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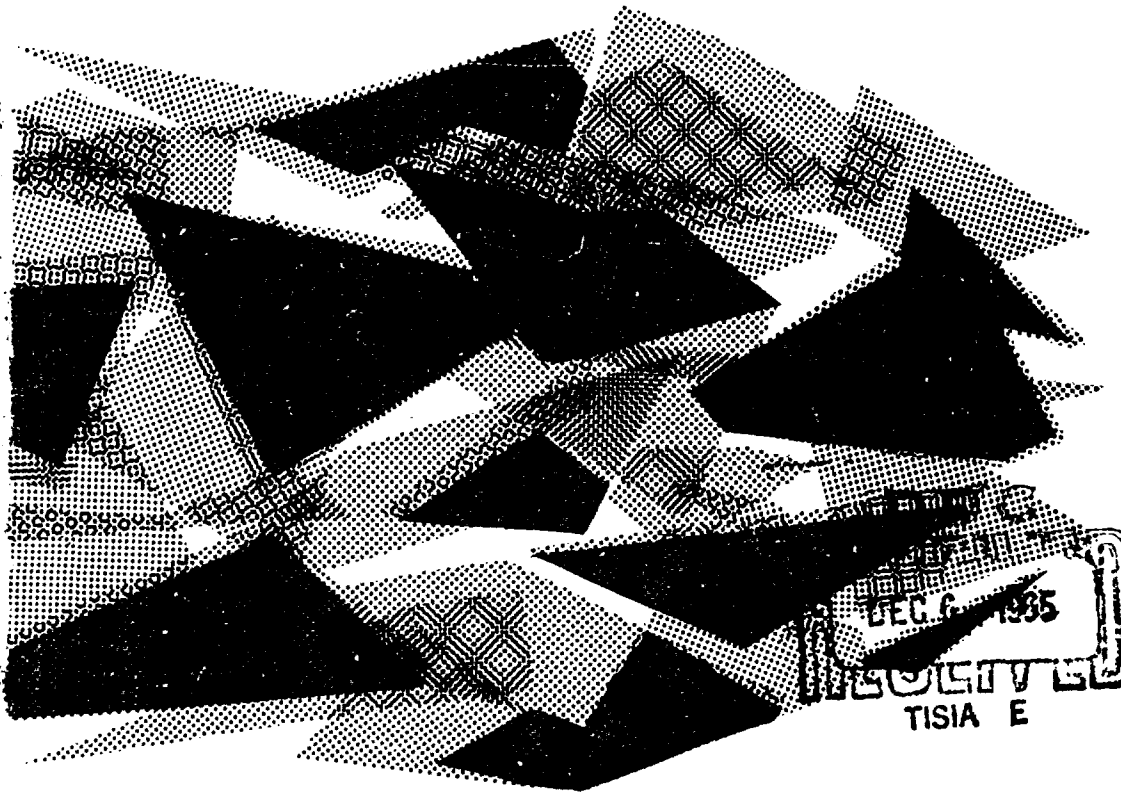
ROHM & HAAS COMPANY

REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

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REPORT NO., S-83

SCALE-UP N_2F_4 -OLEFIN REACTIONS IN A HIGH
PRESSURE LIQUID PHASE FLOW REACTOR
(C)



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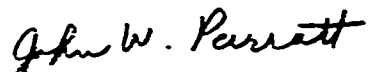
Report No. S-83

SCALE-UP N_2F_4 -OLEFIN REACTIONS
IN A
HIGH PRESSURE LIQUID PHASE FLOW REACTOR (C)

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ABSTRACT

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Difluoramino compounds were continuously synthesized by the high pressure liquid phase reaction of N_2F_4 with an olefin diluted in an appropriate solvent. About 400 pounds of two N_2F_4 adducts were synthesized over a two-year period in a tubular reactor operating in the laminar flow regime. The productivity of the reactor was progressively increased to a rate of about 100 pounds per month. A mathematical model of the flow reactor was developed and used to establish reaction conditions that would not result in prohibitive exotherms.

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GLOSSARY

TVOPA	- 1, 2, 3-Tris[α, β -bis-(difluoramino)ethoxy]propane
A-3	- 2, 3-bis(difluoramino)propyl formate
NFPA	- 2, 3-bis(difluoramino)propyl acrylate
Freon TF	- 1, 1, 2-trichloro-1, 2, 2-trifluoroethane
Freon MF	- trichlorofluoroethane
2D	- Refers to two-dimensional mathematical model
D/P cell	- Pneumatic differential pressure cell with integral flow nozzle

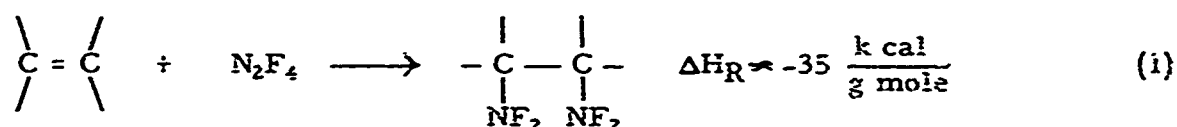
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1. INTRODUCTION

Composite solid propellants based upon binders and plasticizers containing the difluoramino (NF_2) group have been of interest for the past decade. Difluoramino compounds which have been scaled-up to the pilot plant by these Laboratories were based on the addition of tetrafluorochydrazine (N_2F_4) to olefins by the reaction shown in Eq. (1). The first pilot plant unit



was a continuous vapor phase tubular reactor operating at atmospheric pressure, and production rates up to 150 gms/hr¹ were obtained. Although the vapor phase reactor was useful in various programs, vapor phase addition was impractical for the synthesis of many NF plasticizers because neither the olefin nor product was easily vaporized.

This report describes the design and successful demonstration of a liquid phase reactor unit suitable for the continuous production of non-volatile compounds by the exothermic N_2F_4 -olefin reaction. The contacting technique chosen was the absorption of N_2F_4 into a solvent-olefin mixture at 400 - 500 psig. A similar principle had been demonstrated by Rohm & Haas Company for continuous vinylation of alcohols with acetylene.² DuPont³ constructed an experimental unit to show the feasibility of using a continuous

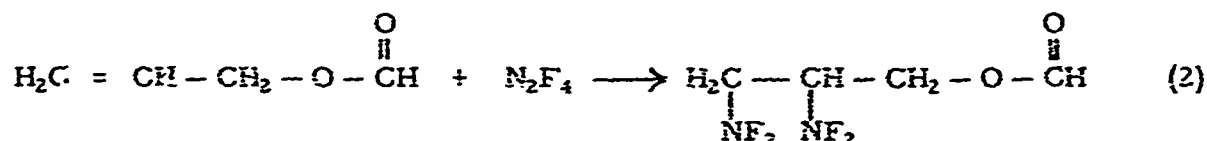
¹Rohm & Haas Company, Quarterly Progress Report on Chemical and Propellant Processing, No. P-63-17, January 15, 1964.

²Nedwick, John J., Ind. Eng. & Chem., Process Design & Development, 1, 1962, 137.

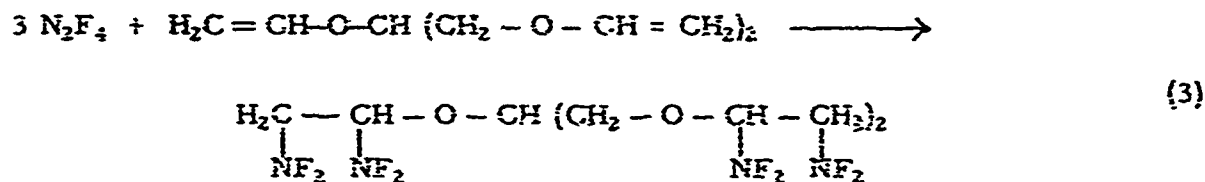
³E. I. du Pont de Nemours & Company, Supply of Experimental High-Energy Solid Propellant Materials, Final Report No. DP-504, July 1, 1962 through September 30, 1963.

tubular reactor for the liquid phase addition of N_2F_4 to olefins, but their unit required batch work-up of the product. The liquid phase reactor installed here provided for continuous work-up (description of unreacted N_2F_4) as well as continuous reaction.

Although design of the liquid phase reactor emphasized the capability of synthesizing a large variety of possible adducts, only two have been synthesized in large quantities to date. About 190 lbs. of 2,3-bis(difluor-amino)propyl formate (A-3) was made by addition of one mole of N_2F_4 to allyl formate according to reaction (2) and about 215 pounds of 1,2,3-tris[α, β -bis-



(difluoramino)ethoxy]propane (TVOPA) was made by the addition of three moles of N_2F_4 to trivinylpropane (TVOP) according to reaction (3).



The A-3 [an intermediate in the synthesis of the propellant binder, 2,3-bis-(difluoramino)propyl acrylate (NFPA)] was formerly synthesized in the continuous vapor phase reactor. The TVOPA was of interest as a plasticizer for the same system. Some of the properties of A-3 and TVOPA are summarized in Appendix A.

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2. CONCLUSIONS AND RECOMMENDATIONS

1. The feasibility of the continuous liquid phase synthesis of N_2F_A adducts in a tubular reactor operating in the laminar flow regime was successfully demonstrated.

2. Mathematical models were used to characterize the reaction exotherms, and explosive reactions were avoided.

3. Scale-up to higher production rates is practical and necessary to the pilot plant program, but this will be seriously restricted in the laminar flow regime.

4. Further studies should be made for scale-up to production in the turbulent flow region.

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3. DISCUSSION

3.1 Advantages of the Liquid Phase Flow Reactor

Use of the liquid phase reactor to prepare N_2F_4 adducts has several advantages compared to a vapor phase reactor. As shown in Table I, these advantages are related to the increase in reaction rate caused by the high reactant concentration in the condensed phase. The advantages of the liquid phase reactor include:

- (1) a substantial reduction of reaction temperature with maintenance of reasonable reaction rates for relatively volatile olefins and adducts;
- (2) a high yield per unit volume of the reactor due to the high concentration of reactants in the liquid phase;
- (3) the extension of continuous flow reaction to non-volatile systems which otherwise would require autoclave operation. This consideration was particularly important for propellant plasticizers, for which low vapor pressure was an essential requirement.

Table I
Comparison of Liquid and Vapor Phase Reactors in A-3 Synthesis

	<u>Liquid Phase Reactor</u>	<u>Vapor Phase Reactor</u>
Reactor Temp., °C	103 - 130	210
N_2F_4 inlet concentration, moles/liter	1.5	0.03
Space-time yield, moles/liter-hr.	3.0	0.3

3.2 Operation Summary

A two-stage reactor operating in the laminar flow regime was used for the synthesis of A-3 and TVOPA. The reactor coils were immersed in a boiling water bath. The N_2F_4 was absorbed at an elevated pressure upstream of the first stage. Typical reaction conditions for both TVOPA and A-3 are summarized in Table II.

Table II
Summary of A-3 and TVOPA Operating Conditions

	<u>A-3</u>	<u>TVOPA</u>
Production rate, gms. per hour	425	400
Yield on olefin/recovery, %	90-99+	94-99+
N ₂ F ₄ concentration, gms/cc solvent	0.2	0.2
Solvent	Freon TF	80% Freon TF, 20% chloroform
N ₂ F ₄ :olefin mole ratio	1.05-1.10	3.2-3.3
Reactor pressure, psig	400-450	400-450
Reactor temperature, °C		
Stage I	103	85
Stage II	125-130	115
Reactor volume, ml		
Stage I	311	311
Stage II	425	425
Residence time, minutes	≈28	≈25
Pounds/shift, maximum	6.3	6.0

The N₂F₄ concentration was normally 0.2 grams/cc solvent, resulting in product diluted with 85% solvent. Freon TF (CCl₂F-CClF₂) and a mixed solvent, 80% Freon TF and 20% chloroform, were used as the diluents for A-3 and TVOPA synthesis, respectively. The total residence time in both stages was about 25 minutes. Reaction pressures were varied from 400 to 500 psig with no noticeable effect on conversion or product quality.

Two mathematical models of the reactor were developed, the bulk model and the two dimensional model (Section 3.5). Figure 1 shows the calculated conversions and exotherm profiles for the TVOPA production conditions listed in Table II. Both models indicated a conversion of about 97% and a maximum exotherm of 8-12°C in each stage. About 50-60% of the reaction was carried out in the first stage at a nominal temperature of 85°C, and the

reaction was completed in the second stage at a nominal temperature of 115°C. Experimentally measured conversions were within the range predicted from the theoretical models.

Typical analytical values¹ for TVOPA produced in the flow reactor are shown in Table III. Occasional batches had N-fluoroozoxo concentrations greater than 1% because of high (>0.3%) nitric oxide levels in the N_2F_4 . The source of the alcohol impurity was undetermined, and the impurities corresponding to some of the other infrared absorbance frequencies were not fully identified. Specifications on raw materials used in the synthesis of TVOPA and A-3 are shown in Appendix B.

The two N_2F_4 adducts were synthesized alternately during the 1-3/4 year period since the flow reactor was put into operation. Productivity for each reaction was increased to about 0.9 pounds per hour. In a recent calendar month 79 pounds of TVOPA was made using a single shift operation. Operation was relatively trouble-free and down time required for equipment repair was reduced to less than 25% of the total operation time.

The liquid phase flow reactor was designed for a maximum production rate of about one pound per hour, corresponding to a Reynolds number of about 400. Further scale-up appears practical within the laminar flow regime, and equipment has been obtained to increase the capacity to about three pounds per hour. Additional mathematical characterization is required for turbulent flow where the heat transfer rate would be considerably higher, and hence more favorable for further increased reaction rate.

¹Test details are reported in Rohm & Haas Company, Quarterly Progress Report on Chemical and Propellant Processing, P-64-10, January 22, 1965.

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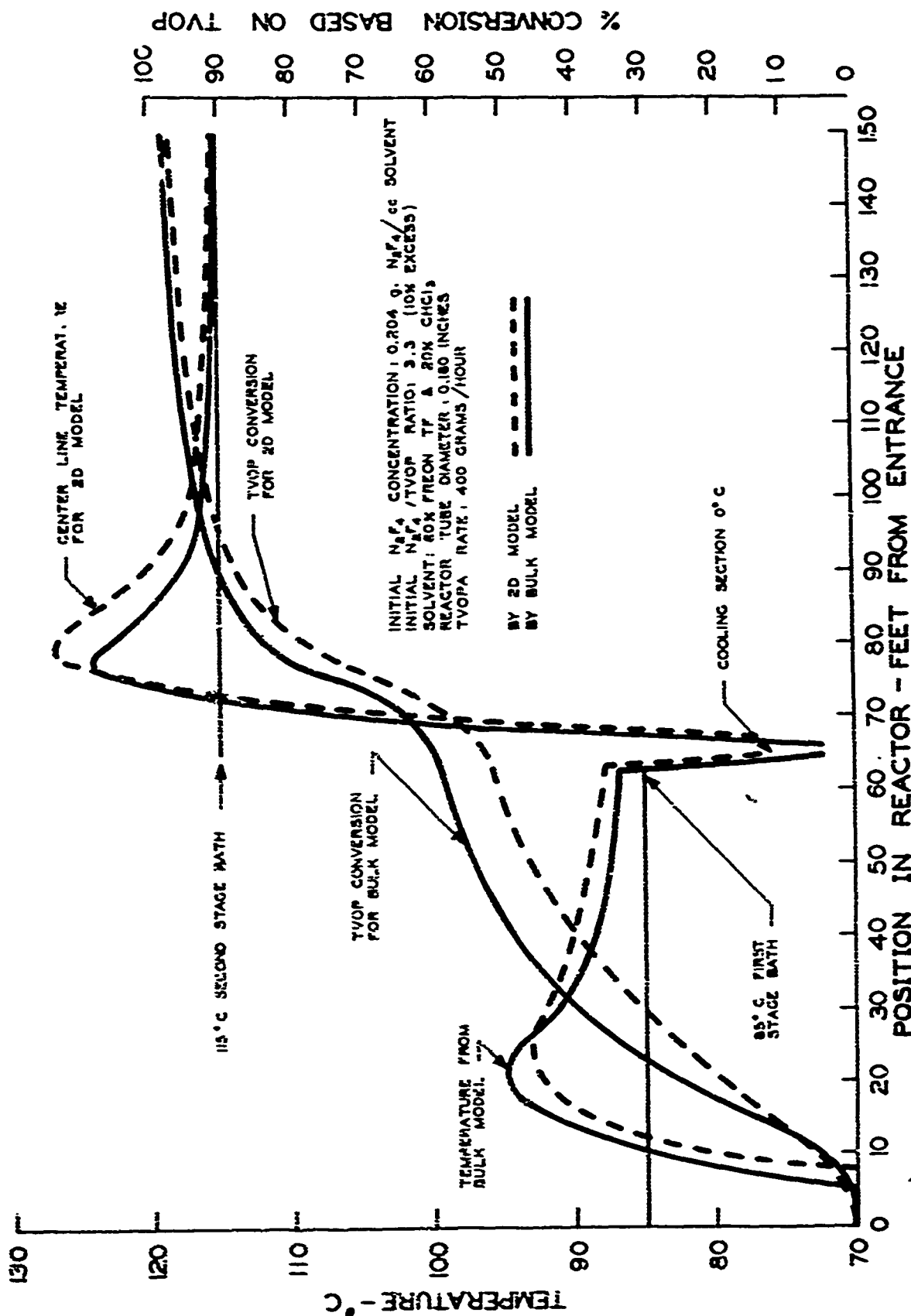


FIG. 1 CALCULATED TEMPERATURE AND EXOTHERM HISTORY FOR TVOPA PRODUCTION IN A TWO-STAGE REACTOR

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Table III
Quality Control Tests on TVOPA

	<u>Typical Range^(a)</u>
I. Infrared Analysis	
A. %	
2.78 μ - (alcohol as ethanol)	0.07 - 0.045
6.60 μ - (N-fluoroazoxy as pentakis adduct)	0.10 - 0.45
6.10, 6.18 μ - (residual olefin as TVOP)	nil - trace
B Absorbance Units	
5.78 μ (carbonyl)	0.025 - 0.045
5.92 μ (fluorimino)	0.125 - 0.150
6.23 μ (fluorimino)	0.040 - 0.085
II. Differential thermal analysis (10°C/min)	
Start, °C	160 - 185
Peak, °C	260 - 270
III. Difluoramino content ^(b)	
Ferrous reducibles, meq/ml	36.5 - 37.5
IV. Impact sensitivity	
Picatinny, kg cm (RDX = 10.5 kg-cm)	10.9 - 25.3

(a) Typical values found for TVOPA synthesized from N₂F₄ greater than 99.5% assay.

(b) Test is described in Rohm & Haas Company, Advanced Propellant Synthesis Report No. S-59, March 31, 1965.

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3.3 Apparatus

A flow sheet of the system, which was designed for the completely remote control of the N_2F_4 pressurization, reaction, depressurization, and continuous work-up, is shown in Fig. 2. (A detailed description of each section is included in Appendix C.) Gaseous N_2F_4 was metered with a two-stage diaphragm compressor from a storage cylinder to a mixing tee for absorption into the solvent-olefin solution. The N_2F_4 metering was automatically controlled by a closed-loop pneumatic system consisting of a differential pressure meter, a two-mode set point controller, and a pneumatic stroke controller on the first stage of the compressor. The solvent and olefin were premixed and metered by a positive displacement pump. Because the heat of solution of N_2F_4 in the solvent is 4 to 6 kcal/mole,¹ the absorption and mixing were accomplished in a cooled section of the pipe line. The three-component solution was fed to the two-stage tubular reactor, which was maintained at an elevated pressure by the downstream application of nitrogen pressure on the domes of two Grove Mity-Mite let-down valves, which were mounted in series. Prior to depressurization through the let-down valves, the reactor effluent was cooled to less than 20°C. The unreacted N_2F_4 was continuously desorbed from the depressurized liquid with a nitrogen sweep in a countercurrent wetted wall column. The product was collected in another bay following an air sparge in a hold-up vessel. The air- N_2F_4 laden nitrogen was further diluted with nitrogen and discharged through a 2-inch aluminum stack at 50 feet above ground level.

Each reactor stage consisted of a coil of 0.180-inch I. D. tubing totally immersed in a liquid water bath contained in a totally enclosed 6-inch pipe. The system was designed for a reaction pressure up to 500 psig, temperatures from 20 to 170°C, and production rates up to about one pound per hour of adduct.

¹Rohm & Haas Company, Quarterly Progress Report on Physical Chemistry, P-62-25, April 1963.

