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THE EFFECTS OF THERMAL TREATMENT ON PROPERTIES OF Fe-Mo OXIDE CATALYSTS

by

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To My Wife

ABSTRACT

In this study the structural and compositional changes that Fe-Mo oxide catalysts undergo during treatment in air at elevated temperatures (up to 900K) were investigated. Commercial and laboratory prepared catalysts were examined. The changes in catalyst properties were determined by low temperature nitrogen adsorption, scanning electron microscopy, X-ray diffraction, X-ray fluorescence and thermogravimetric analysis. The activities of the catalysts for the oxidation of methanol in air to formaldehyde were measured using an integral bed reactor.

The results showed that treatment at elevated temperatures resulted in the growth and segregation of $Fe_2(MoO_4)_3$ and MoO_3 crystals resulting in a loss of specific surface area and changes in specific activity. The changes in specific activity can be explained in terms of molybdenum depletion from a molybdenum-rich iron molybdate phase.

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I - INTRODUCTION

Iron molybdenum oxide, which consists of a mixture of normal iron molybdate, $Fe_2(MoO_4)_3$, and molybdenum oxide, MoO_3, is one of the most widely used catalysts in the production of formaldehyde from methanol. In the industrial process that uses this catalyst, the conversion of methanol in one single pass through a fixed bed reactor is >98% and the selectivity to formaldehyde is about 90 - 95%.

A significant amount of work on Fe-Mo oxide catalysts can be found in the literature. Most of this deals with the determination of the structure(s) and the active component of the catalyst and also with the mechanism of the reaction of oxidation of methanol to formaldehyde. One of the aspects which has been ignored in most studies is the deactivation of this type of catalyst with use.

Experience with industrial reactors has shown that after an initial period of constant, or even increasing activity, the activity of the catalyst starts to decline. Since this industrial process does not have facilities to recover unreacted methanol, the methanol conversion per pass has to be maintained at greater than 98% at all times. As the activity of the catalyst starts to decline the required methanol conversion is maintained by increasing the reactor temperature. For example, in the initial period of production, when the catalyst is active, a typical value of initial temperature is 500K. As the catalyst activity begins to decline the reactor temperature is increased in 5 to 10K intervals to an approximate final value of 560K. When this temperature is reached, the activity and selectivity of the catalyst has declined to such a degree that it is no longer acceptable and the catalyst is removed and a fresh charge of catalyst is introduced. It is important to point out that the typical values of temperatures given are reactor wall temperatures; the temperature of the catalyst bed, due to the exothermic nature of the reaction, may be as much as 75K higher at the hot spot in the reactor. The life of the catalyst depends on the operating conditions, but it is typically between 6 and 12 months.

In order to obtain some knowledge of this phenomenon of deactivation, the present study was undertaken to determine changes in the properties of Fe-Mo oxide catalysts during various treatments at elevated temperatures. The treatments used were intended to simulate the catalyst at various stages of deactivation. The catalysts, after treatment, were examined by various instrumental techniques such as Scanning Electron Microscopy, X-Ray Diffraction, X-Ray Fluorescence, BET Adsorption and Thermogravimetric Analysis. The activity of the treated catalysts for the conversion of methanol to formaldehyde was determined using an integral bed reactor.

II - LITERATURE SURVEY

II.1 Formaldehyde Production Processes

Formaldehyde is widely used in the manufacture of many products but the main use today is in the production of resins and glues such as phenolic resins, urea-formaldehyde resins, melamine resins, polyacetal resins and acrylic esters [1].

Over 90% of the formaldehyde is currently produced from methanol and only a small fraction is still being prepared by direct oxidation of hydrocarbons.

Production from methanol is carried out by two catalytic processes. The classic procedure uses a silver catalyst and employs a rich methanol-air mixture, whereas, the second method makes use of an iron-molybdenum oxide catalyst and a lean methanol-air mixture. The two processes are competitive and the selection depends upon many things such as product end use, size of plant and type of operation [2].

Over the silver catalyst the reaction occurs in two steps - dehydrogenation of methanol and oxidation of hydrogen, i.e.

$$CH_3OH \xrightarrow{Ag} CH_2O + H_2 \qquad (1)$$

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O \qquad (2)$$

If an iron-molybdenum oxide catalyst is used, the reaction proceeds by a one-step oxidation process, i.e.

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow{\text{Fe-Mo oxide}} CH_2O + H_2O \qquad (3)$$

In both processes side reactions, which include destruction or direct combustion of the reacting methanol or degradation or combustion of the formaldehyde produced, can occur.

The difference in the operating conditions for the two processes are pronounced. Since methanol and air form explosive mixtures at concentrations ranging between 8 to 37 volume % methanol at atmospheric pressure the two processes must operate outside these limits.

The dehydrogenation of methanol over a silver catalyst requires an excess of methanol versus air and therefore the process operates with methanol/air mixture above the upper flammability limit. Air is only added to supply the energy, by oxidation of the hydrogen, necessary to maintain the operating temperature at the desired 600-700°C level. The gaseous products contain about 20 volume % hydrogen due to the lack of oxygen. The high operating temperatures result in side reactions. In order to minimize the by-product formation very short residence times are used and the product stream is immediately quenched at the exit of the reactor. The short residence time employed results in incomplete methanol conversion (60 - 80%) and consequently distillation equipment is needed to recover the unreacted methanol for recycling.

On the other hand, the oxidation process using a mixture of iron-molybdenum oxide catalyst operates at temperatures between 250 and 400°C. Since this type of catalyst becomes inert in presence of an excess of methanol and require a relatively high oxygen partial pressure to maintain its activity, it must operate with an excess of air and therefore below the lower limit of flammability. Due to the excess of air and lower temperature the selectivity is very high. The catalysts that are now used are based on Fe_2O_3 - MoO_3 mixtures with an excess of MoO_3 over the stoichiometric amount corresponding to the normal ferric molybdate $Fe_2(MoO_4)_3$. In the industrial process that uses this catalyst an overall conversion of methanol greater than 97% and a selectivity to formaldehyde better than 94% have been reported [3].

II.2 Iron-molybdenum Oxide Catalysts

Adkins and Peterson [4] first prepared this catalyst in 1931. They pointed out the high activity and selectivity of this catalyst at relatively low reaction temperature for the oxidation of methanol to formaldehyde. The authors concluded that the most satisfactory catalyst was found to be an equimolar mixture of iron oxide and molybdenum oxide; with this catalyst they obtained a maximum conversion to formaldehyde of about 91% when feeding 10 g of methanol in 93 l of air at 373°C. This experimental work served as the basis for a considerable number of patents [5-8] devoted mainly to the improvement in the method of preparation of the catalyst.

The catalysts employed are in general obtained by coprecipitation of iron and molybdenum salts and they have a molar ratio of MoO_3 to Fe_2O_3 varying from 3.6 to 11.1.

(i) Phase Composition and Nature of the Active Component

In one of the first investigations made by Boreskov and coworkers [9, 10] a study of the chemical composition, its effect upon the activity and selectivity in the oxidation of methanol to formaldehyde and the nature of the catalytically active component was carried out. They prepared various catalysts with different Mo to Fe ratios. Their experimental data show that the maximum of specific catalytic activity is obtained for an atomic Mo/Fe ratio of 1.7 (or 63 atom % of Mo); for Mo/Fe < 1.7 the catalytic activity is rapidly reduced to very low values while for Mo/Fe > 1.7 the catalytic activity decreases slower and linearly to the value of pure MoO_3. The catalyst with Mo/Fe = 1.7 has a specific activity which is 40 - 70 times greater than that of the oxides from which it has formed. They also found that for pure Fe_2O_3 and in mixed catalyst with Mo/Fe ≤ 1 the selectivity for the formation of formaldehyde was very low. On the other hand pure MoO_3 had a high selectivity but a very low activity. Therefore, they concluded that the catalytic properties of the mixed catalysts are not linear functions of the properties of the oxide components and suggested that a reaction takes place between the original components forming a chemical compound with Mo/Fe = 1.5 to 1.7. In order to identify the active component they examined the catalysts by X-ray diffraction, electron paramagnetic resonance, infrared spectroscopy and thermography. The results showed the following:

1) In the catalysts with Mo/Fe = 1.5, after calcination at 400°C, only one phase is present, normal iron molybdate [$Fe_2(MoO_4)_3$] which is formed in the case of precipitation as an amorphous phase, and crystallizes upon heating to 350°C. With increasing content both of iron and of molybdenum in the catalysts, the crystallization of $Fe_2(MoO_4)_3$ occurs at higher temperatures.

2) With broad variations in composition of the crystallized catalysts, only two phases are present, $Fe_2(MoO_4)_3$ and MoO_3 for Mo/Fe > 1.5, and $Fe_2(MoO_4)_3$ and Fe_2O_3 for Mo/Fe < 1.5.

3) On the basis of these investigations, it was concluded that the activity of iron-molybdenum oxide catalysts is due to the formation of normal ferric molybdate which is the active component. The fact that

commercial catalysts, in order to have high activity, need an excess of molybdenum over the stoichiometric amount corresponding to $Fe_2(MoO_4)_3$ does not quite agree with the conclusion of these investigators.

Pernicone et al. [11] showed that pure MoO_3 and pure $Fe_2(MoO_4)_3$ have much lower activity than a MoO_3 - $Fe_2(MoO_4)_3$ catalyst mixture with a molar ratio of 9:1. They explained their experimental results by assuming that both MoO_3 and $Fe_2(MoO_4)_3$ are catalysts for the reaction of oxidation of methanol but that $Fe_2(MoO_4)_3$ is actually the most active component and that it may have a promoting effect on the MoO_3. Another important aspect that they consider is the surface acidity of the catalyst. Pure MoO_3 showed higher acidity than mixed catalysts, but the latter showed a higher catalytic activity than the former; in fact, acid catalyst such as Al_2O_3 and SiO_2 are inactive for this reaction. Therefore, surface acidity is not the only factor that influences catalytic activity and redox properties play an important factor. One possible explanation that they gave is that these acid sites due to pure MoO_3 are the active sites for methanol adsorption and the role of $Fe_2(MoO_4)_3$ is to produce an adequate reducibility of the catalyst in order to increase the product desorption rate that seems to be the rate controlling step. In conclusion, $Fe_2(MoO_4)_3$ to be an active catalyst must be Fe deficient, i.e. have a Mo excess with respect to the stoichiometric amount. To verify the validity of this hypothesis, Fagherazzi and Pernicone [12] carried out an X-ray structural study on MoO_3 - $Fe_2(MoO_4)_3$ and pure $Fe_2(MoO_4)_3$ catalysts and they found a larger unit cell for the $Fe_2(MoO_4)_3$ in the Mo rich catalyst. They concluded that the active phase is an iron molybdate containing Mo in excess of the stoichiometric amount (referred to as Fe-deficient). They also pointed out that heating the amorphous hydrous iron molybdate at 380°C results in the segregation of MoO_3 and crystallization of both MoO_3 and Fe-defective iron molybdate. Therefore the Fe-defective iron molybdate, which is present in the catalysts with Mo/Fe >1.5, was postulated to be the active phase. They also mention that complete segregation of MoO_3 to give pure $Fe_2(MoO_4)_3$ should occur by heating at higher temperatures which should lead to reduced activity.

Peirs and Leroy [13] found the highest catalytic activity for a catalyst with a Mo/Fe = 3 activated at 330°C; they also detected the two characteristic phases of MoO_3 and ferric molybdate.

(ii) Mechanism of the Catalytic Oxidation

The mechanism of methanol oxidation over Fe and Mo oxide catalysts has been studied in detail by various investigators. For example Jiru *et al*. [14] postulated the following two-stage oxidation-reduction mechanism similar to that observed by Mars and Van Krevelen [15] for the oxidation of aromatic hydrocarbons on V_2O_5, in which the lattice oxygen of the catalyst participates in the reaction, *i.e.*

$$CH_3OH(g) + Cat_{ox} \xrightarrow{k_1} CH_2O(g) + H_2O(g) + Cat_{red} \quad (4)$$

$$O_2(g) + Cat_{red} \xrightarrow{k_2} Cat_{ox} \quad (5)$$

This mechanism was verified by oxygen balance in the rate of interaction between methanol and catalyst without oxygen in the gaseous phase and by the rate of interaction between oxygen and partially reduced catalyst without methanol in the gaseous phase. The two steps could be repeated without lowering the activity of the catalyst. Other results obtained by these workers, with regard to physical changes of the catalyst during reduction-oxidation, which support the redox mechanism are: one, during the oxidation reaction the catalyst changes its yellowish colour into greyish blue; and two, the electrical resistance decreases during the oxidation of methanol while after re-oxidation, it increases to almost its initial value.

