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DESIGN OF A HIGH PRESSURE REACTION SYSTEM AND THE UNCATALYZED HIGH PRESSURE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE

A Thesis
Submitted to the Faculty of Graduate Studies Through the
Department of Chemical Engineering in Partial Fulfilment
of the Requirements for the Degree of
Master of Applied Science at the
University of Windsor

by

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ABSTRACT

A high pressure reaction system was designed to operate up to a maximum pressure of 15,000 psig. Tests indicated that the system was operable up to 11,200 psig.

Exploratory studies on the high pressure oxidation of pseudocumene by sulfur dioxide, were carried out. Experiments were conducted for reaction temperatures of 251.9°C ± 3.0C° and 272.5°C ± 3.0C°. A pseudocumene concentration of 3.72 gmole/ℓ and 1.19 gmole/ℓ was used. The oxidation of pseudocumene by sulfur dioxide under pressure was demonstrated to be feasible. One of the products was identified as a methyl substituted carboxylic acid.

The reaction rate was observed to be strongly dependent upon the pseudocumene concentration.

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R.J.M.

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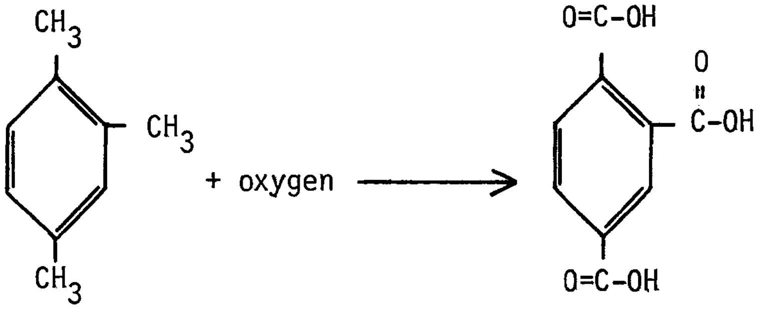
I. INTRODUCTION

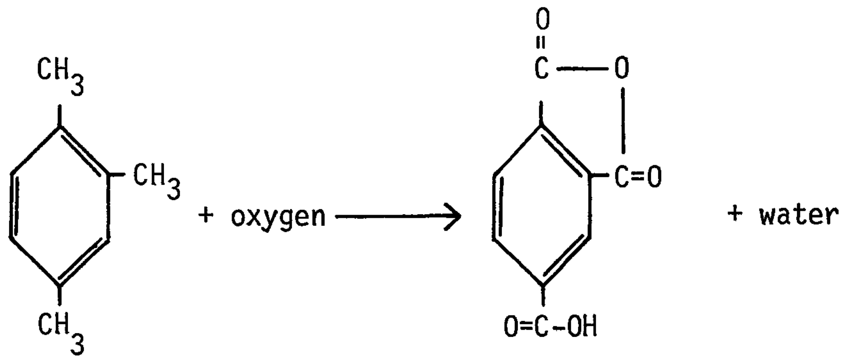
Although various polymethylbenzenes can be recovered from C_9 and C_{10} reformate streams only three of them seem to be attaining the commercial status enjoyed by the xylenes. They are pseudocumene, mesitylene and durene. [9] Hemimellitene, prehnitene, isodurene, pentamethylbenzene and hexamethylbenzene are still in the research or product development stage [8]. Production of pseudocumene is approximately one million pounds annually, whilst that of mesitylene and durene is much smaller.

Typical C_9 streams contain about 41% by weight pseudocumene, whilst C_{10} streams contain only 8% by weight durene. As raw material, this relative abundance of pseudocumene fosters research in novel applications.

New uses for these polymethylbenzenes have been found in plastics, coatings, plasticizers, synthetic fibres, pharmaceuticals and paints. Pseudocumene's most important derivatives are its oxidation products trimellitic acid and trimellitic anhydride.



Pseudocumene Trimellitic Acid



Trimellitic Anhydride

Oxidation of pseudocumene to produce carboxylic acids is a logical starting point when considering novel uses, since its homologue toluene is readily oxidized to form benzoic acid. However the difficulty in synthesizing a polycarboxylic acid from a polymethylbenzene is that one methyl group reacts easily enough, but the others resist oxidation. [12] Consequently catalyzed vapour phase and liquid phase oxidation processes have been developed to synthesize the polycarboxylic acids. On the basis of existing information, it appears that pseudocumene cannot be successfully oxidized to trimellitic acid or anhydride by vapour phase oxidation. The only contrary report has been made by Ibling. [13] Ibling reported that several tests were conducted in the Ruhröl Chemie Werk, West Germany, in which the oxidation of pseudocumene produced trimellitic anhydride in yields of 35 to 40%. Efforts by Rao [14] and Preudhomme [15] to carry out this oxidation resulted in rupture of the benzene ring for the range of conditions they studied. Preudhomme's ammoxidation runs resulted in the production of maleic imide and water. The catalyzed liquid phase oxidation of pseudocumene is feasible and has been reported by Towle and Baldwin [10].

Liquid phase oxidation is used for production of a greater variety of products, from a wider range of starting materials. Often the advantage over vapour phase oxidation is one of less severe oxidation conditions [11]. Some exploratory studies on the liquid phase, catalyzed and uncatalyzed oxidation of pseudocumene have been carried out indicating its feasibilty [16].

In view of the foregoing discussion this project was undertaken to:

(i) design a high pressure reactor system permitting the study of various chemical reactions.

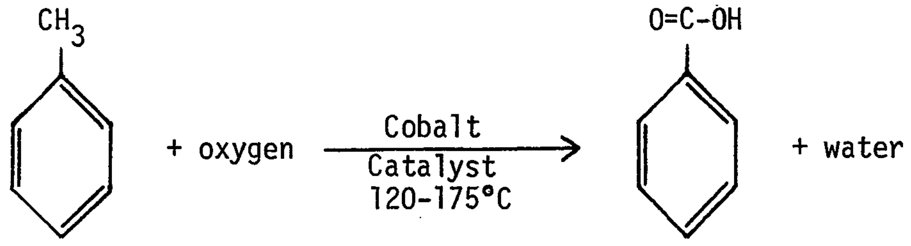
(ii) carry out further exploratory studies on the liquid phase uncatalyzed oxidation of pseudocumene by sulfur dioxide.

II. LITERATURE SURVEY

Although the oxidation of many alkyl substituted aromatic hydrocarbons to produce carboxylic acids has been explored extensively, little attention has been paid to the liquid phase oxidation of the higher polymethylbenzenes, particularly pseudocumene. In what follows, a concise review of liquid phase oxidation of pseudocumene is presented, subsequent to the mention of the oxidation of toluene, and the liquid phase oxidation of p-xylene.

A. Two Phase Oxidation of Toluene and the Liquid Phase Oxidation of p-Xylene.

Experiments by Kaeding [29] indicated that toluene could be oxidized to benzoic acid at temperatures between 120°C and 175°C in a reaction mixture containing a soluble cobalt catalyst in concentration of 0.1 to 0.3% by weight. Benzoic acid was also the usual end product for a variety of oxidizing agents such as persulfate, chromic acid, alkaline permanganate, dilute nitric acid, oxygen and chlorine. The following equation represents the reaction.

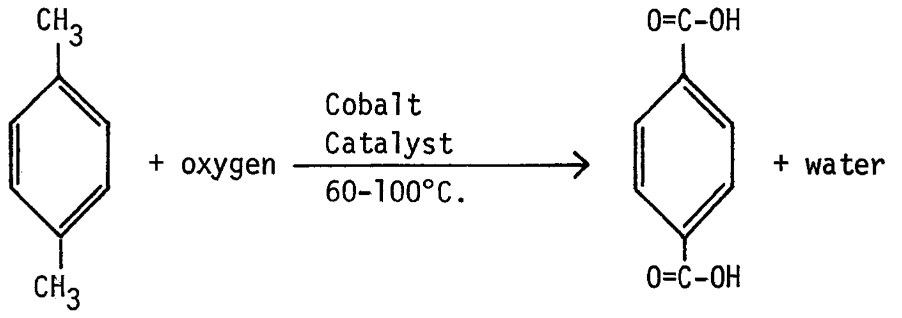


(II-1)

Toluene

Benzoic Acid

Yamamota et al. [28] reported that terephthalic acid can be synthesized by the liquid phase oxidation of p-xylene in acetic acid, in the presence of acetaldehyde as accelerator and cobalt acetate as catalyst. The reaction was carried out between 60°-100°C using oxygen as the oxidizing agent. The reaction is represented by the following equation.



(II-2)

p-xylene Terephthalic Acid

Terephthalic acid was produced in 98% yields under optimum conditions.

Towle and Baldwin [10] have reported the liquid phase air oxidation of p-xylene to terephthalic acid using a heavy metal catalyst and some form of bromine.

B. Liquid Phase Oxidation of Pseudocumene.

Kachurina [25] and Kazanskii [26] reported the catalyzed two step oxidation of pseudocumene to trimellitic acid. First the liquid phase air oxidation under pressure with a cobalt stearate catalyst was carried out. Secondly water and nitric acid were added under a pressure of 100-200 psig., in the presence of HCl and NH_4Cl. The yield of trimellitic acid was 97%.

Patents by Backlund [17, 18, 19] indicate that pseudocumene can be oxidized in the liquid phase to trimellitic acid by the addition of nitric acid to a pseudocumene and water mixture. The reaction was carried out at 200-250°C, 100 psig. pressure and in the presence of HCl, HBr, NH_4Cl and NH_4Br. The acid was added when the reactant had reached 160°C. The total reaction time was about 1.5 hours giving a 89.5% yield.

Pseudocumene oxidation to trimellitic acid by chromic acid in glacial acetic acid or by potassium permanganate and sodium hydroxide has been accomplished [24].

Hofman et al. [27] have reported that the base-catalyzed oxidation of pseudocumene to trimellitic acid can be carried out. The reaction occurred on contacting pseudocumene with potassium t-butoxide or potassium hydroxide in hexamethylphosphoramide at room temperature. Oxygen was passed through the reaction mixture. However, only a 10% yield of trimellitic anhydride was obtained after a reaction time of three hours.

The commercial oxidation process known as the Mid-Century process is a one step liquid phase air oxidation process for the production of aromatic polycarboxylic acids. [10] This process incorporates a heavy metal catalyst such as cobalt, molybdenum or manganese with some form of bromine to effect the acid production. The use of bromine represents a unique feature, because it is used as a regenerative source of chain initiating free radicals. For most aromatic acids, reaction times of one half to three hours are required. Reaction temperatures may vary from 125 to 275°C, while a pressure of about 40 atmospheres is employed to maintain the liquid phase. A 5-15% excess of oxygen is required to prevent undesirable byproduct formation. Byproduct separation from the acid is achieved by incorporating into the reaction mixture a solvent such as acetic acid, in which the byproducts are soluble and the acid insoluble.

These oxidations maybe carried out batchwise, semi continuous, or in a continuous manner. In a typical batch operation, the components - hydrocarbon, solvent and catalyst system - are charged to the reactor and heated to the reaction temperature. Heat is removed by condensing and refluxing solvent vapors. Upon completion of the reaction, the contents are discharged into a surge vessel. Product acid is separated from the solvent by centrifuging or filtration.

The first acid to be produced from this process was trimellitic acid from the oxidation of pseudocumene. However, no information pertaining to the kinetics of this system is available in the literature except for the work of Shipman. [16].

Shipman [16,20,21,22,23] investigated some reactions of alkyl substituted aromatic compounds with sulfur dioxide. He reported that toluene was oxidized to benzoic acid, xylenes to phthalic acids and pseudocumene to trimellitic acid. The overall reaction is represented by the following equation,

$$RCH_3 + 1.5\ SO_2 \longrightarrow RCOOH + 1.5\ S. + H_2O \qquad \text{(II-3)}$$

High pressure reactors of 100 ml, 1 l, and 25 l, were used. These reactors were made of stainless steel and were magnetically stirred. Electric furnaces effected the necessary heating.

The common experimental procedure employed was to charge the reactor with a known weight of the organic compound used, assemble the reactor into the furnace and heat to reaction temperature, then pressurize with sulfur dioxide. During the reaction the pressure dropped as the sulfur dioxide was consumed. More sulfur dioxide was added periodically from a compressor. The products could be removed upon completion of the reaction by blow off through a dip pipe or by cooling the reactor and dismantling it.

Shipman's findings may be summarized as follows:

1) Presence of a methyl group substituted on the aromatic ring leads to a higher yield of the corresponding carboxylic acid. However, as the number of methyl groups substituted in the benzene ring increases, the yield of the carboxylic acid decreases.
2) The rate of oxidation is not affected by the addition of free radical initiators or inhibitors, metal salts as sulfates, sulfites of alkalai transition metals, or chlorine compounds.
3) The reaction is catalyzed by bromine, iodine and their compounds.
4) In addition to the oxidation of polymethylbenzenes sulfur dioxide may react in the following ways:
    (i) bring about oxidative coupling of alkyl substituted aromatic compounds and benzene.
    (ii) dehydrogenate or aromatize alicyclic compounds.
    (iii) form cyclic sulfones with olefins.
    (iv) form cyclic sulfites with olefin oxides.
    (v) oxides form ethers from aliphatic alcohols.
5) Heat of reaction of the polymethylbenzenes was estimated to be 50 kcal./methyl group.
6) The activation energies for the oxidation of toluene, xylenes and pseudocumene are all within the range 92±2 kcal./mole.

7) The overall reaction rate is approximately proportional to the square of the hydrocarbon concentration.

8) The reaction rate decreases with increasing pressure.

9) The reaction rate nor the product varied significantly with the purities of the reactants.

10) The reaction is not affected by the presence of a few atmospheres of oxygen or air.

11) The reaction is completely inhibited by metallic silver or copper.

12) The yield of trimellitic acid is inversely proportional to the reaction rate.

13) The major byproduct from p-xylene was p-toluic acid and from pseudocumene it was 4-methylphthalic acid.

14) Small amounts of tarry products were often found amongst the products.

15) In excess sulfur dioxide the reaction proceeds as stoichiometrically indicated.

16) If the reaction is stopped before completion, aldehydes and hydrogen sulfide are found in significant quantities, suggesting that the reaction proceeds by way of several steps.

Shipman determined the rate of reaction by measuring the pressure drop and elapsed time. The pressure dropped due to the consummation of sulfur dioxide. The sulfur dioxide was added intermittently, restoring the pressure and decreasing the mole fraction of pseudocumene. Pressure drops were accumulated and plotted against time. The slope determined from the resulting curve indicated the rate.

Water soluble carboxylic acids were separated from the crude product by water extraction; however Shipman fails to mention how the carboxylic acids were identified.

III. SYSTEM DESIGN AND EXPERIMENTAL SET UP

The liquid phase noncatalyzed oxidation of pseudocumene was carried out in a batch reactor. Figure 1. indicates schematically the overall system. Under its own vapour pressure the liquid oxidizing agent sulfur dioxide was charged into the reactor from an inverted gas cylinder. A high pressure liquid handling pump was installed into the feed line between the gas cylinder and the reaction vessel, such that by closing a valve the fluid could be directed through the pump and into the reactor. Thus, the system could be maintained at a desired pressure by force feeding the fluid from the low pressure side into the high pressure side.

The reactants were stirred by subjecting a magnetic stirrer inside the reactor to a rotating magnetic field induced by a revolving permanent magnet mounted on a motor shaft.

Reaction temperatures were attained by heating the reactor contents with cylindrical heaters strapped to the reactor.

Electronic temperature and motor control units were employed to control temperature and shaft speed of the motor. Appendix I indicates the respective designs in greater detail.

The reaction vessel itself was fitted with thermocouples, a safety valve, pressure gauge, cooling coil, sample and feed lines.

A. Reactor Design.

The stainless steel reactor was built from 316 stainless steel round bar stock measuring 8 in. in diameter and 12 in. long. Stainless steel No. 316 was chosen over other materials for the following reasons.