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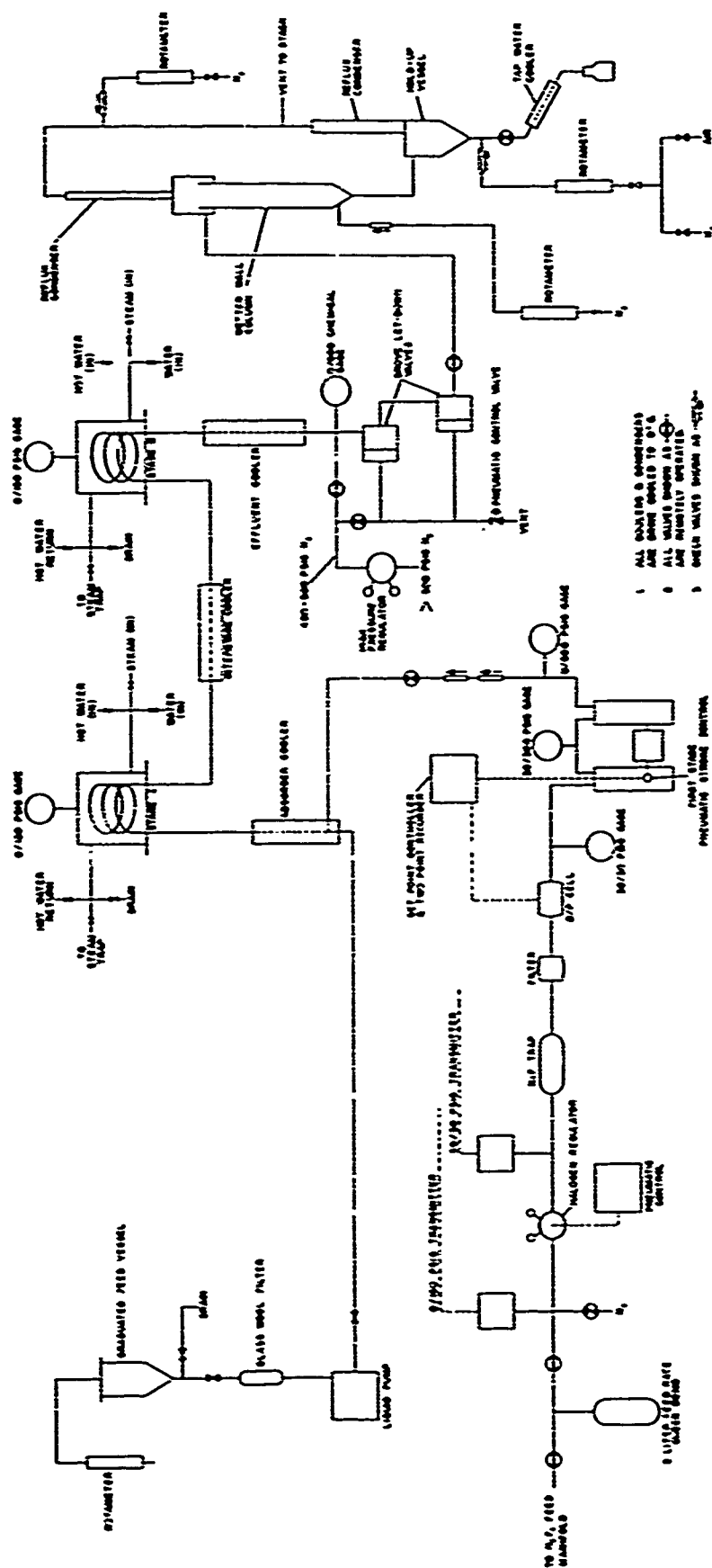


FIG. 2 FLOW DIAGRAM OF LIQUID PHASE REACTOR

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3.4 Operating Techniques

The detailed standard operating procedure is included in Appendix D.

During the steady-state portion of the batch, operational requirements were mainly limited to checking and adjusting process variables, including N_2F_4 feed rate, N_2F_4 suction pressure, olefin solution feed rate, stage temperatures, and nitrogen and air flows to the product collection system. About 6-1/2 to 7 hours of steady-state operation was possible for a single shift. The process was controlled by one operator during this period. Typically, the start-up, which was limited to equipment checkout and filling out batch cards, consumed about 15 minutes. The shut-down took about 45 minutes, the period required to flush the reactor with one reactor volume of chloroform, which was collected with the product. For personnel entry into the reactor bay the shut-down procedure was extended to include flushing the N_2F_4 from the compressor manifold with nitrogen, which added 15 minutes to the shut-down.

Before each start-up the N_2F_4 compressor manifold and the reactor coils were leak checked by pressurization and holding, usually overnight, but for at least 15 minutes. No pressure drop was acceptable in either section, and a leak-free system was easily maintained. Because air can initiate an explosive N_2F_4 reaction, special precautions were taken to insure that air was completely purged from the system. For start-up following the simple overnight shutdown, the purge procedure was usually not required. If air was admitted to a section, the N_2F_4 compressor manifold was flushed with nitrogen and the solvent-olefin feed line as well as the reactor coil were flushed with solvent.

3.5 Exotherm Characterization

The addition of N_2F_4 to olefins is highly exothermic, and the product is subject to thermal degradation. Therefore, exotherm control was a serious consideration in the reactor design and operation.

Two mathematical models^{1,2,3} of the coupled heat transfer-reaction rate process in the flow reactor were developed to identify possible hazardous operating conditions and predict the effect of changes in the operating conditions on exotherms and conversions. The models (for laminar flow operation) were:

(1) The bulk model, which assumed a slug flow profile with concentrations and temperatures varying only along the tubular axis.

(2) The two dimensional model (2D model), which accounted for both radial and axial variations of temperature and concentrations under fully developed laminar flow.

Some findings from these models are presented in Appendix E, and the Fortran program listings for both models are given in Appendix F. Both models were used to determine reaction conditions which would limit the risk of an explosion. Selection of pilot plant reactor conditions was guided by the results from the mathematical analyses, and no explosive primary exotherm was encountered in the pilot plant. The mathematical models suggest that current reactor temperatures are only 15-20°C below the region of probable explosion, but their validity has not been determined experimentally. Reaction rate data used in the models were obtained from experiments in batch reactors (Appendix G).

3.6 Solvent Selection

Freon TF was selected as the basic solvent, primarily on the criterion of complete miscibility with N_2F_4 , olefin, product, and reaction by-products. Other important requirements were non-flammability and stability in the presence of common chemicals, materials of construction, and N_2F_4 even at the elevated reaction temperature.

¹Rohm & Haas Company, Quarterly Progress Report on Chemical and Propellant Processing, No. P-64-3, August 6, 1964.

²Ibid, No. P-64-10, January 22, 1965.

³Rohm & Haas Company, Application of Flow Reactor Models to Process Simulation, No. E-54, October 9, 1964.

Since the olefins and products were soluble in most organic solvents, N_2F_4 solubility was a limiting factor. Incomplete solubility of N_2F_4 was unacceptable, because with even a small fraction of the gas present as a second phase the residence time in the reactor would be significantly reduced. The solubility of N_2F_4 was measured in five non-flammable solvents:^{1,2,3} (1) Freon TF; (2) Freon MF; (3) chloroform; (4) carbon tetrachloride; and (5) methylene chloride. Of this group, Freon TF was about twice as good as the next best solvent, chloroform. The minimum 400 psig reactor pressure was established from N_2F_4 solubility measurements in the absence of the olefin (Appendix H); the effect of the olefin and/or product was not determined. All A-3 runs and the early TVOPA runs were made with pure Freon TF, but after initial trouble with reactor tube plugging, chloroform was added to the Freon TF for TVOPA synthesis to dissolve TVOP polymer (Section 3. 7).

3. 7 Operational Problems

Mechanical Problems

Although corrosion of the compressor parts by N_2F_4 was minor (Appendix I), considerable difficulties were encountered in obtaining and maintaining the necessary compressor capacity. Apparently, the formation of even a small amount of powdery corrosion product interfered with the check valve seating. The period between shut-downs forced by check valve leakage was substantially increased (from one to four months) by three modifications: (1) a sodium fluoride trap was added to absorb traces of hydrogen fluoride from the N_2F_4 feed; (2) bondable "Teflon" discs were cemented to the type 316 stainless steel valves to convert the seating to Teflon-to-metal from metal-to-metal; and (3) all the gas-wetted parts were thoroughly cleaned with a hot Triton®-water mixture each time check valve leakage occurred.

¹Rohm & Haas Company, Quarterly Progress Report on Physical Chemistry, P-62-25, April 1963.

²Ibid., No. P-63-25, February 7, 1964.

³Esso Research and Engineering Company, Quarterly Progress Report on Research on Advanced Solid Propellants, No. 61-3, September 19, 1961.

Reactor Plugging

Reactor plugging was sometimes encountered during the first batch immediately after change-over in adduct production. Apparently, solid by-products were gradually deposited on the reactor walls throughout the synthesis of both adducts, and the plugging was attributed to the dislodging of these solids by the change of reactant-product mixture. Because the pressure drop remained about constant through any series of batches with the same adduct, these solids were thought to be deposited as a thin film throughout the reactor tube. It was evident that the quantity of deposited solids was negligible compared to the quantity of adduct synthesized; 78 pounds of TVOPA was made without evidence of plugging.

A steam and water cleaning schedule was found to eliminate solids prior to interchange of adduct production (A-3 to TVOPA or vice versa). Before start-up acetone and then methylene chloride were used to remove all traces of water from the reactor coils.

Although TVOP polymerizes very slowly, enough polymer was formed under the N_2F_4 reaction conditions ($100^\circ C$ and a high concentration of NF_2 free radicals) to increase the pressure drop severely in a 0.118-inch I. D. tubular reactor during an operating period of an hour or more. Two process changes were required to eliminate this problem: (1) mixed solvent (4:1 ratio of Freon TF to chloroform) was chosen in which the TVOP polymer was at least partially soluble; and (2) the tube diameter was increased to 0.180-inch I. D.

3.8 Safety

About 3.5 pounds of N_2F_4 was lost from partial decomposition which occurred on one occasion with the opening of a main cylinder valve, and six explosive incidents were encountered during the two-year period the reactor was in operation. No personnel injury occurred, and equipment damage was minor. These incidents are discussed in Appendix J.

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The synthesis of N_2F_4 adducts in the liquid phase reactor had a significant safety advantage, since the potentially explosive reactant-product mixture was heavily diluted with solvent. Thus, the 85% solvent dilution of the reactor effluent allowed non-remote handling of a desensitized product. Solvent dilution during reaction apparently eliminated explosion propagation through the liquid phase. All six explosions experienced during reactor operation were confined to short sections where the explosion initiated. In four instances the explosion occurred in the N_2F_4 mixing and absorption section during apparently trouble-free operation when the downstream section was filled with the reactants-product solution.

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APPENDIX A

Properties of TVOPA and A-3

Physical properties for both A-3 and TVOPA are itemized in Table IV.

Table IV
Properties of TVOPA and A-3

	<u>TVOPA</u>	<u>A-3</u>
Appearance	clear liquid	clear liquid
Volatility	equivalent to triethylene glycol dinitrate	6.5 mm Hg at 50°C
Freezing point	< -30°C	< -30°C
Specific gravity	1.54 $\frac{28}{4}$	1.43 $\frac{20}{4}$
Viscosity, 30°C, cp	33	
Molecular weight	482	190
Weight % N ₂ F ₄	64.7	54.6
Toxicity ^(a)	400-500	225

(a) LD₅₀ in mg/kg of body wt. in acute oral tests on white, male Wistar rats; both compounds are classed as "highly toxic" on this basis.

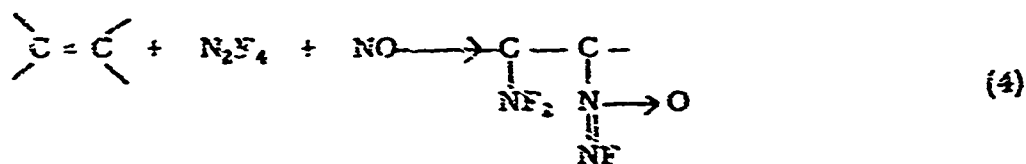
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APPENDIX B

Raw Material SpecificationsN₂F₄

Minimum N₂F₄ purity for TVOPA synthesis was set at 93 wt. % and for A-3 synthesis at 97 wt. %. For TVOPA synthesis nitric oxide content was limited to a maximum value of 0.3 wt. %.

Although the effect of impurities in N₂F₄ was not fully established, nitric oxide appeared to react preferentially during TVOPA synthesis to yield the fluoroazoxy impurity by the reaction shown in equation 4.



As shown in Fig. 3, the fluoroazoxy impurity in TVOPA increased about 3.5% (as the pentakis adduct) for each 1% NO in the N₂F₄ feed. A larger amount of NO could be tolerated in the A-3 synthesis, probably because of the fractionation of fluoroazoxy effected by subsequent reaction and purification steps in the NFPA synthesis.

Trivinoxypropane

Minimum assay of TVOP as determined by gas chromatography was set at 95%. Conversion calculations assumed 100% TVOP purity.

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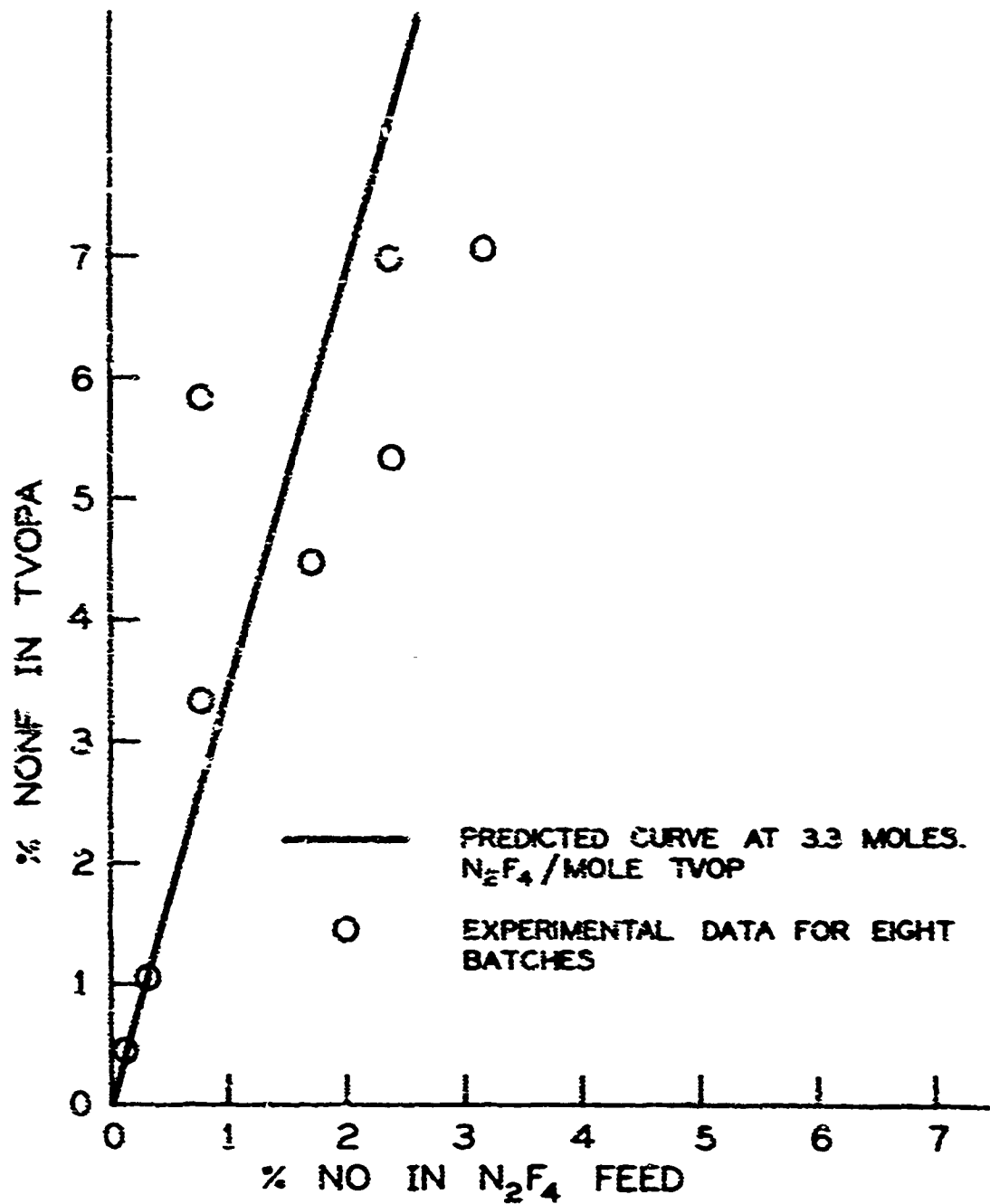


FIG. 3 FLUOROAZOXY CONTENT IN PRODUCT VERS. NITRIC OXIDE CONTENT IN N_2F_4

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APPENDIX C

Detailed Equipment Description

A flow sheet for the liquid phase flow reactor is shown in Fig. 2. The N_2F_4 compressor system, the two-stage tubular reactor, and the product work-up system were located for completely remote operation in a bay barricaded by 12-inch reinforced concrete walls. An 8-inch thick Plexiglas[®] sight port was provided for visual observation of the reactor bay from the control area, and the explosive limit on the bay was set at 5 lbs. Because N_2F_4 was condensable at the desired operating pressure, the entire reactor bay was thermostatted at 40°C (3.5°C above the critical temperature of N_2F_4)¹. The N_2F_4 feed cylinders were located in an adjacent barricaded bay, and a second adjacent barricaded bay was used for product collection. The solvent-olefin feed tank and pump were located in the control area.

N_2F_4 Cylinder Manifold

The N_2F_4 cylinder manifold, shown in Fig. 4, served a dual purpose. First, it provided for ready replacement of N_2F_4 feed cylinders during any portion of the flow reactor operation; and second, it allowed recombination of nearly empty cylinders by compression into another gas cylinder. There were two independent cylinder manifolds containing one and three cylinders, respectively.

¹Rohm & Haas Company, Quarterly Progress Report on Air Force High Energy Solid Propellant Program, No. AF-8, February 9, 1961.

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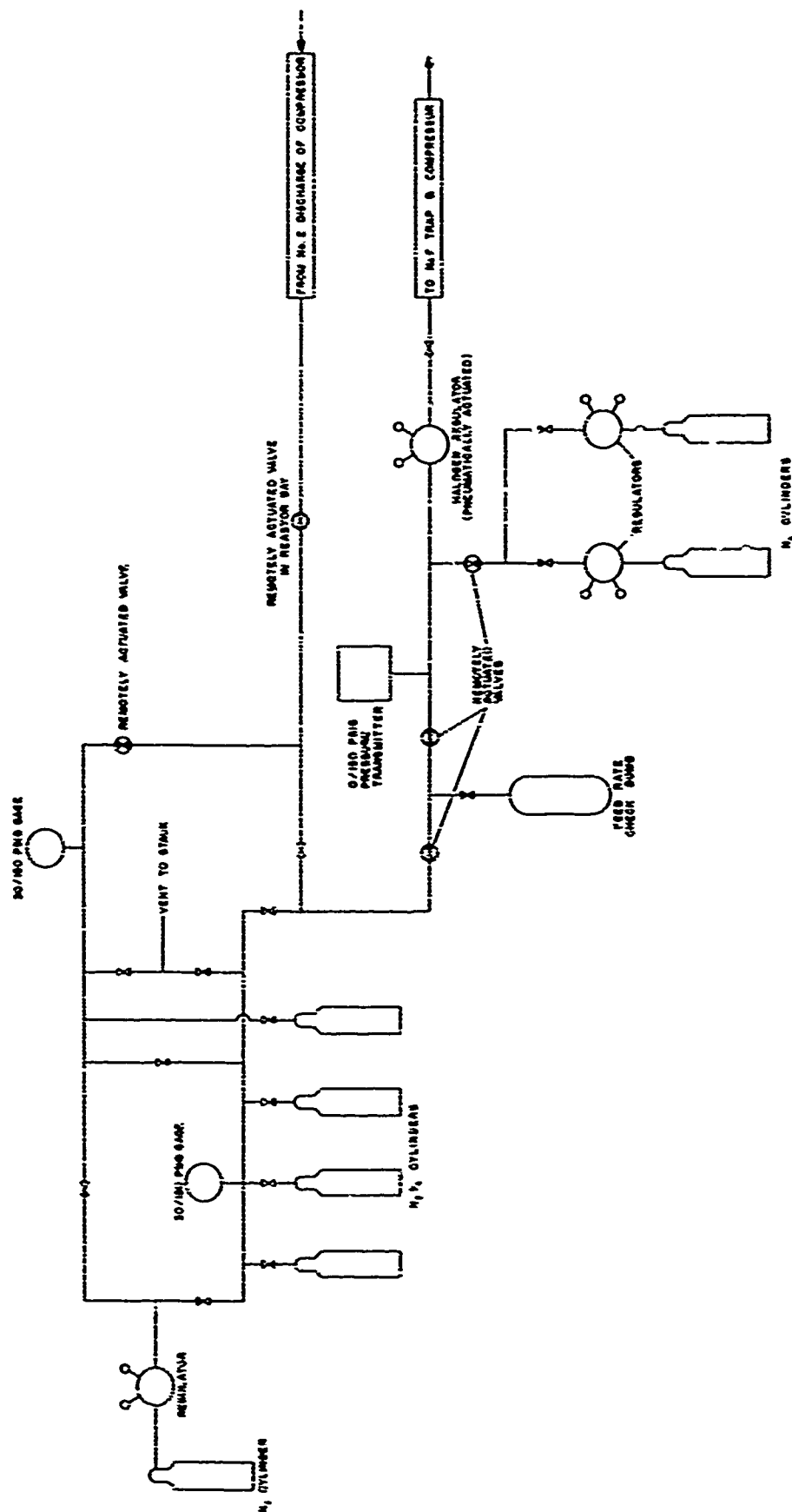


FIG. 4 N₂F₄ FEED MANIFOLD

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The N_2F_4 was fed from a single cylinder, and about five hours was required to reduce the pressure from 130 psig to the 16 psig standard suction pressure of the compressor. Usually the three cylinders in a bank were emptied before any in that bank was replaced. Before cylinder removal and before the opening of a newly installed cylinder, the manifold was purged of air by five alternate fillings with 100 psig N_2 and ventings to atmosphere. The small amount of remaining atmospheric nitrogen was fed with the N_2F_4 . The operating procedure for cylinder interchange is discussed in Appendix D.