The oxidation of methanol and formaldehyde was carried out by the same research group [16, 17] on MoO_3, Fe_2O_3 and mixed catalysts. On pure MoO_3 at 320°C, without oxygen in the gas phase, the first dose of methanol produced mainly formaldehyde and water but a further dose of methanol produced mainly CO, CO_2 and H_2; also, with fresh catalyst formaldehyde does not react while with the used sample formaldehyde is oxidized. On pure Fe_2O_3 at 220°C, without oxygen in the gas phase, complete oxidation of methanol and formaldehyde occurs with formation of CO, CO_2 and H_2 and these products are the same with several doses of methanol. On MoO_3 - Fe_2O_3 mixed catalyst at 100°C, without oxygen in the gas phase, formaldehyde and water were the reaction products and the product composition did not change with several doses. Therefore, they supposed that the mechanism of the selective methanol oxidation is the same on mixed catalyst as that on MoO_3 in its unreduced state, and it is caused by Mo^{6+} ions. An alcoholate bonding might be formed which decomposes under formation of formaldehyde and water; one H atom from the methanol molecule being bonded to a surface oxygen. If a similar complex is formed on Fe_2O_3 it is very unstable because of the complete oxidation observed. Thus, in conclusion, they suggest that the role of Fe^{3+} ions is to hinder the reduction of Mo^{6+} ions and increase the lability of lattice oxygen available for the oxidation process.

These results are similar to those found by Pernicone and coworkers [18-20]. These authors assumed that the dissociative adsorption of methanol occurs on two types of centers, an anionic vacancy that would have the function of a Lewis acid center and an O^{2-} ion that would behave as a Brönsted basic center. The O^{2-} forms an hydroxyl and the anionic vacancy is occupied by a methoxyl. Then the surface reaction should occur by transfer of an H^+ ion from the methoxyl to a near O^{2-} ion, with the formation of a second hydroxyl and electron transfer to the reducible cation (either Mo^{6+} or Fe^{3+}), this producing the CH_2O formation on the anionic vacancy. After that, water can be removed from the two hydroxyls and desorbed with CH_2O and formation of a new adsorption center. In their opinion, the presence of Fe^{3+} ions increases the number of methanol adsorption centers and at the same time facilitates the desorption of products. This step seems to be the rate-controlling since their experimental results showed that neither the adsorption of reactants nor the surface reaction are the rate-controlling steps. Other authors [21-22] arrived at the same conclusion with respect to the adsorption of methanol and oxygen.

In order to have a further evidence of the redox mechanism and clearly define the role of the two metals in the catalytic system, Trifiro _et al_. [23] reduced the mixed catalyst with N_2/H_2 and N_2/NH_3 mixtures and they found that iron molybdate, $Fe_2(MoO_4)_3$, is the first component of the system $MoO_3 - Fe_2O_3$ that is reduced to give ferrous molybdate, $FeMoO_4$. They represented the mechanism as follows:

$$Fe^{3+} \text{ molybdate} + CH_3OH \longrightarrow Fe^{2+} \text{ molybdate} + CH_2O + H_2O \qquad (6)$$

$$Fe^{2+} \text{ molybdate} + \tfrac{1}{2} O_2 \longrightarrow Fe^{3+} \text{ molybdate} \qquad (7)$$

Therefore, the conclusion of these investigators is that Fe^{3+} acts as the transfer agent of oxygen and water between the surface and the gas phase.

(iii) Kinetics of the Reaction

The opinions of various authors about the rate equation that can describe best the oxidation process differ. The different rate expressions proposed and their applicability will be discussed here.

The simplest kinetic equation proposed for the oxidation of methanol is the one corresponding to a first order reaction with respect to CH_3OH and of zero order with respect to O_2, i.e.

$$r = k\, p_{CH_3OH} \tag{8}$$

where

r - rate of reaction, [mole/(g-sec)].
k - rate constant, [mole/(g-sec-Torr)].
p_{CH_3OH} - partial pressure of methanol, [Torr].

The experimental data obtained by various investigators [9, 13, 29] were well fitted by this expression.

However, according to the two steps oxidation-reduction mechanism mentioned before (Equations 4 and 5), Jiru et al. [14] proposed the following rate expression for the oxidation of methanol at low partial pressure of reactants,

$$r = \frac{k_1 \, p^m_{CH_3OH}}{1 + \alpha(k_1 \, p^m_{CH_3OH}/k_2 \, p^n_{O_2})} \qquad (9)$$

where

r - rate of oxidation of methanol, [mole/(g-sec)].

p_{CH_3OH}, p_{O_2} - partial pressure of methanol and oxygen, [Torr].

k_1 - rate constant of oxidation of methanol by oxygen from catalyst Cat_{ox}, [mole/(g-sec-Torr)].

k_2 - rate constant of oxidation of catalyst Cat_{red} by oxygen, [mole/(g-sec-Torr)].

α, m, n - constants; calculation from experimental data gave $m = n = 1$, $\alpha = 0.5$.

The experiments were carried out in an integral reactor at atmospheric pressure and 270°C using a catalyst containing 17.5 wt % of Fe_2O_3 and 82.5 wt % of MoO_3 (Mo/Fe = 2.6).

In a subsequent work [24] from kinetic data obtained by means of a recycle reactor they recommended the value m = n = 0.5.

The same kinetic equation has been used by other authors [25]. Pomerantsev and Mukhlenov [26] considered also the influence of the formaldehyde formed in the reaction according to the following equation:

$$r = \frac{k\, p_{CH_3OH}^{0.5}}{[1 + (0.5\, p_{CH_2O}/p_{CH_3OH}\, p_{O_2}^{0.5})]^{0.5}} \qquad (10)$$

However, the data obtained by Pernicone *et al.* [18] using a flow and pulse reactor method did not verify these types of equation especially when high partial pressures of reactants were used. They pointed out that the oxidation-reduction mechanism proposed gives only an approximate description of a more complex phenomenon, although the basic idea that the lattice oxygen participates in the reaction was not excluded.

Bibin and Popov [27] made a detailed study of the reaction in the kinetic region by a circulating flow method and they found that water formed in the reaction has an inhibiting effect and must be included in the reaction rate expression. They fitted their experimental results by the equation,

$$r = \frac{k_1 \, C_{Me}}{1 + a_1 \, C_{Me} + a_2 \, C_{H_2O}} \tag{11}$$

where

r - rate of reaction, [μ mole/(m^2-sec)].
C_{Me}, C_{H_2O} - concentration of methanol and water, [mole/m^3].
k_1, a_1, a_2 - reaction constants.

The temperatures of the reaction were in the range of 225 - 308°C and catalysts with a Mo/Fe = 1.7 - 1.8 were used.

The effect of water was also considered by Evmenenko and Gorokhovatskii [28] along with the effect of oxygen; their experimental data were described by the equation:

$$r = k \frac{C_{Me}}{1 + b_1 C_{Me} + b_3 C_{H_2O}} \cdot \frac{C_{O_2}}{1 + b_2 C_{O_2}} \tag{12}$$

which they also derived theoretically considering the following Langmuir-Hinshelwood type mechanism:

$$CH_3OH\ (g) + [\ \ ] \rightleftarrows [CH_3OH]_{ads} \qquad (13)$$

$$O_2\ (g) + [\ \ ] \rightleftarrows [O_2]_{ads} \qquad (14)$$

$$[CH_3OH]_{ads} + [O_2]_{ads} \rightleftarrows CH_2O\ (g) + [H_2O]_{ads} + [\ \ ] \qquad (15)$$

$$[H_2O]_{ads} \rightleftarrows H_2O\ (g) + [\ \ ] \qquad (16)$$

where

[ ] - catalyst adsorption site
b_1, b_2, b_3 - are the corresponding adsorption constants

(iv) Changes in the Properties of the Catalyst

Although this problem has not been very well studied some investigators pointed out the necessity of periodically regenerating or eventually replacing the catalyst due to loss of activity with use. For example Hodgins and Shelton [30] noted the following changes in the catalyst after 36 days of operation: a) the color changed from greenish-yellow to greenish-grey, b) the MoO_3 content decreased about 8%, c) using X-ray diffraction, the fresh catalyst showed no pattern but in the used one the crystalline pattern of MoO_3 appeared.

Since the rate of sublimation of MoO_3 is appreciable at 700°C they attribute its loss to volatilization. Also they consider that at the same time a redistribution apparently separates the original amorphous MoO_3 from the amorphous Fe_2O_3 in contact with it and therefore the active centers are lost.

Peirs and Leroy [13] studied by electron probe microanalysis the morphological variations of the catalyst related with the loss of activity. They used for the study a catalyst with atomic ratio Mo/Fe = 3 activated at 330°C for which they found the maximum specific activity. For the fresh catalyst, the two peaks in the electronic images obtained at Mo/Fe = 2.4 and 3.2 corresponded to the two phases, ferric molybdate and MoO_3. However, the histrogram of the used catalyst showed the presence of only one peak at Mo/Fe = 1.4. The authors attribute this effect to the disappearance of the MoO_3 phase and the partial destruction of ferric molybdate. Also, they have found that a bluelike residue is formed at the base of the reactor where they measured a considerable decrease of temperature. The analysis by X-rays and electronic images of this residue showed the presence of the Mo and O and the absence of Fe; quantitative analysis gave a ratio O/Mo of about 3 explaining in this form that the residue is MoO_3 generally called "molybdenum blue". Therefore this phenomenon would explain the disappearance of the peak corresponding to the MoO_3 phase.

A study of the variations occurring during high temperature treatment was carried out by Trifiro et al. [31]. They concluded that there are three ranges of temperature in which some marked change in the properties of the catalyst occurred. Over the first range, 300 - 350°C, a sharp increase of electrical conductance, the starting of CO production in the oxidation of methanol and the starting of bulk reduction of the catalyst in N_2-NH_3 flow were noted. They attributed these effects to the higher rate of electronic transfer between Fe^{2+} and Fe^{3+} that occurs in the process of the reoxidation of the catalytic surface. This reoxidation can occur not only with oxygen but also from the reduction of the bulk Fe^{3+}. The second variation took place at 500°C and consisted in an almost total reoxidation of Fe^{2+} in air with elimination of water, a decrease of the isomerization power in the oxidation of 1-butene and in the formation of CO_2 in the oxidation of methanol. They also pointed out that due to the more severe oxidation conditions the reduced form of the catalyst does not have the same structure as that of the oxidized form and this variation can cause the decomposition of molybdate to the single oxides. The third variation occurred at 600°C and it is characterized by a definite and sharp decrease in the surface area and by the breakdown of catalytic activity for 1-butene oxidation and cyclohexene epoxidation. They linked this loss of activity to a sintering phenomena occurring at this temperature.

III - EQUIPMENT AND EXPERIMENTAL PROCEDURES

III.1 Catalysts

Two different Fe-Mo oxide catalysts were employed in this work; one was a commercial catalyst obtained from the Lummus Company. Table 1 gives the physical and chemical properties of this catalyst as specified by the manufacturer.

TABLE 1: Properties of Lummus Catalyst as Specified by Manufacturer

Fe	9.5 wt %
Mo	50.0 wt %
Surface area	4 m^2/g
Pore volume	0.2 cc/g

The other catalyst was prepared in the laboratory by co-precipitation of Fe-Mo oxide from ferric chloride ($FeCl_3 . 6H_2O$) and ammonium paramolybdate

[$(NH_4)_6 Mo_7O_{24}.4H_2O$] solutions by a procedure similar to that described by Allyl et al. [32].