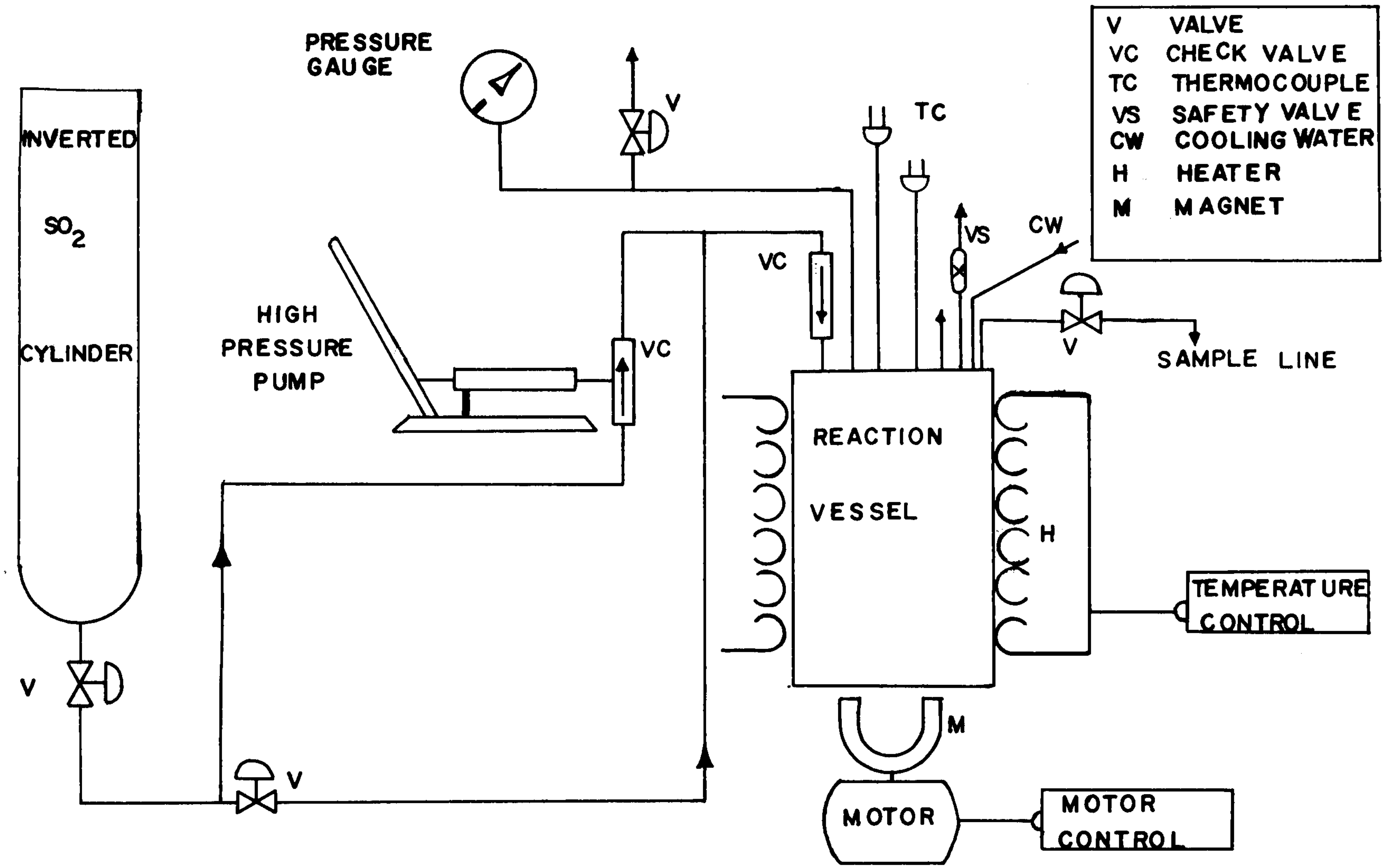


FIGURE I SCHEMATIC DIAGRAM OF EXPERIMENTAL SET UP

i) A reaction system was to be designed which would be sufficiently general in design as to permit the study of various reactions under high pressure. Therefore it was desirable to have the reaction vessel constructed from a material which is noncatalytic to most reactions that may be studied. In particular, the oxidation of pseudocumene is catalyzed by bromine, iodine, silver, copper, their compounds and perhaps other materials. However, the reaction is not catalytically influenced by stainless steel [5].

ii) Stainless steel has a relatively high tensile strength.

1) Calculation of the Wall Thickness for the Reactor. [1]

For internal pressure where the tensile stress, S_t, is a maximum at the inside surface of the cylinder, the equation for thick walled vessels is,

$$\underset{\text{Max}}{S_t} = \left[\frac{b^2 + a^2}{b^2 - a^2}\right] p_i \qquad \text{(III-1)}$$

where p_o = zero guage, a = internal radius

b = outside radius

p_i = maximum internal pressure

S_t = maximum yield strength.

Now the tensile stress produced by the internal pressure must equal the yield stress of the material. This equation is derived from the more general expression by setting the radius r, equal to the internal radius a. Hence:

$$S_t = \frac{a^2 p_i}{b^2 - a^2}\left[1 + \frac{b^2}{r^2}\right] \qquad \text{(III-2)}$$

$$S_t = \frac{a^2 p_i}{b^2 - a^2} \left[1 + \frac{b^2}{a^2} \right]$$

$$S_{t\,Max} = \frac{b^2 + a^2}{b^2 - a^2} \quad p_i$$

Similarly for internal pressure the compressive stress is given by,

$$S_r = \frac{a^2 p_i}{b^2 - a^2} \left[1 - \frac{b^2}{r^2} \right] \qquad \text{(III-3)}$$

The working stress, S_w, is the actual stress the material experiences when underload. It is almost synonymous with allowable stress which is the maximum safe stress a material may carry. The yield point is selected as the basis for determining S_w in structural steel because it is the stress at which a large permanent strain may occur. However, for other cases the allowable stress is usually based on the ultimate strength. Therefore,

$$S_w = \frac{S_{ult.}}{N}$$

where S_{ult} = ultimate stress

N = safety factor.

Although 316 stainless steel has a tensile stress of 90,000 - 150,000 psi. [2], a maximum value for the ultimate tensile strength of 70,000 psi. was chosen to ensure safety. An arbitrary safety factor of 2. was chosen; hence a working stress of 35,000 psi. was obtained.

A design condition imposed is that the internal radius, a, be 2.0 in. Also another design condition imposed is that the maximum internal pressure to be sustained by the reactor is 15,000 psig.

Applying equation (III-1), the outside radius, b, is computed as follows:

$$35{,}000 = \left[\frac{2^2 + b^2}{b^2 - 2^2}\right] 15{,}000$$

$$b^2 = 10.00$$

$$b = 3.16 \text{ in.}$$

Let the wall thickness be Δr.

Therefore $\Delta r = b - a. = (3.16 - 2.00)$

$\Delta r = 1.16$ in.

The wall thickness must be at least 1.16 in. to withstand an internal pressure of 15,000 psi.

The compressive stress involved is computed by equation (III-3) For $r = 2.0 = a$.

$$S_r = \frac{(2)^2 \times 15{,}000}{10 - (2)^2} \left[1 - \frac{10}{4}\right] \text{psi}$$

$$S_r = -15{,}000 \text{ psi.}$$

The compressive stress is then 15,000 psi. at the inside wall of the reactor. The negative sign merely indicates the stress is compressive as opposed to tensile. Similarly at the outer wall of the reactor the tensile and compressive stresses are as follows:

$$S_t = 20{,}000 \text{ psi.}$$

$$S_r = 0 \text{ psi.}$$

Table 1. summarizes these computations.

Table 1. Stresses on Inner & Outer Surface of Reaction Vessel

	a = 2.0"	b = 3.16"
S_t	35,000 psi.	20,000 psi.
S_r	-15,000 psi.	0 psi.

However, suppose the wall thickness was increased to 2.0 in., then what internal pressure would the reactor withstand?

Applying equation (III-1)

$$35{,}000 = \frac{4\,p_i}{16-4}\left[1 + \frac{16}{4}\right]$$

$$p_i = 21{,}000 \text{ psi.}$$

This would represent a 40% over design.

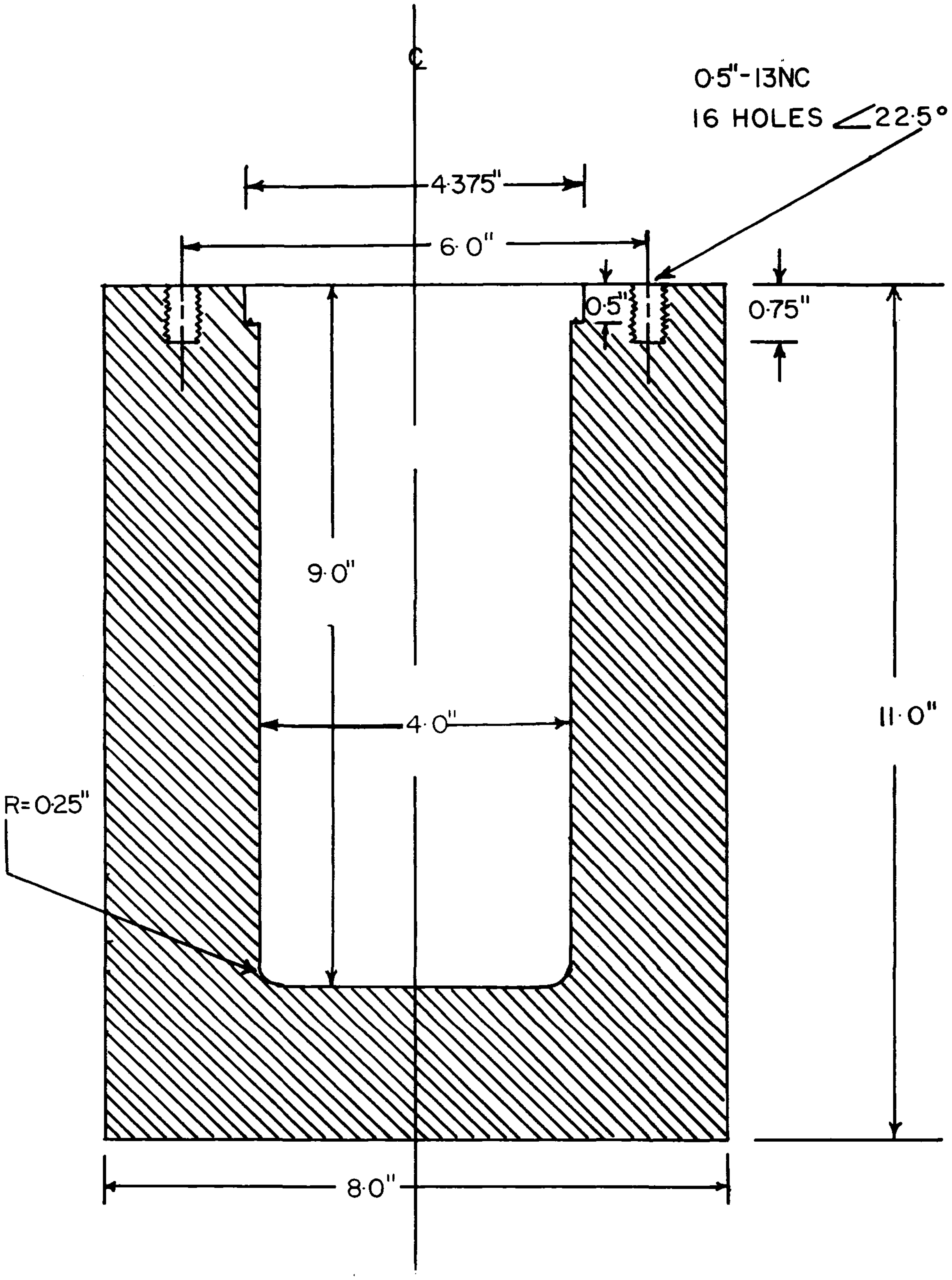
Therefore, the reactor will have a 2.0 in. wall thickness, with an inside radius of 2.0 in. and a corresponding outside radius of 4.0 in. The maximum design pressure will be 15,000 psi., thereby incorporating a 40% over design.

For a 2.0 in. wall thickness the tensile stress at the outer wall by application of equation (III-1) is 14,000 psi. Similarly, the compressive stress is 0 psi. Table 2. summarizes these computations.

Table 2. Stresses on Inner & Outer Surface of Reaction Vessel

	a = 2.0"	b = 4.0"
S_t	35,000 psi.	14,000 psi.
S_r	-21,000 psi.	0 psi

FIGURE 2 DESIGN SPECIFICATIONS FOR REACTOR BODY
CROSS SECTION VIEW·
SCALE 1" = 2"



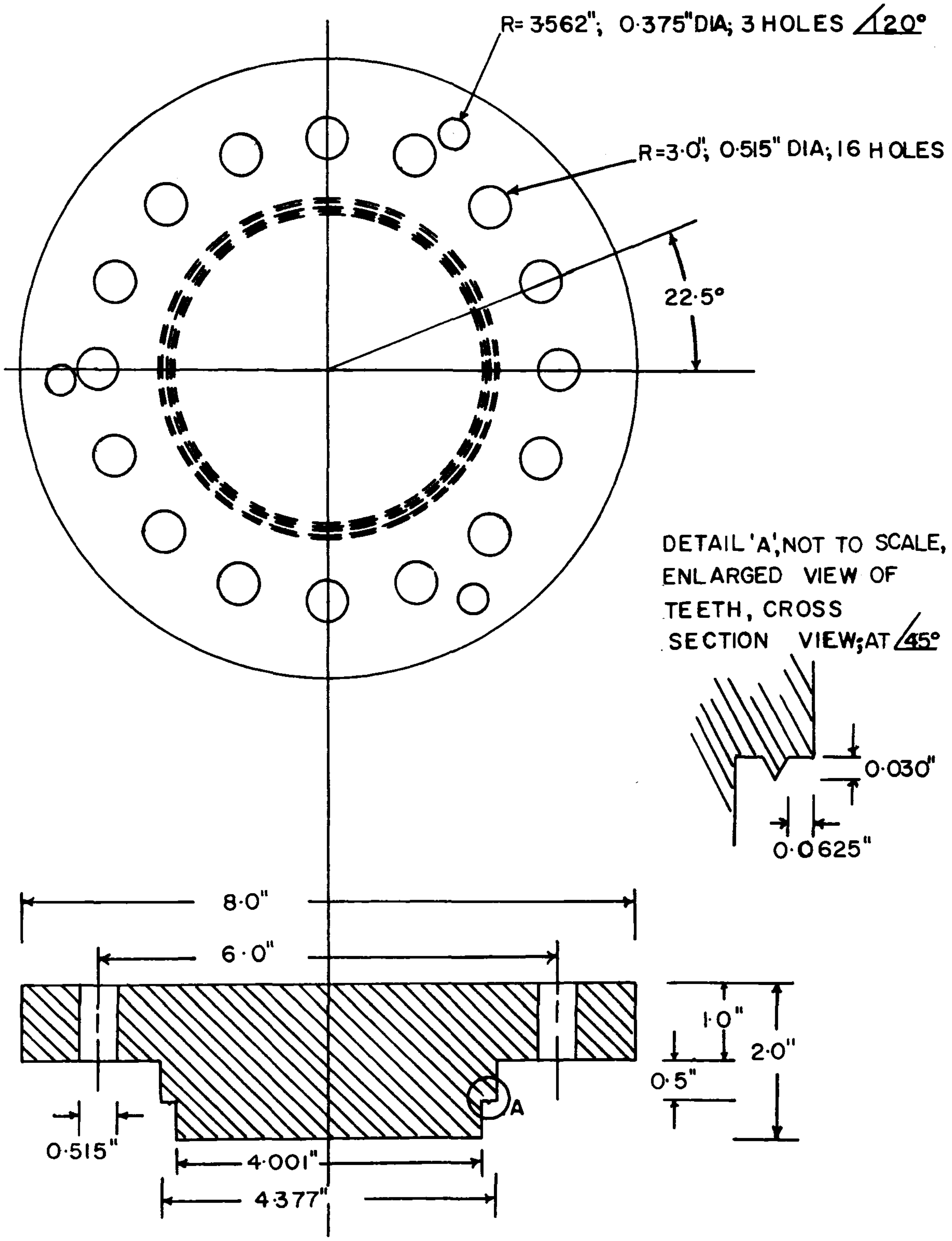


FIGURE 3 DESIGN SPECIFICATIONS FOR REACTOR HEAD PRIOR TO EQUIPMENT INSTALLATION
SCALE 1"= 2"

Figures 2 and 3 indicate the design specifications for construction of the reactor body and head, based upon the foregoing design calculations. With the reactor head in position the inside dimensions of the reactor are 4.0 in. x 8.0 in. The length to diameter ratio is 2.0 .