Following an incident discussed in Appendix J, flame protection was provided during the opening of main N_2F_4 cylinder valves. Personnel were protected by a 12-inch reinforced concrete wall against which the cylinders were fixed. A two-foot long cable was inserted through the wall to open the valve. Care was taken to insure that the main cylinder valve was fully opened to take advantage of a second stem seal which was independent of the packing.

About 1/2 pound of N_2F_4 was recovered from each exhausted feed cylinder by recombination with the two-stage compressor. Typically, the compressor evacuated the 15-16 psig heels in the spent cylinders to 10-15 inches vacuum while discharging to as much as 110 psig. Mass spectral analyses confirmed a negligible change of N_2F_4 quality by this procedure. Six to nine cylinders could be emptied in a single day.

N_2F_4 Compressor System

A two stage, double diaphragm Lapp compressor having a nominal capacity of about 0.75 pounds of N_2F_4 per hour (15 psig to 500 psig) was used to compress the N_2F_4 . The double diaphragm feature was chosen to avoid the mixing of N_2F_4 with the hydrocarbon oil if a leak should occur in the diaphragm, and the interdiaphragm space was filled with No. 3 Kei-F oil. However, no difficulty was encountered with diaphragm leakage.

A feed back control system was used to maintain the N_2F_4 feed rate to within $\pm 3.5\%$ of the desired value. The feed rate was measured by a Fisher-Porter differential pressure transmitter (D/P cell) with an integrally mounted flow nozzle. The unit was continuously adjustable through a 0-20 to 0-200 inches of water range. A Minneapolis-Honeywell two-mode set-point recording controller (proportional plus automatic reset) was used to actuate the pneumatic stroke controller located on the first stage of the compressor. The D/P cell was attached to the suction side of the compressor. Suction pressure was controlled to 16 ± 0.5 psig with a Matheson Company halogen regulator. The regulator was modified for remote operation by substitution of pneumatic for mechanical actuation of the non-process side of the diaphragm. Continual adjustment of the pneumatic manual loader was required to maintain the suction pressure within ± 0.5 psig because pressure in the N_2F_4 supply cylinder dropped about 25 psi per hour during a run.

Periodic independent checks of the N_2F_4 feed rate confirmed the rate indicated by the D/P cell. A 2.5-liter cylinder was located downstream of the N_2F_4 feed cylinder, and the rate was checked by determining the pressure drop in this small cylinder over a period of four minutes. The small cylinder was immediately refilled (to feed cylinder pressure) by opening a connecting valve to the feed cylinder. This technique provided a rapid check on the D/P cell readout without seriously interfering with the absolute N_2F_4 feed rate.

Activated sodium fluoride was used in the HF trap. This was prepared by heating sodium bifluoride ($1/4" \times 1/4"$ pellets) overnight at $300^\circ C$ while passing nitrogen through the bed to eliminate hydrogen fluoride.

Solvent and Olefin Feed

The solvent and olefin were premixed and metered with a 2300 cc/hr. capacity Lapp diaphragm pump. A glass wool filter was required to separate any material which otherwise interfered with the seating of

Hastelloy ball checks. Clear polyethylene tubing was used to connect the filter to the suction side of the metering pump, and this section was periodically checked to insure that the pump was not drawing air.

Mixing and Absorption

The N_2F_4 was mixed with the solvent-olefin in a cooled two-foot section of 1/4-inch I.D. tubing to control the heat of solution (4-6 kcal/mole) of N_2F_4 in the solvent.

Reactors

As shown in Fig. 5, each reactor chest was constructed from a schedule 40 6-inch water pipe, 30 inches long, vertically mounted, and insulated with about 2 inches of vermiculite. Each chest had provision for cooling with tap water, heating to 170°C with injected steam, and heating with hot water to about 95°C. A steam inlet was located at the bottom of the pipe, and the condensate overflow was from the top so that the tubular coils were totally immersed in the liquid bath. The tubular reactor was constructed by coiling 0.18 inch I.D. type 316 stainless steel tubing. The short section of tubing connecting the first and second stage was brine cooled.

Cooling and Depressurization

The effluent from the second stage of the reactor was cooled to less than 20°C before depressurization through two Grove back-pressure regulators which were mounted in series. The regulators controlled the reactor pressure by balancing nitrogen pressure on the upper side of the Teflon diaphragm against the pressure on the process side. As the process pressure exceeded the nitrogen balance pressure, the diaphragm opened, permitting process fluid to flow through an outlet nozzle. Because of the build up of a small amount of solid by-products on the outlet nozzle, sealing with one regulator was not always possible. Adequate sealing was obtained with the addition of the second regulator.

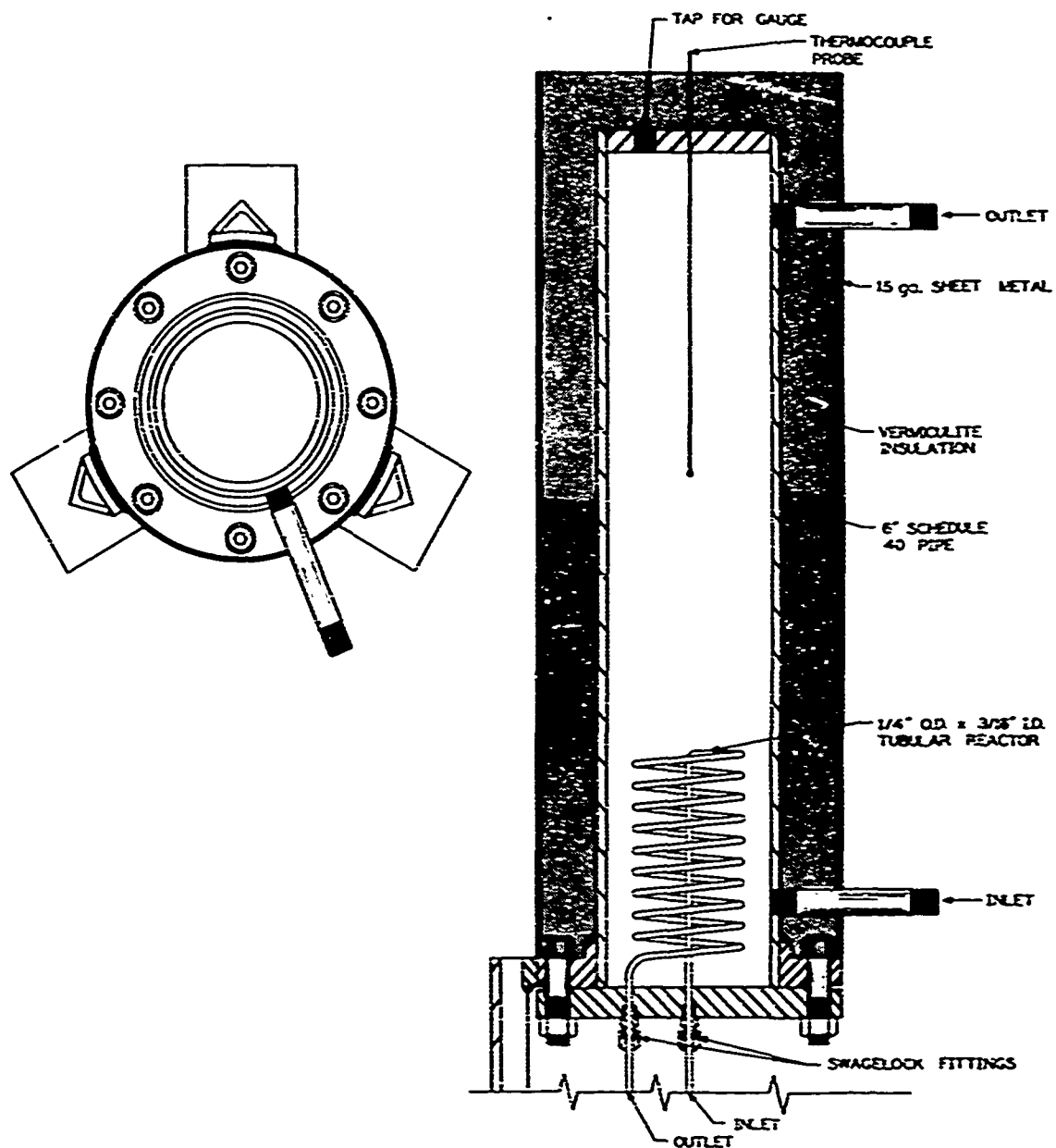


FIG. 5 TUBULAR REACTOR ARRANGEMENT IN REACTOR CHEST

N₂F₄ Desorption

Since both reactor effluents (TVOPA and A-3) readily wet 316 stainless steel, a wetted wall column (Fig. 6) was chosen for countercurrent desorption of the dissolved N₂F₄ in the depressurized effluent. The liquid was fed through the annulus and distributed to the column by overflowing around the inner perimeter. Nitrogen was fed to the bottom of the column at 1 liter per minute to dilute and sweep out the desorbed gas. The column temperature was about 40°C, which was the temperature of the thermostatted reaction bay. The column was 3 feet by 7/8-inch I.D. with a 1/8-inch annulus at the top formed by welding a 1 inch length of a larger, outer tube which extended 1/2-inch above the column.

Complete desorption of the N₂F₄ was confirmed by the absence of its characteristic odor in the effluent. Since there was concern that NF adducts containing absorbed N₂F₄ would deflagrate upon exposure to air, the product was air sparged (200 cc/min) in a hold-up vessel before collection in an adjacent bay. Because of the possibility of transmittal of such a deflagration, personnel were not allowed to enter the product collection bay while the air sparging operation was in progress. Entry was allowed while the hold-up vessel was temporarily used for the product collection, but only after the air was purged by nitrogen.

Liquid seals were used to prevent the nitrogen or air from flowing through the desorber drain line to the hold-up vessel or air flowing through the hold-up vessel drain line to the product collection bay. Two translucent polyethylene-U-tubes were installed so that a three-foot head differential was necessary for gas flow through the liquid lines. Repeated observation of the liquid levels confirmed that the seals were effective; typical liquid head differentials were in a range of 0 to 12 inches.

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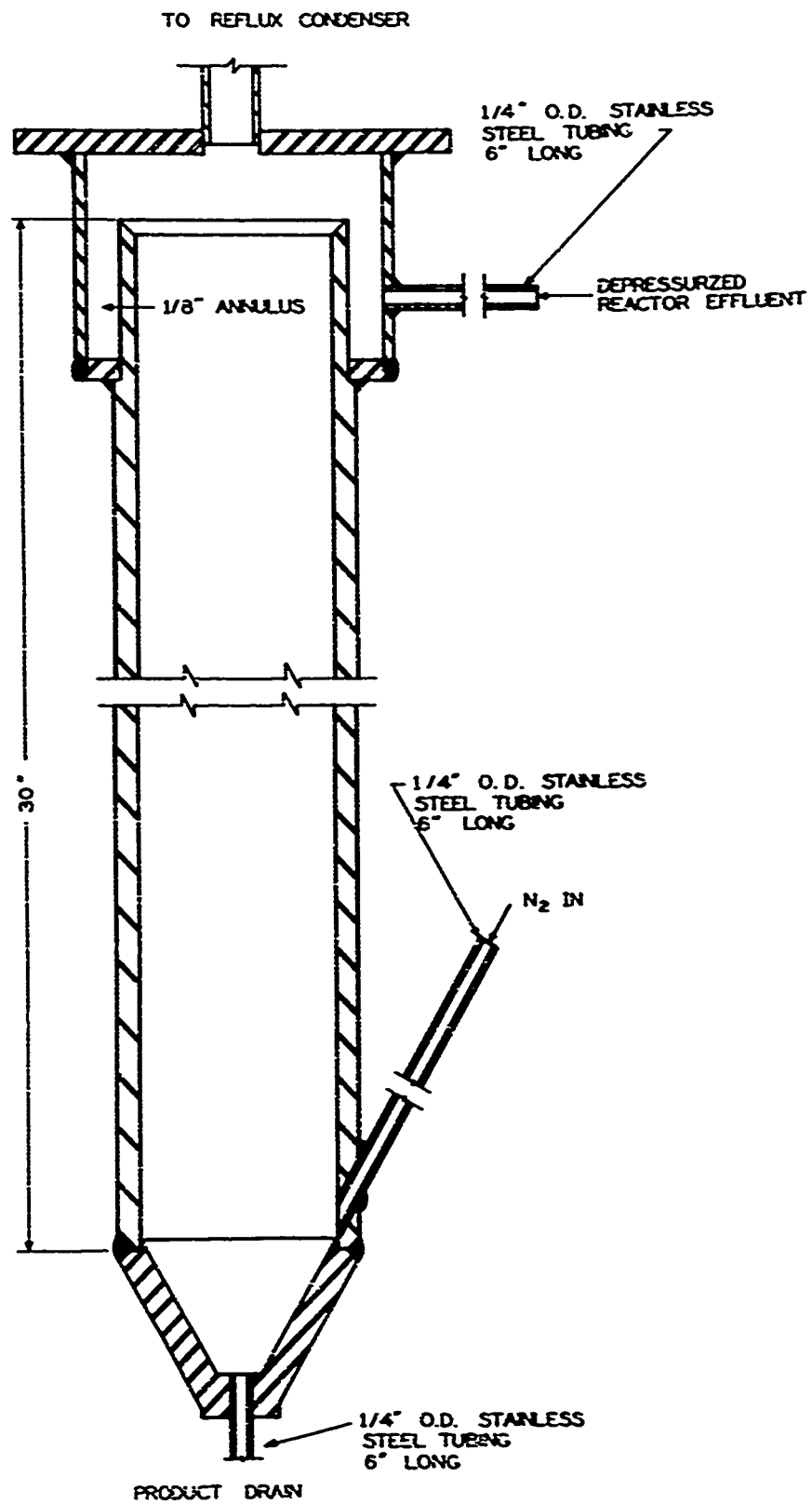


FIG. 6 WETTED WALL COLUMN

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Venting of Unreacted N_2F_4

The unreacted N_2F_4 was vented directly to the atmosphere through a two inch aluminum stack at a 50 foot elevation. The nitrogen- N_2F_4 stream from the wetted wall column was diluted to about 30% with additional nitrogen, and upon entry to the stack, this mixture was further diluted with air so that the net concentration of original nitrogen- N_2F_4 mixture was reduced to less than 1% upon exhaustion to the atmosphere.

Materials of Construction

All pressurized process lines, with the exception of the N_2F_4 feed lines to the suction side of the compressor, all valves, and all process vessels were constructed of type 316 stainless steel. Hoke toggle valves with a Teflon tip were modified for remote actuation with an air cylinder. The N_2F_4 feed manifold was constructed of 1/4 inch copper tubing. Where possible, polyethylene tubing, either black or clear, was used for remote process lines operated at atmospheric pressure.

APPENDIX D

Standard Operating Procedure
for
High Pressure Liquid Phase Flow Reactor

General

The Section Safety Regulations are considered a part of this operating procedure and all applicable regulations must be observed.

Personal Protective Equipment

1. Safety goggles are required at all times except in the Bay H control area.
2. Safety goggles and rubber gloves are required while preparing solvent and olefin and while adding the mixture to the feed tank in Bay H.

Equipment Required

See Figures 2 and 4.

Process Description

The preparation of the product involves the liquid phase reaction of N_2F_4 dissolved in a suitable solvent with another reactant. The reaction is carried out in a jacketed tubular coil.

Safety Limits

The following limits must be observed, except for gas cylinders and 1/4-inch copper lines. Solvent used for dilution should not be considered explosive.

- | | |
|---|---|
| 1. Explosives in Reactor Bay: | 1000 grams |
| 2. Explosives in Control Room: | zero |
| 3. Explosives in Product Collection Room: | 10 pounds (never more than one day's run) |
| 4. Explosives in Cylinder Room: | zero |
| 5. Explosive charge per adduct container: | 6 pounds |

Safety Considerations

1. Once the door to the reaction area has been closed, never open it until shutdown procedure (for entry into the reactor bay) is followed. The door to the reaction area is not considered closed until the seven latches are secured.
2. Keep the door to the N_2F_4 cylinder storage bays closed except when it is necessary to take readings or move cylinders.
3. Handling of Product:
 - a.
 - i. Always carry product samples in a rubber boot.
 - ii. Two-gallon polyethylene containers with handles may be hand carried.
 - iii. Ten-gram samples are to be hand carried with the port directed away from the body.
 - b. No more than six pounds of product will be added to any single storage container.
 - c. Never transport the product or samples in the east corridor of Bldg. 7555.
 - d. Open a product bottle which contains 35% or more concentrated adduct remotely if it has been stored longer than eight hours.
4. The west door to the Bay H control area should be closed at all times.
5. While handling solvent, etc. (in Bay H), be sure the exhaust fan is on.

Hazardous Properties of Chemical Compounds

1. N_2F_4 is considered highly toxic and can, even at low concentration, produce systemic injury if repeatedly inhaled. NEVER WORK OR REMAIN IN AN AREA WHERE THERE IS ANY PERCEPTIBLE ODOR OF N_2F_4 . Personnel exposure must be limited to N_2F_4 stored at less than 130 psig in cylinders rated at greater than 2500 psig rupture pressure because of explosion hazard. Exceptions may be made by the supervisor.
2. Mixtures of N_2F_4 and air sometimes will initiate decomposition of the product, and the decomposition products may increase the product sensitivity to air. For this reason it is very important to leak test the flow reactor system before each run.
3. Treat N_2F_4 as if it were oxygen, that is, use oxygen fittings, valves, gages and regulators. NEVER ALLOW N_2F_4 TO COME IN CONTACT WITH GREASE OR SIMILAR HYDROCARBONS. SOME EXCEPTIONS WILL BE MADE WITH KEL-F GREASES, BUT ONLY AT THE DIRECTION OF THE SUPERVISOR. All process equipment must be degreased for oxygen usage.

4. No personnel should be in Bays E and F when N_2F_4 is introduced into the reactor feed lines. Before opening an N_2F_4 cylinder, be sure that the upstream remote valve to the system is closed.
5. The product is sensitive to shock and impact. For this reason it should be handled carefully. All bottles and vials containing this material must be clearly labeled as explosives.
6. Ingestion, inhalation, and contact of the product with the skin should be carefully avoided.

A. Preliminary Systems Check Out

1. All operating personnel should have completed at least two simulated emergency shutdowns.
2. If reactors are below $80^\circ C$, turn on heated water to both reactor stages and set water heater to $180^\circ F$ (at $80^\circ C$ set reactor temperature to that designated).
3. Check brine cooling system and turn on circulating pump.
4. Turn on air to the panel board and set regulator for instrument air controllers at 60 psig.
5. Set instrument air at 20 psig.
6. Close both N_2 back pressure valves on the panel board and N_2 feed to compressor, work-up vessel, wetted wall column, and dilution.
7. Turn on electricity to panel board.
8. Turn on lights in reaction area.
9. Turn on reaction area heater and set temperature at $40-42^\circ C$.
10. Turn on hot water to the Stage II compressor head and use hot water as necessary to maintain $49-50^\circ C$ head temperature.
11. Turn on tap water to product cooling section.
12. Turn on all three nitrogen cylinders and replace if pressures are as follows: (vent air by filling and breaking at cylinder)
 - a. Back Pressure N_2 : below 600 psig
 - b. Emergency N_2 : below 1000 psig
 - c. Sparge N_2 : below 1000 psig
 - d. N_2F_4 feed cylinder: as specified, and record analysis in log book

13. Do not replace any cylinder in the middle of a run; exceptions may be made by the supervisor.
14. Keep a cylinder log book for the N_2F_4 cylinders showing:
(This is in addition to inventory requirements.)
 - a. Date installed; Initial Pressure; Analysis
 - b. Batch Numbers Used for
 - c. Date Removed; Final Pressure
15. Turn on the exhaust fans in Bay F and Bay N.
16. Be sure glove for shutting down steam valves is "mounted" on panel board.
17. Close the drain valve on the vent trap.