Portions of these two catalysts were heated in flowing air at various temperatures for varying periods of time. The samples were placed in a U-shaped Vycor tube and heated in a Thermolyne muffle furnace. The temperature of the furnace was controlled by a Thermo Electric 400 temperature controller. At the exit of the tube, outside the furnace, a glass wool plug was used to collect possible products of sublimation. The various treatment conditions used to obtain the catalyst samples are given in Table 2.

For the samples pretreated at temperatures greater than 670K white crystals were collected in the glass wool plug, and the wall of the U-tube near the glass plug became blue. The crystals were kept for subsequent analysis.

III.2 Activity Measurements

The activity of the catalysts described in Table 2 for the conversion of methanol in air to formaldehyde was determined in a fixed bed reactor. The equipment that was constructed for this purpose and the

TABLE 2: Description of Catalyst Treatment

Catalyst Number*	Temperature (K)	Length of Time (Hr.)
1	Fresh Lummus Catalyst, No Treatment	
2	500	137
3	500	572
4	520	450
5	670	17
6	770	18
7	820	18
8	870	20
9	820	42
10		Fresh Untreated (dried in air at 423 K for 24 hr.)
10'	530	12
11	870	20
A	820	48
B	870	25
C	870	72
D	910	15
E	900	48

* For catalyst number 2 to 9 and A to E, the starting catalyst was fresh Lummus catalyst; for catalysts 10, 10' and 11 the starting catalyst was the sample prepared in the laboratory. Samples A, B, C, D and E were heated in TGA equipment.

procedure followed will now be discussed in detail.

(i) Equipment

A schematic diagram of the equipment is shown in Figure 1. The feed to the reactor consisted of an air-methanol mixture. The air came from the house supply. It was dried by passing through a 12.7 cm dia., 30 cm long, aluminum oxide bed and fine particles were removed by a sintered metal filter (Nupro Cat. No. SS 316-2F-15). The upstream pressure was set by means of a single stage regulator (Fisher Governor Co. Type 67F R 224). The air flow rate was measured by means of a calibrated rotameter (Matheson, Cat. No. 621 PBX ~~with~~ dual float tube, Cat. No. 603). The air flow rate was controlled with the rotameter needle valve. The rotameter readings were converted to flow rate according to the method described in Appendix A. The calibration included compensation for the variation of pressure in the rotameter. The pressure in the rotameter was measured by the mercury filled manometer shown in Figure 1.

Methanol was fed into the air stream as a liquid by means of a precalibrated syringe pump which provided uniform (±2%) and reproducible flow rates. The needle of the syringe was placed in contact with the bottom of the

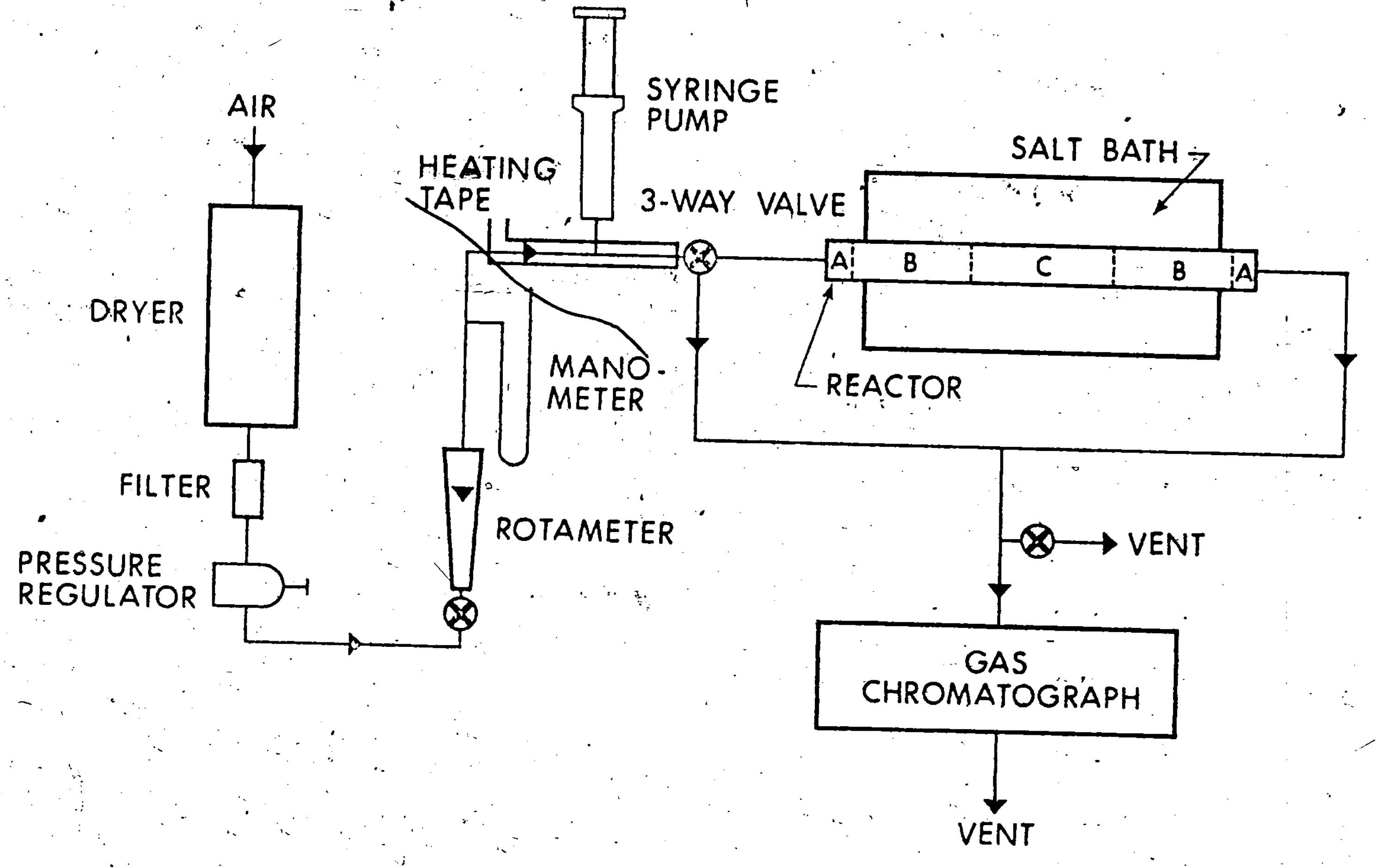


Figure 1: Schematic Diagram of Equipment Used for Activity Measurements

(A = Glass wool plugs; B = Pyrex beads; C = Catalyst mixed with Pyrex beads).

tube of the air line to prevent drop formations which would result in pressure fluctuations. The air was preheated by means of heating tape to approximately 100°C in order to preheat the feed and also to assure complete evaporation of methanol. The air-methanol mixture could be routed to the reactor or to the gas chromatograph for analysis by means of a three-way valve. Feed stream composition were calculated from air and methanol feed rates and checked by gas chromatographic analysis.

The reactor was constructed out of a 1.9 cm, schedule 40, 316 stainless steel pipe. Its length was 76 cm. The feed was preheated by means of a coil immersed in a salt bath which consisted of a mixture of equal quantities by weight of KNO_3 and $NaNO_3$; this mixture forms an eutectic which has a melting point of 222°C [33]. A cross section of the reactor and salt bath is shown in Figure 2. (This construction is not well suited for obtaining isothermal rate data. This reactor was initially designed to measure autothermal effects). The reactor was easily removable by loosing the four bolts that fastened it to the plate welded to the salt bath reservoir. Asbestos and copper gaskets did not provide an adequate seal; finally, an aluminum gasket, which provided a tight seal, was used. The feed flowed counter-

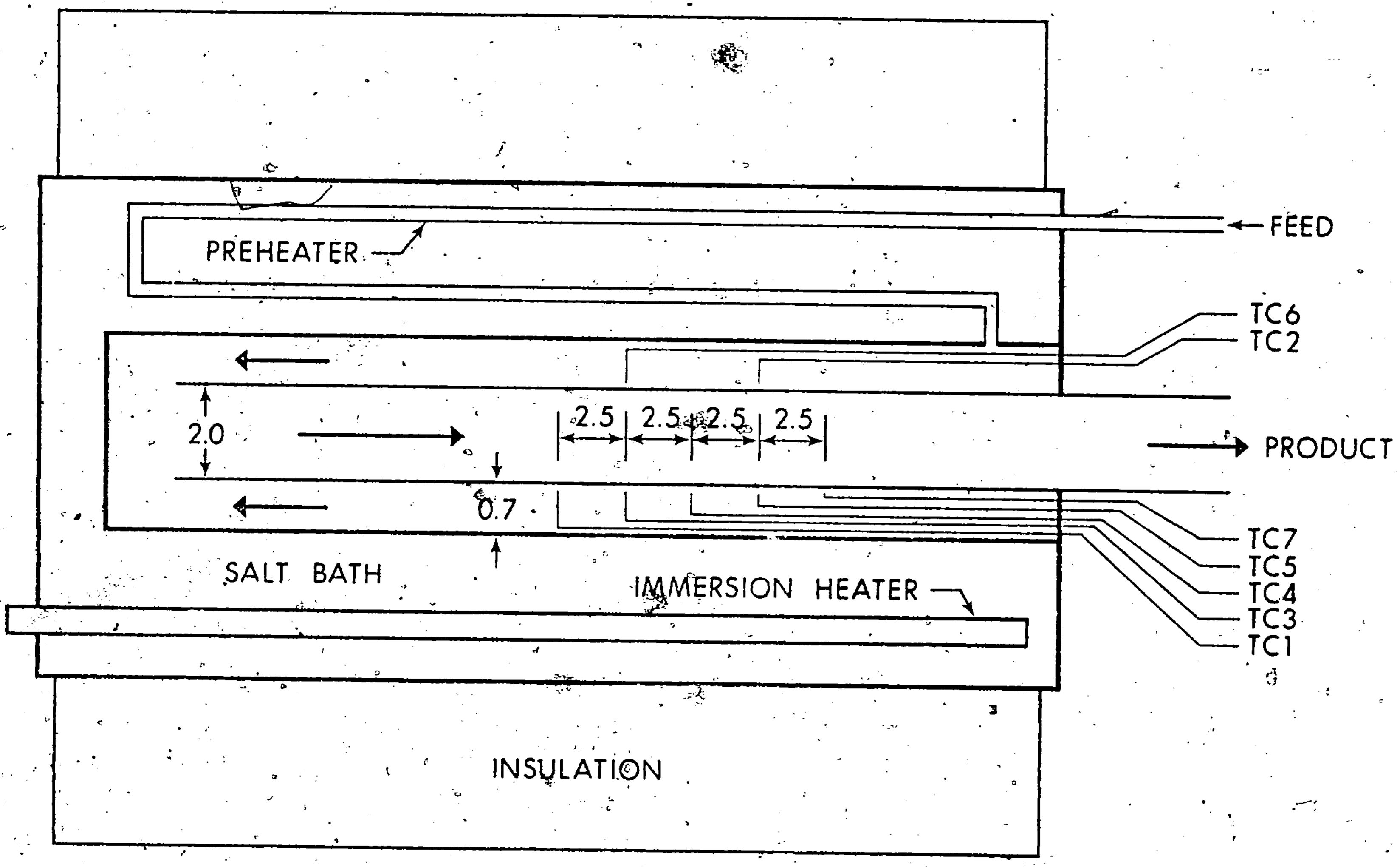


Figure 2: Cross Section of Reactor. (TC2 and TC6 are thermocouples welded to the outside wall of the reactor; all other thermocouples are located at the center of the reactor, dimensions indicated are in centimeters).

currently through the annular region around the reactor as shown in Figure 2. The bath was heated by four 1550 watt U-shaped immersion heaters (0.8 cm in diameter and 1.4 m long) immersed in the bath; two of the heater elements were connected to a variable voltage supply and the other two to the temperature controller. The whole container was surrounded by 5 cm of asbestos insulation.

Temperatures at various positions in the catalyst bed and along the reactor wall (see Figure 2) were obtained by seven iron-constantan thermocouples. Two thermocouples, TC2 and TC6, were joined to the wall of the reactor and the five remaining thermocouples were positioned inside the reactor in order to obtain the temperatures at various positions in the catalyst bed. The thermocouples used were 1.6 mm O.D. (1/16"), stainless steel sheathed, grounded hot junction, purchased from Thermoelectric Company. The output of thermocouples TC2 to TC7 were recorded by a Speedomax Type G, Leeds and Northrup, 16 point variable-range, variable-zero temperature recorder. The range normally set on this recorder was 200 to 400°C. Thermocouple TC1 was connected to a West (Model JPGB) temperature indicator-controller which controlled the temperature of the salt bath by regulating the current to two of the immersion heaters.

