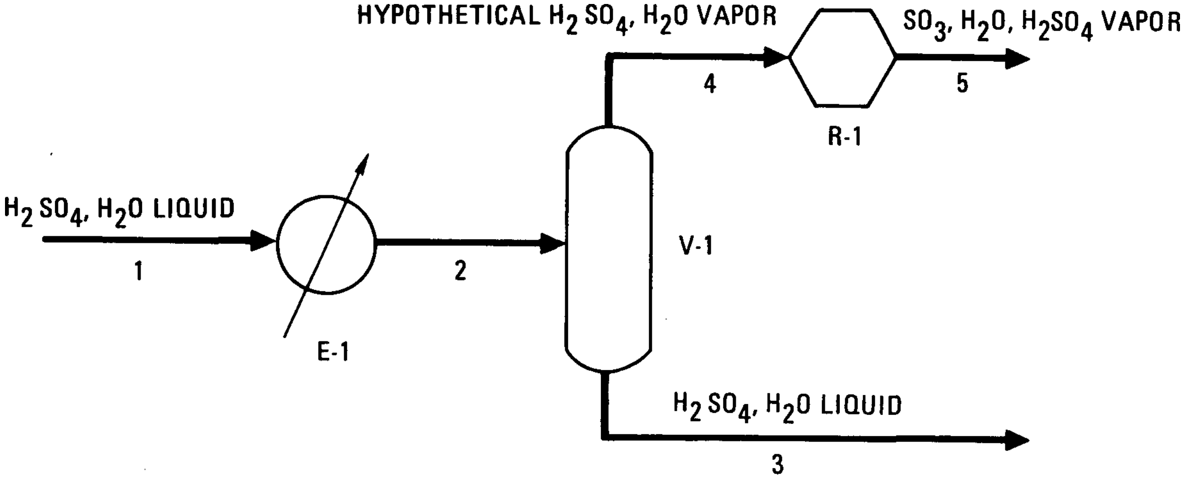
where:

$y^a_{H_2SO_4}$ = apparent mole fraction of H_2SO_4 in vapor phase

$y^a_{H_2O}$ = apparent mole fraction of H_2O in vapor phase



Process Engineering Flowsheet



DESIGN Model

Fig. A.1. Modeling of H_2SO_4 concentration step with DESIGN code

$p^a_{H_2SO_4}$ = apparent partial pressure of H_2SO_4

$p^a_{H_2O}$ = apparent partial pressure of H_2O

p^a_T = apparent total pressure

$p_{H_2SO_4}$ = true partial pressure of H_2SO_4

p_{SO_2} = true partial pressure of SO_3

p_{H_2O} = true partial pressure of H_2O

Apparent K values then follow from:

$$K^a_{H_2SO_4} = \frac{y^a_{H_2SO_4}}{x_{H_2SO_4}}$$

$$K^a_{H_2O} = \frac{y^a_{H_2O}}{(1 - x_{H_2SO_4})}$$

where:

$K^a_{H_2SO_4}$ = apparent K value of H_2SO_4

$K^a_{H_2O}$ = apparent K value of H_2O

$x_{H_2SO_4}$ = mole fraction of H_2SO_4 in liquid

In Table A.2 the input instructions for the simulator run with DESIGN are shown; actually two parallel simulations were performed; the relevant statements for the simulation described here are indicated. The initial

TABLE A.2
INPUT INSTRUCTIONS FOR DESIGN SIMULATOR RUN
(Lines marked with → are relevant to example described in text)

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             ECHO PRINT OF INPUT DATA            29DEC77                   0: 4:24
→*H2SO4 CONCENTRATION * WATER SPLITTING *
→HXE1=E-1,1,-2,TEM OUT(K)=613.15
→FLA2=V-1,2,-4,-3
→REA3=R-1,4,-5,STO COE=-1,1,1,CON=0.158223,HEA(CAL/GMOL)=-24176,LIM=201,
→ISO
 REA50=R-50,44,-50,STO COE=1,-1,-1,CON=1.0,HEA(CAL/GMOL)=-24176,LIM=1068,
 ISO
 HXE41=E-10,50,-45,TEM OUT(K)=573.15
 FLA42=V-8,45,-46,-35
 REA43=R-8,46,-47,STO COE=-1,1,1,CON=3.76046E-2,HEA(CAL/GMOL)=-24277,
 LIM=201,ISO
→GENERAL
→COM=201,62,1068
→CHE FIL='SULF','IS42','WSGA'
→FLO(KGMOL/SEC)1=1.6175,0.8333,0.0000
→TP(K,ATM)1=573,15,2.0
 FLO(KGMOL/SEC)44=0.2146,0.7189,0.0404
 TP(K,ATM)44=613.15,2.0
→KKEY=1
→EXC TAB
→MAS UNI=3,TIM UNI=2,TEM UNI=2,PRE UNI=4,DUTY UNI=7
→END

 THERMO DATA FILE OPENED FOR READ
 FILE NAME IS:  SULF/IS42(WSGA)
```

results of this H_2SO_4 concentration subunit showed that the apparent K-values and hypothetical reactor approach functioned well, giving a material balance which was more accurate than that for the hand calculations, and which enabled the calculations to be done in a reasonably short time. Table A.3 presents a comparison of the material balance obtained by hand and with the DESIGN code.

The results on the heat balance, however, given in Table A.4, are not yet sufficiently accurate. This is due to residual deviations in the curve fittings performed with the DISTILL preprocessor run on our enthalpy data, mainly on the heat of mixing, which we for the moment have accepted. We are confident, however, that by choosing different curve fitting options we will be able to decrease these residuals and thereby improve on the accuracy.

TABLE A.3
COMPARISON OF MATERIAL BALANCE

	Eng. Flowsheet	DESIGN	Eng. Flowsheet	DESIGN	Eng. Flowsheet	DESIGN	Eng. Flowsheet	DESIGN
Stream No.	9a	1	9b	2	11	3	12	5
Temp., K	573.16	573.16	613.16	613.16	613.16	613.16	613.16	613.16
Press., 10^5 Pa	2.027	2.027	2.027	2.027	2.027	2.027	2.027	2.027
H_2SO_4, kMol/s	1.6175	1.6175	1.5858	1.6175	1.4172	1.4031	0.1686	0.1805
H_2O, kMol/s	0.8333	0.8333	0.8650	0.8333	0.3004	0.2973	0.5646	0.5699
SO_3, kMol/s	0.0000	0.0000	0.0317	0.0000	0.0000	0.0000	0.0317	0.0339
TOTAL, kMol/s	2.4508	2.4508	2.4825	2.4508	1.7176	1.7004	0.7649	0.7843

TABLE A.4
COMPARISON OF HEAT DUTIES OF E-11 BASED ON DESIGN'S MATERIAL BALANCE

	Design	Hand Calc.
Heating up 573.16K → 613.16K, MJ/S	13.95	14.51
Vaporization at 613.16K, MJ/S	26.94	27.05
Decomposition at 613.16K, MJ/S	3.45	3.45
Mixing, MJ/S	13.19	16.16
Total, MJ/S	57.53	61.17