2) Determination of the Number of Bolts to be Inserted into the Reactor Head.

The bolts employed were 2.0 in. long 1/2 in. diameter unbrako socket head cap screws. These were chosen because of their high tensile strength, 185,000 psi. per bolt. [4].

Let n, be the number of bolts required.

$$S_w = \frac{185,000}{2}$$

$$S_w = 92,500 \text{ psi.}$$

Now

Pressure x Area = number of bolts x area/bolt x tensile strength/bolt.

$$15,000 \times \pi(2)^2 = n \times \pi\left[\frac{1}{4}\right]^2 \times 92,500$$

$$n = 11 \text{ bolts}$$

However, to ensure a smooth and even application of pressure on the gasket and to incorporate a 45% safety factor, sixteen bolts were used. Figure 3 indicates that the holes for the bolts are at an angle of 22.5° from each other and at a distance of 3.0 in. from the centre of the reactor head. Each hole is tapped to a depth of 0.75 in. [ref. Figure 2.]

3) Determination of Thermal Stress.

The reactor is designed to have a maximum operating temperature of 400°C. The thermal stress is calculated by multiplying the elongation by the modulus of elasticity. The producer of unbrako cap screws was unable to provide the physical properties of his product. Consequently, the thermal coefficient of expansion for carbon steel is used in this calculation.

The thermal coefficient of expansion for 316 stainless steel is $8.9 \times 10^{-6} \frac{\text{in}}{\text{in}^\circ\text{F}}$.

The thermal coefficient of expansion for carbon steel is $6.7 \times 10^{-6} \frac{\text{in.}}{\text{in}^\circ\text{F}}$.

The difference in the coefficient of expansion between the stainless steel and the carbon steel is $2.2 \times 10^{-6} \frac{\text{in.}}{\text{in}^\circ\text{F}}$.

Suppose the reactor temperature is 750°F. whilst the ambient temperature is 70°F. This represents a change of 680F°.

Hence the elongation ε is $2.2 \times 10^{-6} \times 680 \frac{\text{in}}{\text{in.}}$

The modulus of elasticity for stainless steel is 28×10^6 psi.

$$\therefore \quad S_{th} = \varepsilon M.$$

$$= 2.2 \times 680 \times 28 \text{ psi.}$$

$$S_{th} = 41{,}880 \text{ psi.}$$

The thermal stress is then 41,880 psi. In addition to this there is the design pressure which the bolts must withstand. This amounts to 940 psi. per bolt. Each bolt must withstand a stress of 42,820 psi. Similarly the stainless steel must withstand this pressure. If the tensile stress of the stainless steel were to drop by 25% at 750°F. the stainless steel would have a tensile stress of 56,000 psi. Therefore it is seen that both the bolts and the stainless steel could adequately withstand the thermal stress. These calculations of course assume that there is no tolerance between the male and female threads. However, they provide a good estimate of the thermal stress.

B. Design of Cooling Coil.

The design of the cooling coil is based on substituting the physical properties of water as estimates for the physical properties of the reacting system whenever the correct information is lacking. This serves as a first order estimate. The function of the cooling coil is to remove the heat of reaction produced, thereby aiding in controlling the temperature.

The heat of reaction for the oxidation of pseudocumene to trimellitic acid is estimated to be 50 kcal. per methyl group substituted on the benzene ring. Therefore it would be 150 kcal. per gmole of pseudocumene. Suppose that it is desired to react six gmole of pseudocumene. The heat of reaction would then be 3,570 Btu. According to Shipman the majority of the reaction occurs within two hours. This would then require the removal of 1,785 Btu/hr.

Both resistances to heat transfer from the reacting fluid and from the cooling water must be estimated. First the outside fluid film coefficient h_o will be estimated.

A Reynolds number of 2,000 is assumed to exist within the reactor. The Reynolds number for the fluid inside the cooling tube is estimated on a flow velocity of eight feet per second. Hence the Reynolds number

N_{Re} for the cooling water is 34,800. [See Figure 4 for physical dimensions].

For water the Prandtl number N_{Pr} is:

$$N_{Pr} = 6.93$$

Ackley[5] has shown that the equation of Chilton and Drew [6]

$$\frac{hc\ de}{k} = 0.17\ (N_{Re})^{0.67}\ (N_{Pr})^{0.37}\ (Vis)^m \left[\frac{de}{D}\right]^{0.5}$$

where m = 0.97 @ 3 cps.

0.18 @ 1,000 cps.

hc = agitated film coefficient when using coils.

de = outside diameter of tubing.

k = thermal conductivity

D = vessel diameter

may be used to estimate the film coefficient for both the inner wall of the vessel and the outer wall of tubular surfaces contained within the vessel. This equation is applicable for a Reynolds number range of $400 < N_{Re} < 15 \times 10^5$.

Therefore according to the equation of Chilton and Drew

$$\frac{hc\ de}{k} = 0.17 \times (2000)^{0.67} \times (6.9)^{0.37} \left[\frac{9}{16 \times 4}\right]^{0.5}$$

$(vis)^m$ is taken to be 1.

$$\therefore \quad \frac{hc\ de}{k} = 21.3$$

$$hc = 21.3 \times 0.347 \times \frac{16 \times 12}{9} \quad \frac{Btu}{ft^2 hr °F}$$

$$hc = 157.5\ Btu/ft^2 hr °F$$

Secondly, the inside film coefficient will be determined.

This film coefficient is obtained by using the equation of Dittus and Boelter [7]

$$(N_{nu})mb = 0.0243\ (N_{Re})mb^{0.8}\ (N_{pr})mb^{0.4}$$

$$= 0.0243\ (34{,}800)^{0.8}\ (6.9)^{0.4}$$

$$\frac{h_iD}{k} = 225$$

$$h_i = 225 \times 0.347 \times \frac{12 \times 16}{9}\ \frac{\text{Btu}}{\text{hr ft}^2\text{°F}}.$$

$$h_i = 1665\ \frac{\text{Btu}}{\text{hr ft}^2\text{°F}}$$

The overall heat transfer coefficient U_o is calculated as follows:

$$\frac{1}{Uo} = \frac{1}{h_c} + \frac{\Delta \times A_o}{kA_m} + \frac{1}{h_i}\frac{Ao}{Ai}$$

$$A_o = \pi \frac{9}{16 \times 12} \ell$$

$$A_m = \pi \frac{7}{16 \times 12} \ell$$

$$A_i = \pi \frac{5}{16 \times 12} \ell$$

$$\frac{1}{U_o} = \frac{1}{157.5} + \frac{\frac{0.125}{12}}{10.7}\left[\frac{9}{7}\right] + \frac{1}{1665}\left[\frac{9}{5}\right]$$

$$\frac{\text{Btu}}{\text{hr°F ft}^2} \qquad \text{ft}\ \frac{\text{Btu}}{\text{hr ft°F}} \qquad \frac{\text{Btu}}{\text{hr°F ft}^2}$$

$$\frac{1}{U_o} = 0.00634 + 0.001251 + 0.00260\ \frac{\text{Btu}}{\text{hr°Fft}^2}$$

$$\frac{1}{U_o} = 0.010191\ \frac{\text{Btu}}{\text{hr°Fft}^2}$$

$$U_o = 98.12 \quad \text{Btu/hr°F ft}^2$$

$$A_o^1 = \pi D \ell = \frac{\pi\ 9}{12 \times 16} \times \frac{13.5}{12} = 0.1655 \text{ ft}^2$$

$$A_o = A_o^1 + \text{area of fins.}$$

$$A_o = 0.1655 + 0.0972 \text{ ft}^2$$

$$A_o = 0.2627 \text{ ft}^2$$

Suppose the reactor is operating at 750°F. and the water is at 70°F. The amount of heat removed by the coil is as follows:

$$Q = U_o A_o \Delta T.$$

$$= 98.12 \times 0.2627 \times 680 \ \frac{\text{Btu}}{\text{hrft}^2\text{°F}} \ \text{ft}^2\text{°F}$$

$$Q = 17{,}527.7 \ \frac{\text{Btu}}{\text{hr.}}$$

Since upon reacting six moles of pseudocumene only 1,785 $\frac{\text{Btu}}{\text{hr.}}$ must be removed, then it is seen that the cooling capacity of the coil is ten times as great as is actually required. This first order approximation shows that the cooling coil will be capable of handling the heat load. This is of prime importance if violently exothermic reactions are to be studied in the future.

Figure 4. illustrates the design specifications for the cooling coil. The cooling coil is constructed from No. 316 stainless steel.

The ends of the cooling coil were fitted with 1/4 in. tubing, 1/8 in. NPT compression fittings.

In addition to the cooling coil, a safety valve, thermocouples, pressure gauge, feed, sample line and a bleed valve were installed into the reactor head. The design specifications for installation of these components are illustrated in figures 5 and 6. Only the area

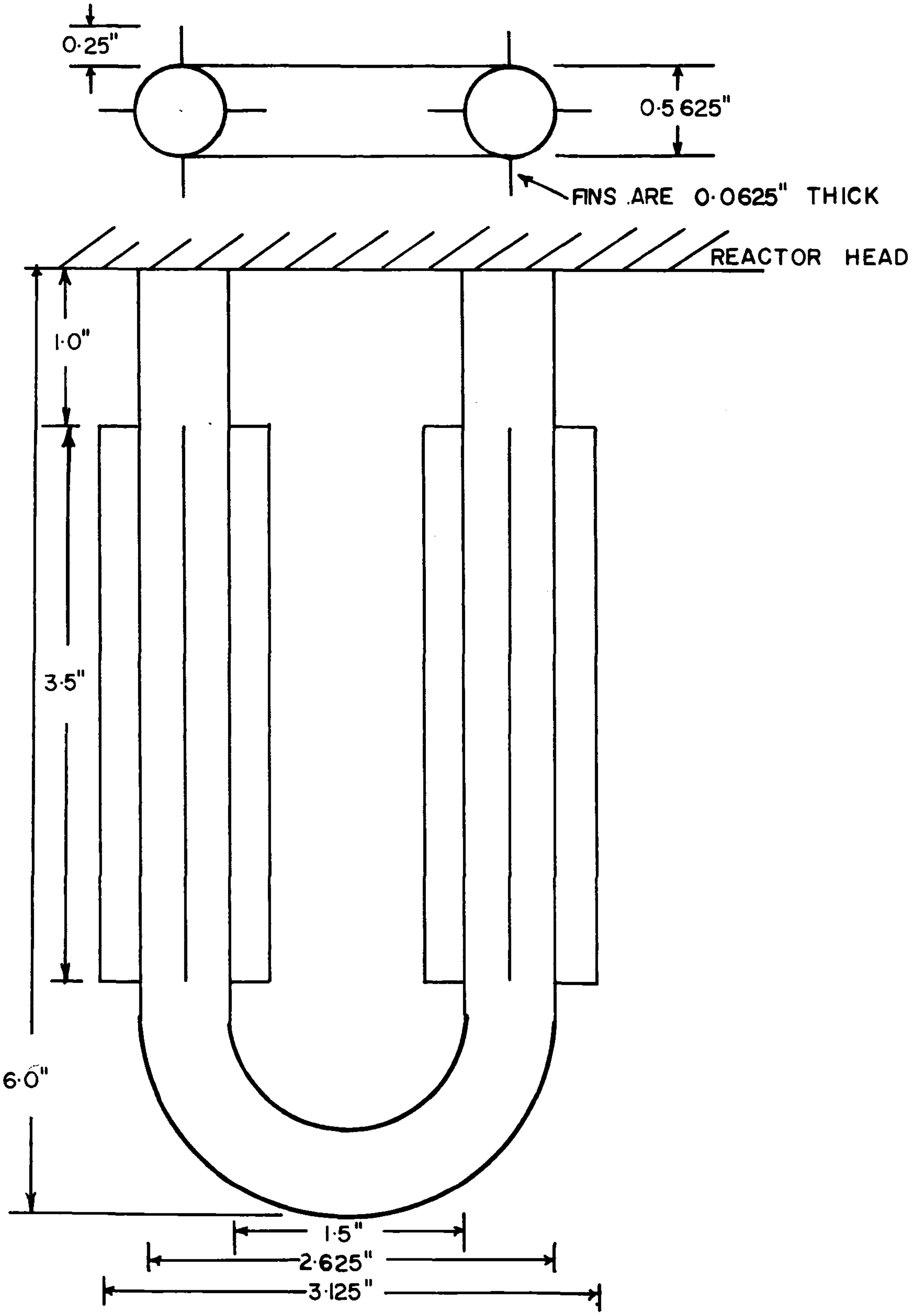


FIGURE 4 DESIGN SPECIFICATIONS FOR COOLING COIL TO BE INSTALLED INTO REACTOR HEAD
SCALE 1" = 1"

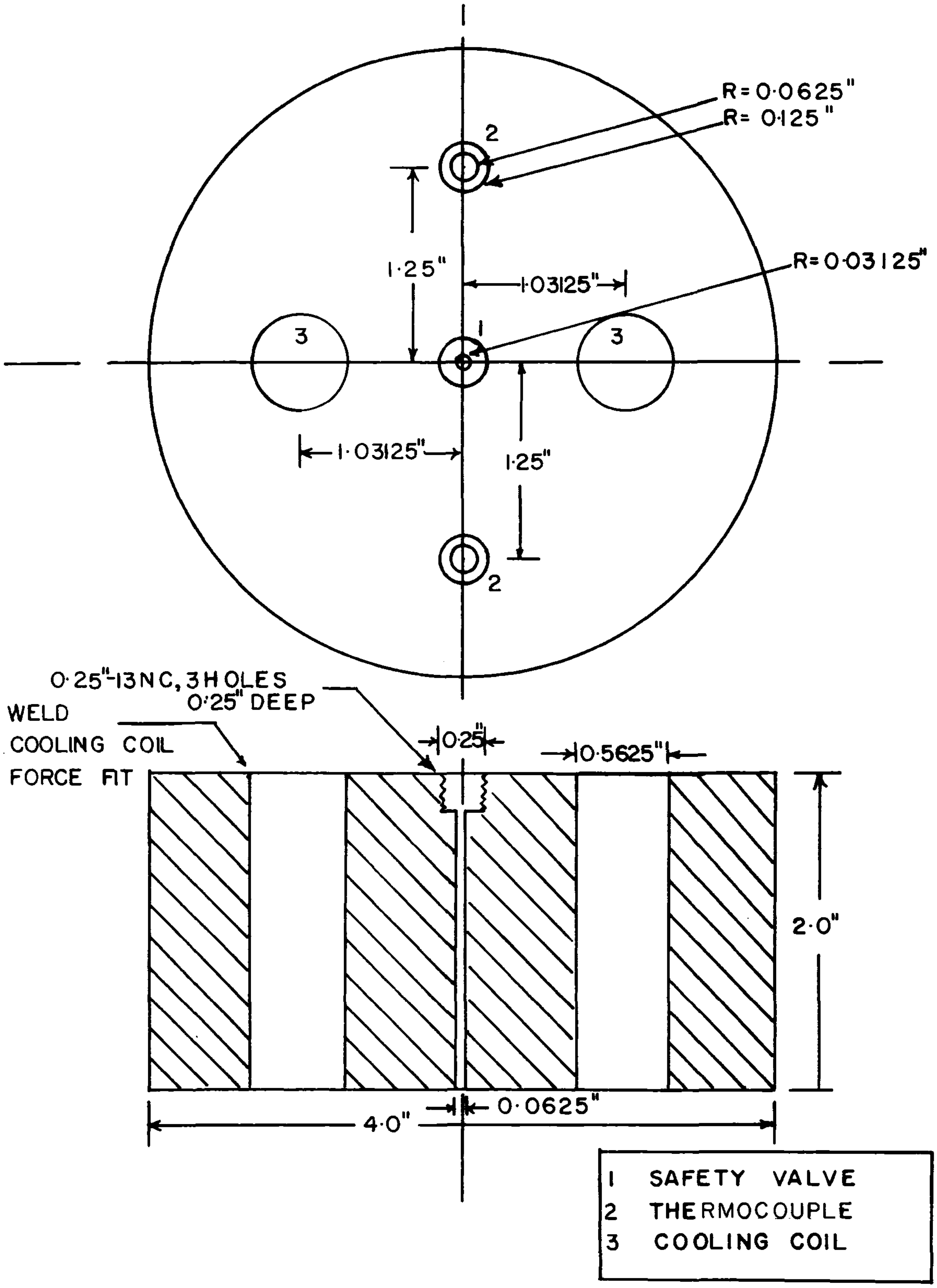


FIGURE 5 DESIGN SPECIFICATIONS FOR INSTALLATION OF SAFETY VALVE, THERMOCOUPLES & COOLING COIL INTO REACTOR HEAD. SCALE 1"= 1"