A constant current was passed through the other two heaters. Very good temperature control was obtained in this way and the temperature of the different thermocouples inside the reactor did not fluctuate more than 3°C once a steady temperature in the bath was obtained.

The pressure in the reactor was regulated by adjusting the regulating valve in the vent line before the GC inlet in order that the reading on the mercury manometer, attached to the inlet line of the reactor, corresponded to the required pressure. When the feed stream was analysed this valve was adjusted to obtain the same pressure drop as in the case when the product stream was analysed.

(ii) Materials

The methanol used as a reactant in the experimental runs was supplied by Mallinckrodt Chemical Works Ltd. and had a purity greater than 99.7%.

Aluminum oxide about 6-16 mesh supplied by The British Drug Houses Ltd. was used as a desiccating agent for the air. Periodically it was regenerated by heating at 250°C for 24 hours.

Sodium nitrate and potassium nitrate, industrial grade, purchased from Olin Chemicals were used to fill the salt bath.

The catalyst prepared in the laboratory was obtained from ammonium molybdate crystal [$(NH_4)_6\,Mo_7O_{24}\cdot 4H_2O$] supplied by Allied Chemical Canada Ltd. and ferric chloride ($FeCl_3\cdot 6H_2O$) supplied by The British Drug Houses Ltd.

Helium supplied by the Liquid Air Company was used as a carrier gas for gas chromatography.

(iii) Operation of Equipment

The first step consisted in charging the reactor with the catalyst under study. A 15 cm catalyst bed length was used. The upstream and downstream zones of the remaining of the reactor were filled with 0.5 mm Pyrex glass beads. Glass wool plugs were placed on both ends of the reactor (see Figure 1). For the first run, in which a charge consisting of only fresh Lummus catalyst pellets, it was noted that considerable temperature differences existed along the catalyst bed ($\sim 30^{\circ}C$ for reaction temperatures between 230° - $270^{\circ}C$). In order to reduce this temperature gradient in the bed, the catalysts for all the other experimental runs were diluted with Pyrex beads (1:1 volume ratio of glass beads to catalyst).

After the reactor had been placed inside the bath and all the bolts and fittings tightened the air stream was allowed to flow through the reactor and leaks were eliminated. Then the desired temperature was set in the controller and the calrod heaters were turned on. Approximately four hours of heating time were required to achieve the set temperature in the bath. When steady state temperature conditions in the reactor had been obtained the syringe pump was turned on, the air flow rate was adjusted to its desired value and the feed stream was routed to the gas chromatograph for analysis. After the feed had been analysed, the air-methanol stream was passed through the reactor. The temperature of the catalyst bed rose by as much as 25°C when this was done. The magnitude of the temperature rise was dependent on the initial reactor temperature and the feed composition. Approximately two hours were allowed for the temperature to reach a uniform value along the catalyst bed (variations ±3°C along catalyst bed), after that the product stream was analysed. Several product analyses were carried out for each run.

(iv) Gas Chromatographic Analysis

The components of the feed and product streams were separated by gas chromatography using a Beckman GC2 chromatograph. The chromatograph was equipped with a thermal conductivity cell and a Beckman pneumatically-operated sampling valve (Cat. No. 102396). The volume of the sample loop used was 0.5 cc.

The following is a description of the chromatographic column used, the operating conditions and the components separated.

Column	6.35 mm O.D., 1.8 m long, spiral stainless steel tube. The first 0.9 m section was packed with Porapak T, 80 - 100 mesh, and the other 0.9 m section with Porapak Q-S, 80 - 100 mesh. Both packings were purchased from Waters Associates (Cat. No. 27078 and 27090).
Column Temperature	165°C
Filament Current	180 ma.
Carrier Gas	Helium

Gas Flow Rate	Carrier side - 50 cc/min. Reference side - 25 cc/min.
Components Separated	"Air"(nitrogen and oxygen), formaldehyde, water and methanol.

The conditions given above were experimentally determined to be optimum considering separation and time of analysis.

The products were identified by their respective retention times obtained by passing pure samples of the gas involved through the column. For quantitative analysis the composition of the samples was computed from the area under the peaks of the various components and their respective correction factors. The output signal from the thermal conductivity cell was analysed on-line by an IBM 1800 computer and peak integrations were obtained electronically by using the Chromatograph Monitoring Program (CMP) [34]. The job defined for this analysis along with the procedure employed is given in Appendix B. Also a typical chromatogram with its corresponding computer output is shown in the same Appendix.

The correction factors for water and "air" relative to methanol were obtained by calibration runs using samples of known composition according to the method described in Appendix B. The correction factor for component i, F_i, relative to methanol is defined by:

$$F_i = \frac{A_{CH_3OH}\ x_i}{A_i\ x_{CH_3OH}} \tag{17}$$

where

A_{CH_3OH} - area under methanol peak

A_i - area under peak for component i

x_{CH_3OH} - mole fraction of methanol

x_i - mole fraction of component i

The correction factor for formaldehyde was obtained by material balance calculation of product samples, i.e. the moles of formaldehyde in the product were equal to the moles of methanol reacted and the moles of water formed since no other reaction products besides water and formaldehyde were detected under the experimental conditions used.

The correction factors obtained in this work were 1.0, 1.02, 1.40 and 1.66 for methanol, air, formaldehyde and water, respectively. Appendix B gives in detail the method employed to calculate these values. The ratio F_{H_2O}/F_{CH_3OH} is in fair agreement with the value given by Dietz [35] and Messner et al. [36] but the F_{air}/F_{CH_3OH} ratio is different by ~25%. The reason for the variation in the air response factor from the value reported in the literature is probably due to the method by which the peak area was determined. The air peak is a very sharp peak of very short duration and hence has a different shape than the other peaks. Nevertheless, the area under the air peak as obtained by CMP was very reproducible.

III.3 Characterization Techniques

To determine the properties of the catalyst listed in Table 2 a variety of instrumental techniques were used. Each technique is described below.

(i) Scanning Electron Microscopy (SEM)

Information on surface morphology and crystal structure of the different samples of catalyst was obtained from scanning electron micrographs.

The SEM is not a normal microscope in which the transmitted image of an object is magnified by electron lenses to produce high magnification [37]; rather, the image in the system is built up from point to point observations of the surface characteristics resulting from the interaction of the electron beam with the specimen surface. The backscattered and secondary electrons emitted from the instantaneous point of impact can be detected by a scintillation counter and the output after amplification is used to modulate the recording intensity of the beam, generally the brightness of a cathode-ray display tube; this variation in brightness recorded produces the high magnified "image" of the object. In this way if the specimen surface has properties (as for example variations in topography or in the size of crystals) which cause the scattering of electrons to vary from point to point, then a two-dimensional image of the specimen surface will be built up on the screen of the display tube which will represent the object as seen in the "light" of the applied radiation. A photography of this image can be obtained if desired. Therefore, it can be seen that with this technique one can obtain more information about the catalyst surface than employing other kinds of microscopes.

A S4 Stereoscan model, scanning electron microscope manufactured by Cambridge Scientific Instruments Ltd. was used for this purpose. The catalyst samples were coated with a thin film (thickness < 20 nm) of gold prior to examination since the Fe-Mo oxide mixtures are electrical insulators. Magnifications of up to 13000X were used.

(ii) X-Ray Diffraction (XRD)

X-ray diffraction studies on catalyst powders were carried out in order to determine the crystallographic structure of the samples. A Philips X-ray diffraction spectrometer was used for this purpose. The diffraction patterns were obtained using Fe filtered Co $K\alpha$ radiation, a Geiger-counter, and a Philips spectrogonimoter.

(iii) Low Temperature Nitrogen Adsorption (BET)

The specific surface area of the samples was determined by physical adsorption of nitrogen at 77K applying the BET method. This is a well known procedure and therefore the details of the experimental technique will not be discussed here. In the present work, the surface areas of all the samples were obtained by the method described by Gregg and Sing [38]. The samples were evacuated for 2 hr. at 250°C before adsorption measurements. A standard Pyrex glass, high vacuum BET equipment was employed for these determinations. A Texas Instruments Co. fused quartz precision pressure gage (model 141A) was used for pressure measurements. Helium was used for dead-volume determinations.

(iv) Atomic Absorption Spectroscropy (AA)

A model 290B Perkin Elmer atomic absorption spectrophotometer was to be used to determine the Fe and Mo content of the samples. The AA method requires the preparation of solutions of the sample to be analysed but attemps to dissolve the Fe-Mo oxide were unsuccessful. The samples were treated first with hot aqua regia and boiled to dryness. Then the residue was collected with HCl (1:2) and boiled again to almost dryness. After making the solutions with HCl (1:5) there always remained an insoluble black solid. Finally, NH_4OH was tried as a solvent but also without satisfactory results.

(v) X-Ray Fluorescence (XRF)

In order to determine the Mo:Fe ratio of the catalysts the non-destructive XRF technique was employed.

The analyses were conducted on a Philips X-ray fluorescence spectrometer. Tungsten radiation and a LiF 200 analysing crystal were used. The characteristic radiations were detected quantitatively by a scintillation counter and plotted on a recorder chart.

(vi) Thermogravimetric Analysis (TGA)

TGA studies were carried out using a Model 950 DuPont Thermogravimetric Analyser. The weight loss of the samples were continuously plotted on the chart of the Model 900 DuPont Differential Thermal Analyser as a function of time and temperature. The method consisted in suspending one catalyst pellet in one of the arms of the microbalance of the apparatus. The samples were heated at a constant rate of 10°C/min from room temperature to the desired final temperature for each run and then the mode of operation was changed to isothermal. Since the weight losses were small, in general, compared with the total weight of the pellet, zero suppression was used to obtain greater sensitivity. Air was passed over the catalyst during all the weight loss measurements.

IV - RESULTS

IV.1 Scanning Electron Microscopy (SEM)

A large number of areas of the various catalyst samples were examined by SEM. The surface of the catalyst pellet was not uniform but showed different characteristics from one part of the pellet to the next. Figure 3 is a representative micrograph showing this effect. Despite these variations within each sample, definite trends with various treatments were observed. Figure 4 and 5 illustrate the marked difference in structure of the fresh (Catalyst 3) and a catalyst after extensive thermal treatment (Catalyst E). Figures 6 to 10 are representative sections of the ~~surfaces~~ for various catalyst samples.