B. Start-up

1. If for some reason the liquid level is below the drain valve in the Lapp pump, charge 100 ml of the chosen solvent (without olefin) and pump (full stroke) until the liquid level is just above the stopcock in the feed flask. Be sure the clear polyflex line connecting the filter to the liquid pump is filled with liquid.
2. Turn on sparge N_2 cylinder and set pressure regulator at 30 psig.
3. Close the valves to the wetted wall column and do not open until item No. 26.
4. If no overnight leak check has been applied: (no pressure drop should be allowed for 15 minute check or for overnight)
 - a. Leak check at 30 psig for 15 minutes and include:
 - (1) lines to main valve sparge N_2 cylinder
 - (2) lines to main valve N_2F_4 cylinder
 - (3) lines to mixing tee above compressor; do not turn on compressor to fill system
 - (4) sparge N_2 system

After venting the high pressure gage on the N_2 cylinder, observe the pressure recorder as well as the two discharge gages on the compressor.
 - b. At the same time leak check the reactor system at the desired operating pressure to:
 - (1) mixing tee
 - (2) both the let-down vessel and the Grove valve, but not the column

- c. At the same time leak check both N_2F_4 feed manifolds to 100 psig with N_2 or N_2F_4 pressure if above 15 psig; included are the remote N_2F_4 feed valve, vents, main cylinder valves, and No. 2 remote discharge valve. No pressure drop should be allowed even on an overnight check.
- d. Vent the reactor system.
5. If air has been introduced to either the compressor or reactor systems, vent the reactor and compressor system and:
 - a. At full stage I stroke, pump N_2 through the reactor system by filling at standard suction pressure and evacuating to 1-2 psig vacuum five times. All drain valves should be opened and a collection vessel should be under the work up vessel drain.
 - b. Dispose of any liquid in explosive scrap and close drain valves.
6. Open the N_2 manifold valve on the panel board.
7. Turn on the N_2 to the column at 1.0 l/min. (if different setting is used, record).
8. Turn on the N_2 to the dilution at 2.5 l/min. (if different setting is used, record).
9. Turn on air to the work-up vessel at 0.2 l/min. (if different setting is used, record).
- 9a. Turn on air to aluminum stack on the roof.
10. Be sure the door to the reaction area is closed and the red warning lights are on.
11. Adjust the pneumatic control valve.
12. Adjust both reactor stage temperatures as designated. While adjusting proceed to items 13-26.
13. Measure out the specified solvent and also measure out the specified quantity of olefin. Record the volumes on the batch card and measure the total volume before charging. Be sure these ingredients are completely mixed.
14. Set the solvent pump and charge the designated solvent-olefin mixture to the solvent feed tank.
15. Close the N_2F_4 feed valve and open the main N_2F_4 cylinder valve.
16. Adjust the halogen regulator to below 16 psig suction pressure.
17. Being sure the nitrogen feed valve is closed, open the N_2F_4 feed valve to the manifold.
18. Reset the halogen pressure regulator to the designated suction pressure.

19. Record null and full stroke compressor readings.
20. Apply pressure to the dome of the Grove valve.
21. If necessary, apply back-pressure to the system and close the back pressure valve.
22. Be sure collection jug is under work-up vessel outlet. Never remove jug without placing another 1000 cc collection vessel at the outlet.
23. Turn on the compressor adjusting the set point controller to the desired N_2F_4 feed rate.
24. When the downstream pressure reaches the back pressure, open the mixing tee valve.
25. If the compressor system did not contain N_2F_4 , run for three minutes before going to item 26.
26. Turn on the solvent pump and start timer.
27. Open the column valves.
28. Wait 20 minutes and open the work-up vessel drain valve.

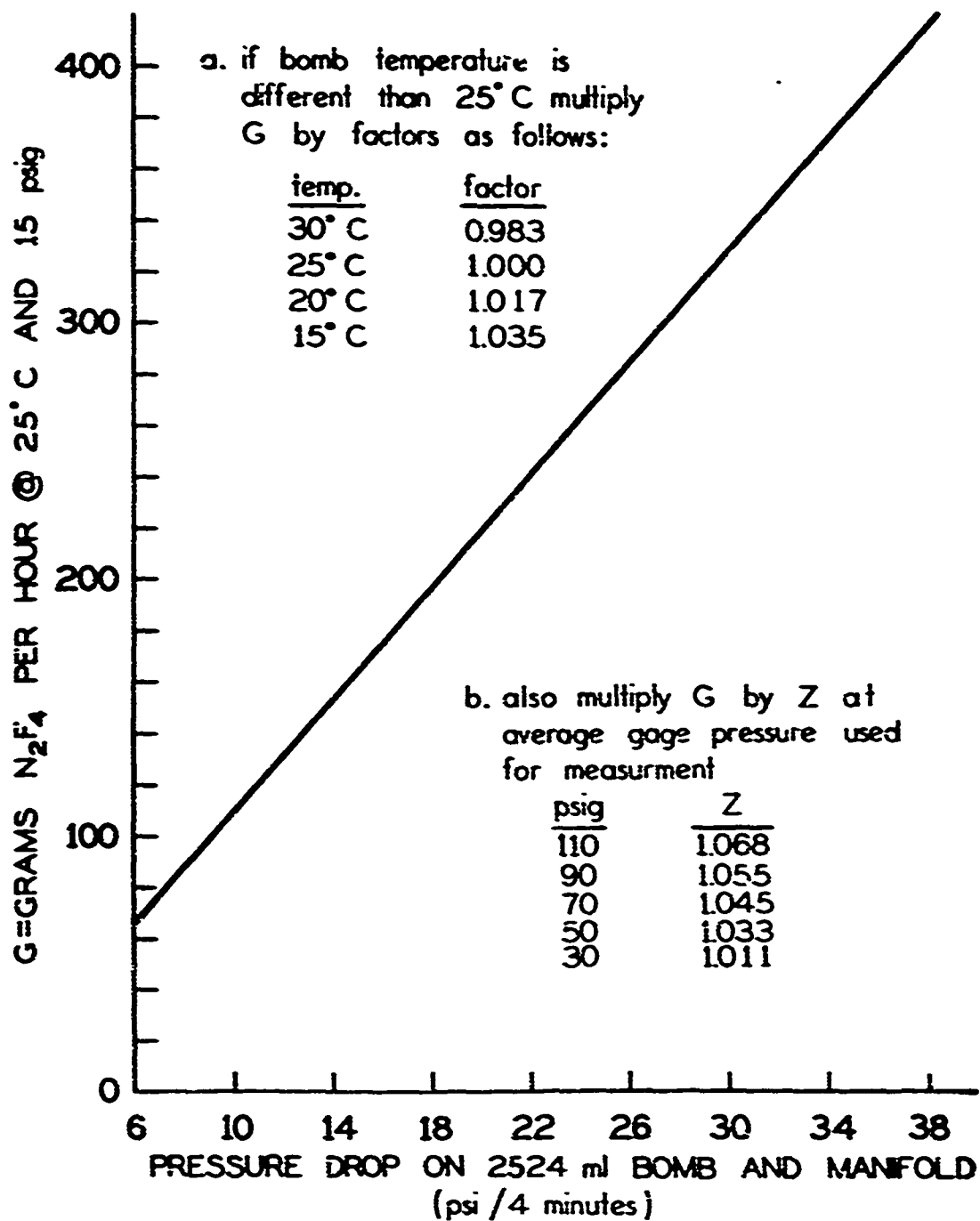
C. Operation

1. If it is necessary to go into the product collection bay:
 - a. Close valve to work-up vessel.
 - b. Turn off air.
 - c. Turn on N_2 to work-up vessel at 0.5 l/min., and after five minutes go to d.
 - d. Enter product collection bay for a maximum period of 15 minutes.
 - e. After leaving product collection bay switch to air flush at 0.2 l/min.
 - f. Open work-up vessel drain valve and continue collection.
2. Periodically check the N_2F_4 feed rate indicated by the D/P cel. This can be done by isolating the feed cylinder from the 2200 cc calibrated bomb as follows:
 - a. Measure the pressure drop over a four minute interval.
 - b. Find the feed rate from the graph, Figure 7.Adjust the D/P cell setting as required to maintain the designated N_2F_4 feed rate.
3. Record the items listed on the batch card at least every 45 minutes.
4. Observe the solvent rotameter, and if the flow should stop, shut down by the emergency shut down procedure.

5. If the polyethylene legs on the column and work-up vessel do not run full, notify supervisor, do not shut down, and do not enter Bay N.
6. If a new N_2F_4 feed cylinder is to be turned on during a run, do the following in the order listed. If trouble occurs (such as a stuck valve), go backwards from the step you are on to continue feeding from the near empty cylinder. If the problem is not readily solvable, shut the reactor down by the shut-down procedure and notify the supervisor.
 - a. Close the remote N_2F_4 feed valve.
 - b. Record the pressure and close the main cylinder valve on the nearly empty cylinder.
 - c. Open the main cylinder valve on the full cylinder.
 - d. Record the cylinder pressure.
 - e. Set the manual valves to feed through the remote N_2F_4 feed valve.
 - f. Being sure there are no personnel in Bays E or F, remotely open the N_2F_4 feed valve.
7. Be sure the clear polyflow tube between the filter and the liquid pump is filled with liquid.

D. Shutdown Procedure

1. With the solvent pump running, quickly collect the excess solvent-olefin mixture in the designated receiver. Drain to just above the stopcock and add (exactly) 1800 ml solvent mixture (use 1000 ml for overnight shutdown where same adduct is to be made the next day). Record time at completion. Wait 2 minutes and then proceed to item 2.
2. Close the N_2F_4 feed valves and all main N_2F_4 cylinder valves.
3. At 8 psig suction close the mixing tee valve and turn off compressor.
4. After feeding at least 300 ml solvent, open the pump to full stroke.
5. Turn off the solvent pump when the liquid level in the glass feed tank is about 3/4-in. above the stopcock and close the column feed valve and drain valve to let down vessel.
6. Turn off the N_2 to the dome and depressurize by venting through the pneumatic valve and then close pneumatic valve and repressurize.
7. If this is an overnight shut down, apply the leak check as in the start-up instructions. Record each pressure and temperature for each bay.
8. Be sure the work-up vessel has been emptied of liquid. Do this by increasing the N_2 dilution to 15 l/min. for at least 3 minutes.

FIG. 7 N_2F_4 FEED RATE CALIBRATION GRAPH

9. If shut down is for entry into the reaction bay, very slowly over a period of at least 15 minutes vent the reactor by opening the Grove valve and the column valves and the drain valve on the work-up vessel. Clean the N_2F_4 feed lines by the following technique (be sure there is a collection vessel under the work-up vessel):
 - a. Open the N_2 feed valve to pressurize the compressor system and turn on the compressor.
 - b. After about 15 seconds, close the N_2 feed valve and open the mixing tee valve.
 - c. When the suction pressure reaches 1-2 psig repeat a and b five times and then pressurize the suction lines to at least 5 psig.
 - d. Close mixing tee valve and shut off compressor.
10. After the solvent is collected, turn off the following:
 - a. Bay lights and warning lights if the reactor bay can be entered.
 - b. All main N_2F_4 cylinder valves.
 - c. Compressor.
 - d. Sparge N_2 cylinder.
 - e. Temperature recorder.
 - f. Air to stack and work-up vessel.Also:
 - g. Open drain valve on the vent trap.
 - h. Do not turn off room heater or cooling system including pump.
11. Store the unused solvent-olefin mixture and label as follows:
 - a. Gross weight.
 - b. Tare weight.
 - c. Net weight (note on batch card).
 - d. Nominal concentration of each component.
 - e. Date.
 - f. Batch No.

E. Emergency Shut Down Procedure

1. If any unusual difficulty occurs, follow this procedure immediately in the sequence listed.
2. Turn off N_2F_4 feed valve to compressor and close mixing tee valve.
3. Close work up vessel drain valve.

4. Cool stage II with tap water to the stage I temperature. While waiting, turn on emergency alarm. Only one operator is to remain in Bay H to complete procedure through Item 10.
5. Cool stage I with tap water, and when both reactors are less than 40°C, proceed.
6. Turn off solvent pump.
7. Turn on N₂ feed to compressor and open mixing tee valve.
8. Set first stage compressor stroke control to 15 psig.
9. Turn pneumatic bleed valve to 15 psig and close N₂ valve to the dome.
10. Consult supervisor. (No watch is necessary after completion of item 8.)

F. Changing N₂F₄ Cylinder

1. Isolate manifold where cylinder is to be added.
2. Close all main N₂F₄ cylinder valves in this manifold.
3. Pressurize the manifold to 100 psig with N₂ and vent. Do this at least five times.
4. Remove the N₂F₄ cylinder.
5. Replace with a new cylinder.
6. Fill the system to 100 psig with N₂ and vent five times.

G. Routine Maintenance (once per month or oftener as required)

1. Each item should be tagged with the date and service received.
2. Grease bearings on compressor motor.
3. Check gear box level on compressor motor.
4. Inspect oil in each compressor stage and, if necessary, change.
5. Inspect oil in solvent pump and, if necessary, change.
6. Sparingly grease all air cylinder rods.
7. Drain air filter and, if necessary, replace.
8. Add make up brine to the cooling system.

H. Interchange of Product

1. If the next batch is to be a different adduct, follow this procedure after following the procedure for entry into the reactor bay.
2. Set the reactor coils for atmospheric pressure operation and flush the brine from the cooling lines with air.
3. Heat both reactors to 103°C with steam.
4. Pump 1000 ml of water through the unit and collect in the product collection bay.
5. Cool the reactors to less than 30°C.
6. Pump 500 cc water.
7. Pump 500 cc acetone.
8. Pump 1500 cc methylene chloride.
9. Dump the solvent water mixture in explosive scrap.
10. The unit is now ready to run on a different adduct.

APPENDIX E

Exotherm Characterization

The addition of N_2F_4 to olefins was exothermic by about 35 kcal/gm mole of N_2F_4 added. For example, 105 kcal were liberated by the addition of 3 moles of N_2F_4 to one mole of TVOP. Exotherm control appeared necessary to avoid explosive incidents. Two mathematical models were developed to characterize the reaction exotherm based upon laboratory kinetic studies. These models were:

- (1) The bulk model which assumed a slug flow profile with concentrations and temperatures varying only along the tubular axis.
- (2) The two-dimensional model (2D) which included radial diffusion of temperature and both reactants under fully developed laminar flow.

The maximum temperature limit was based upon differential thermal analysis of TVOPA thermal decomposition. Since the DTA indicated that TVOPA began to decompose at above 150°C, operating conditions were chosen never to exceed a 140°C reactant temperature. The operating bath temperature was set at 10°C below the temperature where the exotherm caused a 140°C reactant temperature. This criterion provided an adequate safety factor to allow for expected process deviations such as $\pm 2^\circ\text{C}$ variation in bath temperatures, $\pm 3.5\%$ variation in N_2F_4 feed rate, and $\pm 1\%$ variation in the solvent + olefin feed rate.

Computer studies based on the mathematical models indicated that current operating conditions were about optimum for the temperature requirements outlined above. Three commercially available tube diameters - 0.118 inch I. D., 0.180 inch I. D. and 0.305 inch I. D. - were compared. Lower bath temperatures were required with increased tube diameters because of the decreased heat transfer surface to volume ratio. Consequently, the quantity in process was found to decrease with decreasing tube diameter. Since the

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0.118 I. D. was easily plugged during TVOPA synthesis, the 0.180 inch I. D. was selected for the tubular reactor.

A minimum TVOP conversion of 95% was chosen to minimize purification requirements. Excess N_2F_4 was required to obtain reasonable coil lengths at this conversion. Since the expected gas and liquid feed rate variations could vary the N_2F_4 concentration by $\pm 5\%$, a 10% excess appeared to be an acceptable compromise of reactor length and N_2F_4 usage. Further increases were not justified because of the high cost of N_2F_4 compared to the savings in reactor length. For example, only a 12% reduction in reactor length was calculated for 30% excess N_2F_4 .

The N_2F_4 concentration of 0.104 grams N_2F_4 /cc solvent was found to minimize reactor length for a reactor with two to five stages. About 40% reduction in total coil length was calculated for a three stage reactor compared to a two stage reactor. However, the reduction depended upon operation of the last stage at 125°C, and the effect of a 125°C bath temperature on TVOPA product quality has not been determined.

Results from both the 2D model and the bulk model were considered in selecting the operating conditions for the pilot plant reactor. The centerline temperature from the 2D model was used and compared with the bulk temperature from the bulk model. The maximum permissible first stage bath temperature obtained from the bulk model was 85°C, or about 5°C below the 90°C obtained from the 2D model. Both models indicated a runaway reaction at 12°C above their respective bath temperatures. For other stages where at least 30% of the TVOP was already converted, there was not a significant difference between the maximum permissible bath temperatures calculated from the two models. Because the limit was on the centerline temperature with the 2D model, its average (bulk) temperature was less than that for the bulk model. Consequently, the 2D model required a longer reactor tube for equivalent conversion. No attempt was made to determine the validity of either model and reaction conditions were selected conservatively. Bath

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temperatures were based on the bulk model and reactor length was chosen from the 3D model. A comparison of the exotherm and conversion predictions is shown in Fig. 2.

The interstage addition of TVOP was investigated as a technique of reducing reactor length for a three stage reactor. The N_2F_4 was added to the solvent containing some TVOP, and additional TVOP was added to the second stage to limit the excess N_2F_4 to 10%. Computer results for these conditions showed a reduction of about 10% in the total tube length at a final stage temperature of 125°C. This small decrease was not sufficient to justify the addition of a second liquid pump for the TVOP.

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APPENDIX F

Listing of FORTRAN Programs for Mathematical Models

The FORTRAN listings of the computer programs used in making the calculations discussed in this report are provided on the following pages, along with printouts of a typical problem. Preceding the FORTRAN listings is an explanation of the input data required by the program. The format used to read the input data can be obtained from the FORTRAN listings.

2D Flow Model Computer ProgramInput Data for 2D Flow Model Computer Program

<u>Fortran Symbol</u>	<u>Meaning</u>	<u>Units for 9.18" I.D. Tubing</u>	
J	No. of pairs of points describing bath temperature		
INPT	1. 2D print out showing all radial points 2. 2D print out showing only centerline points and bulk conversion		
NK	number of radial increments	10	
IBTA	number of DELX increments between points (A)	50 100	for CAPR of 0.100
FK	thermal conductivity of reacting solution	0.253	BTU/hr-ft. ² -°F
DFT	diffusion coefficient of reacting species M	0.00009	ft. ² /hr
DFN	diffusion coefficient of reacting species N	0.00015	ft. ² /hr
A	constant in reaction rate expression	0.321 exp + 18	or mol ² /gm mole
B	constant in reaction rate expression	0.1975 exp + 5	°R
TA ^o	constant to convert to absolute temperature (TAR = 460)		°R
AA	exponent for conc. CN in reaction rate expression	1	
EB	exponent for conc. CM in reaction rate expression	1	
T10	initial temperature of solution entering reactor	-20	°C
DELX	spatial increments in axial direction	0.0125 0.0100	ft. for CAPR of 0.100

<u>Fortran Symbol</u>	<u>Meaning</u>	<u>Units for 0.15" I.D. Tubing</u>	
DELTA	spatial increments in radial direction	0.00075	ft.
RR	radius of tube	0.0075	ft.
XX	maximum length in reactor (to stop comp.)	_____	ft.
HO	heat transfer coefficient (tube wall to bath)	200	BTU/hr.-ft. ² .-°F
PRC6	problem identification number	_____	
T	TVOP feed rate	100	gms. TVOP/hr.
CON	fraction TVOP converted on input	_____	%/100
CAPR	N ₂ F ₄ concentration at 6% TVOP conversion	_____	gms. N ₂ F ₄ /cc solvent
LCR	mole ratio at 6% TVOP conversion	_____	moles N ₂ F ₄ moles TVOPA
XA1	distance to first environment temperature point	_____	ft.
TS1	temperature at first environment temperature point	_____	°C
XA2	distance to second environment temperature point	_____	ft.
TS2	temperature at second environment temperature point	_____	°C
XAj	distance to j th environment temperature point	_____	ft.
TSj	temperature at j th environment temperature point	_____	°C

(a) Chosen to satisfy inequality as outlined in Rohm & Haas Company, Report No. S-54, Application of Flow Reactor Models to Process Simulation, October 9, 1964.