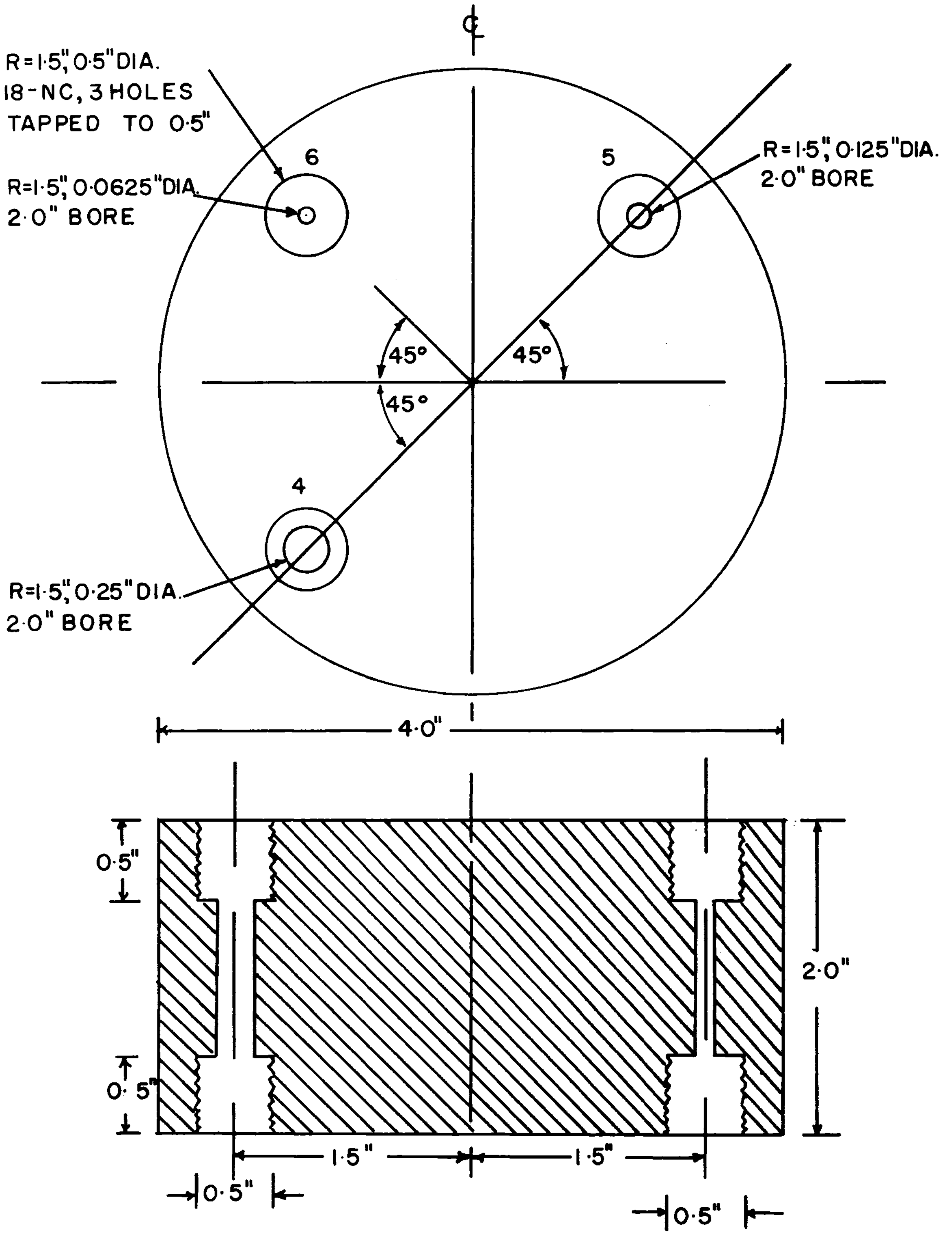


FIGURE 6 DESIGN SPECIFICATIONS FOR INSTALLATION OF FEED & SAMPLE LINES, BLEED VALVE & PRESSURE GAUGE CONNECTION INTO REACTOR HEAD.
SCALE 1"=1"

4 FEED LINE
5 SAMPLE LINE
6 BLEED VALVE & PRESSURE GAUGE CONNECTION

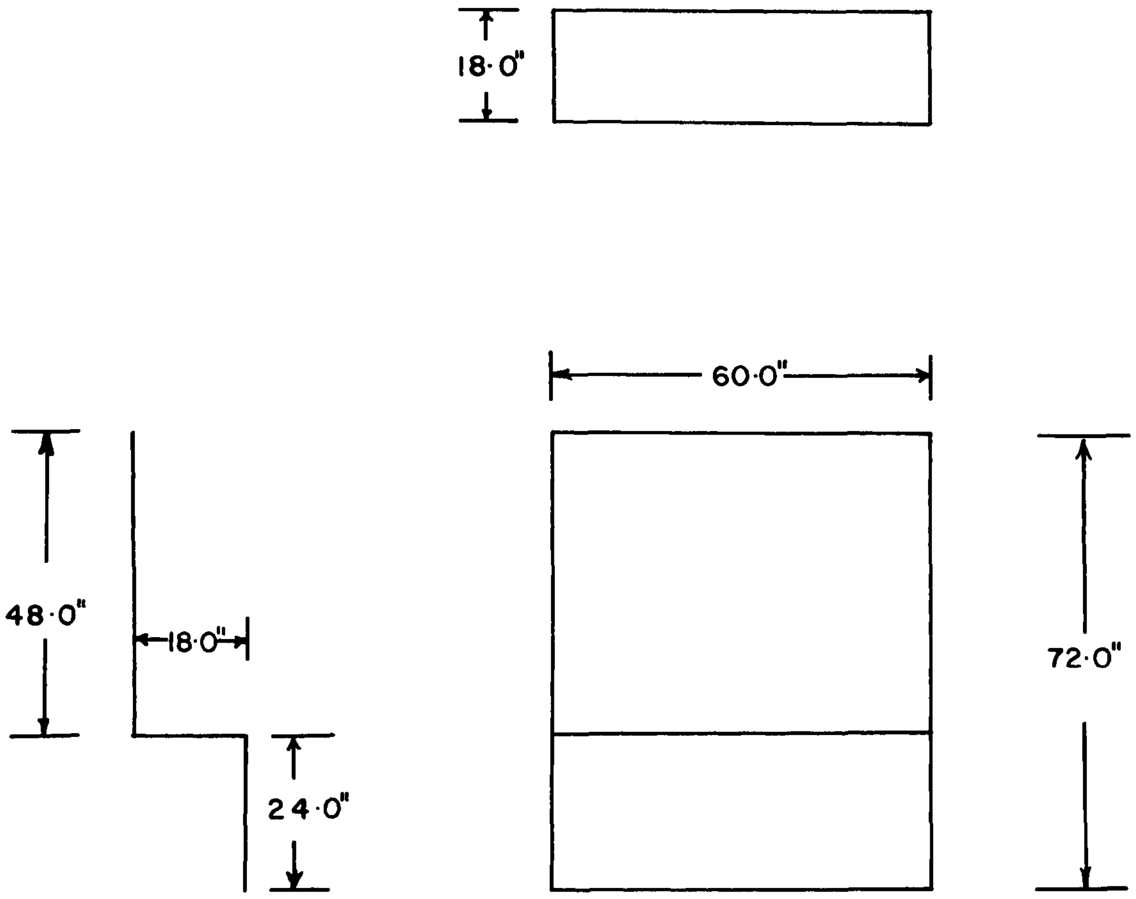


FIGURE 7 FRONT PANEL OF PROTECTIVE SHIELD CONSTRUCTED FROM 0·25" STEEL PLATE
FRONT, TOP & SIDE VIEW. SCALE 1 CM = 12"

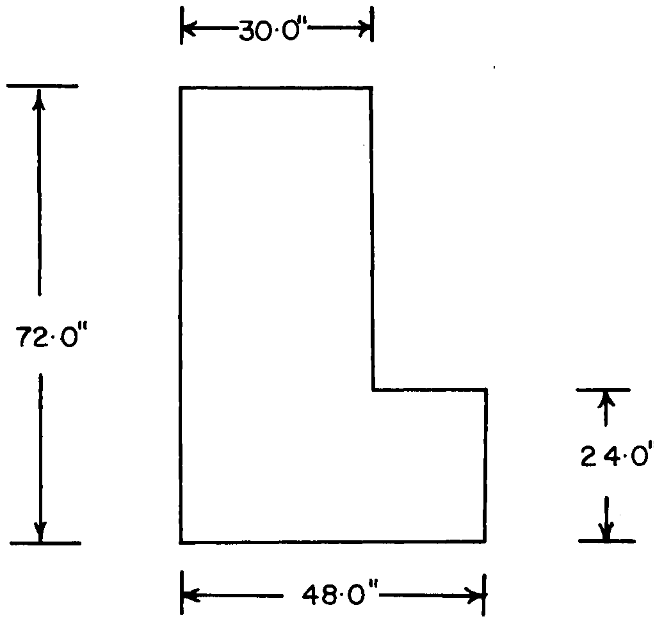


FIGURE 8 LEFT SIDE PANEL OF PROTECTIVE SHIELD. SCALE 1 CM = 12"

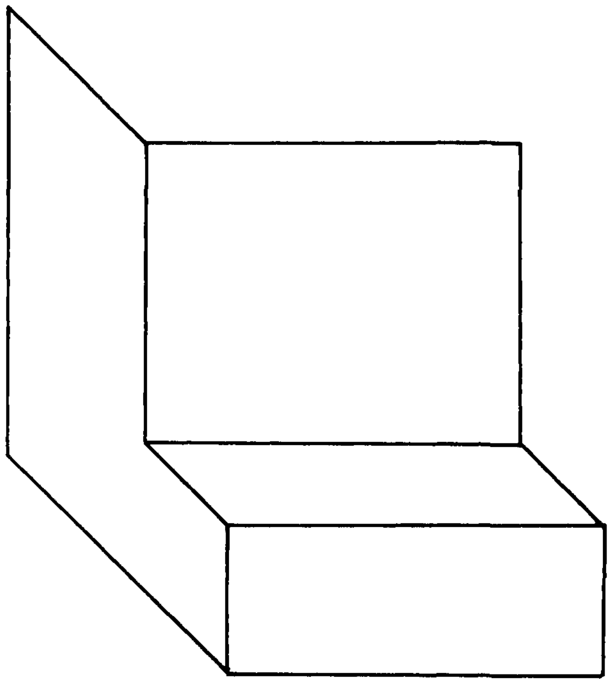
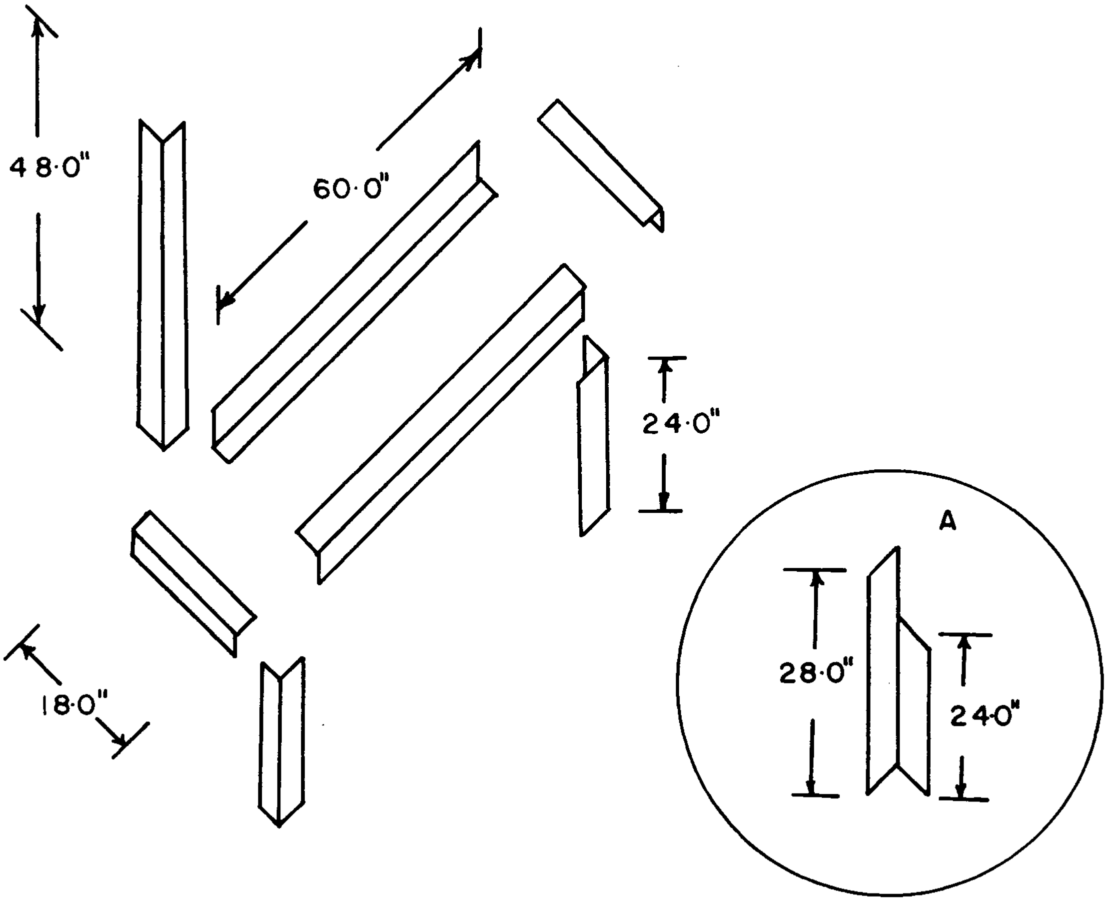


FIGURE 9 SKETCH OF PROTECTIVE SHIELD. NOT TO SCALE



SPECIFICATIONS

ONE 48·0"X2·0"X2·0"X0·125"
TWO 60·0"X2·0"X2·0"X0·125"
TWO 18·0"X2·0"X2·0"X0·125"
TWO 24·0"X2·0"X2·0"X0·125"
ONE AS IN "A", 2·0"X2·0"X0·125"

FIGURE 10 EXPLODED VIEW INDICATING ANGLE IRON LAYOUT FOR PROTECTIVE SHIELD. NOT TO SCALE which is directly over the reactor volume is indicated in the drawings.

Figures 8, 9, 10 illustrate the design of the protective shield which is constructed from 0.25 in. steel plate.

The volume of the reactor with all the equipment in place is calculated to be 1568 cm^3. [Ref. Appendix I].

The heaters for the reactor were connected in parallel in order that the maximum power may be obtained. In this configuration a total 30.4 amperes of electricity is drawn. The power output is 3,500 watts.

Appendix I contains the part list, calibration curves and design information for the auxiliary equipment.

IV. PROCEDURE

The reactor was charged with pseudocumene and then assembled. Sulfur dioxide was then charged to the reactor under its own vapor pressure through a check valve. In order to completely fill the reactor, the bleed valve was opened until the reaction mixture emerged and then shut off. The system was then brought to the reaction temperature and maintained at the temperature with the aid of the cooling coil. The pressure was monitored with time.

At the end of the reaction, the products were either blown off via the sample line or the system was cooled, the reactor dismantled and the products removed for analysis.