On the basis of these micrographs we can make the following observations:

(i) Lummus Catalysts

All catalysts contained the plate-like MoO_3

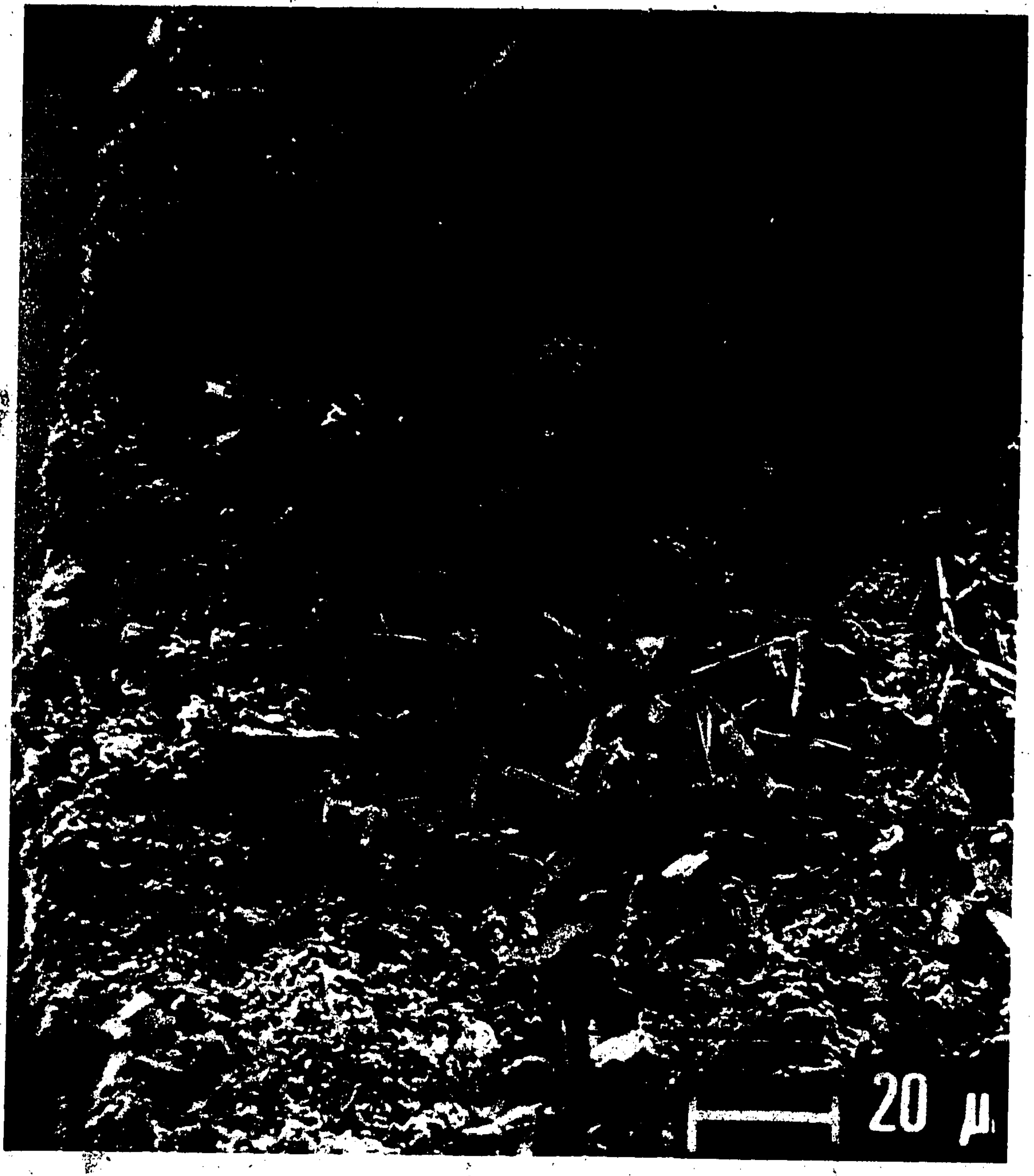
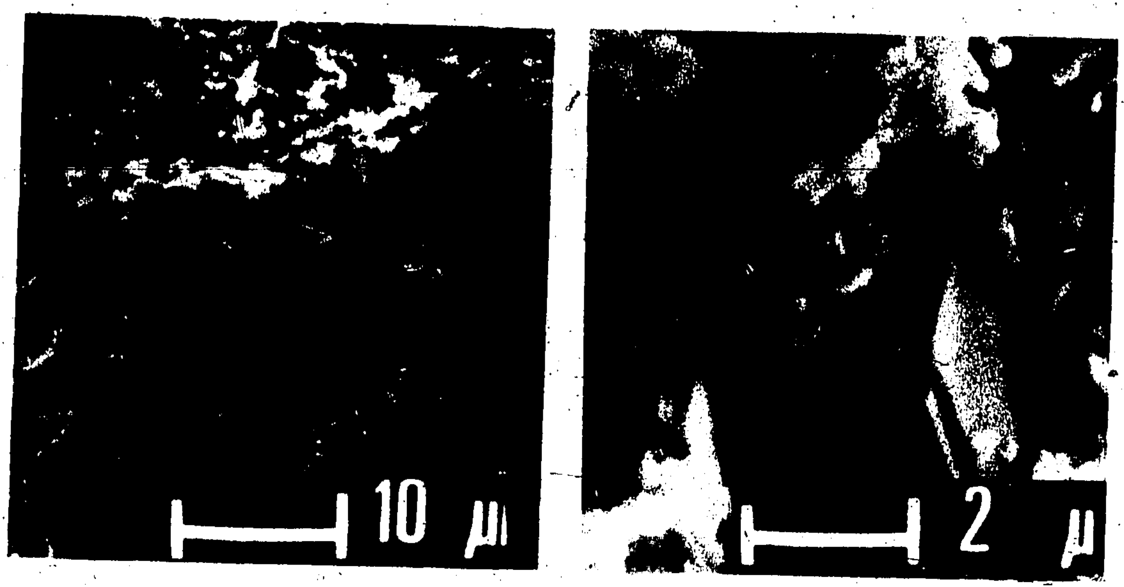


Figure 3: SCANNING ELECTRON MICROGRAPH OF CATALYST B

Figure 4: SCANNING ELECTRON MICROGRAPH OF FRESH, ACTIVATED CATALYST (SAMPLE # 3)

Figure 5: SCANNING ELECTRON MICROGRAPH OF CATALYST HEATED AT 630°C (SAMPLE E)