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FORTRAN Listing
2D Model of Flow Reactor

LINE	EXTERNAL FORMULA NUMBER	SOURCE STATEMENT	INTERNAL FORMULA NUMBER(S)	PAGE 1
C	110005-A	LIQUID PHASE FLOW REACTOR FOR WILCOUGHBY	1	
C	110005-B	LIQUID PHASE FLOW REACTOR, TWO-DIMENSIONAL MODEL, PROGRAM 11	2	
C	110005-C	DCM WILCOUGHBY, ROMP AND MASS COMPANY	3	
		TEMPERATURE T1(50), T2(50), CT1(50), CT2(50), CR1(50), CR2(50), CP1(50),	4	
		CP2(50), X1(100), T5(100), DT1(50), UR1(50), C1(50), DELT(50), G2(50),	5	
		ZC1(50), ZC2(50), CF1(50), C2(50), C3(50), C4(50), C5(50), C6(50), C7(50),	6	
		CF3(50), C8(50), C9(50), C10(50), C11(50)	7	
10		FORMAT (5E14.7)	8	
11		FORMAT (4E15)	9	
12		FORMAT (64M) TWO-DIMENSIONAL MODEL OF LIQUID PHASE FLOW REACTOR.	10	
		PROGRAM 2/1	11	
13		FORMAT (16M) PROBLEM NUMBER E14.7/1	12	
14		FORMAT (24M) EQUATIONS UNSTABLE, STOP	13	
15		FORMAT (7M) TIME = E14.7, 16M DISTANCE = E14.7, 30M ENVIRONMENT	14	
		15M TEMPERATURE = E14.7	15	
17		FORMAT (22M) TEMPERATURES FOLLOW, T1(50) = E14.7	16	
18		FORMAT (18(2E14.7))	17	
19		FORMAT (13M) C1 CONCENTRATIONS FOLLOW, CT1(50) = E14.7	18	
20		FORMAT (13M) C2 CONCENTRATIONS FOLLOW, CR2(50) = E14.7	19	
21		FORMAT (13M) C3 CONCENTRATIONS FOLLOW, CP3(50) = E14.7	20	
22		FORMAT (18M) C1(50), C2(50), C3(50), C4(50), C5(50), C6(50), C7(50),	21	
		C8(50), C9(50), C10(50), C11(50)	22	
23		FORMAT (18M) C1(50), C2(50), C3(50), C4(50), C5(50), C6(50), C7(50),	23	
		C8(50), C9(50), C10(50), C11(50)	24	
24		FORMAT (18M) DELT(50), CT1(50), CT2(50), CR1(50), CR2(50), CP1(50),	25	
		CP2(50), X1(100), T5(100), DT1(50), UR1(50), C1(50), DELT(50), G2(50),	26	
25		FORMAT (18M) DELT(50), CT1(50), CT2(50), CR1(50), CR2(50), CP1(50),	27	
		CP2(50), X1(100), T5(100), DT1(50), UR1(50), C1(50), DELT(50), G2(50),	28	
26		FORMAT (18M) DELT(50), CT1(50), CT2(50), CR1(50), CR2(50), CP1(50),	29	
		CP2(50), X1(100), T5(100), DT1(50), UR1(50), C1(50), DELT(50), G2(50),	30	
27		FORMAT (18M) J(15,50), I(15,50), K(15,50), L(15,50), M(15,50),	31	
28		FORMAT (18M) N(15,50), O(15,50), P(15,50), Q(15,50), R(15,50),	32	
29		FORMAT (18M) S(15,50), T(15,50), U(15,50), V(15,50), W(15,50),	33	
30		FORMAT (18M) X(15,50), Y(15,50), Z(15,50), A(15,50), B(15,50),	34	
		C(15,50), D(15,50), E(15,50), F(15,50), G(15,50), H(15,50),	35	
		I(15,50), J(15,50), K(15,50), L(15,50), M(15,50), N(15,50),	36	
		O(15,50), P(15,50), Q(15,50), R(15,50), S(15,50), T(15,50),	37	
		U(15,50), V(15,50), W(15,50), X(15,50), Y(15,50), Z(15,50),	38	
		A(15,50), B(15,50), C(15,50), D(15,50), E(15,50), F(15,50),	39	
		G(15,50), H(15,50), I(15,50), J(15,50), K(15,50), L(15,50),	40	
		M(15,50), N(15,50), O(15,50), P(15,50), Q(15,50), R(15,50),	41	
		S(15,50), T(15,50), U(15,50), V(15,50), W(15,50), X(15,50),	42	
		Y(15,50), Z(15,50), A(15,50), B(15,50), C(15,50), D(15,50),	43	
		E(15,50), F(15,50), G(15,50), H(15,50), I(15,50), J(15,50),	44	
		K(15,50), L(15,50), M(15,50), N(15,50), O(15,50), P(15,50),	45	
		Q(15,50), R(15,50), S(15,50), T(15,50), U(15,50), V(15,50),	46	
		W(15,50), X(15,50), Y(15,50), Z(15,50), A(15,50), B(15,50),	47	
		C(15,50), D(15,50), E(15,50), F(15,50), G(15,50), H(15,50),	48	
		I(15,50), J(15,50), K(15,50), L(15,50), M(15,50), N(15,50),	49	
		O(15,50), P(15,50), Q(15,50), R(15,50), S(15,50), T(15,50),	50	
		U(15,50), V(15,50), W(15,50), X(15,50), Y(15,50), Z(15,50),	51	
		A(15,50), B(15,50), C(15,50), D(15,50), E(15,50), F(15,50),	52	
		G(15,50), H(15,50), I(15,50), J(15,50), K(15,50), L(15,50),	53	
		M(15,50), N(15,50), O(15,50), P(15,50), Q(15,50), R(15,50),	54	
		S(15,50), T(15,50), U(15,50), V(15,50), W(15,50), X(15,50),	55	
		Y(15,50), Z(15,50), A(15,50), B(15,50), C(15,50), D(15,50),	56	
		E(15,50), F(15,50), G(15,50), H(15,50), I(15,50), J(15,50),	57	
		K(15,50), L(15,50), M(15,50), N(15,50), O(15,50), P(15,50),	58	
		Q(15,50), R(15,50), S(15,50), T(15,50), U(15,50), V(15,50),	59	
		W(15,50), X(15,50), Y(15,50), Z(15,50), A(15,50), B(15,50),	60	
		C(15,50), D(15,50), E(15,50), F(15,50), G(15,50), H(15,50),	61	
		I(15,50), J(15,50), K(15,50), L(15,50), M(15,50), N(15,50),	62	
		O(15,50), P(15,50), Q(15,50), R(15,50), S(15,50), T(15,50),	63	
		U(15,50), V(15,50), W(15,50), X(15,50), Y(15,50), Z(15,50),	64	
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		G(15,50), H(15,50), I(15,50), J(15,50), K(15,50), L(15,50),	66	
		M(15,50), N(15,50), O(15,50), P(15,50), Q(15,50), R(15,50),	67	
		S(15,50), T(15,50), U(15,50), V(15,50), W(15,50), X(15,50),	68	
		Y(15,50), Z(15,50), A(15,50), B(15,50), C(15,50), D(15,50),	69	
		E(15,50), F(15,50), G(15,50), H(15,50), I(15,50), J(15,50),	70	
		K(15,50), L(15,50), M(15,50), N(15,50), O(15,50), P(15,50),	71	
		Q(15,50), R(15,50), S(15,50), T(15,50), U(15,50), V(15,50),	72	
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		C(15,50), D(15,50), E(15,50), F(15,50), G(15,50), H(15,50),	74	
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		O(15,50), P(15,50), Q(15,50), R(15,50), S(15,50), T(15,50),	76	
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		G(15,50), H(15,50), I(15,50), J(15,50), K(15,50), L(15,50),	79	
		M(15,50), N(15,50), O(15,50), P(15,50), Q(15,50), R(15,50),	80	
		S(15,50), T(15,50), U(15,50), V(15,50), W(15,50), X(15,50),	81	
		Y(15,50), Z(15,50), A(15,50), B(15,50), C(15,50), D(15,50),	82	
		E(15,50), F(15,50), G(15,50), H(15,50), I(15,50), J(15,50),	83	
		K(15,50), L(15,50), M(15,50), N(15,50), O(15,50), P(15,50),	84	
		Q(15,50), R(15,50), S(15,50), T(15,50), U(15,50), V(15,50),	85	
		W(15,50), X(15,50), Y(15,50), Z(15,50), A(15,50), B(15,50),	86	
		C(15,50), D(15,50), E(15,50), F(15,50), G(15,50), H(15,50),	87	
		I(15,50), J(15,50), K(15,50), L(15,50), M(15,50), N(15,50),	88	
		O(15,50), P(15,50), Q(15,50), R(15,50), S(15,50), T(15,50),	89	
		U(15,50), V(15,50), W(15,50), X(15,50), Y(15,50), Z(15,50),	90	
		A(15,50), B(15,50), C(15,50), D(15,50), E(15,50), F(15,50),	91	
		G(15,50), H(15,50), I(15,50), J(15,50), K(15,50), L(15,50),	92	
		M(15,50), N(15,50), O(15,50), P(15,50), Q(15,50), R(15,50),	93	
		S(15,50), T(15,50), U(15,50), V(15,50), W(15,50), X(15,50),	94	
		Y(15,50), Z(15,50), A(15,50), B(15,50), C(15,50), D(15,50),	95	
		E(15,50), F(15,50), G(15,50), H(15,50), I(15,50), J(15,50),	96	
		K(15,50), L(15,50), M(15,50), N(15,50), O(15,50), P(15,50),	97	
		Q(15,50), R(15,50), S(15,50), T(15,50), U(15,50), V(15,50),	98	
		W(15,50), X(15,50), Y(15,50), Z(15,50), A(15,50), B(15,50),	99	
		C(15,50), D(15,50), E(15,50), F(15,50), G(15,50), H(15,50),	100	

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EXTERNAL FORMULA NUMBER		SOURCE STATEMENT		INTERNAL FORMULA NUMBERS	
59	Y2=CXAT/AL	55	.32		
60	Y3=X3/AX	56	.33		
61	Y4=X4/AX	57	.34		
62	C=V1+0.29*Y2+0.46+0.213*Y3+0.234*Y4	58	.35		
63	WRITE (6,12)	59	.36	.37	
64	WRITE (6,13) PRD9	60	.38	.39	.40
65	WRITE (6,22) C,FX,DEX,OFT,CFM	61	.41	.42	.43
66	WRITE (6,23) A,B,TAX,AA,EB	62	.44	.45	.46
67	WRITE (6,24) DELM,CTO,CNO,CPC,TIO	63	.47	.48	.49
	TIO=1.8 *TIC + 32.	64	.50		
68	WRITE (6,25) DELX,DELR,RR,RRX,MO	65	.51	.52	.53
69	WRITE (6,26) VEL,V,CON,CAPR,SMALR	66	.54	.55	.56
70	WRITE (6,27) J,IMPT,AK,IBTS	67	.57	.58	.59
71	WRITE (6,28)	68	.60	.61	
72	WRITE (6,29) (X(1),T(1),I=1,J)	69			
C	CONVERT TS TO DEGREES F	70	.62	.63	.64 .65 .66
	DO 1000 I=1,J	71	.67		
1000	TS(I)=1.8 *TS(I) + 32.	72			
C	PRELIMINARY CALCULATIONS FOLLOW	73	.68	.69	
73	DELX=DELR*VEL	74	.70		
74	IMALL=AK+1	75	.71		
75	AVEL=RR*RR*VEL	76	.72		
76	R=0.0	77	.73		
77	DO 85 I=1,IMALL	78	.74		
78	CTI(I)=CIC	79	.75		
79	CTI(I)=CNO	80	.76		
80	CTI(I)=CPC	81	.77		
81	CTI(I)=TIO	82	.78		
82	DTI(I)=DELX/(2.0*VEL*(1.-R/RR+R/RR))	83	.79		
83	R=R+DELX	84	.80		
84	CONTINUE	85	.81	.82	
85	ICNT=ICNT+1	86	.83		
86	ALP=1-FX/DEX/C	87	.84		
87	IF (ALP-CA) 89,91,91	88	.85		
88	CC=CFR	89	.86		
89	GO TO 92	90	.87		
90	CFR=CFR	91	.88		
91	PRD9=PRD9+93.54,94	92	.89		
92	CF=CFR	93	.90		
93	CONTINUE	94	.91		
94	FA=DELR/RR	95	.92		
95	FA=DELR/DELR	96	.93		
96	CON2=CON2+FA*FA*FA*FA*FA	97	.94		
97	CON2=FA/2.0	98	.95		
98	IF (CON1-CON2) 100,102,102	99	.96		
100	CON3=CON1	100	.97		
101	GO TO 103	101	.98		
102	CON3=CON2	102	.99		
103	CONTINUE	103	.100		
104	CON4=VEL*RR/24*CON3	104	.101		
105	FA=FA-CON4 100,100,100	105	.102		
106	WRITE (6,14)	106	.103		
107	GO TO 10	107	.104	.104	
108	CONTINUE	108	.105		
109	R=0.0	109	.106		
110	TT=0.0	110	.107		
111	VT=0.0	111	.108		

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PAGE 2

MAIN EXTERNAL FORMULA NUMBER	SOURCE STATEMENT	INTERNAL FORMULA NUMBER(S)
117 J=1		111 .109
118 X=TS(2)-TS(1)/(X(2)-X(1))		112 .110
119 U(1)=VEL*(1.0-DELTA/RA+DELTA/RA/15.0)+DELTA/2.0*DELTA		113 .111
115 A=DELTA		114 .112
116 DO 118 I=2,N		115 .113
117 U(1)=4.0*VEL*(1.0-R/RA+R/RA)+A*DELTA		116 .114
118 X=DELTA		117 .115 .116
119 U(1)=2.0*VEL*(1.0-(RA-DELTA/4.0)+2.0/RA/RA)+(RA-DELTA/4.0)* DELTA		118 .117
120 T(1)=ELL-TS(1)		119 .118
121 CA=2.0*VEL/DELTA		120 .119
122 CA1=4.0/DELTA/DELTA/CA		121 .120
123 CA1=XPRX/CA1		122 .121
124 CA2=1.-CA1		123 .122
125 CA3=DELTA/CA		124 .123
126 CC1=CPA*CA1		125 .124
127 CC2=1.-CC1		126 .125
128 CC3=1.0/CA		127 .126
129 CC1=CPA*CA1		128 .127
130 CC2=1.-CC1		129 .128
131 CC3=1.0/3.0/CA		130 .129
132 A=DELTA		131 .130
133 DO 149 K=2,N		132 .131
134 CS=2.0*VEL/DELTA*(1.-R/RA+R/RA)		133 .132
135 CS1(1)=VEL/DELTA+CS/DELTA/7CS		134 .133
136 CS1(K)=ALPHA*CS1		135 .134
137 CS1(K)=CPA*CS1		136 .135
138 CS1(K)=CPA*CS1		137 .136
139 CS22=1.0/DELTA/DELTA-0.5/DELTA/CS		138 .137
140 CS2(K)=ALPHA*CS22		139 .138
141 CS2(K)=CPA*CS22		140 .139
142 CS2(K)=CPA*CS22		141 .140
143 CS3(K)=CS-2.0*ALPHA/DELTA/DELTA/CS		142 .141
144 CS3(K)=CS-2.0*CPA/DELTA/DELTA/CS		143 .142
145 CS3(K)=CS-2.0*CPA/DELTA/DELTA/CS		144 .143
146 CS4(K)=DELTA/CS		145 .144
147 CS4(K)=DELTA/CS		146 .145
148 CS4(K)=DELTA/CS		147 .146
149 A=DELTA		148 .147
150 INLET TO MAIN CALCULATION LOOP		149 .148
151 CONTINUE		150 .149
152 IF(X(1)-X) 157,155,155		151 .150
153 J=J+1		152 .151
154 X=TS(1)-TS(2)/(X(1)-X(2))		153 .152
155 GO TO 157		154 .153
156 TE=TS(1)-TS(2)/(X(1)-X)		155 .154
157 DO 159 K=2,N		156 .155
158 G1(K)=A*EXP(1-2/(T1(K)+T2(K))*C1(K)+2A*CT1(K)+2A		157 .156
159 DELTA(K)=CPA*G1(K)		158 .157
160 G2(K)=C1(K)*DELTA(K)		159 .158
161 IF(G2(K)) 165,165,165		160 .159
162 G2(K)=0.0		161 .160
163 DELTA(K)=G2(K)		162 .161
164 G1(K)=DELTA(K)/CT1(K)		163 .162
165 CONTINUE		164 .163
166 C1(1)=C1(1)+C2(1)+C3(1)+C4(1)		165 .164

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MAIN		07/07/65	
EXTERNAL FORMULA NUMBER	SOURCE STATEMENT	INTERNAL FORMULA NUMBER(S)	
511	IF(CN2(1)) 517,515,515	167	.165
512	0(1)=-1CC1+CN1(2)+CC2+CN1(1)/CC3	168	.167
513	DEL C(1)=Q(1)+DT(1)	169	.168
514	CN2(1)=0.0	170	.169
515	CT2(1)=CE1+CT1(2)+CE2+CT1(1)+CE3+Q(1)	171	.170
516	IF(CT2(1)) 517,521,521	172	.171
517	Q(1)=-1CE1+CT1(2)+CE2+CT1(1)/CE3	173	.172
518	DEL C(1)=Q(1)+DT(1)	174	.173
519	CT2(1)=0.0	175	.174
520	CN2(1)=CC1+CN1(2)+CC2+CN1(1)+CC3+Q(1)	176	.175
521	CP2(1)=CP1(1)-DEL C(1)/3.0	177	.176
522	T2(1)=C11+T1(2)+C22+T2(1)-C33+Q(1)	178	.177
530	DO 544 K=2,NK	179	.178
531	CN2(K)=CD1(K)+CN1(K+1)+CD2(K)+CN1(K-1)+CD3(K)+CN1(K)+CD4(K)+Q(K)	180	.179
532	IF(CN2(K)) 533,535,535	181	.180
533	C(K)=-1CD1(K)+CN1(K+1)+CD2(K)+CN1(K-1)+CD3(K)+CN1(K)/CD4(K)	182	.181
534	DEL C(K)=Q(K)+DT(K)	183	.182
535	CN2(K)=0.0	184	.183
536	CT2(K)=CF1(K)+CT1(K+1)+CF2(K)+CT1(K-1)+CF3(K)+CT1(K)+CF4(K)+Q(K)	185	.184
537	IF(CT2(K)) 538,542,542	186	.185
538	Q(K)=-1CF1(K)+CT1(K+1)+CF2(K)+CT1(K-1)+CF3(K)+CT1(K)/CF4(K)	187	.186
539	DEL C(K)=Q(K)+DT(K)	188	.187
540	CT2(K)=0.0	189	.188
541	CN2(K)=CD1(K)+CN1(K+1)+CD2(K)+CN1(K-1)+CD3(K)+CN1(K)+CD4(K)+Q(K)	190	.189
542	CP2(K)=CP1(K)-DEL C(K)/3.0	191	.190
543	T2(K)=C11(K)+T1(K+1)+C22(K)+T1(K-1)+C33(K)+T1(K)-C44(K)+Q(K)	192	.191
544	CONTINUE	193	.192 .193
545	T2(1)=T2(1)+TE+FRAC/DELA*(T1(1)=1)-T1(1)=1	194	.194
546	CN2(1)=CN2(1)+CN2(1)	195	.195
547	CP2(1)=CP2(1)+CP2(1)	196	.196
548	CT2(1)=CT2(1)+CT2(1)	197	.197
550	IF(1CN7-1B7A) 604,555,604	198	.198
555	BACT=0.0	199	.199
556	BACB=0.0	200	.200
557	BACT=0.0	201	.201
558	BACP=0.0	202	.202
559	DO 564 I=2,NK	203	.203
560	BACT+BACT+Q(1)=(T1(1)-T1(1)=1)	204	.204
562	BACB+BACB+Q(1)=(CN1(1)-CN1(1)=1)	205	.205
563	BACT+BACT+Q(1)=(CT1(1)-CT1(1)=1)	206	.206
564	BACP+BACP+Q(1)=(CP1(1)-CP1(1)=1)	207	.207 .209
565	BACT+Q(1)=(T1(1)-T1(1)=1)+BACT/ARVEL+T1(1)=1	208	.208
566	BACB+Q(1)=(CN1(1)-CN1(1)=1)+BACB/ARVEL+CN1(1)=1	209	.209
567	BACT+Q(1)=(CT1(1)-CT1(1)=1)+BACT/ARVEL+CT1(1)=1	210	.210
568	BACP+Q(1)=(CP1(1)-CP1(1)=1)+BACP/ARVEL+CP1(1)=1	211	.211
569	GO TO 1569,1601,1601	212	.212

COMPILER EXPECTS A COMPA BETWEEN BRANCH SYMBOL AND BRANCH LIST.

SOURCE ERROR 232, LEVEL 1. MARKING ONLY.