V. RESULTS AND DISCUSSION OF AN EXPLORATORY STUDY INTO THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE

Following the procedure described in chapter IV, pseudocumene was oxidized in the liquid phase by sulfur dioxide. Two runs were made at the following conditions:

(i) reaction temperature of 272.5°C ± 3.0C° and pseudocumene concentration of 1.19 gmole/ℓ.

(ii) reaction temperature of 251.9°C ± 3.0C° and pseudocumene concentration of 3.72 gmole/ℓ.

The observations for the experimental runs are summarized under the following headings:

A) Observed Pressure Behaviour.

B) Product Separation and Analysis.
   (i) Extraction Process.
   (ii) Product Composition.
   (iii) Product Identification.

A) Observed Pressure Behaviour.

Figure 11 and 12 are indicative of the behaviour of total pressure with time during the respective runs. At the higher temperature and lower concentration of pseudocumene, the reaction commenced almost immediately; while at a higher pseudocumene concentration and lower temperature a rather long induction period was observed. Once the reaction began, however, the pressure drop per minute for the linear portion of the curve is about four times as great for the run with

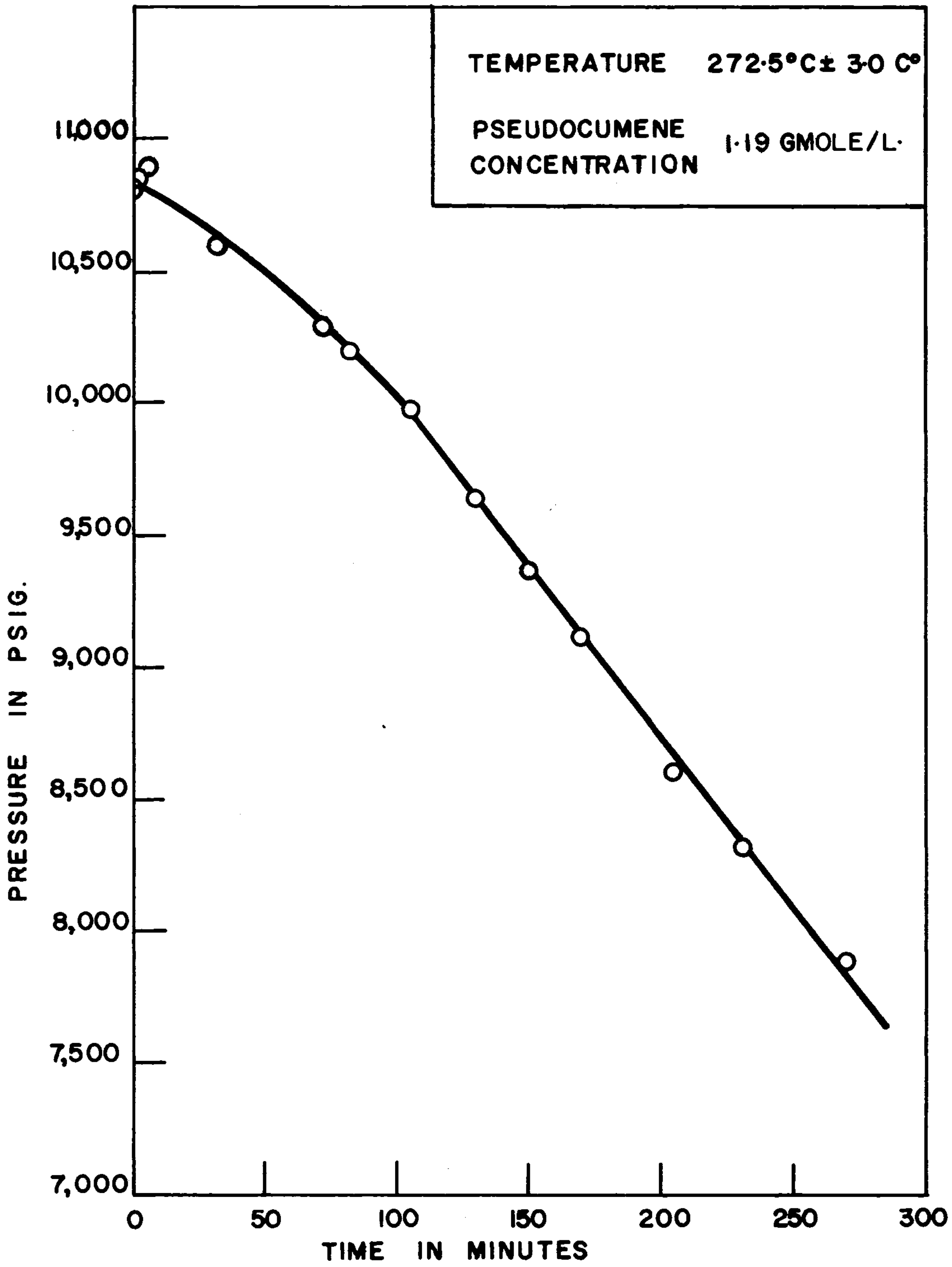


FIGURE II RUN I PRESSURE VERSUS TIME CURVE FOR THE REACTON BETWEEN PSEUDOCUMENE & SULFUR DIOXIDE MIXTURE

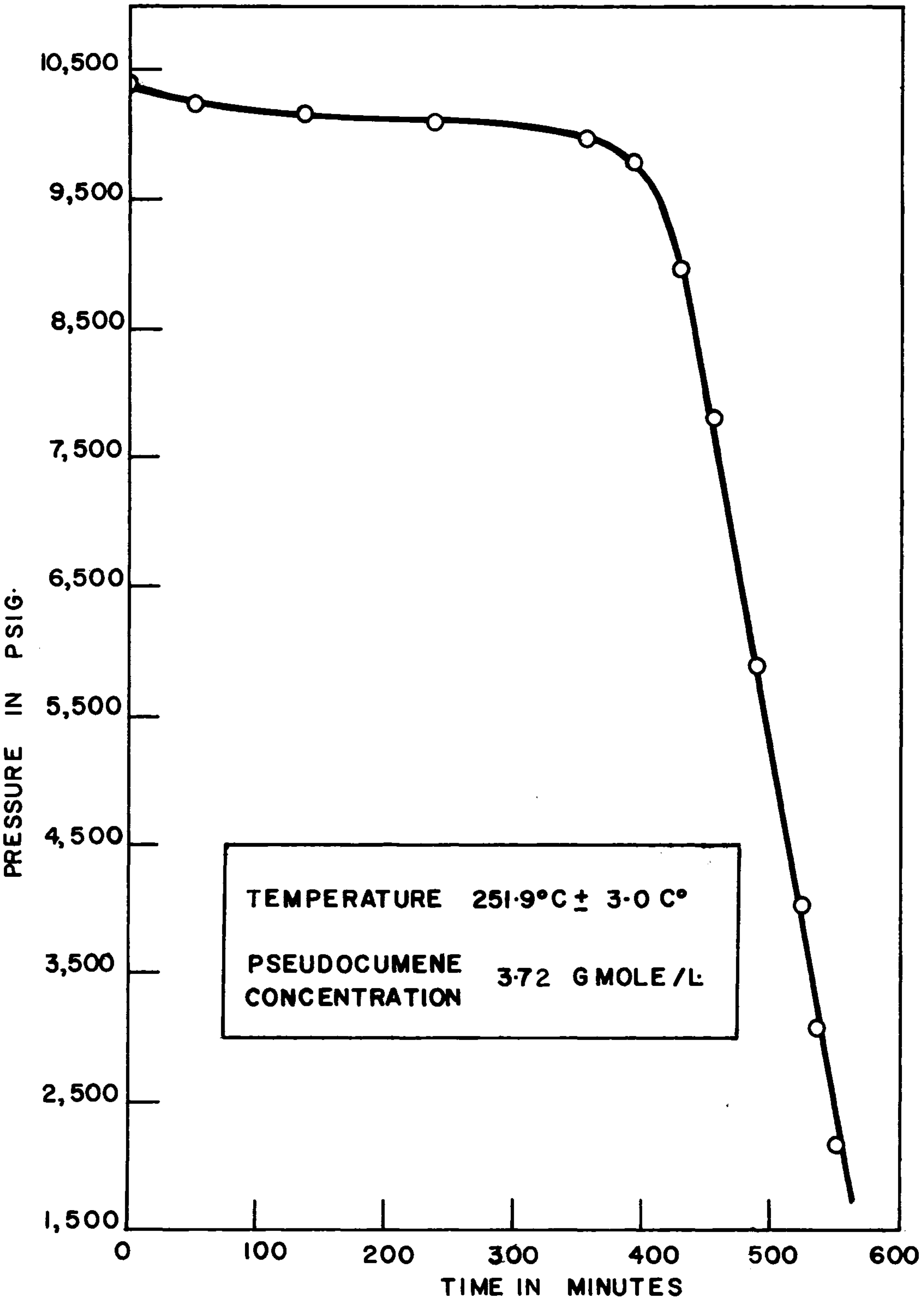


FIGURE 12 RUN 2 PRESSURE VERSUS TIME CURVE FOR THE REACTION BETWEEN PSEUDOCUMENE & SULFUR DIOXIDE MIXTURE

lower temperature and higher pseudocumene concentration.

Both runs were made under isothermal conditions with the temperature varying not more than ± 3.0C°.

The data accompanying figures 11 and 12 is listed in appendix III.

B) Product Separation and Analysis.

The products obtained from the oxidation runs were of a black-brown colour and subjected to the following treatment and analysis.

(i) Extraction Process.

The product was dissolved in acetone and filtered. The residue was washed with water. No product was obtained upon evaporation of the washing water. An extraction was carried out on the filtrate using copious quantities of distilled water and petroleum ether. Decolourizing carbon was used to remove impurities in the resulting solutions which were then filtered out. The purified product was crystallized from the water solution and dried. Similarly products were crystallized from the petroleum ether solutions.

(ii) Product Composition.

It is assumed that the reaction products constitute a homogeneous mixture and therefore the samples analyzed are representative.

(1) Run No. 1.

An 11.22 gram sample of crude product was purified according to the extraction process indicated in the preceding section. The following products were obtained.

Per cent based upon the dried sample.

black crud	16.77%

light brown product	25.90%
yellow product crystallized from carbon disulfide solution	16.14%
white product crystallized from distilled water	4.03%
white product crystallized from petroleum ether	18.25%
reddish-brown and black solid resembling pieces of rusted iron	16.77%
products accounted for	97.86%
products unaccounted for	2.14%
TOTAL	100.00%

Per cent based upon undried sample.

fluid	58.02%
black crud	7.04%
light brown product	10.87%
yellow product crystallized from carbon disulfide solution	6.77%
white product crystallized from distilled water	1.69%
white product crystallized from petroleum ether solution	7.66%
reddish-brown and black solid resembling pieces of rusted iron	7.04%
products accounted for	99.09%
products unaccounted for	.91%
TOTAL	100.00%

The fluid obtained is a mixture of pseudocumene and water. The individual amounts of each were not ascertained. Based upon the assumption that the fluid is all pseudocumene the product yield would be 25.7%.

(2) Run No. 2.

A 20.68 gram sample of crude product was analyzed and found to have the following composition.

Per cent based upon the dried sample.

black crud	72.16%
sulfur	8.06%
white product	12.27%
yellow deposit	4.48%
products accounted for	97.57%
products unaccounted for	2.43%
TOTAL	100.00%

Per cent based upon the undried sample.

fluid	46.03%
black crud	39.26%
sulfur	4.35%
white product	6.62%
yellow deposit	2.42%
product accounted for	98.68%
product unaccounted for	1.32%
TOTAL	100.00%

Similarly as in Run No. 1, the fluid was a mixture of pseudocumene and water; the relative amounts of each were not ascertained. However if the fluid is assumed to be pseudocumene a yield of 54.7% results.

A total of 13.52 grams of solid sulfur were deposited inside the reactor in Run No. 1 and 91.83 grams were deposited in Run No. 2.

(iii) Product Identification.

Efforts were directed mainly towards establishing whether any carboxylic acid products are formed. All other compounds are not of much interest from a commercial point of view and can be properly classified as byproducts.

Melting points were determined as an initial step in product identification. The black crud from Run No. 1, exhibited a melting point range of 305-310°C, while that of Run No. 2 emitted a yellow vapor at 150°C with subsequent melting at 209 to 230°C.

The dirty yellow solid product obtained from Run No. 1, melted to form an amber liquid in the range 119-122°C. This solid dissolved readily in carbon disulfide. This substance is believed to be sulfur since it has the melting point of sulfur and is highly soluble in carbon disulfide. The same product was also obtained from Run No. 2.

The reddish-brown product from Run No. 1, melted between 195-205°C, forming a tarry black liquid. This substance was insoluble in water. However, its infrared spectrogram indicated that in all probability it was a carboxylic acid. An elemental analysis revealed it to be composed of 65.86% carbon, 4.21% hydrogen, 16.83% oxygen and 11.70% sulfur. It should be mentioned here that the sample purity was somewhat questionable.

The mustard yellow solid product obtained from Run No. 2, began to sublime at 155°C. At 235°C slight decomposition occurred exhibiting a colour change - cream yellow to light brown. At 280°C sublimation was complete.

A pale yellow solid product obtained from Run No. 1, prior to the quantitative sampling, had a definite melting point range of 282-285°C. The pale yellow product did not exist in the quantitative sample as such. However, it may have been extracted from the quantitative sample as a purified product, having a white colour. On one occasion the product sublimed at 270°C. Previously a slight colour change to an amber brown at 237°C had indicated product decomposition. A sample of this product was dissolved in neutral distilled water. The resulting solution had a pH of approximately 5. The infrared spectogram of this product indicates an aromatic carboxylic acid containing at least one methyl group on the ring. The elemental analysis for this product indicated a composition of 61.97% carbon, 4.59% hydrogen, 31.02% oxygen and 2.02% sulfur. A sodium fusion and test for sulfur did not indicate any sulfur content. The sulfur test was repeated several times. This absence of sulfur in the compound would appear to indicate that the 2.02% sulfur existed as an impurity in the sample sent for analysis. The sample was dissolved in distilled water and treated with sodium bicarbonate; an evolution of colourless gas was observed. This is indicative of a carboxylic acid group.

No melting point was obtained in the range from 20°C to 300°C for the white solid product obtained from Run No. 1. However slight sublimation of the product occurred at 180°C. Similarly from Run No. 2 the white powder product decomposed and simultaneously vaporized at 290°C. The decomposition began at 155°C and was very slow.

Upon decomposition the product changed colour from white to amber to light brown. A purified sample of this powder sublimed between 255-290°C with no decomposition. Test for sulfur content was negative. The elemental analysis for this sample indicated a composition of 49.95% carbon, 4.27% hydrogen, 33.74% oxygen, 1.40% sulfur and 14.16% ash. However, again the purity of the sample is questionable. A distilled water solution of this product yielded a pH of 5. This solution was treated with sodium bicarbonate and an evolution of a colourless gas was observed. This is indicative of the carboxylic acid group. The infrared spectrogram of this product indicated that it was an aromatic carboxylic acid with at least one methyl group on the benzene ring.

On the basis of this information speculation can be made as to the structure of the acid obtained. Of the mono and di, carboxylic acids of pseudocumene, the pale yellow product resembles the dicarboxylic acid most, on the basis of an elemental analysis, even though the samples were likely to be impure. The comparison is given in Table 3.

Table 3. Speculative Comparison of the Pale Yellow Product with the Dicarboxylic Acid of Pseudocumene

	%C	%H	%O
dicarboxylic acid of pseudocumene	59.98	4.48	35.54
yellow product	61.97	4.59	31.12

The equivalent weight of the dicarboxylic acid of pseudocumene is 180·07 gm. An effort was made to elucidate the equivalent weight of the acid by titration, using phenolthalein as indicator. Table 4 indicates the equivalent weights so determined.

Table 4. Equivalent Weight of Acid Products

Run	Product Description	Equivalent Weight gm/eq.
1	pale yellow product	120.69 121.21
1	white product	179.31 157.10
2	white	187.19 180.29

However, the information so far obtained is insufficient to conclusively establish the structure of the acid product.