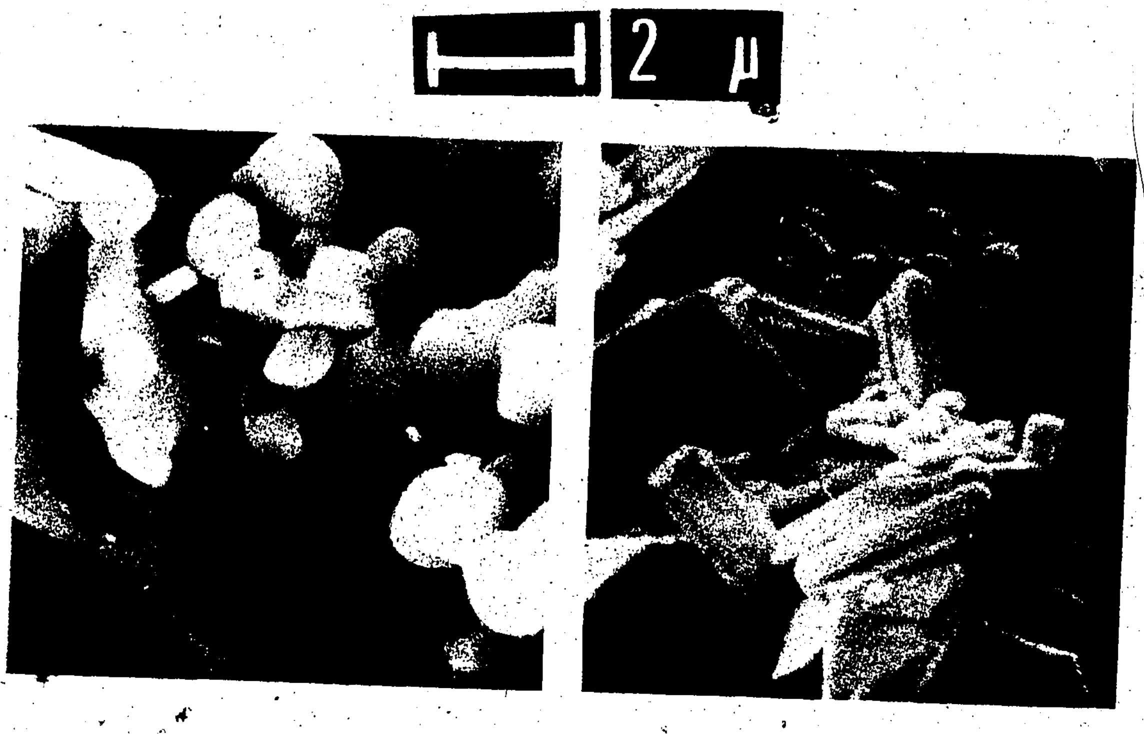
CATALYST 1 CATALYST 1

CATALYST 3 CATALYST 5

Figure 6: SCANNING ELECTRON MICROGRAPHS OF CATALYSTS 1, 3, AND 5

CATALYST 6

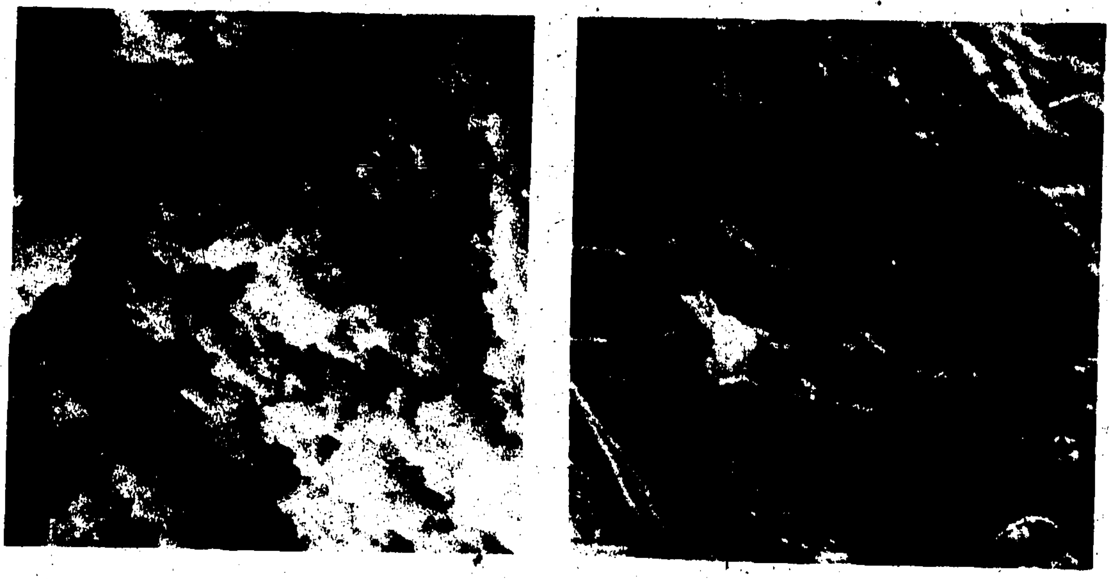
CATALYST 7



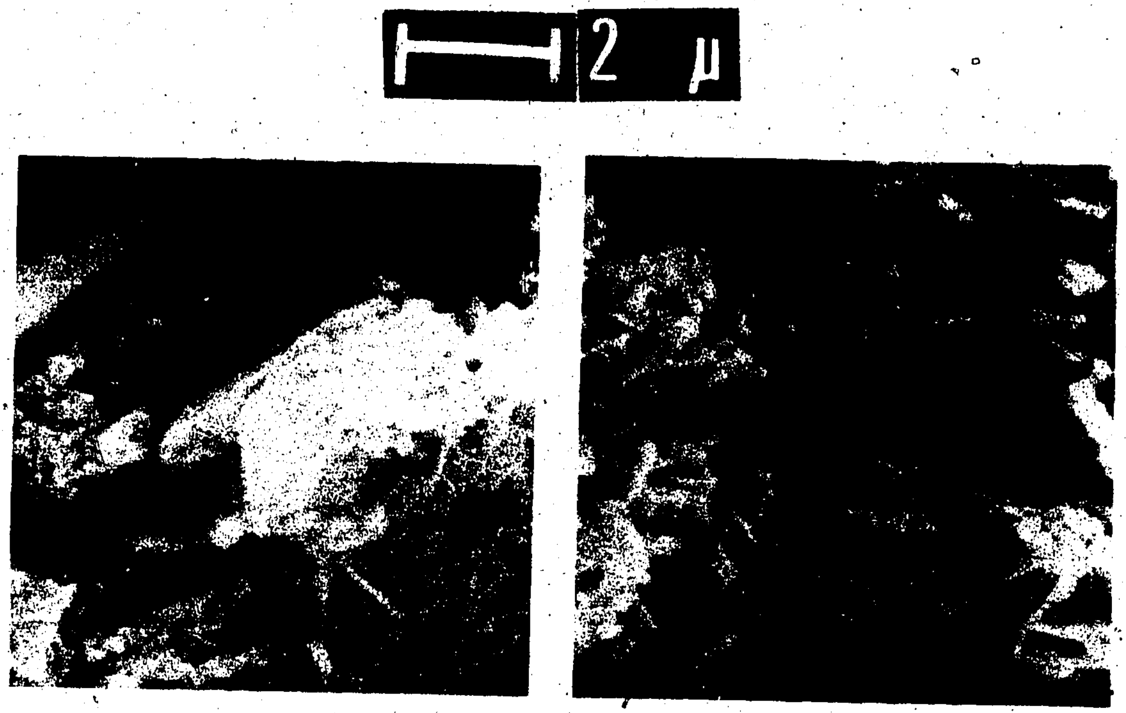
CATALYST 8

CATALYST 9

Figure 7: SCANNING ELECTRON MICROGRAPHS OF CATALYSTS 6, 7, 8, AND 9

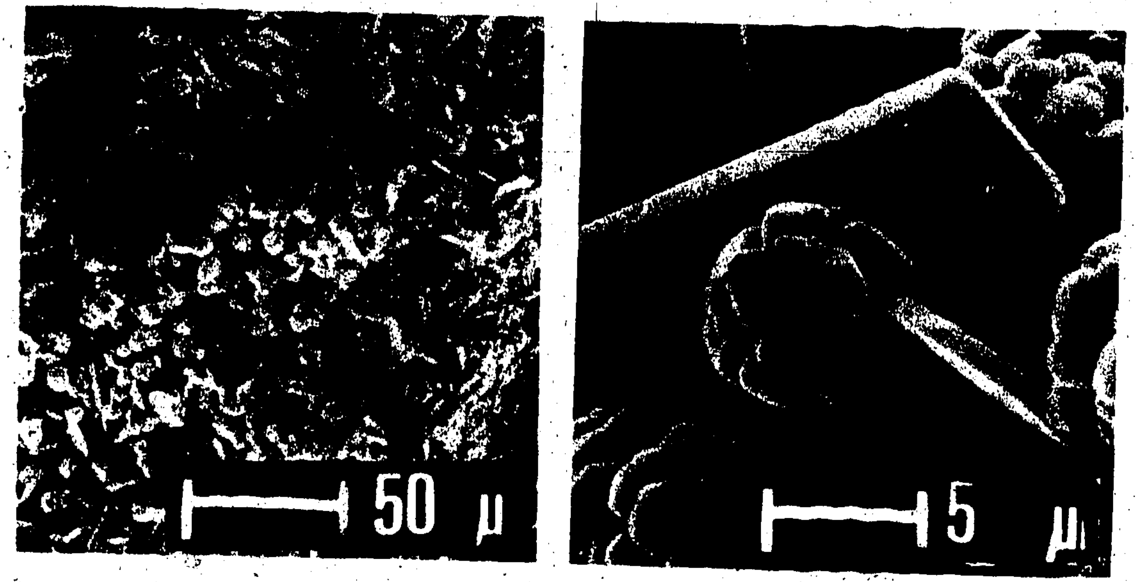


CATALYST 10.　　　　　　　　CATALYST 10

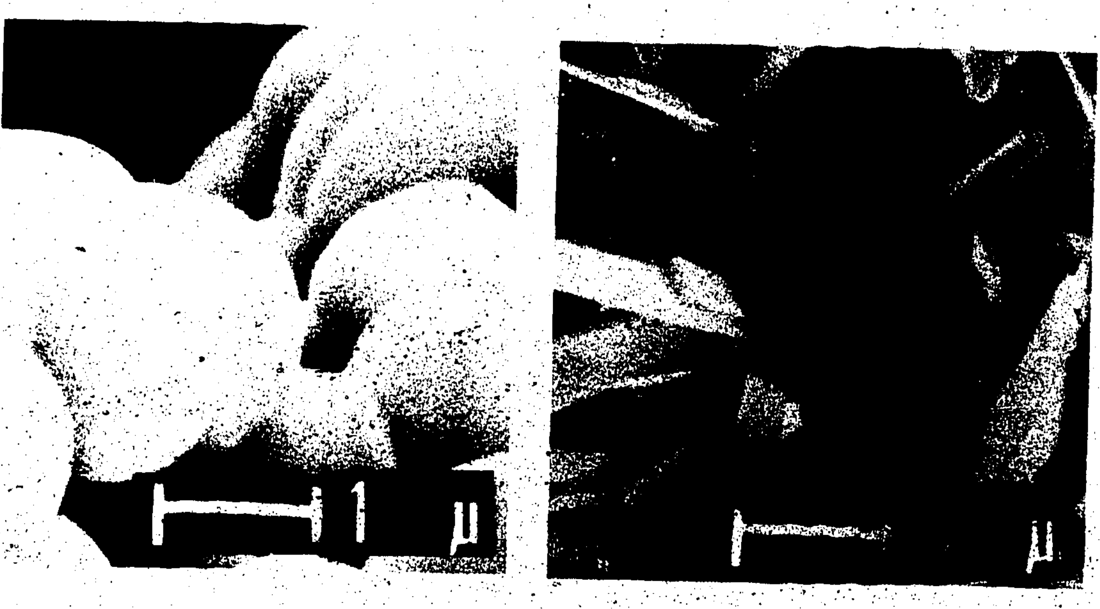


CATALYST 10′　　　　　　　　CATALYST 10′

Figure 8: SCANNING ELECTRON MICROGRAPHS OF CATALYSTS 10 AND 10′



CATALYST 11　　CATALYST 11



CATALYST 11　　MoO_3 CRYSTALS

Figure 9: SCANNING ELECTRON MICROGRAPHS OF CATALYST 11 AND MoO_3 CRYSTALS

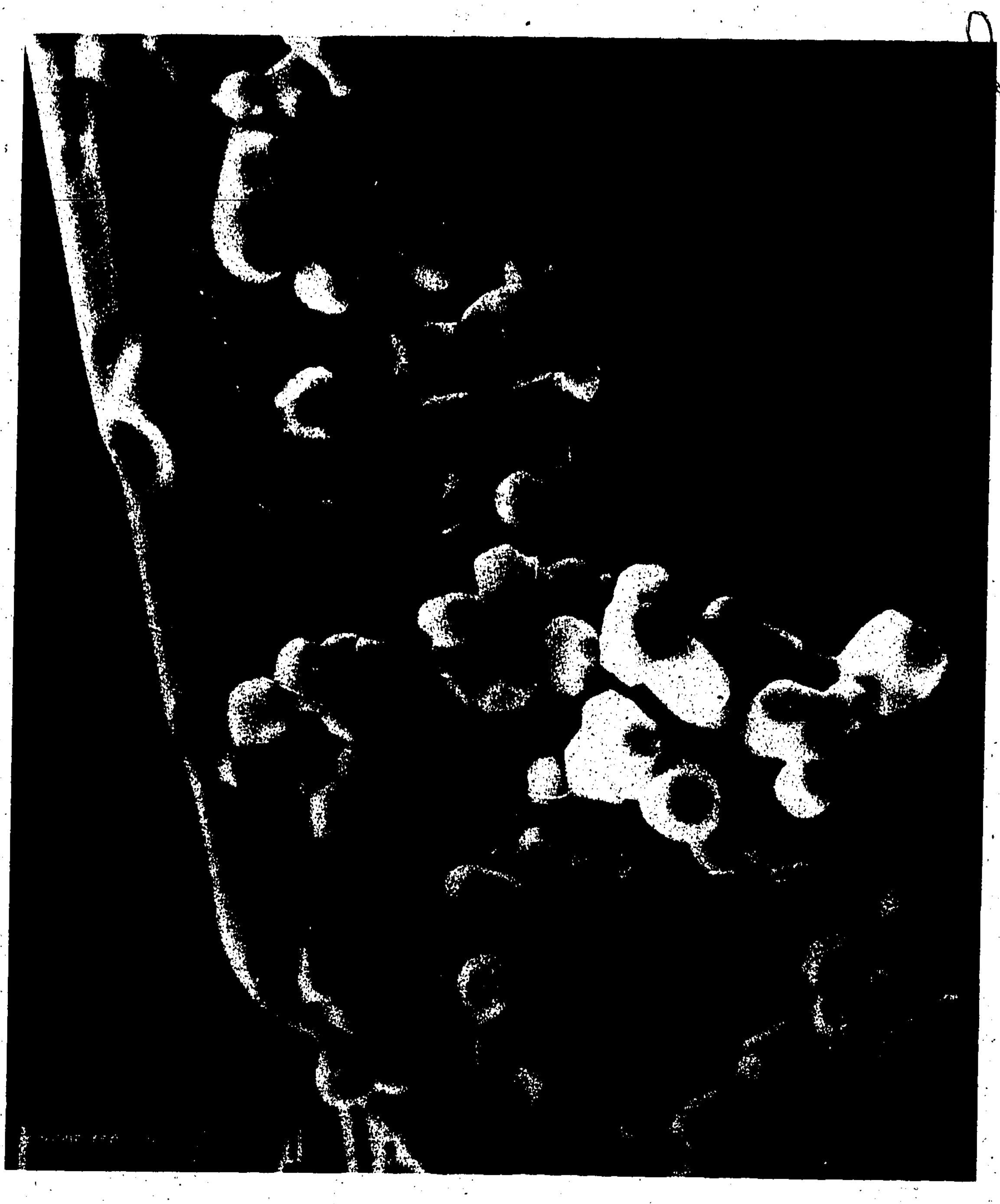


Figure 10: SCANNING ELECTRON MICROGRAPH OF CATALYST E

crystals [39] but the size of these crystals varied from catalyst to catalyst. That these plate-like structures are indeed MoO_3 crystals can be seen in Figure 9 in the bottom right-hand micrograph. The material used for obtaining this micrograph was the sublimated crystalline material collected during the pretreatment of Catalyst 9. These crystals were attached to the glass wool plug at the exit of the U-shaped tube used to preheat the sample. XRF showed that the only metal contained in this material was molybdenum.

A more marked change with treatment occurs in the non-MoO_3 phase of the catalyst. According to the literature this material is assumed to be normal iron molybdate, $Fe_2(MoO_4)_3$, but no determination of the composition of this phase was carried out in this work. By examination of the micrographs it can be seen that a significant variation in the crystal size occurs with treatment at elevated temperatures. This phase, for the fresh Lummus catalysts, appears to be made up of small spheroids ($<0.2\mu$ in diameter) forming a sponge-like structure. Heating this catalyst, even at low temperature (Catalyst 3) causes this phase to change to well developed spheroids. As the temperature of treatment is increased the size of these spheroids increases from

~0.3μ for Catalyst 3 to more than 1μ for Catalyst 8. For Catalyst 9, heated at 820K, for a long period of time, the micrograph shows that an effect, in addition to the growth of crystals, appears to take place causing the plate-like structures of MoO_3 to become three-dimensional in nature, with ledges on the surface.

Examination of numerous micrographs showed that some parts of the surfaces presented spheroids in close contact with MoO_3 crystals. In these areas of contact, a "pitted" structure in the crystals was observed. This effect can be observed in Figure 7 (Catalyst 8) and Figure 10.

(ii) Laboratory Prepared Catalysts

A different structure is observed in the catalyst prepared in our laboratory (Catalyst 10); it can be seen in the corresponding micrograph (Figure 8) that this sample consists of sponge-like and fibrous structures. The sponge-like structure is probably $Fe_2(MoO_4)_3$ and the fibre-like material is possibly MoO_3. Mild temperature treatment (Catalyst 10') causes the fibers to become more well-defined and plates of MoO_3 start to appear. Some indication of formation of spheroids is also present. Severe treatment (Catalyst 11) causes the formation of the characteristic phases of MoO_3 plates and $Fe_2(MoO_4)_3$ spheroids. Micrographs of Catalyst 11 (Figure 9) show a structure which is similar to that of the Lummus catalys[illegible] treated at high temperature although the crystal growth in Catalyst 11 is more pronounced than in any of the [illegible] catalysts.

IV.2 X-Ray Diffraction (XRD)

The results of XRD studies are presented graphically in Figures 11 and 12. The XRD patterns show the characteristic diffraction lines of MoO_3 and $Fe_2(MoO_4)_3$. The lines due to these two phases are indicated on the figures. The line assignments for MoO_3 and $Fe_2(MoO_4)_3$ were taken from the ASTM diffraction files [40, 41]. The lines listed for iron molybdenum oxide, $Fe_2O_3.3\text{-}4\ MoO_3$, [41] were taken as the $Fe_2(MoO_4)_3$ lines.