569 WRITE (6,16) TT,X,TE	213	.214	.215	.216
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PAID EXTERNAL FORMULA NUMBER	SOURCE STATEMENT	07/27/65 INTERNAL FORMULA NUMBER(S)	PAGE 5
513	WRITE (6,177) BLK7	214	.217 .218 .219
521	WRITE (6,18) (T1(1),1-1,IMALL)	215	.220 .221 .222 .223 .224
522	WRITE (6,19) BCC7	216	.225 .226 .227
523	WRITE (6,18) (CT1(1),1-1,IMALL)	217	.228 .229 .230 .231 .232
524	WRITE (6,20) BCCN	218	.233 .234 .235
525	WRITE (6,18) (CN1(1),1-1,IMALL)	219	.236 .237 .238 .239 .240
526	WRITE (6,21) BACP	220	.241 .242 .243
527	WRITE (6,18) (CP1(1),1-1,IMALL)	221	.244 .245 .246 .247 .248
600	IF (X-XPR) 602,602,601	222	.249
601	GO TO 30	223	.250
602	ICNT=1	224	.251
603	GO TO 605	225	.252
604	ICNT=ICNT+1	226	.253
605	X=X+DELX	227	.254
606	TI=TI+DELT	228	.255
607	DO 611 1-1,IMALL	229	.256
608	T1(1)=T2(1)	230	.257
609	CN1(1)=CN2(1)	231	.258
610	CT1(1)=CT2(1)	232	.259
611	CP1(1)=CP2(1)	233	.260 .261
612	GO TO 3-6	234	.262
1001	IF (IFLAG) 1003,1003,1002	235	.263
1002	WRITE (6,1005)	236	.264 .265
	IFLAG=-1	237	.266
1003	RATIO=SCCP/ISCP*50CT	238	.267
	P=ITE-32.3/1.8	239	.268
	BLKTR=BLKT-32.3/1.8	240	.269
	TONER=TT(1)-32.3/1.8	241	.270
	WRITE (6,1004) TT,X,TE,BLKTR,TONER,RATIO	242	.271 .272 .273
	GO TO 600	243	.274
1004	FORMAT(6E18.7)	244	
1005	FORMAT(81X#CENTER/42X11#ENVIRONPENT25X4#LINE/10X4#TIME12X#DISTAN	245	
	1CESX11#TEMPERATURE10X5#TOLK10X11#TEMPERATURE8X10#CONVERSION1	246	
	END	247	.275

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Sample Problem
2D Model of Flow Reactor

Summary of Output Data Not Included with Input Data

Time	period in reactor, hrs.
Distance	position in reactor, ft.
Environment temperature	bath temperature, °C
T_{bulk}	averaged reactant temperature, °C

Centerline temperature, °C

Conversion = moles TVOPA/ moles TVOP input

CTO	moles TVOP/ liter solution (input)
CNO	moles N_2F_4 / liter solution (input)
CPO	moles TVOPA/ liter solution (input)
VEL	reactant velocity, ft/ hr

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TWO-DIMENSIONAL MODEL OF LIQUID PHASE FLOW REACTOR. PROGRAM 2

PROBLEM NUMBER U.1000000E 01
 C= 0.2429242E-00 FK= 0.3300000E-01 DEN= 0.9131815E 02 DF1= 0.9000000E-04 DFN= 0.1800000E-03
 A= 0.3210000E 13 B= 0.1972000E 05 TAR= 0.4600000E 03 XX= 0.1000000E 01 B3= 0.1000000E 01
 DELX= 0.4183177E 05 CYC= 0.4485359E-03 CNO= 0.1547060E-02 CPO= 0. 110= 0.
 DELT= 0.1250000E-01 DELTA= 0.7500000E-03 RR= 0.7500000E-02 EXE= 0.1550000E 03 MO= 0.2000000E 03
 VEL= 0.3535105E 03 Y= 0.1410000E 03 CCR= 0. CAPR= 0.2040000E-00 LCR= 0.3300000E 01
 J= 6 INPT 2 SC= 10 ISTA= 80
 XX VALUES TS VALUES
 J. 0.8500000E 02
 0.6220000E 02 0.8500000E 02
 0.6230000E 02 0.
 0.6420000E 02 0.
 0.6430000E 02 0.1150000E 03
 0.1550000E 01 0.1150000E 03

TIME	DISTANCE	ENVIRONMENT TEMPERATURE	TBULK	CENTER LINE TEMPERATURE	CONVERSION
0.	0.	0.8500000E 02	0.4252667E-00	0.	0.
0.2828770E-02	0.9999993E 00	0.8500000E 02	0.2894344E 02	0.1780945E 01	0.5565841E-03
0.5657577E-02	0.1999997E 01	0.8500000E 02	0.4292871E 02	0.1407043E 02	0.2125490E-02
0.8486303E-02	0.2999993E 01	0.8500000E 02	0.5295094E 02	0.2879588E 02	0.4607519E-02
0.1131504E-01	0.3999997E 01	0.8500000E 02	0.6058370E 02	0.4174382E 02	0.6055105E-02
0.1414383E-01	0.4999996E 01	0.8500000E 02	0.6645922E 02	0.5197901E 02	0.1257322E-01
0.1697259E-01	0.5999995E 01	0.8500000E 02	0.7111718E 02	0.5984374E 02	0.1826785E-01
0.1980135E-01	0.6999994E 01	0.8500000E 02	0.7477933E 02	0.6613496E 02	0.2519173E-01
0.2263011E-01	0.7999993E 01	0.8500000E 02	0.7771015E 02	0.7115808E 02	0.3335144E-01
0.2545837E-01	0.8999992E 01	0.8500000E 02	0.8007984E 02	0.7521923E 02	0.4270018E-01
0.2828764E-01	0.9999991E 01	0.8500000E 02	0.8201559E 02	0.7854322E 02	0.5314961E-01
0.3111640E-01	0.1099993E 02	0.8500000E 02	0.8361045E 02	0.8129313E 02	0.6458221E-01
0.3394516E-01	0.1199997E 02	0.8500000E 02	0.8493276E 02	0.8358689E 02	0.7686221E-01
0.3677392E-01	0.1299995E 02	0.8500000E 02	0.8603295E 02	0.8550982E 02	0.8984449E-01
0.3960268E-01	0.1399996E 02	0.8500000E 02	0.8694833E 02	0.8712419E 02	0.1033812E-00
0.4243145E-01	0.1499995E 02	0.8500000E 02	0.8770769E 02	0.8847593E 02	0.1173263E-00
0.4526021E-01	0.1599995E 02	0.8500000E 02	0.8833214E 02	0.8950003E 02	0.1315420E-00
0.4808897E-01	0.1699993E 02	0.8500000E 02	0.8833901E 02	0.9052358E 02	0.1458966E-00
0.5091773E-01	0.1799992E 02	0.8500000E 02	0.8924237E 02	0.9126896E 02	0.1602717E-00
0.5374649E-01	0.1899990E 02	0.8500000E 02	0.8955418E 02	0.9185535E 02	0.1745618E-00
0.5657526E-01	0.1999989E 02	0.8500000E 02	0.8976507E 02	0.9230003E 02	0.1886759E-00
0.5940402E-01	0.2099987E 02	0.8500000E 02	0.8994476E 02	0.9261912E 02	0.2025381E-00
0.6223278E-01	0.2199986E 02	0.8500000E 02	0.9004235E 02	0.9282798E 02	0.2160873E-00
0.6506154E-01	0.2299984E 02	0.8500000E 02	0.9008544E 02	0.9294136E 02	0.2292771E-00
0.6789030E-01	0.2399983E 02	0.8500000E 02	0.9008513E 02	0.9297333E 02	0.2420743E-00
0.7071906E-01	0.2499981E 02	0.8500000E 02	0.9004604E 02	0.9293723E 02	0.2544578E-00
0.7354783E-01	0.2599979E 02	0.8500000E 02	0.8997620E 02	0.9284544E 02	0.2664156E-00
0.7637659E-01	0.2699978E 02	0.8500000E 02	0.8988203E 02	0.9270930E 02	0.2779484E-00
0.7920535E-01	0.2799976E 02	0.8500000E 02	0.8976925E 02	0.9253895E 02	0.2890577E-00
0.8203411E-01	0.2899975E 02	0.8500000E 02	0.8964259E 02	0.9234331E 02	0.2997541E-00
0.8486287E-01	0.2999973E 02	0.8500000E 02	0.8950726E 02	0.9213007E 02	0.3100512E-00
0.8769164E-01	0.3099972E 02	0.8500000E 02	0.8936602E 02	0.9190568E 02	0.3199516E-00
0.9052040E-01	0.3199970E 02	0.8500000E 02	0.8922215E 02	0.9167551E 02	0.3295134E-00
0.9334916E-01	0.3299969E 02	0.8500000E 02	0.8907806E 02	0.9144354E 02	0.3387748E-00
0.9617792E-01	0.3399967E 02	0.8500000E 02	0.8893567E 02	0.9121409E 02	0.3475872E-00
0.9900668E-01	0.3499966E 02	0.8500000E 02	0.8879641E 02	0.9098883E 02	0.3561510E-00
0.1018354E-00	0.3599964E 02	0.8500000E 02	0.8866135E 02	0.9077001E 02	0.3644222E-00
0.1046442E-00	0.3699963E 02	0.8500000E 02	0.8853122E 02	0.9055848E 02	0.3724185E-00
0.1074930E-00	0.3799961E 02	0.8500000E 02	0.8840551E 02	0.9035661E 02	0.3801563E-00
0.1103417E-00	0.3899960E 02	0.8500000E 02	0.8828747E 02	0.9016343E 02	0.3876306E-00
0.1131905E-00	0.3999958E 02	0.8500000E 02	0.8817422E 02	0.8997967E 02	0.3949156E-00
0.1160393E-00	0.4099957E 02	0.8500000E 02	0.8806674E 02	0.8980534E 02	0.4019644E-00
0.1188880E-00	0.4199955E 02	0.8500000E 02	0.8796489E 02	0.8964227E 02	0.4089093E-00

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0.121634E-00	0.4299954E 02	0.8500000E 02	0.8786851E 02	0.8948419E 02	0.4156625E-00
0.1244655E-00	0.4399952E 02	0.8500000E 02	0.8777735E 02	0.8933672E 02	0.4219330E-00
0.1272942E-00	0.4499950E 02	0.8500000E 02	0.8769119E 02	0.8919745E 02	0.4282313E-00
0.1301229E-00	0.4599949E 02	0.8500000E 02	0.8760971E 02	0.8906592E 02	0.4343665E-00
0.1329516E-00	0.4699947E 02	0.8500000E 02	0.8753265E 02	0.8894168E 02	0.4403455E-00
0.1357803E-00	0.4799946E 02	0.8500000E 02	0.8745975E 02	0.8882427E 02	0.4461772E-00
0.1386090E-00	0.4899944E 02	0.8500000E 02	0.8739067E 02	0.8871322E 02	0.4518584E-00
0.1414377E-00	0.4999943E 02	0.8500000E 02	0.8732521E 02	0.8860811E 02	0.4574254E-00
0.1442664E-00	0.5099941E 02	0.8500000E 02	0.8726311E 02	0.8850852E 02	0.4628543E-00
0.1470951E-00	0.5199940E 02	0.8500000E 02	0.8720433E 02	0.8841406E 02	0.4681603E-00
0.1499237E-00	0.5299938E 02	0.8500000E 02	0.8714855E 02	0.8832435E 02	0.4733505E-00
0.1527524E-00	0.5399937E 02	0.8500000E 02	0.8709466E 02	0.8823903E 02	0.4784267E-00
0.1555811E-00	0.5499935E 02	0.8500000E 02	0.8704378E 02	0.8815792E 02	0.4833957E-00
0.1584098E-00	0.5599934E 02	0.8500000E 02	0.8699523E 02	0.8808057E 02	0.4882609E-00
0.1612385E-00	0.5699932E 02	0.8500000E 02	0.8694855E 02	0.8800747E 02	0.4930266E-00
0.1640672E-00	0.5799931E 02	0.8500000E 02	0.8690449E 02	0.8793828E 02	0.4976964E-00
0.1668959E-00	0.5899929E 02	0.8500000E 02	0.8686201E 02	0.8787385E 02	0.5022737E-00
0.1697246E-00	0.5999928E 02	0.8500000E 02	0.8682130E 02	0.8781430E 02	0.5067620E-00
0.1725532E-00	0.6099926E 02	0.8500000E 02	0.8678224E 02	0.8775943E 02	0.5111643E-00
0.1753819E-00	0.6199924E 02	0.8500000E 02	0.8674472E 02	0.8770917E 02	0.5154835E-00
0.1782106E-00	0.6299923E 02	0.	0.8670825E 02	0.8766343E 02	0.5197943E-00
0.1810393E-00	0.6399921E 02	0.	0.8667344E 02	0.8762178E 02	0.5240950E-00
0.1838680E-00	0.6499920E 02	0.1150000E 03	0.8663911E 02	0.8758329E 02	0.5282957E-00
0.1866967E-00	0.6599918E 02	0.1150000E 03	0.8660571E 02	0.8754794E 02	0.5324964E-00
0.1895254E-00	0.6699917E 02	0.1150000E 03	0.8657344E 02	0.8751567E 02	0.5366971E-00
0.1923541E-00	0.6799915E 02	0.1150000E 03	0.8654221E 02	0.8748644E 02	0.5408978E-00
0.1951827E-00	0.6899914E 02	0.1150000E 03	0.8651201E 02	0.8745921E 02	0.5450985E-00
0.1980114E-00	0.6999912E 02	0.1150000E 03	0.8648284E 02	0.8743398E 02	0.5492992E-00
0.2008401E-00	0.7099911E 02	0.1150000E 03	0.8645469E 02	0.8741075E 02	0.5535000E-00
0.2036688E-00	0.7199909E 02	0.1150000E 03	0.8642756E 02	0.8738952E 02	0.5577007E-00
0.2064975E-00	0.7299908E 02	0.1150000E 03	0.8640143E 02	0.8737029E 02	0.5619014E-00
0.2093262E-00	0.7399906E 02	0.1150000E 03	0.8637630E 02	0.8735306E 02	0.5661021E-00
0.2121549E-00	0.7499905E 02	0.1150000E 03	0.8635217E 02	0.8733783E 02	0.5703028E-00
0.2149836E-00	0.7599903E 02	0.1150000E 03	0.8632904E 02	0.8732360E 02	0.5745035E-00
0.2178123E-00	0.7699902E 02	0.1150000E 03	0.8630691E 02	0.8731137E 02	0.5787042E-00
0.2206410E-00	0.7799900E 02	0.1150000E 03	0.8628578E 02	0.8730114E 02	0.5829049E-00
0.2234697E-00	0.7899899E 02	0.1150000E 03	0.8626565E 02	0.8729291E 02	0.5871056E-00
0.2262984E-00	0.7999897E 02	0.1150000E 03	0.8624652E 02	0.8728568E 02	0.5913063E-00
0.2291271E-00	0.8099895E 02	0.1150000E 03	0.8622839E 02	0.8727945E 02	0.5955070E-00
0.2319558E-00	0.8199894E 02	0.1150000E 03	0.8621126E 02	0.8727422E 02	0.5997077E-00
0.2347845E-00	0.8299892E 02	0.1150000E 03	0.8619513E 02	0.8726999E 02	0.6039084E-00
0.2376132E-00	0.8399891E 02	0.1150000E 03	0.8617900E 02	0.8726676E 02	0.6081091E-00
0.2404419E-00	0.8499889E 02	0.1150000E 03	0.8616387E 02	0.8726453E 02	0.6123098E-00
0.2432706E-00	0.8599888E 02	0.1150000E 03	0.8614974E 02	0.8726330E 02	0.6165105E-00
0.2460993E-00	0.8699886E 02	0.1150000E 02	0.8613661E 02	0.8726307E 02	0.6207112E-00
0.2489280E-00	0.8799885E 02	0.1150000E 03	0.8612448E 02	0.8726384E 02	0.6249119E-00
0.2517567E-00	0.8899883E 02	0.1150000E 02	0.8611335E 02	0.8726561E 02	0.6291126E-00
0.2545854E-00	0.8999882E 02	0.1150000E 03	0.8610322E 02	0.8726838E 02	0.6333133E-00
0.2574141E-00	0.9099880E 02	0.1150000E 03	0.8609409E 02	0.8727215E 02	0.6375140E-00
0.2602428E-00	0.9199879E 02	0.1150000E 03	0.8608596E 02	0.8727692E 02	0.6417147E-00
0.2630715E-00	0.9299877E 02	0.1150000E 02	0.8607883E 02	0.8728269E 02	0.6459154E-00
0.2659002E-00	0.9399876E 02	0.1150000E 03	0.8607270E 02	0.8728946E 02	0.6501161E-00
0.2687289E-00	0.9499874E 02	0.1150000E 03	0.8606757E 02	0.8729723E 02	0.6543168E-00
0.2715576E-00	0.9599873E 02	0.1150000E 03	0.8606344E 02	0.8730600E 02	0.6585175E-00
0.2743863E-00	0.9699871E 02	0.1150000E 03	0.8606031E 02	0.8731577E 02	0.6627182E-00
0.2772150E-00	0.9799870E 02	0.1150000E 03	0.8605818E 02	0.8732654E 02	0.6669189E-00
0.2800437E-00	0.9899868E 02	0.1150000E 03	0.8605605E 02	0.8733831E 02	0.6711196E-00

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0.2828763f-00	0.9999866E 02	0.1150000E 01	0.1164253E 01	0.1173022E 03	0.9075658E 00
0.2856989E-00	0.1009933E 03	0.1150000E 03	0.1173364E 03	0.1171546E 03	0.9101836E 00
0.2885274E-00	0.1019986E 03	0.1150000E 03	0.1162944E 01	0.1170223E 03	0.9125808E 00
0.2913559E-00	0.1029936E 03	0.1150000E 03	0.1161876E 03	0.1169032E 03	0.9150666E 00
0.2941845E-00	0.1039986E 03	0.1150000E 03	0.1161147E 03	0.1167957E 03	0.9173491E 00
0.2970130E-00	0.1049986E 03	0.1150000E 03	0.1160066E 03	0.1166993E 03	0.9195357E 00
0.2998416E-00	0.1059986E 03	0.1150000E 03	0.1159076E 03	0.1165097E 03	0.9216327E 00
0.3026701E-00	0.1069986E 03	0.1150000E 03	0.1157974E 03	0.1163297E 03	0.9236460E 00
0.3054986E-00	0.1079986E 03	0.1150000E 03	0.1156912E 03	0.1161446E 03	0.9255810E 00
0.3083272E-00	0.1089986E 03	0.1150000E 03	0.1155764E 03	0.1159343E 03	0.9274422E 00
0.3111557E-00	0.1099986E 03	0.1150000E 03	0.1154616E 03	0.1157233E 03	0.9292341E 00
0.3139842E-00	0.1109986E 03	0.1150000E 03	0.1153468E 03	0.1155160E 03	0.9309607E 00
0.3168128E-00	0.1119986E 03	0.1150000E 03	0.1152319E 03	0.1153070E 03	0.9326255E 00
0.3196413E-00	0.1129986E 03	0.1150000E 03	0.1151171E 03	0.1151005E 03	0.9342730E 00
0.3224699E-00	0.1139986E 03	0.1150000E 03	0.1150022E 03	0.1148931E 03	0.9357831E 00
0.3252984E-00	0.1149986E 03	0.1150000E 03	0.1148875E 03	0.1146856E 03	0.9372818E 00
0.3281269E-00	0.1159986E 03	0.1150000E 03	0.1147727E 03	0.1144781E 03	0.9387356E 00
0.3309555E-00	0.1169986E 03	0.1150000E 03	0.1146579E 03	0.1142706E 03	0.9401894E 00
0.3337840E-00	0.1179986E 03	0.1150000E 03	0.1145431E 03	0.1140631E 03	0.9416432E 00
0.3366126E-00	0.1189986E 03	0.1150000E 03	0.1144283E 03	0.1138556E 03	0.9430970E 00
0.3394411E-00	0.1199986E 03	0.1150000E 03	0.1143135E 03	0.1136481E 03	0.9445508E 00
0.3422697E-00	0.1209986E 03	0.1150000E 03	0.1141987E 03	0.1134406E 03	0.9459526E 00
0.3450982E-00	0.1219986E 03	0.1150000E 03	0.1140839E 03	0.1132331E 03	0.9473544E 00
0.3479268E-00	0.1229986E 03	0.1150000E 03	0.1139691E 03	0.1130256E 03	0.9487562E 00
0.3507553E-00	0.1239986E 03	0.1150000E 03	0.1138543E 03	0.1128181E 03	0.9501580E 00
0.3535839E-00	0.1249986E 03	0.1150000E 03	0.1137395E 03	0.1126106E 03	0.9515598E 00
0.3564124E-00	0.1259986E 03	0.1150000E 03	0.1136247E 03	0.1124031E 03	0.9529616E 00
0.3592410E-00	0.1269986E 03	0.1150000E 03	0.1135099E 03	0.1121956E 03	0.9543634E 00
0.3620695E-00	0.1279986E 03	0.1150000E 03	0.1133951E 03	0.1119881E 03	0.9557652E 00
0.3648981E-00	0.1289986E 03	0.1150000E 03	0.1132803E 03	0.1117806E 03	0.9571670E 00
0.3677266E-00	0.1299986E 03	0.1150000E 03	0.1131655E 03	0.1115731E 03	0.9585688E 00
0.3705552E-00	0.1309986E 03	0.1150000E 03	0.1130507E 03	0.1113656E 03	0.9599706E 00
0.3733837E-00	0.1319986E 03	0.1150000E 03	0.1129359E 03	0.1111581E 03	0.9613724E 00
0.3762123E-00	0.1329986E 03	0.1150000E 03	0.1128211E 03	0.1109506E 03	0.9627742E 00
0.3790408E-00	0.1339986E 03	0.1150000E 03	0.1127063E 03	0.1107431E 03	0.9641760E 00
0.3818694E-00	0.1349986E 03	0.1150000E 03	0.1125915E 03	0.1105356E 03	0.9655778E 00
0.3846979E-00	0.1359986E 03	0.1150000E 03	0.1124767E 03	0.1103281E 03	0.9669796E 00
0.3875265E-00	0.1369986E 03	0.1150000E 03	0.1123619E 03	0.1101206E 03	0.9683814E 00
0.3903550E-00	0.1379986E 03	0.1150000E 03	0.1122471E 03	0.1099131E 03	0.9697832E 00
0.3931836E-00	0.1389986E 03	0.1150000E 03	0.1121323E 03	0.1097056E 03	0.9711850E 00
0.3960121E-00	0.1399986E 03	0.1150000E 03	0.1120175E 03	0.1094981E 03	0.9725868E 00
0.3988407E-00	0.1409986E 03	0.1150000E 03	0.1119027E 03	0.1092906E 03	0.9739886E 00
0.4016692E-00	0.1419986E 03	0.1150000E 03	0.1117879E 03	0.1090831E 03	0.9753904E 00
0.4044978E-00	0.1429986E 03	0.1150000E 03	0.1116731E 03	0.1088756E 03	0.9767922E 00
0.4073263E-00	0.1439986E 03	0.1150000E 03	0.1115583E 03	0.1086681E 03	0.9781940E 00
0.4101549E-00	0.1449986E 03	0.1150000E 03	0.1114435E 03	0.1084606E 03	0.9795958E 00
0.4129834E-00	0.1459986E 03	0.1150000E 03	0.1113287E 03	0.1082531E 03	0.9809976E 00
0.4158120E-00	0.1469986E 03	0.1150000E 03	0.1112139E 03	0.1080456E 03	0.9823994E 00
0.4186405E-00	0.1479986E 03	0.1150000E 03	0.1110991E 03	0.1078381E 03	0.9838012E 00
0.4214691E-00	0.1489986E 03	0.1150000E 03	0.1109843E 03	0.1076306E 03	0.9852030E 00
0.4242976E-00	0.1499986E 03	0.1150000E 03	0.1108695E 03	0.1074231E 03	0.9866048E 00
0.4271262E-00	0.1509986E 03	0.1150000E 03	0.1107547E 03	0.1072156E 03	0.9880066E 00
0.4299547E-00	0.1519986E 03	0.1150000E 03	0.1106399E 03	0.1070081E 03	0.9894084E 00
0.4327833E-00	0.1529986E 03	0.1150000E 03	0.1105251E 03	0.1068006E 03	0.9908102E 00
0.4356118E-00	0.1539986E 03	0.1150000E 03	0.1104103E 03	0.1065931E 03	0.9922120E 00
0.4384404E-00	0.1549986E 03	0.1150000E 03	0.1102955E 03	0.1063856E 03	0.9936138E 00
0.4412689E-00	0.1559986E 03	0.1150000E 03	0.1101807E 03	0.1061781E 03	0.9950156E 00