VI. CONCLUSIONS AND RECOMMENDATIONS

The reaction system designed operates successfully up to 11,200 psig., with the aluminium gasket employed. Temperature control can be achieved to within ± 3.0C°.

The uncatalyzed oxidation of pseudocumene by sulfur dioxide in the liquid phase is feasible. An aromatic carboxylic acid is produced by this oxidation and the reaction rate is strongly dependent upon the pseudocumene concentration. Studies employing a constant pseudocumene concentration with temperature as a variable and vice versa could be readily undertaken to elucidate the kinetics of this oxidation. Experiments to ascertain whether an excess of sulfur dioxide is required to oxidize the three methyl groups of pseudocumene may be worthwhile.

The blow off of products, when hot, allows loss of any water vapor formed, consequently the reactor should be cooled and dismantled to recover the products. An alternative would be the installation of a trap to recover the blow off.

Since product identification was not very easy, greater efforts should be made to establish a suitable analytical procedure to qualitatively and quantitatively analyze the products. A distillation of the sample to determine the amount of unreacted pseudocumene and water present would be worthwhile.

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VIII. NOMENCLATURE

S_r	compressive stress
S_t	tensile stress
$S_{t\ Max}$	maximum tensile stress
S_w	working stress
Sult	ultimate stress
S_{th}	thermal stress
a	internal radius
b	outside radius
P_o	outside guage pressure
P_i	internal pressure
r	radius
N	safety factor
n	number of bolts required
π	pi
ε	elongation
M	modulus of elasticity
N_{Re}	Reynolds number
N_{Pr}	Prandtl number
h_c	agitated film coefficient when using coils
h_i	inside film coefficient
d_e	outside diameter of tubing
k	thermal conductivity
D	vessel diameter
m	exponent

(vis)	viscosity
N_{nu}	Nusselt number
mb	mean bulk
U_o	overall heat transfer coefficient based upon outside area
Δx	wall thickness of cooling coil
A_o	outside area
A_i	inside area
A_m	mean area
A'	outside surface area of tube
ℓ	length of cooling coil
Q	heat load
ΔT	temperature difference
gmole/ℓ	gram mole per liter
°C.	degrees centigrade
C°	centigrade degrees
T_b	normal boiling point temperature
T_c	critical temperature
M*	molecular weight
P_c	critical pressure
Δp	change in pressure

APPENDIX I.

DESIGN DETAILS & PARTS SPECIFICATION

(i) Parts List.

The following constitutes a parts list for the system designed.

No.	Catalogue No.	
1	10-4792-J	1/8 in. pencil type thermocouples include 12 in. long leads
2	10-4792-L	
3	W125	1/8 in. Ermeto W125 connection
4		1/4 in. O.D., 0.083 in. I.D. super pressure rating of 60,000 psi., made of 316 S.S.
5		1/8 in. O.D., 1/16 in. I.D. AE annealed tubing, with a pressure rating of 15,000 psi. made from 316 S.S.
6		5/16 in. O.D., 1/16 in. I.D. super pressure quality tubing, pressure rating 100,000 psi., made of 316 S.S.
7	30VM4081	1/4 in. x 0.083 in., Valve, 30,000 psi. connection nomenclature F250C
8	60VM4072	1/4 in. x 0.083 in., Valve, 60,000 psi. connection nomenclature F250C.
9	CK04400	1/4 in. x 0.083 in., O-Ring check valve (supply O-Ring to withstand liquid SO_2)
10	CL4400	1/4 in. x 0.083 in. elbows.
11	60F4433	Couplings 1/4 in. AE Cone Female F250C To 1/4 in. AE Cone Female F250C
12	60F4533	Couplings 1/4 in. AE Cone Female F250C To 5/16 in. AE Cone Female F312C100
13	CT4440	1/4 in. x 0.083 in., F250C Tees (AE Cone)
14		9/16 in. x 5/16 in., 15,000 psi. super pressure quality tubing 316 S.S.
15	P483	0-15,000 psig., 316 S.S. bourbon tube, pressure gauge, minor interval values 100 psi., F250C connection, 4-1/2 in. dia. include interchangeable dial cover retaining rings to permit panel mounting.

No.	Catalogue No.	
16	CS4600	1/4 in. x 1/8 in. Universal Safety head connection nomenclature SW250.
17		Inconel rupture discs - disc size 1/4 in. rupture rating 15,000 psi.
18	HN30N	Hand pump, 30,000 psi.

The above items are purchased from Valve Engineers, Division of Autoclave Engineers Inc., Erie, Pennsylvania.

19	1100H14	0.081 in. thick aluminium sheet for gaskets. Aluminium sheet is 99% aluminium purchased from Atlas Alloys, Windsor, Ont.
20		Metalon pipe insulation for 8 in. I.D. pipe. I.D. insulation 8.5 in.
20	UPMF 12/2	Selector switch for thermocouples. Thermovolt Instruments.
21	#316	Stainless steel round bar stock 8 in. dia. x 11 in. long oversize for machine cleaning.
22	#316	Stainless steel round bar stock 8 in. dia. x 12 in. long oversize for machine cleaning.
23		1/4 in. male threaded needle valve. Matheson of Canada, Limited.
24	4-8708-SP	875 watt 8 in. length 8-1/4 in. inside dia. 16 groves, 115 volts, 1/4 cylindrical electrical heating units. Hevi-duty Electric Co., Watertown, Wisconsin.
25	SP-87	Horseshoe magnet 155 lb. holding force. Alnico 5.
26	SP-257	1/2 in. x 3-1/2 in. Alnico centreless ground piece magnet bar with 316 stainless steel sheath. Storch Products Co. Ltd., Detroit, Michigan.
27	6-150	Cinch Jones Barrier Terminal. Block dimensions 1-13/16 in. x 35/32 in.

(ii) To Determine the Volume of the Reaction Vessel.

$$\text{Volume of the reaction vessel} = \pi \times 4 \times 8 = 32\,\pi\ \text{in}^3 = 1647.39\ \text{cm}^3$$

Volume occupied by the cooling coil	54.73 cm^3
Volume occupied by the thermocouples	1.01 cm^3 1.11 cm^3
Estimated volume of the feed tube	5.23 cm^3
Estimated volume of the sample line	0.33 cm^3
Estimated volume of the magnetic stirrer	13.82 cm^3
Estimated volume of the bolt heads	2.51 cm^3
	78.74 cm^3

Vessel volume	1647.39 cm^3
Total occupied volume	78.74 cm^3
Free volume	1568.65 cm^3

The free volume of the reactor is calculated to be 1568.65 cm^3. Figure 13 represents the calibration curve for the pressure gauge. The pressure gauge has a range from 0-15,000 psi.

Table 5. Data for Pressure Gauge Calibration

Gauge Reading psi.	Correct Reading psi.
2,000	1,950
4,000	3,975
6,000	5,975
8,000	7,950
10,000	9,950
12,000	12,025
14,000	14,150
14,500	14,750

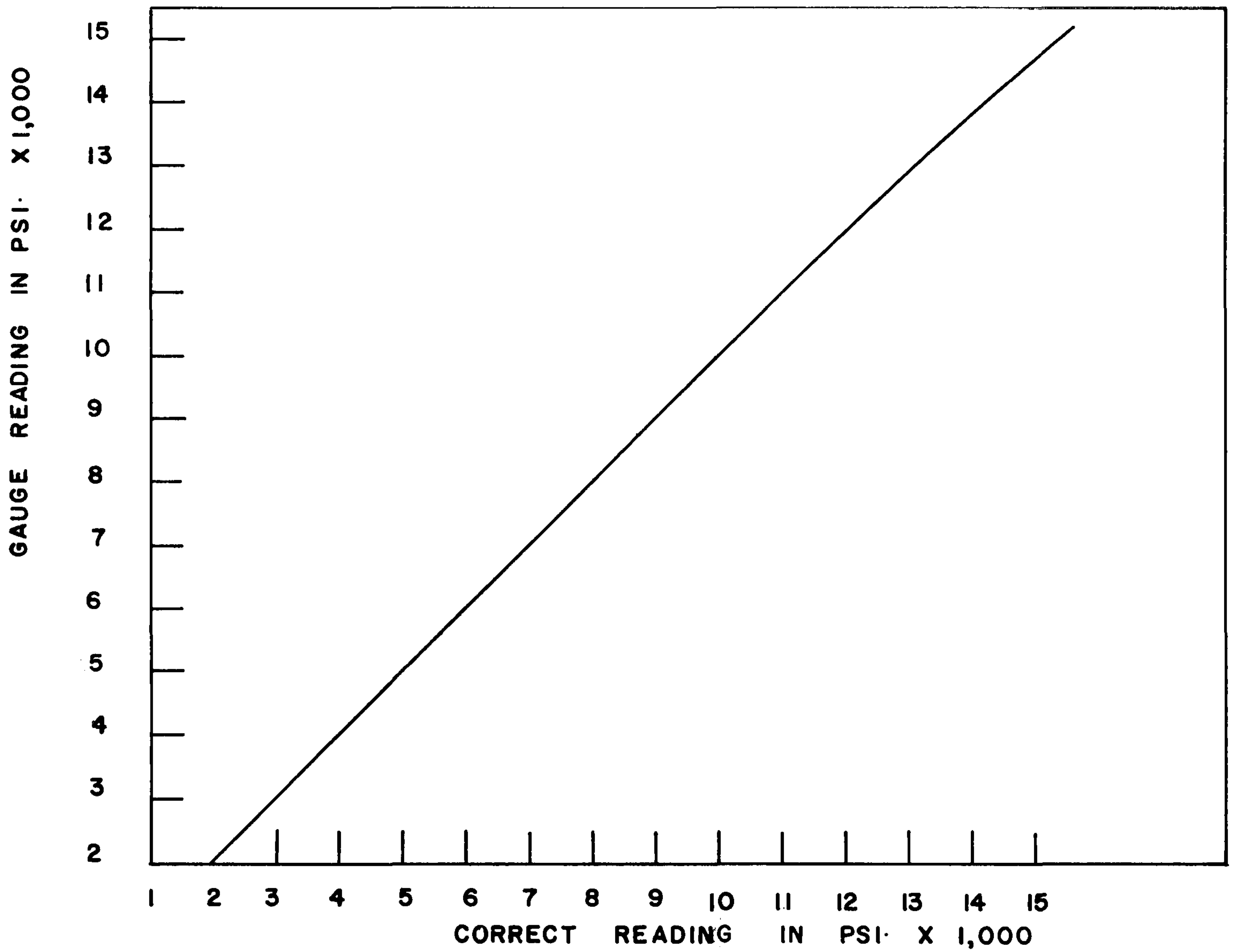


FIGURE 13 CALIBRATION CURVE FOR PRESSURE GAUGE

Table 6. Data for Thermocouple Calibration.

Thermocouple No. 1 °C	Thermocouple No. 2 °C	Mercury Thermometer ± 0.1C°
98.4	95.3	96.2
78.2	75.2	75.9
61.9	62.0	62.1
57.3	57.1	57.2
52.8	50.7	52.2
48.9	48.1	48.8
41.9	41.5	42.5

The average temperature deviation based on the mercury thermometer is ± 0.9C° for both thermocouples.

Figure 14 and 15 are the schematic diagrams for the temperature controller, and motor controller.

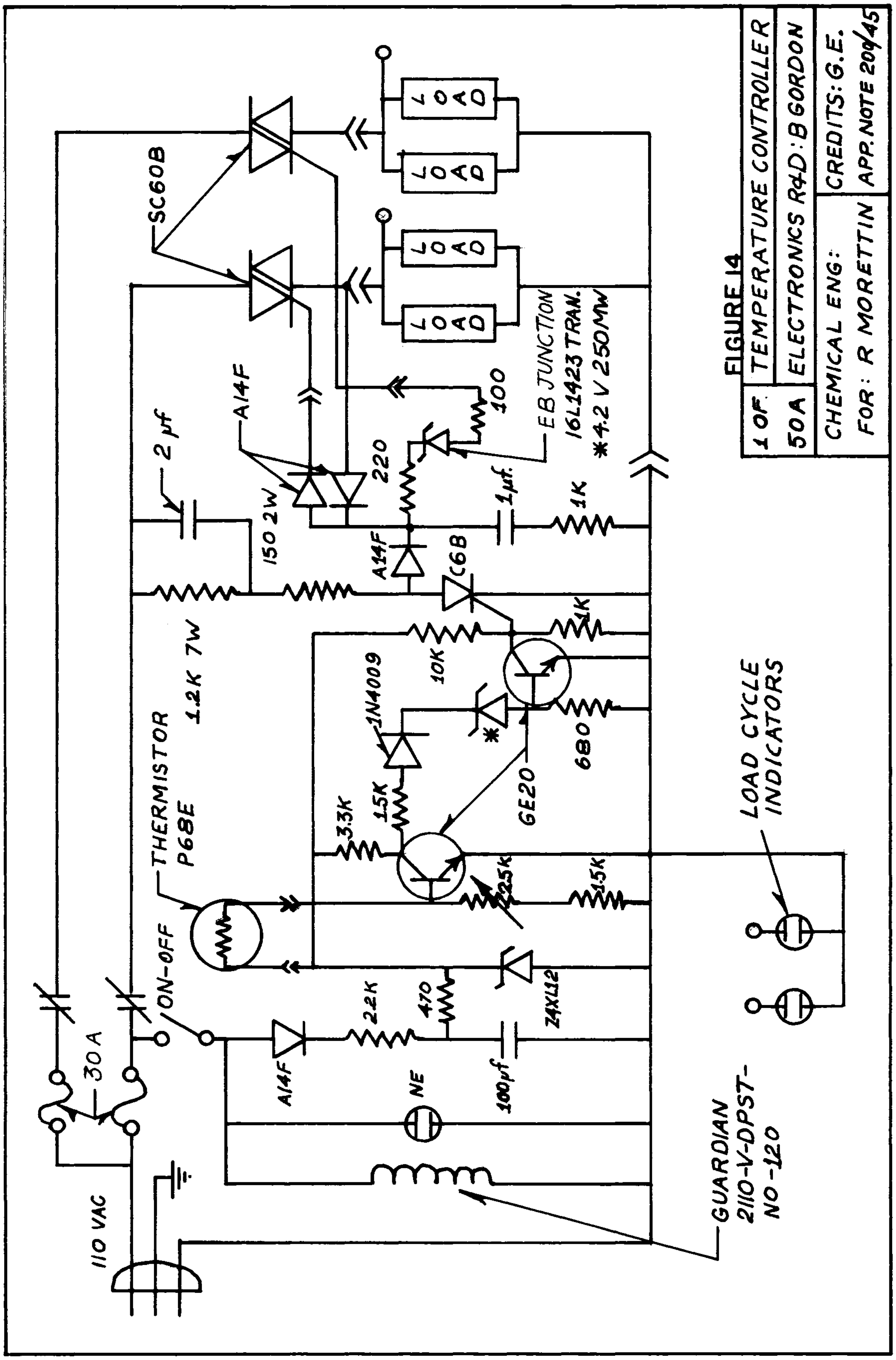


FIGURE 14

TEMPERATURE CONTROLLER

ELECTRONICS R&D: B GORDON

CHEMICAL ENG:

FOR: R MORETTIN

CREDITS: G.E.