The diffraction patterns for the Lummus Catalysts (Figure 11) all clearly show the presence of MoO_3 and $Fe_2(MoO_4)_3$ crystal phases. All these samples have about the same degree of crystallinity as indicated by the intensity and sharpness of the diffraction lines; Catalysts 5, 8 and 9 having slightly above average intensities for the MoO_3 lines.

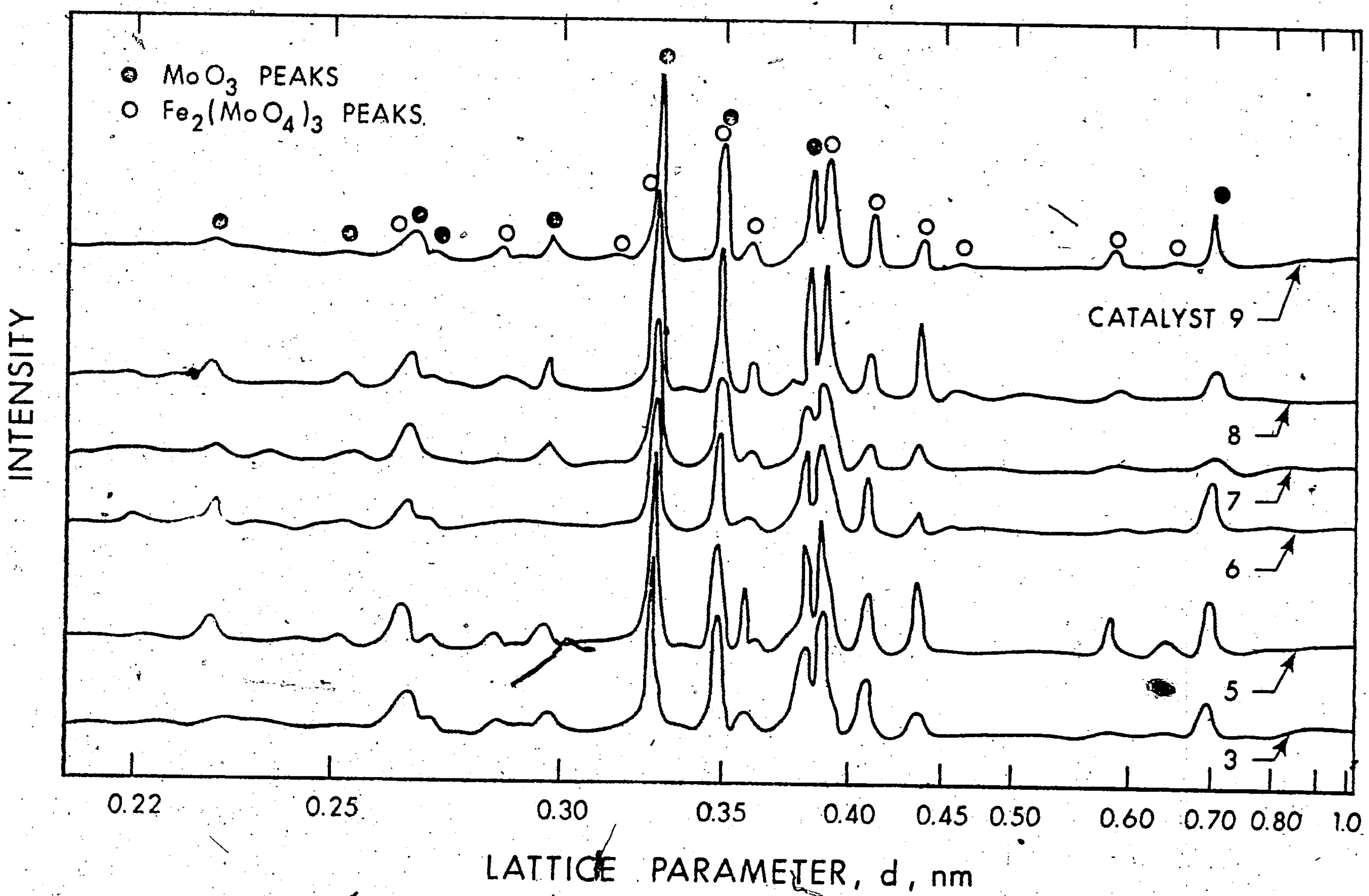


Figure 11: X-Ray Diffraction Patterns of Catalysts 3 and 5 to 9.

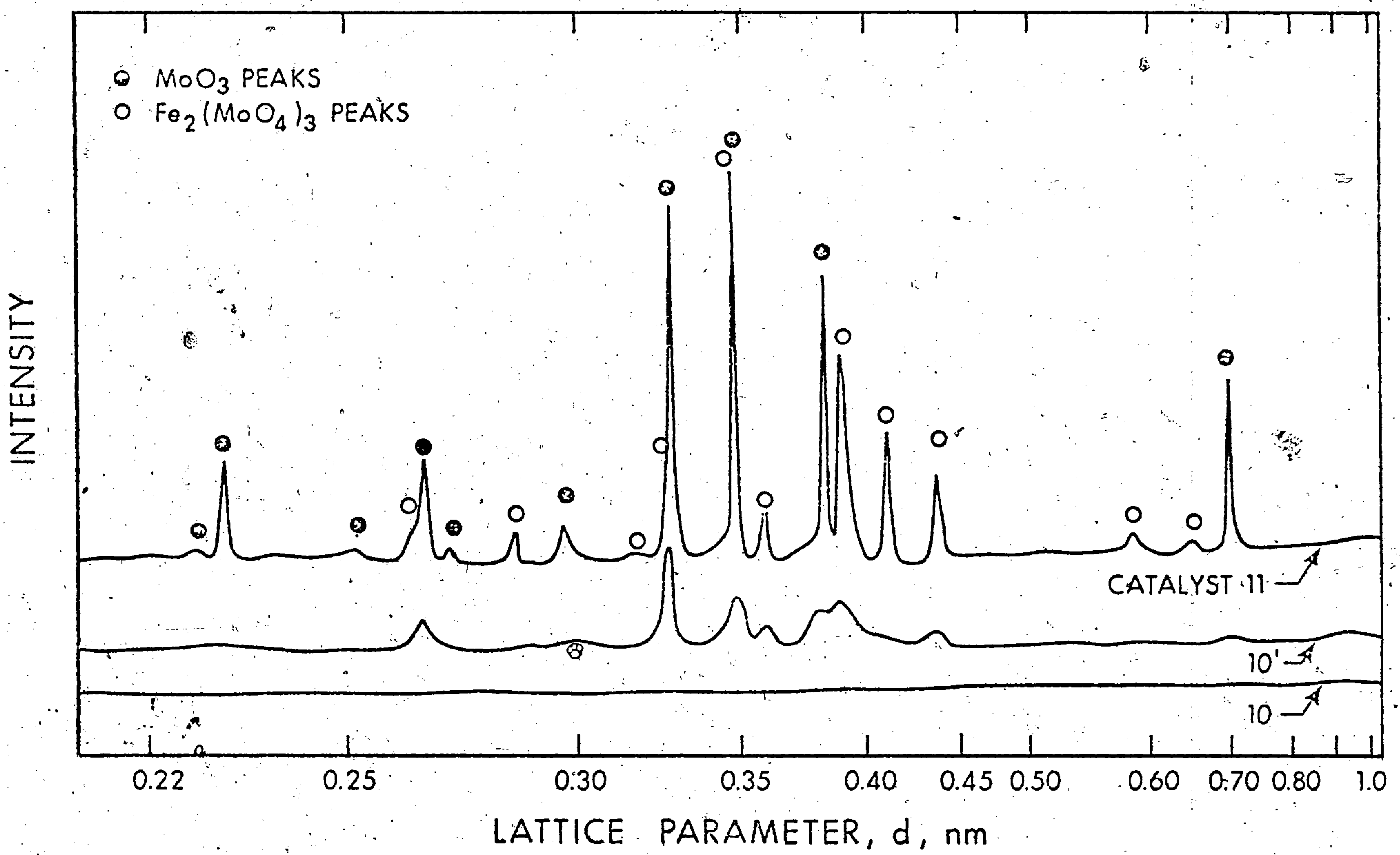


Figure 12: X-Ray Diffraction Patterns of Catalysts 10, 10', and 11.

The XRD results for the samples prepared in the laboratory (Figure 12) show a much greater variance than the Lummus catalysts. Catalyst 10 was found to be amorphous. Treatment at very low temperatures produces a slightly crystalline structure as it can be seen in the pattern for Catalyst 10'. Increasing the temperature a more definite crystalline structure is observed. Catalyst 11 is the most crystalline of all the samples examined.

These results agree well with structural features observed by SEM since for Catalyst 10 the distinct well formed crystals, which form the two characteristic phases, were not observed. Micrographs of Catalyst 10' show the presence of some crystals, in agreement with the XRD results. The large well-defined crystals observed by SEM for Catalyst 11 also agree with the high degree of crystallinity observed by XRD.

IV.3 Surface Area Determinations

The specific surface areas were obtained by the BET method. The data from the experiments were processed according to the computer program presented in Appendix C. As an example, the complete table of results for Catalyst 1 is also given in Appendix C. Plots of the

BET equation with 8 to 10 points per isotherm in the range of P/P_{sat} between 0.05-0.35 all resulted in straight lines (see Figure C-1). In order to test the reproducibility of the method, duplicate determinations were carried out for Catalysts 5 and 11 and the same values were obtained.

In Table 3 the measured specific surface areas are listed. It can be seen that as the temperature of pretreatment increases the specific surface area decreases. For Catalyst 3 the decrease of surface area is more pronounced due to the long treatment period of time (572 hr., compared to 15 to 42 hrs. for other samples).

Again, the qualitative SEM results agree well with the measured decrease in surface area with thermal treatment. The decrease in specific surface area is in accordance with the observed crystal growth. Although the fresh Lummus catalyst (Catalyst 1) had a lower surface area than the prepared catalyst (Catalyst 10'), similar treatment of these fresh catalysts (20 hr. at 870K) to give Catalysts 8 and 11, resulted in a much larger decrease in surface area for Catalyst 10'.

Low temperature nitrogen adsorption isotherms to pressures up to 0.98 of the saturation pressure showed

TABLE 3: Results of Catalyst Characterization

Catalyst	Surface Area (m^2/g)	Mo/Fe Atomic Ratio by XRF	Mo/Fe Atomic Ratio by Weight Loss
1	3.78	3.1	–
3	3.31	3.1	–
5	3.53	3.0	–
6	3.22	3.0	3.1
7	2.42	2.9	3.0
8	1.21	2.7	–
9	1.66	2.8	–
10	8.70	3.4	–
10'	10.72	3.7	–
11	0.25	3.0	–
A	–	2.6	3.0
B	–	2.1	2.9
D	–	1.8	2.9
E	–	1.8	2.8

that the isotherms were of Type IV (BDDT classification) [38]. Analysis of these isotherms showed that the catalysts did not contain any appreciable amount of pores with radii in the 0.001 to 0.03μ range. The micrographs show pores $>0.1\mu$; these are too large to be determined by low temperature nitrogen adsorption. It is concluded from these results that these catalysts do not contain micropores.

IV.4 Catalyst Composition

X-Ray Fluorescence (XRF) was used to estimate the Mo/Fe atomic ratio of the catalysts. The results of these determinations are shown in Column 3 of Table 3. The reported values were obtained by multiplying the Mo/Fe ratio of XRF peak heights by a response factor. This response factor for the Lummus catalysts was calculated from the measured Mo/Fe peak height ratio and the known composition (see Table 1). This resulted in a response factor of 0.356. The response factor for Catalysts 10, 10', and 11 was obtained from the calculated composition of Catalyst 10 and the measured Mo/Fe peak height ratio. The Mo/Fe atomic ratio of Catalyst 10 was 3.4 based on the amount of $FeCl_3 \cdot 6H_2O$ and $(NH_4)_6MoO_7O_{24} \cdot 4H_2O$ used in its preparation. The response factor for these catalysts was 0.365. The use of XRF peak areas rather than peak heights resulted in similar values of the Mo/Fe atomic ratios.