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Bulk Flow Model Computer ProgramInput Data for Bulk Flow Model Computer Program

<u>Fortran Symbol</u>	<u>Meaning</u>	<u>Units for 0.16" I.D. Tubing</u>
XMX	Maximum length in reactor	_____ ft.
DELT	Time increment for calculations	_____ hrs.
HI	Inside tube heat transfer coefficient	8.85 BTU/hr-ft ² -°F
HO	Outside tube heat transfer coefficient	220 BTU/hr-ft ² -°F
CW	Thermal conductance through tube wall	3400 BTU/hr-ft ² -°F
A	Pre-exponential factor	3.21×10^{17} 1/hr
B	(E/R) constant in rate expression	1.11×10^5 °C
TAR	Constant to convert to absolute temperature	273 °C to °K
AA	Exponent in rate expression	1.0
BB	Exponent in rate expression	1.0
R	Radius of tube	7.5×10^{-3} ft.
FLCR	Mole ratio N_2F_4 /TVOP at 0% conversion	_____ gm moles N_2F_4 /gm moles TVOP
CAPR	Gms. N_2F_4 /cc solvent at 0% conversion	_____ gms N_2F_4 /cc solvent
Y	TVOP feed rate	_____ gms/hr
TIO	Initial temperature of fluid entering reactor	10°C
PROB	Problem identification number	_____
FC	Initial fraction reacted (0 if problem starts with 1st stage)	_____
$j^{(a)}$	Number of points to describe environment temperature	_____
IBTA ^(b)	Printout frequency	_____
XX(1)	Distance to 1st environment temperature point	0 ft.
TS(1)	Temperature of 1st environment temperature point	_____ °C
XX(2)	Distance to 2nd environment temperature point	_____ ft.
TS(2)	Temperature at 2nd environment temperature point	_____ °C
XX(j)	Distance to j^{th} environment temperature point	_____ ft.
TS(j)	Temperature at j^{th} environment temperature point	_____ °C

(a) [XX(1), TS(1)], [XX(2), TS(2)], etc. are considered pairs and j instructs the computer about the number of pairs to be read.

(b) If for example IBTA is 5, the calculator is instructed to print every fifth calculation it makes.

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FORTTRAN Listing Bulk Model of Flow Reactor

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00000 * PROGRAM NO. 42
00000 C BULK ANALYSIS II - LIQUID PHASE FLOW REACTOR
00000 C DON WILLOUGHBY, HORN AND HAAS COMPANY 3/15/65
00001 DIMENSION TS(500),XX(500)
00001 10 FORMAT(5E14.7)
00007 11 FORMAT(2I5)
00014 12 FORMAT(20X,PROBLEM NUMBER ,E14.7/)
00034 13 FORMAT(25X,EQUATIONS UNSTABLE, STOP)
00035 14 FORMAT(0M ,XX=E14.7,0M ,DELT=E14.7,0M ,NI=C14.7, 0M
00035 1 NO=E14.7,0M ,UN=E14.7)
00132 15 FORMAT(0M ,A=E14.7,0M ,B=E14.7,0M ,TAR=E14.7,0M ,AA=
00132 1E14.7,0M ,BB=E14.7)
00205 16 FORMAT(0M ,R=E14.7,0M ,FLCR=E14.7,0M ,CAPR=E14.7,0M ,Y=
00205 1E14.7,0M ,T10=E14.7)
00268 17 FORMAT(0M ,J=15,12M ,IOTA=15)
00302 18 FORMAT(20M ,XX ,TS ,)
00325 19 FORMAT(2E14.7)
00333 20 FORMAT(0M ,CT0=E14.7,0M ,CNO=E14.7,0M ,SED=E14.7,0M ,DELM=
00333 1E14.7,0M ,C=E14.7)
00406 21 FORMAT(9E13.3)
00414 22 FORMAT(10X,TIME HOURSXXMM-FFETX12BULK TEMP.-C1M F NOT COUNTED
00414 1X,CT113X,CT113X,CP17X10MALL TEMP.7X2NTS)
00502 30 READ 10, ,XX,DELT,NI,NO,UN,A,B,TAR,AA,BB,R,FLCR,CAPR,Y,T10,
00502 1PROD,FC
00547 31 READ 11,J,IOTA
00556 32 READ10,(XX(I),TS(I),I=1,J)
00602 33 PRINT 12,PROD
00607 34 PRINT 14,XX,DELT,NI,NO,UN
00624 35 PRINT 15, A,B,TAR,AA,BB
00641 36 PRINT 16,R,FLCR,CAPR,Y,T10
00656 37 PRINT 17,J,IOTA
00665 38 PRINT 18
00670 39 PRINT 19,(XX(I),TS(I),I=1,J)
00714 40 CNO=CAPR/(104.0+CAPR*(83.0+176.0/FLCR))
00734 41 CT0=CNO/FLCR
00744 42 CP0=0.0
00750 43 V1=83.1+CNO
00756 44 V2=176.0+CT0
00764 45 V3=1.0-V1-V2
00774 46 DEN=(104.0+CNO*170.0+CT0*1.95+V3)*62.4
01024 47 DELM=3620000.0/DEN
01032 48 X3=0.00445*V3
01040 49 X4=0.0025*V3
01044 50 AX=X3*X4+CNO*CT0
01060 51 Y1=CP0/AX
01066 52 Y2=CT0/AX
01074 53 Y3=X3/AX
01102 54 Y4=X4/AX
01118 55 C=(Y1*0.29+Y2*0.46+Y3*0.213+Y4*0.234)
01144 56 PRINT 20,CT0,CNO,DEN,DELM,C
01163 57 C=C*1.0
01171 57 T1=T10
01179 58 CT1=CT0
01201 59 CN1=CNO
01203 60 CP1=CP0

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01211 552 CP1=FC-CTC
01217 553 CT1=CT1-CP1
01225 554 CH1=CH1-3.8-CP1
01234 61 AREA=3.1416-R-R
01244 62 VEL=Y/(178.0-C78-AREA+28317.0)
01256 65 TT=0.0
01272 66 X=0.0
01274 67 ICHT=18TA
01302 68 UT=1.0/M1+1.0/M2+1.0/UM
01330 69 U=1.9/UT+9.0/5.0
01342 70 M1=M1+1.0
01350 70 CC=VELT/DELW+5/C+2.0/R
01366 71 C1=1.0-CC
01374 72 IF(C1) 73,75,75
01402 73 PRINT 13
01405 74 GO TO 30
01407 75 C2=CC
01413 76 CH=DELW/C
01422 77 DELX=VEL*DEL T
01430 80 J=1
01434 81 XX=(TS(2)-TS(1))/(XX(2)-XX(1))
01442 89 PRINT 22
01445 90 IF(XX(J+1)-X) 91,94,94
01505 91 J=J+1
01513 92 XX=(TS(J+1)-TS(J))/(XX(J+1)-XX(J))
01555 93 GO TO 90
01557 94 TE=TS(J+1)-XX*(XX(J+1)-X)
01612 100 DELCH=AA*EXP (-B/(T1-TAR))*CH1+AA*CT1+BB*DEL T
01644 101 CH2=CH1*DELCH
01672 102 IF(CH2)103,105,105
01700 103 CH2=0.0
01704 104 DELCH=CH1
01711 105 CT2=CT1*DELCH/3.0
01721 106 IF(CT2)107,111,111
01727 107 CT2=0.0
01733 108 DELCT=CT1
01740 109 DELCH=3.0*DELCT
01744 110 CH2=CH1*DELCH
01754 111 CONTINUE
01754 112 CP1=CP1-DELCH/3.0
01765 113 T2=C1+T1+C2+TE+CH+DELCH
02013 156 T3=T1+C+M1+(TE-T1)
02033 157 F=CT1/CT0
02041 160 IF(1CHT-18TA)166,161,161
02051 161 PRINT 21,TT,X,T1,F,CT1,CH1,CP1,T3,TE
99070 162 IF(X-BHX)164,164,163
92104 163 GO TO 30
92116 164 ICHT=1
92116 165 GO TO 167
92116 166 ICHT=1CHT+1
92124 167 X=X*DELX
92132 168 TT=TT*DEL T
92140 169 T1=T2
92144 170 CT1=CT2
92150 171 CH1=CH2
92154 172 CP1=CP2
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Sample Problem
Bulk Model of Flow Reactor

Summary of Output Data Not Included With Input Data

Time	period in reactor, hrs.
z -feet	position in reactor, ft.
F NOT CONVTD	moles TVOP/ moles TVOP input
BULK TEMP-°C	Reactant temperature, °C
CT1	moles TVOP/ liter of solution
CN1	moles N_2F_4 / liter of solution
CP1	moles TVOPA/ liter of solution
Wall temperature	temperature of tube wall, °C
TS	bath temperature, °C

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PROBLEM NUMBER 0.1000000E 01

XIN= 0.1550000E 03 DELT= 0.1000000E-02 NI= 0.0050000E 01 ME= 0.2000000E 03 WE= 0.3000000E 04
 A= 0.3210000E 10 B= 0.1110000E 03 TAR= 0.2730000E 03 AA= 0.1000000E 01 BB= 0.1000000E 01
 R= 0.7500000E-02 FLCR= 0.3300000E 01 CAPR= 0.2040000E 00 Y= 0.1410000E 03 T10= 0.0000000E 00
 J= 6 IDTA= 5
 XX TS

TIME HOURS	X-FEET	BULK TEMP. -C	F	MT	COMPTD	CT1	CR1	CP2	WALL TEMP.	TS
0.000000E 00	0.000000E 00	0.000000E 00	0.100000E 01	0.440000E-03	0.15477E-02	0.000000E 00	0.01100E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.500000E-02	0.17671E 01	0.35254E 02	0.99977E 00	0.440000E-03	0.15476E-02	0.15016E-07	0.02750E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.100000E-01	0.35342E 01	0.55943E 02	0.99911E 00	0.440000E-03	0.15467E-02	0.32311E-06	0.03691E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.150000E-01	0.53013E 01	0.66394E 02	0.99940E 00	0.45700E-03	0.15419E-02	0.19030E-05	0.04252E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.200000E-01	0.70604E 01	0.76202E 02	0.90722E 00	0.46300E-03	0.15297E-02	0.59921E-05	0.04600E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.250000E-01	0.88354E 01	0.81642E 02	0.97159E 00	0.45900E-03	0.15077E-02	0.13323E-04	0.04040E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.300000E-01	0.10603E 02	0.89577E 02	0.94079E 00	0.44495E-03	0.14750E-02	0.24034E-04	0.05020E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.350000E-01	0.12370E 02	0.80600E 02	0.91932E 00	0.43115E-03	0.14341E-02	0.37037E-04	0.05162E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.400000E-01	0.14137E 02	0.90949E 02	0.80455E 00	0.41404E-03	0.13052E-02	0.54144E-04	0.05200E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.450000E-01	0.15904E 02	0.92713E 02	0.84616E 00	0.39004E-03	0.13312E-02	0.72140E-04	0.05340E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.500000E-01	0.17671E 02	0.91900E 02	0.80620E 00	0.37810E-03	0.12750E-02	0.90600E-04	0.05401E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.550000E-01	0.19438E 02	0.94540E 02	0.76677E 00	0.35940E-03	0.12195E-02	0.10930E-03	0.05430E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.600000E-01	0.21205E 02	0.94652E 02	0.72062E 00	0.34210E-03	0.11672E-02	0.12600E-03	0.05439E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.650000E-01	0.22972E 02	0.94335E 02	0.69592E 00	0.32630E-03	0.11190E-02	0.14261E-03	0.05421E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.700000E-01	0.24739E 02	0.93721E 02	0.66611E 00	0.31240E-03	0.10779E-02	0.15099E-03	0.05293E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.750000E-01	0.26506E 02	0.92340E 02	0.64000E 00	0.30810E-03	0.10413E-02	0.16000E-03	0.05350E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.800000E-01	0.28273E 02	0.92130E 02	0.61740E 00	0.29955E-03	0.10093E-02	0.17944E-03	0.05321E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.850000E-01	0.30041E 02	0.91345E 02	0.59732E 00	0.29023E-03	0.98130E-03	0.18076E-03	0.05200E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.900000E-01	0.31808E 02	0.90630E 02	0.57902E 00	0.27100E-03	0.95663E-03	0.19701E-03	0.05254E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.950000E-01	0.33575E 02	0.90024E 02	0.56410E 00	0.26450E-03	0.93445E-03	0.20440E-03	0.05220E 02	0.000000E 02	0.000000E 02	0.000000E 02
1.000000E-01	0.35342E 02	0.89505E 02	0.54007E 00	0.25700E-03	0.91474E-03	0.21110E-03	0.05203E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.105000E 00	0.37109E 02	0.89471E 02	0.53677E 00	0.25174E-03	0.89592E-03	0.21725E-03	0.05103E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.110000E 00	0.38876E 02	0.88710E 02	0.52405E 00	0.24625E-03	0.87806E-03	0.22293E-03	0.05167E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.115000E 00	0.40643E 02	0.88410E 02	0.51335E 00	0.24076E-03	0.86290E-03	0.22823E-03	0.05150E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.120000E 00	0.42410E 02	0.88159E 02	0.50274E 00	0.23570E-03	0.84803E-03	0.23321E-03	0.05142E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.125000E 00	0.44177E 02	0.87947E 02	0.49272E 00	0.23100E-03	0.83394E-03	0.23791E-03	0.05133E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.130000E 00	0.45944E 02	0.87764E 02	0.48323E 00	0.22643E-03	0.82030E-03	0.24234E-03	0.05125E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.135000E 00	0.47711E 02	0.87610E 02	0.47419E 00	0.22239E-03	0.80707E-03	0.24660E-03	0.05110E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.140000E 00	0.49478E 02	0.87473E 02	0.46557E 00	0.21835E-03	0.79573E-03	0.25064E-03	0.05111E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.145000E 00	0.51245E 02	0.87353E 02	0.45732E 00	0.21440E-03	0.78413E-03	0.25451E-03	0.05100E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.150000E 00	0.53012E 02	0.87245E 02	0.44941E 00	0.21077E-03	0.77300E-03	0.25822E-03	0.05101E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.155000E 00	0.54779E 02	0.87147E 02	0.44181E 00	0.20720E-03	0.76231E-03	0.26170E-03	0.05097E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.160000E 00	0.56547E 02	0.87059E 02	0.43450E 00	0.20370E-03	0.75203E-03	0.26521E-03	0.05093E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.165000E 00	0.58314E 02	0.86977E 02	0.42740E 00	0.20047E-03	0.74212E-03	0.26851E-03	0.05090E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.170000E 00	0.60081E 02	0.86903E 02	0.42067E 00	0.19729E-03	0.73254E-03	0.27170E-03	0.05086E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.175000E 00	0.61848E 02	0.86833E 02	0.41411E 00	0.19421E-03	0.72334E-03	0.27477E-03	0.05083E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.180000E 00	0.63615E 02	0.86800E 02	0.40843E 00	0.19282E-03	0.71479E-03	0.27607E-03	0.05080E 02	0.000000E 02	0.000000E 02	0.000000E 02
0.185000E 00	0.65382E 02	0.86803E 02	0.40093E 00	0.19179E-03	0.71007E-03	0.27720E-03	0.051291E 03	0.000000E 02	0.000000E 02	0.000000E 02
0.190000E 00	0.67149E 02	0.86819E 02	0.40542E 00	0.19037E-03	0.71101E-03	0.27842E-03	0.051370E 03	0.000000E 02	0.000000E 02	0.000000E 02
0.195000E 00	0.68916E 02	0.86859E 02	0.39477E 00	0.18914E-03	0.69012E-03	0.28005E-03	0.051439E 03	0.000000E 02	0.000000E 02	0.000000E 02
0.200000E 00	0.70684E 02	0.86925E 02	0.37800E 00	0.17304E-03	0.64253E-03	0.28904E-03	0.05170E 03	0.000000E 02	0.000000E 02	0.000000E 02
0.205000E 00	0.72451E 02	0.87177E 02	0.33379E 00	0.15054E-03	0.61033E-03	0.31244E-03	0.05190E 03	0.000000E 02	0.000000E 02	0.000000E 02
0.210000E 00	0.74218E 02	0.87400E 02	0.28014E 00	0.13513E-03	0.54610E-03	0.33309E-03	0.05192E 03	0.000000E 02	0.000000E 02	0.000000E 02
0.215000E 00	0.75985E 02	0.87622E 02	0.24221E 00	0.11359E-03	0.48140E-03	0.35539E-03	0.05137E 03	0.000000E 02	0.000000E 02	0.000000E 02
0.220000E 00	0.77752E 02	0.87844E 02	0.20312E 00	0.95262E-04	0.42640E-03	0.37373E-03	0.05154E 03	0.000000E 02	0.000000E 02	0.000000E 02
0.225000E 00	0.79519E 02	0.88066E 02	0.17320E 00	0.81229E-04	0.38430E-03	0.38776E-03	0.05159E 03	0.000000E 02	0.000000E 02	0.000000E 02