APP. NOTE 200.45

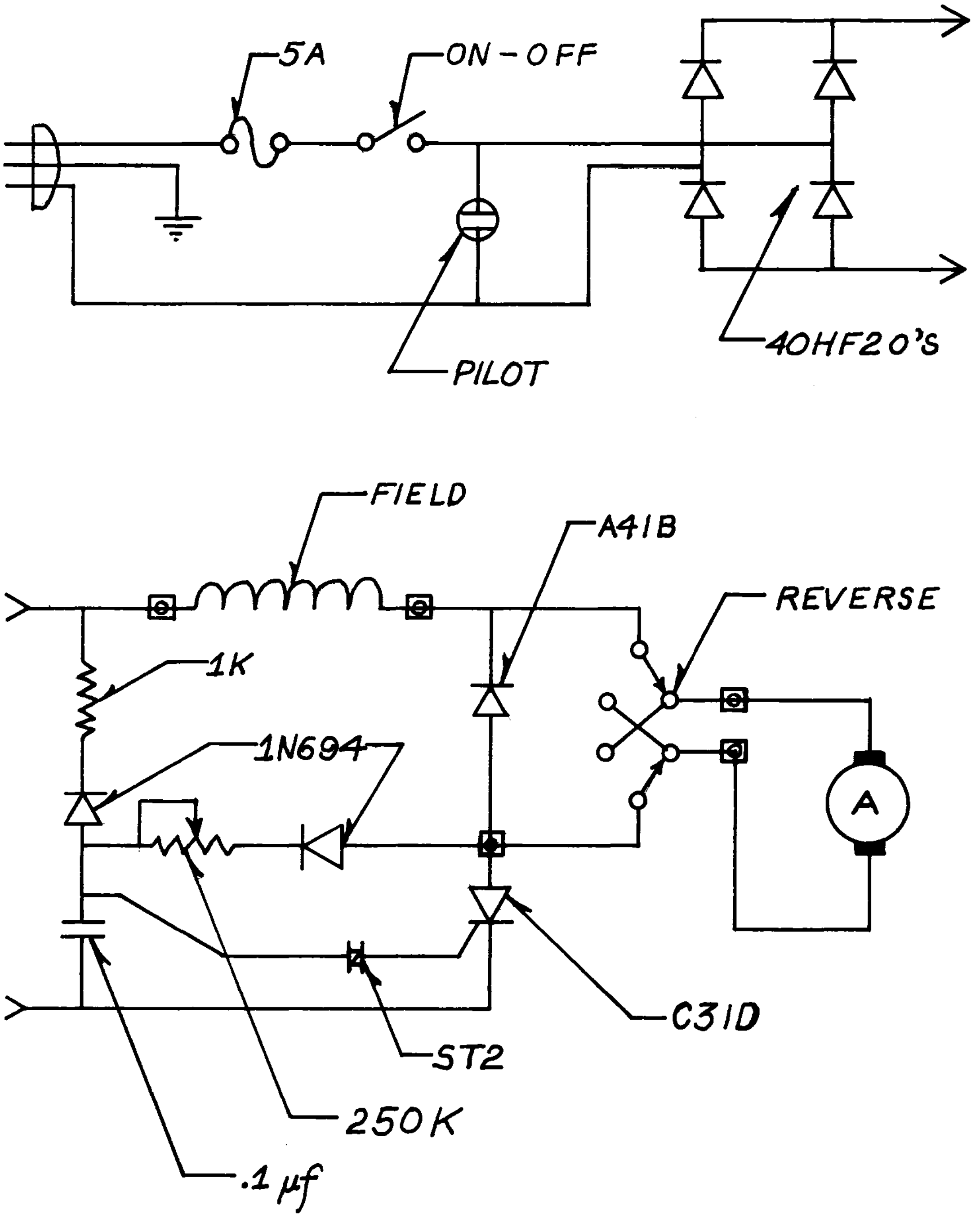


FIGURE 15

S	8/2/69	MOTOR CONTROLLER
B	23/11/69	FOR: CHEM: ENG:
T	10/12/69	ELECTRONICS R&D.
D	3/2/70	BY: B.P. GORDON

(iii) Parts List for Temperature Controller.

No.	Quantity	Code
1	1	1ZV1W Zener; GEZ4XL12
2	2	16L1423 Transistor or BZY56 4.2/4.4 V. Zener
3	2	1N4009 Diodes
4	2	GE A14B Diodes
5	3	GE A14F Diodes
6	2	GE SC60B Triacs
7	3	100 Ω, 1/2 watt Resistors
8	1	2.2 k, 1/2 watt Resistors
9	1	220 Ω, 1/2 watt Resistors
10	2	1.5 k, 1/2 watt Resistors
11	2	1 k, 1/2 watt Resistors
12	1	680 Ω, 1/2 watt Resistors
13	1	10 k, 1/2 watt Resistors
14	2	470 Ω, 1 watt Resistors
15	1	150 Ω, 2 watt Resistors
16	1	1.2 k, 10 watt Resistors
17	1	2.5 k, 1 watt Potentiometer
18	1	100 μf/25 or 50 volt Capacitor
19	1	1 μf Mylar 200 volt Phillips
20	1	2 μf Mylar 200 volt Phillips
21	2	G.E. 20 NPN Si Transistors
22	1	G.E. 81B154 Bead Thermistor (400°C)
23	1	G.E. C6BSCR 1.6A 200 PRV
24	1	Hammond 1429-1 Cabinet

No.	Quantity	Code
25	1	Hammond 1443-22 Chassis
26	1	Hubble Connector #3330
27	1	Hubble Connector #3331
28	1	Hubble Connector #3333
29	1	Hubble Connector #3334
30	1	SPST ON-OFF Switch Selfix
31	1	2180A15 (Red) Pilot Light
32	2	2180A15 (Amber) Pilot Light
33	1	Amphenol 80 PC2F
34	1	Amphenol 80 MC2M
35	1	PC Board 4" x 6"
36	2	Busman Fuses 20 Amp REN.
37	4	Fuse Holder Clips 5674-41
38	1	Plexiglass Insulator
39	1	Guardian D.P.S.T. Relay, 25A, Lews 2110U/120 V. Coil.
40	2	NC 303-NN Heat Sinks
41	1	Length of 4 Lead Cable
42	1	Shielded Cable for Thermistor, 6 ft.

(iv) Parts List for Motor Speed Controller.

No.	Quantity	Code
1	4	40HF20 IR Rectifier Diodes
2	1	Fuseholder
3	1	Moulded Three Wire Line Cord Beldon 17236-S
4	1	D.P.D.T. Switch Reversing.
5	1	4 Pin Socket (F) Cinch S-304-DB
6	1	4 Pin Plug (M) Cinch P-304-CCT
7	1	A14B G.E. Diode
8	2	1N694 Diode
9	1	G.E. ST2 Diac
10	1	C31D G.E. 25 Amp. 400 volt PRV
11	1	SPST Switch (ON-OFF)
12	1	250 k, 1 watt Potentiometer
13	1	1 k, 1 watt
14	1	0.1 μf Capacitor
15	1	Barrier Terminal Strip
16	1	2-1/2 Amp. Slow Blow Fuse
17	1	Hammond 1411 Q

APPENDIX II.

PHYSICAL PROPERTIES

Table 7. Physical Properties of Pseudocumene 1, 2, 4 - Trimethylbenzene.

molecular formula	C_9H_{12}
molecular weight	120.20
melting point	-60.5°C.
boiling point	169.5°C. @ 1 atm.
density	0.889 gm/cm^3
refractive index	1.5044
critical temperature	380.42°C.
critical pressure	27.82 atm.
insoluble in water	
soluble in alcohol, ether, and benzene	

Table 8. Physical Properties of Sulfur Dioxide.

molecular formula	SO_2
molecular weight	64.07
vapour pressure @ 70°F.	34.4 psig.
specific volume @ 70°F.	5.9 ft^3/lb.
melting point	-75.5°C.
boiling point	-10.0°C.
specific gravity, gas 1 atm., 0°C. (Air = 1)	2.264
specific gravity liquid @ 0°C.	1.434
density gas 0°C., 1 atm.	2.927 gm/ℓ
critical temperature	157.5°C.
critical pressure	77.8 atm.
critical density	0.524 gm/cm^3
latent heat of vapourization at boiling point	94.9 cal/gm
latent heat of fusion @ melting point	27.6 cal/gm
specific heat liquid @ 0°C.	0.318 cal/gm°C.
specific heat gas @ 15°C. 1 atm. Cp	0.1516 cal/gm°C.
specific heat gas @ 15°C. 1 atm. Cv	0.1175 cal/gm°C.
specific heat ratio, Gas, Cp/Cv	1.29
thermal conductivity @ 32°F.	$0.0050\ \frac{\text{Btu}}{\text{hr ft}^2\ \frac{{}^\circ\text{F.}}{\text{ft.}}}$
gas viscosity @ 18°C.	0.01242 cps.
solulibility in water @ 0°C.	18.59% (by weight)
irritating gas readily detectible in concentrations of	3-5 ppm.

Commercial grade sulfur dioxide was employed having the following specifications.

Table 9. Specifications for Commercial Grade Sulfur Dioxide.

sulfur dioxide	99.9% min.
moisture	100 ppm. max.
nonvolatiles	50 ppm. max.
acidity (as H_2SO_4)	10 ppm. max.
colour	water white.

Table 10. Physical Properties of Water

molecular formula	H_2O
molecular weight	18.01
refractive index liquid	1.333
specific gravity	1.0
melting point	0°C.
boiling point	100°C.
viscosity liquid	1.002 cps.
heating capacity Cp @ 25°C. 1 atm.	0.998 cal/gm°C.
thermal conductivity k	0.347 $\frac{\text{Btu}}{\text{hr ft °F.}}$

Table 11. Physical Properties of No. 316 Stainless Steel.

Composition	18% Cr., 11% Ni, 25% Mo. 0.10% C. max. Fe. Bal.
Yield strength	30,000 - 120,000 psi.
Tensile strength	90,000 - 150,000 psi.
Elongation	50% in 2 in.
Density	0.29 lbm/in^3
Specific gravity	8.02
Melting point	2500 - 2550°F.
Specific heat (32-212°F)	0.12 Btu/lb$_m$°F.
Thermal expansion coefficient (32-212°F)	8.9 x 10^{-6} in/in°F.
Thermal conductivity (32-212°F)	113 Btu/ft^{2}hr°F in. 10.7 Btu/ft^2°F ft.
Tensile modulus of elasticity	28 x 10^6 psi.
Hardness brinell	165 - 275

Table 12. Physical Properties of Aluminium.

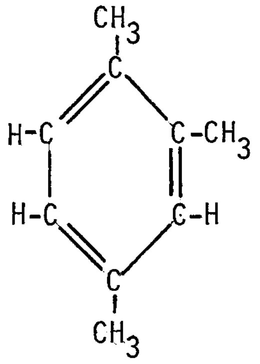
Composition	99% Al.
Yield strength	5,000 - 22,000 psi.
Tensile strength	13,000 - 24,000 psi.
Density	0.098 lbm/in^3
Specific gravity	2.71
Melting point	1190 - 1215°F.
Specific heat (32-212°F)	0.23 Btu/lb°F.
Thermal expansion coefficient @ 68°F.	$13.1 \times 10^{-6} \frac{\text{in}}{\text{in}^\circ\text{F}}$.
Thermal conductivity	$1540 - 1510 \frac{\text{Btu}}{\text{ft}^2\text{hr}^\circ\text{F in}}$.
Tensile modulus of elasticity	10×10^6 psi.
Hardness brinell	23

Table 13. Physical Properties of Carbon Steel.

Composition	0.2% C, 0.25% Si 0.45% Mn. Fe bal.
Yield strength	38,000 - 62,000 psi.
Tensile strength	65,000 - 90,000 psi.
Hardness brinell	130-179
Density	0.284 lb/in^3
Specific gravity	7.86
Melting point	2760°F.
Specific heat (32-212°F)	0.107 Btu/lb°F.
Thermal expansion coefficient (32-212°F)	$6.7 \times 10^{-6} \frac{in}{in}$ °F
Thermal conductivity	360 $Btu/ft^2hr°F$ in.
Tensile modulus of elasticity	30×10^6 psi.

Estimation of the critical temperature and pressure of pseudocumene [30].

A) Critical Temperature.



$$\frac{Tb}{Tc} = 0.567 + \Sigma\Delta T - (\Sigma\Delta T)^2$$

$$\begin{array}{llllll}
3(\ -\overset{\overset{H}{|}}{C}=\ ) & \equiv & 3(0.011) & = & 0.033 & \\
3(\ -CH_3\ ) & \equiv & 3(0.020) & = & 0.060 & \\
3(\ =C=\ ) & \equiv & 3(0.011) & = & \underline{0.033} & \\
 & & & & 0.126 & = \Sigma\Delta T
\end{array}$$

$$T_b = 442.5°K$$

$$\frac{442.5}{T_c} = 0.6772$$

$$T_c = 653.42°K = 380.42°C.$$

B) Critical Pressure.

$$\sqrt{\frac{M^*}{P_c}} = 0.34 + \Sigma\Delta p$$

$$\begin{array}{lllll} 3(\ -\overset{\overset{\displaystyle H}{|}}{C}=\ ) & \equiv & 3(0.154) & = & 0.462 \\ 3(\ =C=\ ) & \equiv & 3(0.198) & = & 0.594 \\ 3(\ -CH_3\ ) & \equiv & 3(0.227) & = & \underline{0.681} \\ & & & & 1.737 \quad = \quad \Sigma\Delta p \end{array}$$

$$\sqrt{\frac{120.20}{P_c}} = 0.34 + 1.737$$

$$P_c = 27.82 \text{ atm.}$$

For these formulae the following symbols apply.

T_b = normal boiling point °K.

T_c = critical temperature.

M^* = molecular weight

P_c = critical pressure.

APPENDIX III

PRESSURE VERSUS TIME DATA FOR THE EXPERIMENTAL RUNS.

Table 14. Data for Run No. 1

Temperature 272.5°C ± 3.0C°

Pressure psig	Time Minutes
10,800	0
10,850	2
10,900	5
10,600	32
10,300	73
10,200	86
9,980	105
9,650	129
9,375	150
9,125	170
8,600	209
8,325	237
7,900	272

Table 15. Data for Run No. 2.

Temperature 251.9°C ± 3.0C°

Pressure psig	Time Minutes
10,400	0
10,250	52
10,190	137
10,100	239
9,990	358
9,800	394
8,990	431
7,825	457
7,100	474
5,900	492
4,750	514
4,050	525
3,100	538
2,200	554