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0.23800E 00	0.31204E 02	0.12240E 03	0.151 3E 00	0.70874E-04	0.35332E-03	0.39911E-03	0.11533E 03	0.11580E 03
0.23520E 00	0.03053E 02	0.12112E 03	0.13464E 00	0.63154E-04	0.33616E-03	0.48903E-03	0.11520E 03	0.11580E 03
0.24800E 00	0.04926E 02	0.11994E 03	0.12197E 00	0.57205E-04	0.31231E-03	0.41173E-03	0.11522E 03	0.11580E 03
0.24500E 00	0.06547E 02	0.11901E 03	0.11103E 00	0.52440E-04	0.29994E-03	0.41654E-03	0.11510E 03	0.11580E 03
0.25920E 00	0.08354E 02	0.11926E 03	0.10345E 00	0.48915E-04	0.29924E-03	0.42847E-03	0.11515E 03	0.11580E 03
0.25520E 00	0.98121E 02	0.11709E 03	0.95321E-01	0.45173E-04	0.27622E-03	0.42391E-03	0.11512E 03	0.11580E 03
0.26800E 00	0.91809E 02	0.11725E 03	0.95134E-01	0.42272E-04	0.26791E-03	0.42672E-03	0.11510E 03	0.11580E 03
0.26500E 00	0.93650E 02	0.11691E 03	0.84672E-01	0.39716E-04	0.25983E-03	0.42928E-03	0.11509E 03	0.11580E 03
0.27000E 00	0.95423E 02	0.11645E 03	0.79704E-01	0.37419E-04	0.25295E-03	0.43157E-03	0.11507E 03	0.11580E 03
0.27500E 00	0.97193E 02	0.11645E 03	0.75372E-01	0.35349E-04	0.24674E-03	0.43364E-03	0.11507E 03	0.11580E 03
0.28000E 00	0.98957E 02	0.11629E 03	0.71355E-01	0.33464E-04	0.24109E-03	0.43552E-03	0.11506E 03	0.11580E 03
0.28500E 00	0.10072E 03	0.11616E 03	0.67673E-01	0.31735E-04	0.23591E-03	0.43725E-03	0.11505E 03	0.11580E 03
0.29000E 00	0.10246E 03	0.11635E 03	0.64243E-01	0.30140E-04	0.23114E-03	0.43884E-03	0.11505E 03	0.11580E 03
0.29500E 00	0.10420E 03	0.11596E 03	0.61140E-01	0.28576E-04	0.22673E-03	0.44031E-03	0.11504E 03	0.11580E 03
0.30000E 00	0.10603E 03	0.11560E 03	0.58239E-01	0.27013E-04	0.22264E-03	0.44167E-03	0.11504E 03	0.11580E 03
0.30500E 00	0.10779E 03	0.11581E 03	0.55531E-01	0.26543E-04	0.21893E-03	0.44294E-03	0.11504E 03	0.11580E 03
0.31000E 00	0.10954E 03	0.11575E 03	0.53803E-01	0.24899E-04	0.21527E-03	0.44413E-03	0.11503E 03	0.11580E 03
0.31500E 00	0.11133E 03	0.11570E 03	0.52637E-01	0.23748E-04	0.21194E-03	0.44524E-03	0.11503E 03	0.11580E 03
0.32000E 00	0.11309E 03	0.11565E 03	0.48019E-01	0.22708E-04	0.20802E-03	0.44628E-03	0.11503E 03	0.11580E 03
0.32500E 00	0.11486E 03	0.11561E 03	0.46334E-01	0.21730E-04	0.20589E-03	0.44726E-03	0.11503E 03	0.11580E 03
0.33000E 00	0.11663E 03	0.11557E 03	0.44373E-01	0.20810E-04	0.20313E-03	0.44810E-03	0.11503E 03	0.11580E 03
0.33500E 00	0.11839E 03	0.11554E 03	0.42523E-01	0.19943E-04	0.20052E-03	0.44904E-03	0.11502E 03	0.11580E 03
0.34000E 00	0.12016E 03	0.11551E 03	0.40777E-01	0.19124E-04	0.19807E-03	0.44994E-03	0.11502E 03	0.11580E 03
0.34500E 00	0.12193E 03	0.11548E 03	0.39126E-01	0.18349E-04	0.19574E-03	0.45084E-03	0.11502E 03	0.11580E 03
0.35000E 00	0.12370E 03	0.11545E 03	0.37503E-01	0.17616E-04	0.19359E-03	0.45173E-03	0.11502E 03	0.11580E 03
0.35500E 00	0.12546E 03	0.11542E 03	0.35981E-01	0.16922E-04	0.19146E-03	0.45267E-03	0.11502E 03	0.11580E 03
0.36000E 00	0.12723E 03	0.11540E 03	0.34575E-01	0.16267E-04	0.18940E-03	0.45273E-03	0.11502E 03	0.11580E 03
0.36500E 00	0.12900E 03	0.11537E 03	0.33340E-01	0.15633E-04	0.18766E-03	0.45335E-03	0.11502E 03	0.11580E 03
0.37000E 00	0.13076E 03	0.11534E 03	0.32276E-01	0.15044E-04	0.18582E-03	0.45369E-03	0.11502E 03	0.11580E 03
0.37500E 00	0.13253E 03	0.11532E 03	0.30841E-01	0.14474E-04	0.18412E-03	0.45431E-03	0.11502E 03	0.11580E 03
0.38000E 00	0.13430E 03	0.11530E 03	0.29716E-01	0.13934E-04	0.18253E-03	0.45505E-03	0.11501E 03	0.11580E 03
0.38500E 00	0.13607E 03	0.11531E 03	0.28413E-01	0.13419E-04	0.18095E-03	0.45577E-03	0.11501E 03	0.11580E 03
0.39000E 00	0.13783E 03	0.11530E 03	0.27569E-01	0.12928E-04	0.17948E-03	0.45606E-03	0.11501E 03	0.11580E 03
0.39500E 00	0.13960E 03	0.11528E 03	0.26566E-01	0.12459E-04	0.17807E-03	0.45653E-03	0.11501E 03	0.11580E 03
0.40000E 00	0.14137E 03	0.11527E 03	0.25618E-01	0.12011E-04	0.17673E-03	0.45693E-03	0.11501E 03	0.11580E 03
0.40500E 00	0.14313E 03	0.11526E 03	0.24697E-01	0.11583E-04	0.17544E-03	0.45748E-03	0.11501E 03	0.11580E 03
0.41000E 00	0.14490E 03	0.11525E 03	0.23823E-01	0.11173E-04	0.17421E-03	0.45781E-03	0.11501E 03	0.11580E 03
0.41500E 00	0.14667E 03	0.11524E 03	0.22987E-01	0.10781E-04	0.17304E-03	0.45821E-03	0.11501E 03	0.11580E 03
0.42000E 00	0.14844E 03	0.11523E 03	0.22104E-01	0.10405E-04	0.17191E-03	0.45858E-03	0.11501E 03	0.11580E 03
0.42500E 00	0.15020E 03	0.11522E 03	0.21410E-01	0.10045E-04	0.17083E-03	0.45894E-03	0.11501E 03	0.11580E 03
0.43000E 00	0.15197E 03	0.11521E 03	0.20744E-01	0.96995E-05	0.16979E-03	0.45920E-03	0.11501E 03	0.11580E 03
0.43500E 00	0.15374E 03	0.11520E 03	0.19975E-01	0.93682E-05	0.16881E-03	0.45962E-03	0.11501E 03	0.11580E 03
0.44000E 00	0.15550E 03	0.11519E 03	0.19253E-01	0.90504E-05	0.16785E-03	0.45994E-03	0.11501E 03	0.11580E 03

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APPENDIX G

Reaction Kinetics

A series of batch reactor runs^{1,2} was made to obtain kinetic data on the synthesis of TVOPA and A-3. For both reactions the data were successfully correlated on the assumption of a second order reaction mechanism. The Arrhenius plots based upon this correlation are shown in Fig. 8.

¹Rehm & Haas Company, Quarterly Progress Report on Chemical and Propellant Processing, No. P-64-3, February 15 1965.

²Ibid, No. P-64-17, August 15, 1964.

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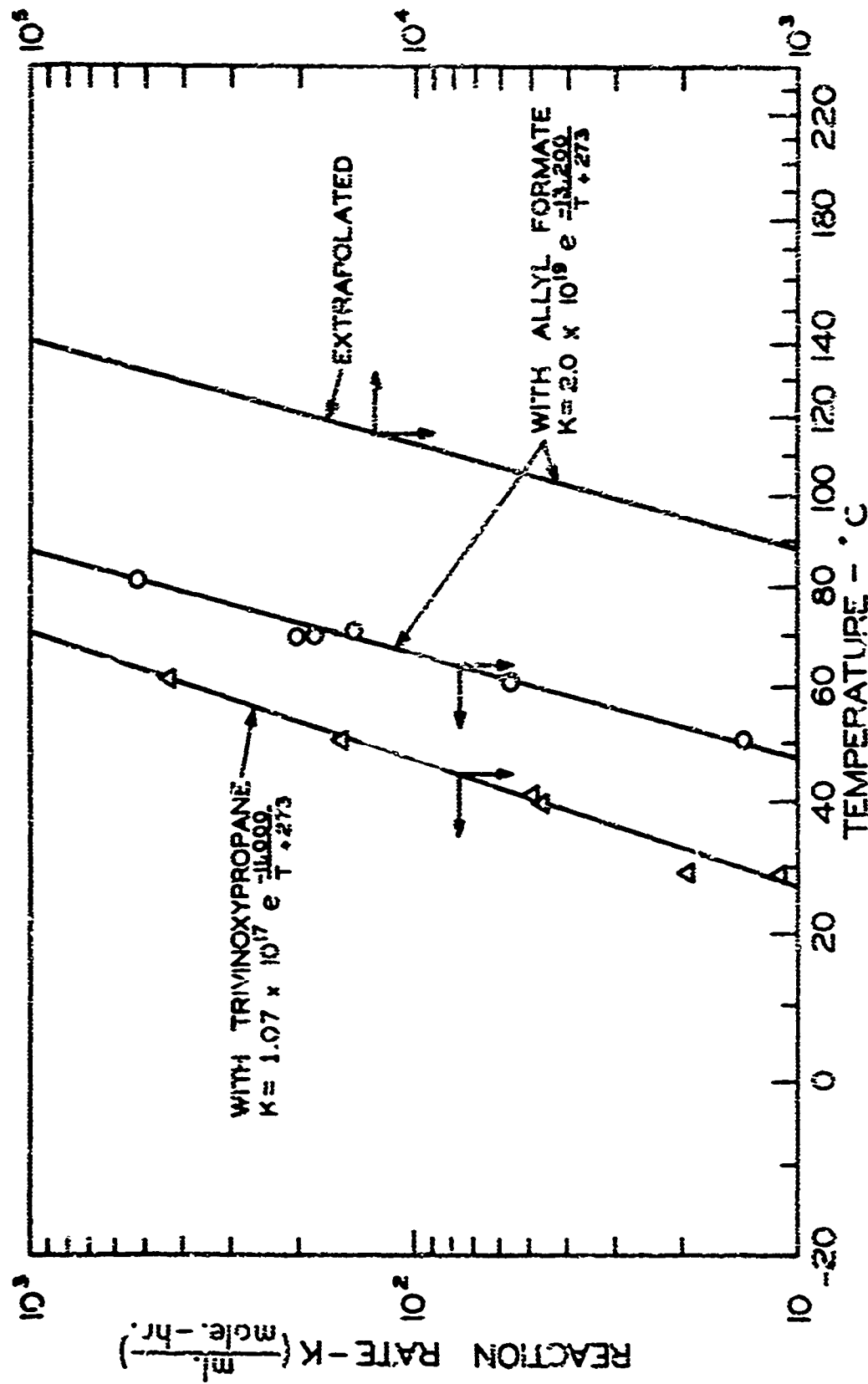


FIG. 8 ARRHENIUS PLOT FOR A-3 AND TVOPA LIQUID PHASE REACTION

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APPENDIX H

N₂F₄ Solubility

A series of N₂F₄ solubility determinations was made by the Physical Chemistry Group, and the results are shown in Table V. The solubility of N₂F₄ in Freon TF and mixed solvent at temperatures from 40-100°C and a total pressure of 300 psia is shown in Fig. 9. Minimum reactor pressure was selected from these values to avoid partial gassing in the first stage of the reactor. For example, the minimum pressure for A-3 synthesis was 415 psia for the 0.204 grams N₂F₄/cc solvent input since the N₂F₄ solubility in mixed solvent was found to be 0.213 at 100°C.

Table V
N₂F₄ Solubility in Various Solvents

Solvent	Temp. °C	Pressure (psi abs.)	Solubility gm N ₂ F ₄ /cc solvent
Freon TF	40	50	.036
	40	100	.139
	40	150	.200
	40	200	.377
	40	300	.869
	60	50	.005
	60	100	.073
	60	200	.213
	60	300	.463
	80	300	.215
ChCl ₃	40	300	.274
	60	300	.162
	80	300	.102
Freon TF:CHCl ₃ , 4:1 by vol.	40	300	.724
	60	300	.361
	80	300	.241
	100	300	.112
	100	300	.104
Freon TF:CH ₂ Cl ₂ , 3:1 by vol.	100	415	.213
	40	50	.035
	40	50	.023
	40	100	.092
	40	150	.183
1, 2-dichloroethane	40	200	.271
	40	300	.052
	40	300	.045
1, 1, 2-trichloroethane	40	300	.032
	40	300	.041
H ₂ O	30	150	.002

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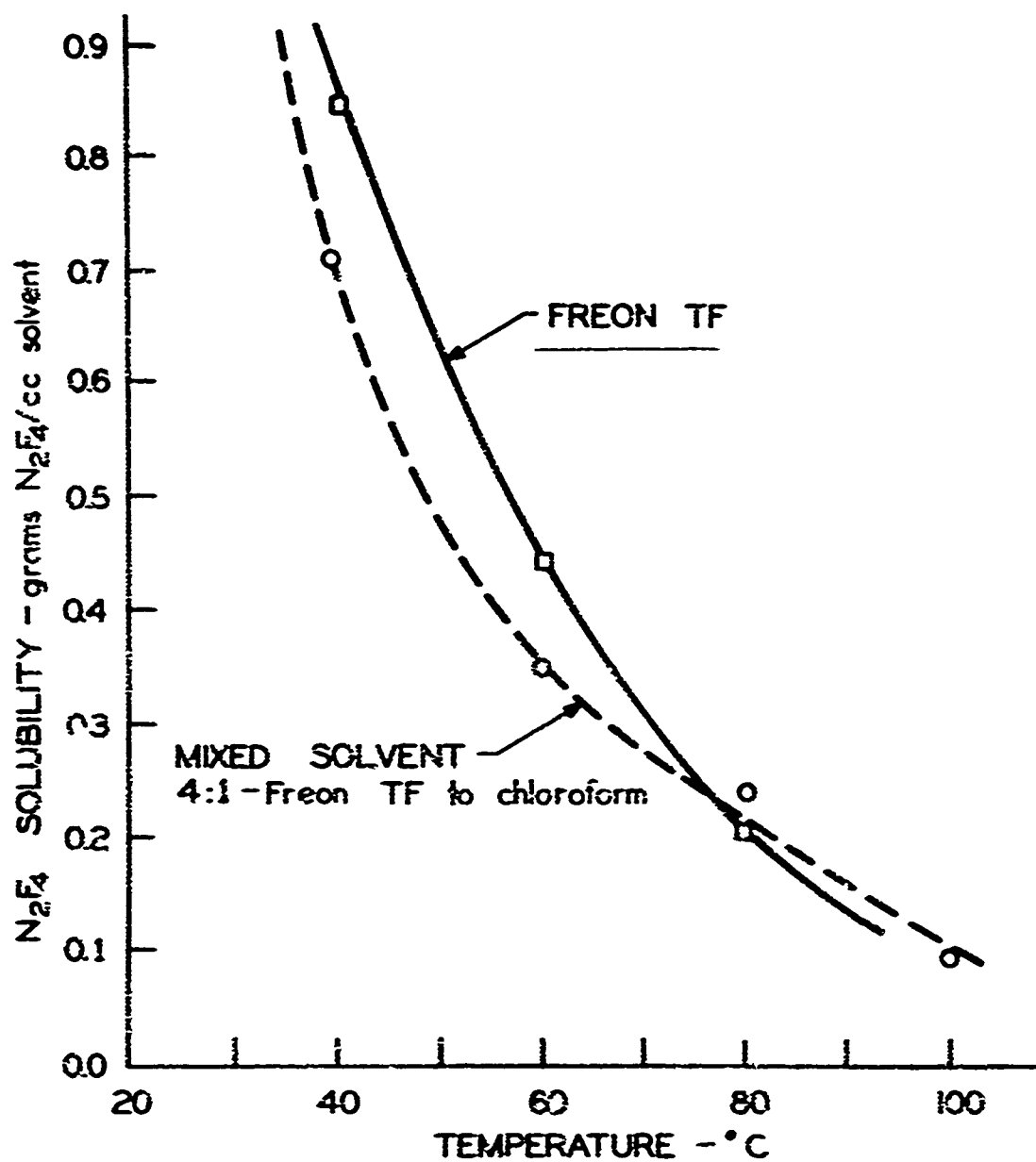


FIG. 9 N_2F_4 SOLUBILITY IN FREON TF AND MIXED SOLVENT VERSUS TEMPERATURE AT 300 PSIA TOTAL PRESSURE

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APPENDIX I

Corrosion Studies

A single corrosion experiment with $> 97\%$ N_2F_4 showed corrosion rates of about 10^{-4} inches per year with Hastelloy C, type 440 stainless steel, and nickel, and about 10^{-5} inches per year with type 316 stainless steel. Exposure was to N_2F_4 free of HF under the test conditions shown in Table VI. The results, summarized in Table VII, showed that all of the materials tested were acceptable for construction and the type 316 stainless steel could be used for precision fitted parts.

The test coupons were about $3/4 \times 3/8 \times 1/16$ inches and were suspended by Teflon string in a 30 ml test cell located downstream of the compressor second stage discharge. About 10% of the N_2F_4 exposure was at > 300 psig and the remainder in the range of 6-30 psig. Exposure was not continuous because equipment changes required periodic flushing with nitrogen and air for personnel entry into the reactor bay.

Table VI
Corrosion Test Conditions

<u>Test</u>	
Exposure, hours	
30 psig N_2F_4	1169
300-500 psig N_2F_4	133
Temperature, °C	35-42
Analysis (Average), %	
N_2F_4	$> 97\%$
NO	$< 3\%$
HF	$\approx 0\%$

Table VII
Summary of Corrosion Tests on N₂F₄

<u>Sample</u>	<u>Corrosion Rate, inches/yr.</u>
Hastelloy C	1.3×10^{-4}
440 Stainless Steel	1.8×10^{-4}
316 Stainless Steel	1.4×10^{-5}
Nickel	2.6×10^{-4}

The coupons were prepared by successive washing with water, acetone, and methylene chloride. Two weighings were made following exposure. The first was made after the coupons were washed by the above procedure, and the second followed a Bon Ami scouring to remove surface films. No additional weight loss was observed after scouring. Estimated error of the corrosion rate was $\pm 50\%$, based upon the accuracy of the balance used to determine the weight loss (excepting 316 stainless steel which was $\pm 100\%$).

APPENDIX J

SafetyN₂F₄ Cylinder Decomposition

About 4 pounds of N₂F₄ (in a single cylinder) was lost because of partial decomposition upon opening of the main cylinder valve. About 13% of the N₂F₄ decomposed to NF₃ and N₂ by the overall reaction:



$$\Delta H_R = -38.85 \frac{\text{kcal}}{\text{mol N}_2\text{F}_4}$$

Following a routine procedure, the main cylinder valve was manually "cracked" to bleed the N₂F₄ into the manifold. The pressure momentarily leveled off at 130 psig and then started rising to 150 psig. Immediately afterwards the operator noticed that the top of the cylinder was "uncomfortably" hot to the touch (ca. 130°F). The incident was particularly disconcerting since the valve had already been opened and closed once to obtain a mass spectral sample.

Previous studies¹ of explosive N₂F₄ reactions indicated a maximum pressure increase of about 14 times the initial pressure (using exploding wire or No. 6 detonators for initiation). These studies were the basis of the 130 psig limit on a standard nitrogen cylinder fitted with an oxygen main valve. Although in this incident the protection offered by the cylinder was adequate, an additional safety factor was later incorporated into the N₂F₄ handling procedure by providing for remote opening and closing of the main cylinder valve.

¹Rohm & Haas Company, Quarterly Progress Report on Interior Ballistics, P-60-13, pp. 1-7, January 19, 1961.

A possible cause of the incident was the initiation of the N_2F_4 by air. Since this incident two cylinders from the same shipment (out of six received) have leaked N_2F_4 during the opening procedure because the stem packing was inadequate. These are the first cylinders with which this difficulty was observed; however, leaks of this kind are not easy to detect because there are valve positions in which sealing does occur. Past experience suggested that, once initiated, the reaction could propagate back through the leak. Leakage is a problem only during opening or closing using the standard practice of tightening the valve in the full open position, because there is a superior second seal independent of the stem seal. For this reason personnel exposure to full N_2F_4 cylinders was permitted when the valve was fully opened or closed.

Explosions in Reactor

Six explosions occurred during operation of the liquid phase flow reactor. Four occurred without warning in the mixing tee (where the N_2F_4 was added to the olefin solution), and two occurred during attempts to eliminate reactor plugs. There was no evidence of propagation through the condensed liquid lines; however, in two instances there was propagation through the 1/8" I. D. N_2F_4 feed tube. Equipment damage was minor, being limited to the mixing tee, a valve, or the tubular reactor coils. Down time for repairs was usually two to three days.

The four explosions in the mixing tee were similar. In each instance no difficulties had been encountered, and all measurements suggested the reactor was operating normally when the explosion occurred. In the first two explosions there was propagation back to the N_2F_4 feed valve. Following the first two incidents, the N_2F_4 feed tube was inserted into the cooled section to insure absorption where the 0.18" I. D. tube was totally surrounded by the 0°C brine bath. This modification limited damage to the mixing tee in the two subsequent incidents.

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Apparently the explosions were not related to N_2F_4 purity, which varied from 97 to 99.5%. A probable cause was initiation by a small amount of air inadvertently introduced with the solvent-olefin feed. Observations confirmed that the air purge technique did not eliminate air in the 30 ml section between the glass wool filter and the suction side of the liquid pump, and as passage through the filter became difficult the pump started taking a little air with each stroke.

The two other explosions were related to reactor plugging which forced premature shut down of the plant. Both occurred during attempts to remove the solid plug so that the N_2F_4 could be cleaned out to allow personnel entry into the reactor bay. The explosions were assumed to be caused by locally excessive N_2F_4 concentrations reacting with either the solids or olefin.

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