APPENDIX IV

INFRARED SPECTRA OF REACTION PRODUCTS

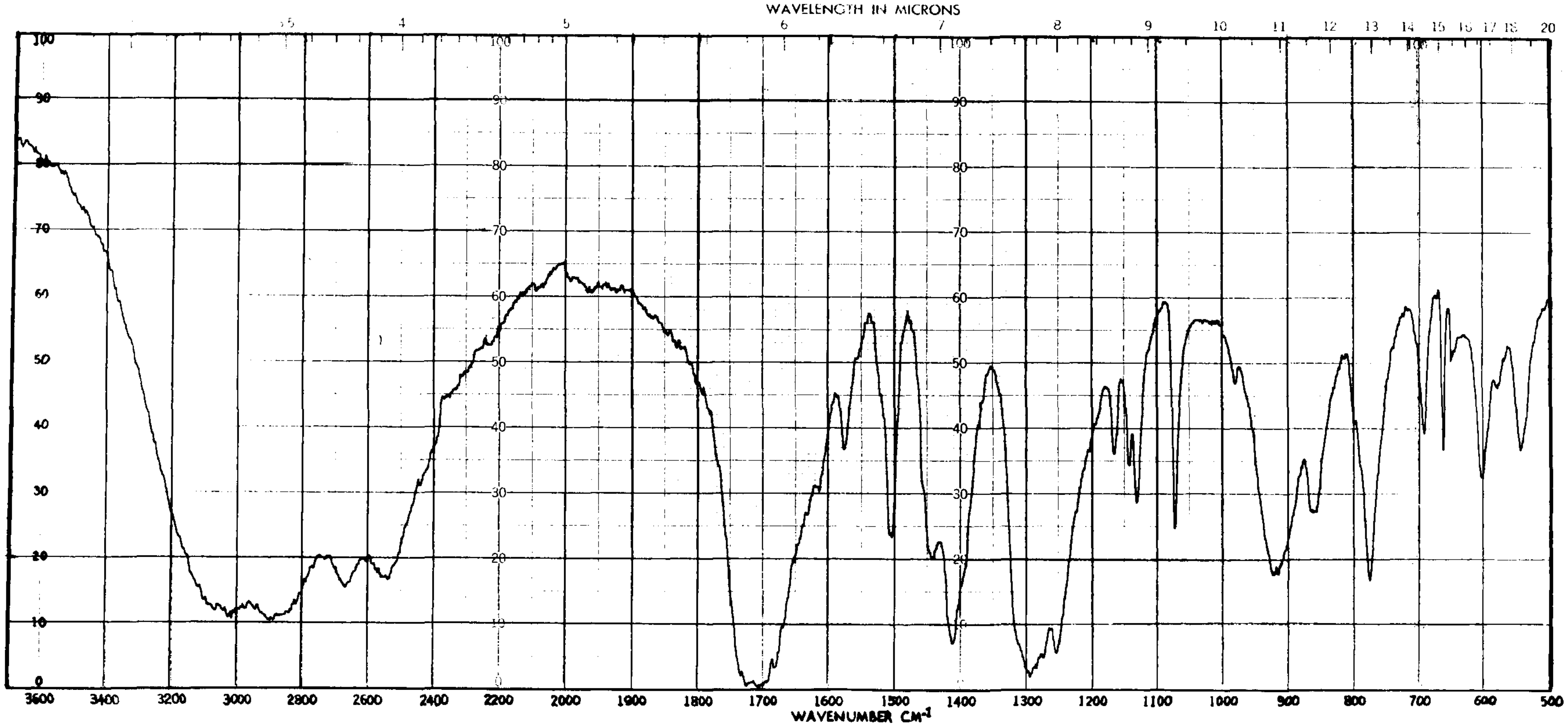


FIGURE 16. INFRARED SPECTRUM OF TRIMELLITIC ACID

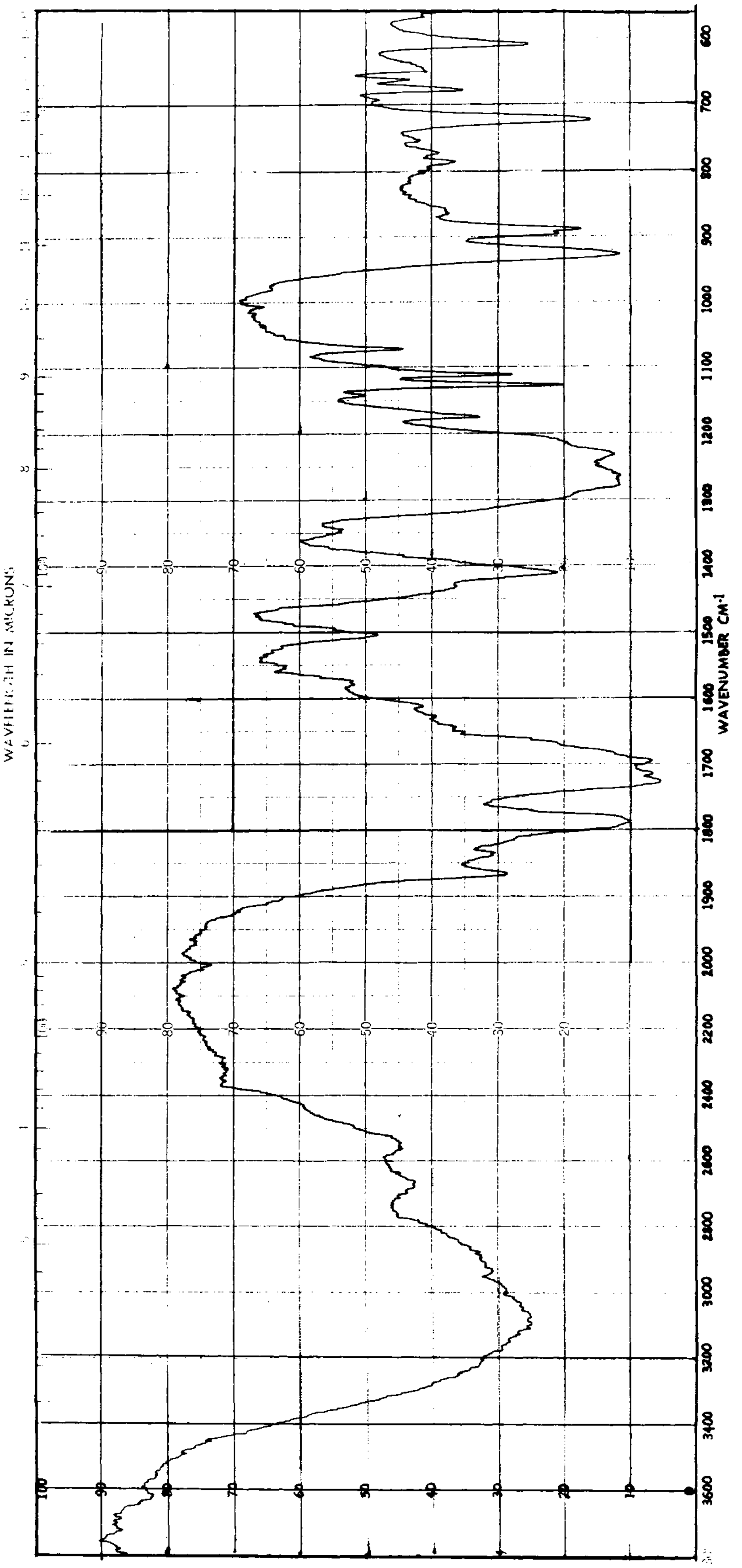


FIGURE 17. INFRARED SPECTRUM OF TRIMELLITIC ANHYDRIDE

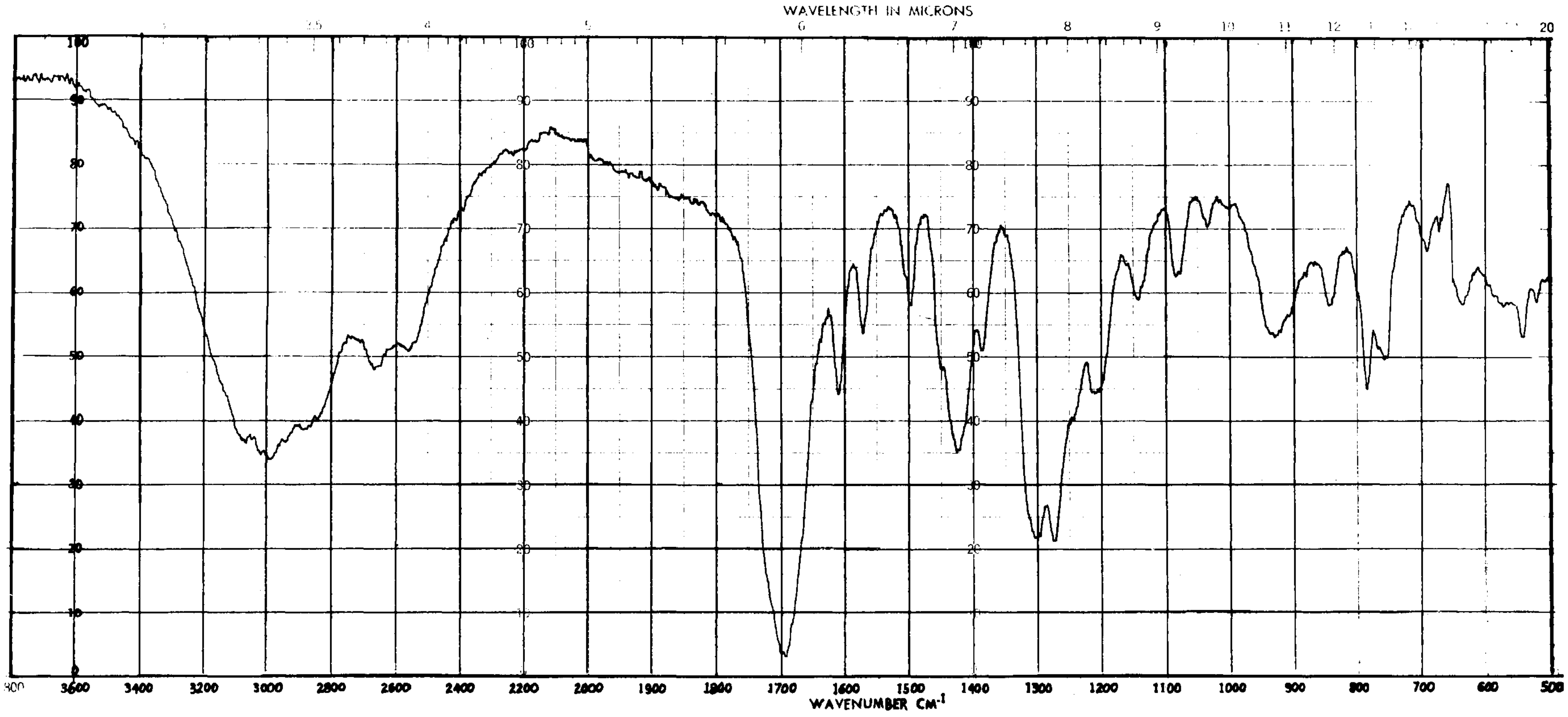


FIGURE 18. INFRARED SPECTRUM OF THE OXIDATION PRODUCT OF PSEUDOCUMENE [PALE YELLOW PRODUCT]

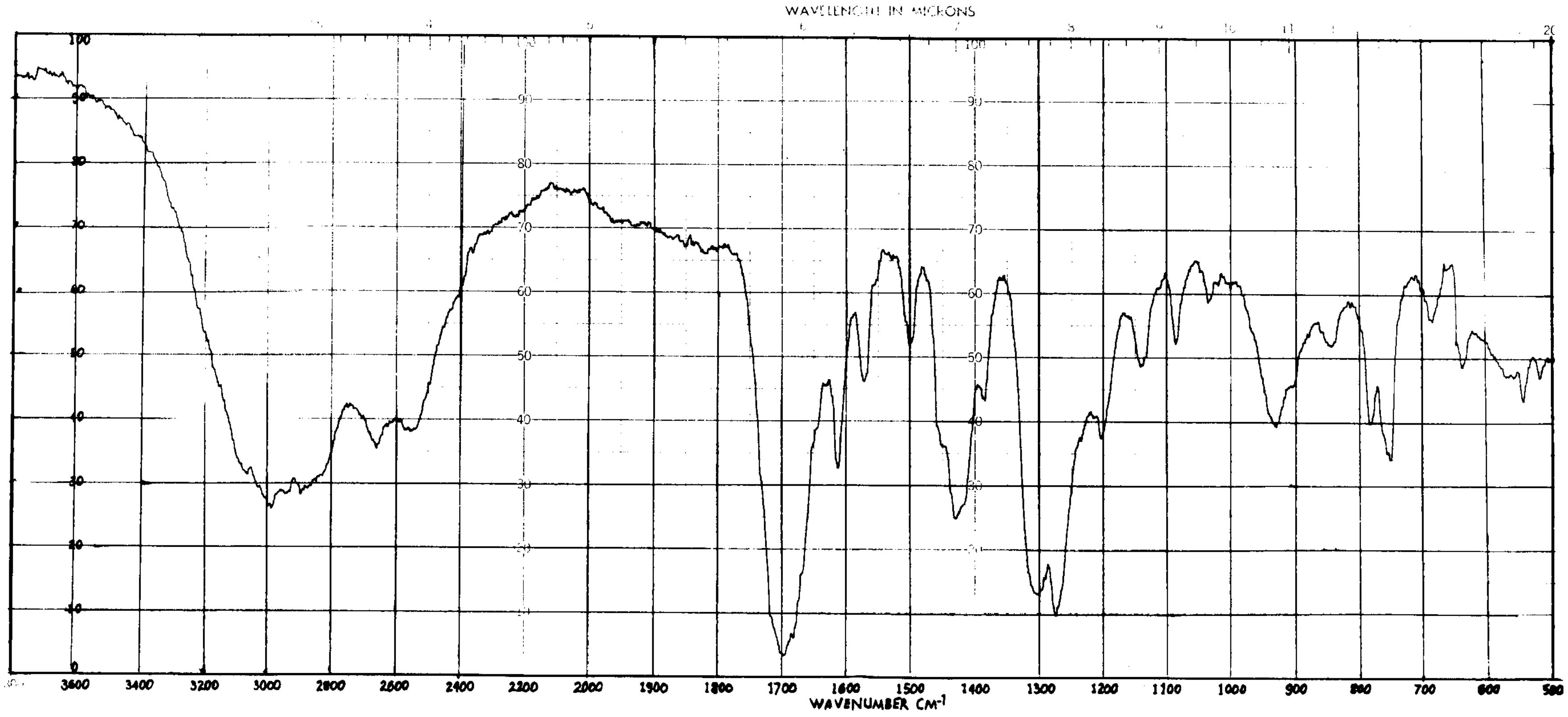


FIGURE 19. INFRARED SPECTRUM OF THE OXIDATION PRODUCT OF PSEUDOCUMENE [MUSTARD YELLOW PRODUCT]

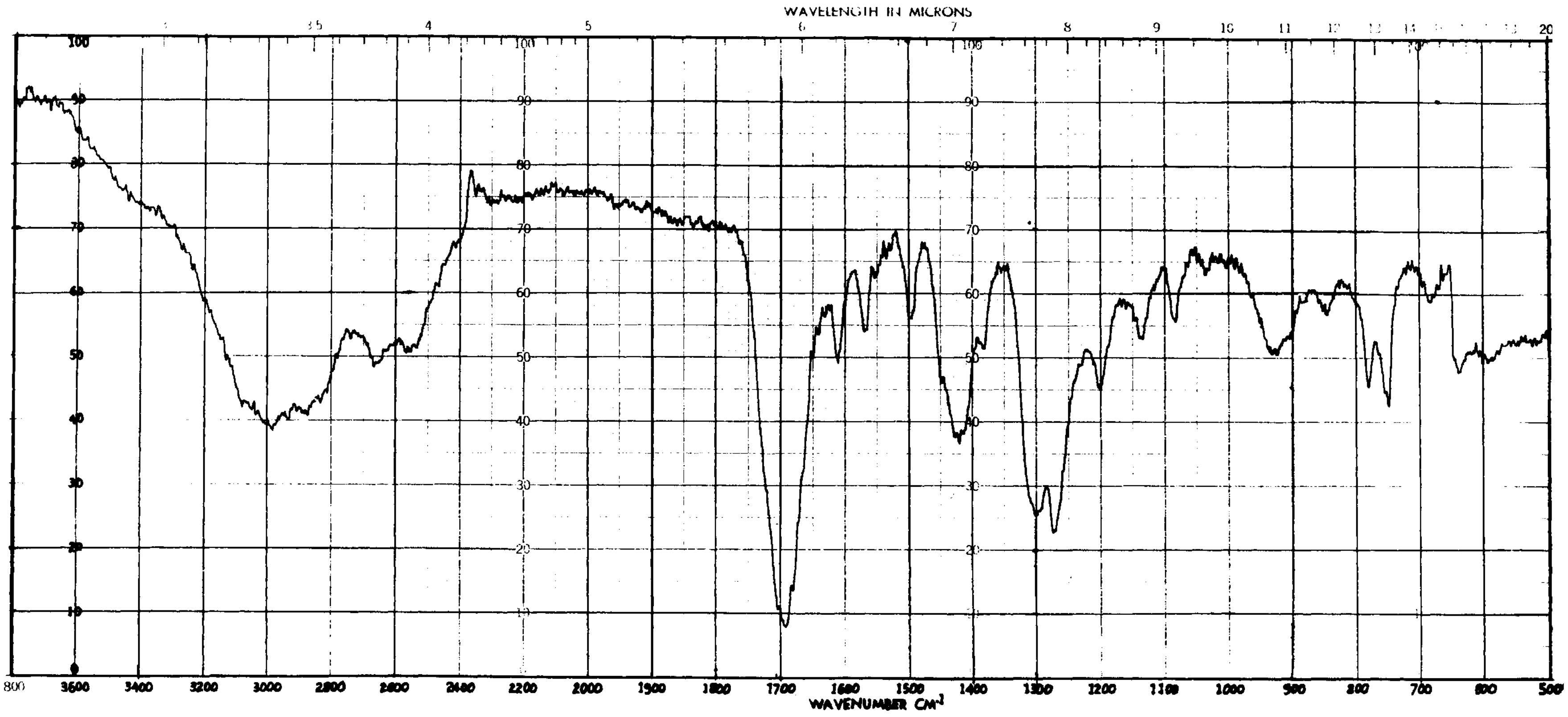


FIGURE 20. INFRARED SPECTRUM OF THE OXIDATION PRODUCT OF PSEUDOCUMENE [WHITE POWDERED PRODUCT]

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1970	Candidate for the Degree of Master of Applied Science in Chemical Engineering at the University of Windsor, Windsor, Ontario, Canada.