The results in Table 3 show a decrease in the Mo/Fe ratio with thermal treatment. This is in agreement with the observed MoO_3 sublimation. The anomalous result for Catalyst 10' which appears to have a higher Mo/Fe ratio than Catalyst 10 (3.7 compared to 3.4) is probably due to the difference in crystallinity of the two samples, since XRF response is a function of crystal structure [42]. The Mo/Fe ratios obtained by XRF, as reported in Table 3, should only be interpreted qualitatively due to the dependence of XRF response on crystal structure and surface morphology.

IV.5 Thermogravimetric Analysis (TGA)

Weight losses of Lummus Catalyst measured by TGA for different treatment conditions are given in Table 4. Throughout the treatment air was passed over the catalyst pellet. A typical weight loss curve is shown in Figure 13. In one of the experiments, after treatment of the sample for 80 hr. at 870K (Catalyst C), the temperature was increased at a rate of 10°C/min and a sharp decrease in the weight of the pellet was noted at 1020K. This effect corresponds to the melting point of

TABLE 4: Thermogravimetric Analysis Measurements

Catalyst	Catalyst Weight (mg)	Temp. (K)	Time (hr)	Total Weight Loss (mg)
A	120.2	820	48	2.0
B	138.0	870	25	3.2
C	147.8	870	80	10.0
D	14[illegible].3	910	15	3.9
E	151.8	900	48	9.0

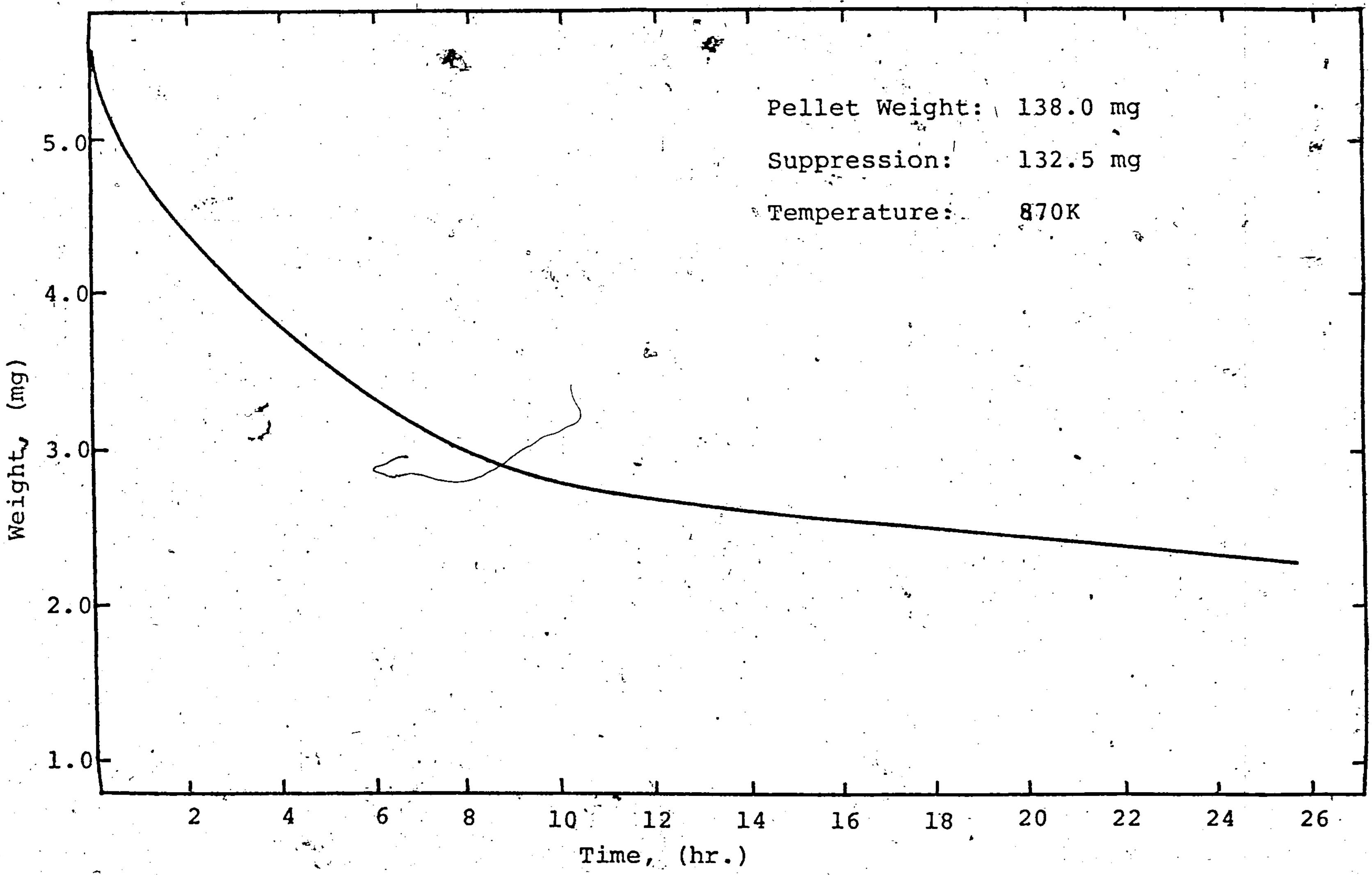


Figure 13: Weight Loss Curve for Catalyst B

ferric molybdate [10].

It is also interesting to note that at temperatures greater than 820K, the wall of the exit of the tube which contained the catalyst became intensely coloured by a blue residue. This colour is characteristic of the molybdenum blues; these are molybdenum oxides with atomic oxygen to molybdenum slightly less than 3. White crystals, which were determined to be MoO_3, also were collected at the exit of the TGA. The vapor pressure of MoO_3 at 1070K is 0.01 atm. and the rate of sublimation is appreciable between 870-970K. Therefore, it can be assumed that the total weight loss was due to sublimation of MoO_3. This assumption appears valid since Catalyst 1 lost $<0.05\%$ of its weight when heated at 520K for 2 hr. Also, the XRF analysis of the white residue showed only the Mo peak.

Table 3, Column 4 shows the values of Mo/Fe ratio calculated from weight loss measurements by TGA (Catalysts A, B, D, E) and during treatment (Catalysts 6 and 7). These values were calculated by assuming that the catalyst has the general empirical formula $Fe_2(MoO_4)_3 \cdot xMoO_3$, that the total weight loss was due to sublimation of MoO_3, and that the starting catalyst (Catalyst 1) had a Mo/Fe atomic ratio of 3.1 (Lummus).

It can be observed that weight loss measurements show that the Mo/Fe atomic ratios obtained by XRF appear to be too low specially in the cases of the catalysts treated in the TGA equipment. One of the reasons of this discrepancy is perhaps the incorrectness in using the same response factor for all catalysts since the XRF signal is sensitive to the surface structure and sample heterogeneity [42].

Another reason, aside from the difference in XRF response due to differences in crystal structure, for the low Mo/Fe atomic ratios obtained by XRF is that the Mo/Fe ratio undoubtedly varies with position in the catalyst pellet. The Mo/Fe ratio is probably lower at the surface of the catalyst pellets than in the interior of the pellet since MoO_3 sublimation occurs from the exterior of the pellet, and loss of MoO_3 from the interior of the pellet would require migration (diffusion) of MoO_3. The XRF measurements were carried out on uncrushed pellets and hence the low Mo/Fe ratios obtained reflect the exterior pellet composition rather than the bulk composition of the catalyst. The weight loss measurements, on the other hand, result in an average composition of the whole pellet.

Attempts to use atomic adsorption spectroscopy in order to get a more accurate Fe and Mo content of the catalysts were frustrated by the inability to find a solvent which completely dissolved the catalysts.

IV.6 Kinetics Studies of the Oxidation of Methanol

Kinetics studies, using the previously described integral-bed reactor, were carried out to determine the activity of the catalysts for the oxidation of methanol to formaldehyde. The approach taken was to evaluate specific rate constants based on various rate functions, and to compare the specific activity of the various catalysts on the basis of the specific rate constants.

(i) Testing of Rate Functions

It was not the objective of this work to obtain a large amount of kinetic data for the determination of a rate function. The aim of the kinetic measurements was to obtain data on the effect of thermal treatment on the activity of the catalysts. During the activity measurements, sufficient kinetic data were obtained to evaluate the applicability of various rate functions proposed in the literature to the catalysts employed in the present study.

The oxidation of methanol to formaldehyde in the presence of Fe-Mo oxide catalysts proceeds practically irreversibly according to the overall equation:

$$CH_3OH(g) + \tfrac{1}{2}O_2(g) \longrightarrow CH_2O(g) + H_2O \qquad (18)$$

A variety of rate functions for this system has been proposed in the literature (see Chapter II). In the present study, the concentration of formaldehyde and water in the feed were always close to zero, and oxygen was always present in large excess. The rate data were therefore analyzed by rate functions which did not include concentration terms for water or formaldehyde. The three rate functions examined were:

$$-r_{CH_3OH} = k_1 \, C_{CH_3OH} \qquad (19)$$

$$-r_{CH_3OH} = k_{\frac{1}{2}} \, C^{\frac{1}{2}}_{CH_3OH} \qquad (20)$$

$$-r_{CH_3OH} = k_0 \, C^{\frac{1}{2}}_{CH_3OH} \, C^{\frac{1}{2}}_{O_2} \qquad (21)$$

where

r_{CH_3OH} - rate of reaction based on surface area, [moles/(m^2-sec)].

k_i - rate constants.

C_{CH_3OH}, C_{O_2} - concentrations of methanol and oxygen, respectively, [moles/m^3].

The values of the rate constants, k_1, $k_{1/2}$, and k_o, based on surface area, were calculated from the measured fractional conversion using the following equations:

$$k_1 = \frac{F_{A_o}}{S.W.C_{A_o}} \left[-\ln\,(1-X_A)\right], \quad [\text{m/sec}] \tag{22}$$

$$k_{1/2} = \frac{2\,F_{A_o}}{S.W.C_{A_o}^{1/2}} \left[1-(1-X_A)^{1/2}\right], \quad [\text{moles}^{1/2}/(\text{m}^{1/2}\text{-sec})] \tag{23}$$

$$k_o = \frac{2^{3/2} F_{A_o}}{S.W.C_{A_o}} \ln \frac{[F_{A_o}\,(1-X_A)/2]^{1/2} - [F_{B_o} - \tfrac{1}{2} F_{A_o} X_A]^{1/2}}{[F_{A_o}/2]^{1/2} - F_{B_o}^{1/2}}, \quad [\text{m/sec}] \tag{24}$$

where

F_{A_o} - feed rate of methanol, [moles/sec].

F_{B_o} - feed rate of oxygen, [moles/sec].

C_{A_o} - feed concentration of methanol, [moles/m^3].

S - specific surface area of catalyst, [m^2/g].

W - weight of catalyst in reactor, [g].

X_A - exit fractional conversion of methanol.

The exit fractional conversion of methanol was calculated in the following three ways:

a. based on methanol analyses

$$X_A = \frac{F_{A_o} - F_{A,e}}{F_{A_o}} \qquad (25)$$

b. based on formaldehyde analyses

$$X_A = \frac{F_{CH_2O,e}}{F_{A_o}} \qquad (26)$$

c. based on water analyses

$$X_A = \frac{F_{H_2O,e} - F_{H_2O,o}}{F_{A_o}} \qquad (27)$$

where

$F_{i,o}$ - feed rate of component i, [moles/sec].

$F_{i,e}$ - product rate of component i, [moles/sec].

Equations 22, 23, and 24 were obtained by integration of the design equation for an isothermal plug-flow reactor, using Equations 19, 20, and 21 as the rate functions and assuming that the vo[illegible]etric flow rate change due to reaction is negligible. Neglecting this volume change introduces an error which is much smaller than the uncertainty in the measured fractional conversions. Appendix D gives the computer program used to calculate the fractional conversions and the rate constant for the various rate functions and definition of X_A^*. The operating conditions of the individual runs and the feed and product compositions are also presented in Appendix D.

Values [illegible] measured fractional conversions and the calculated values of the rate constants, according to Equations 22, 23, and 24, are listed in Table 5. The reported fractional conversions and rate constants are the average value obtained from methanol, water and formalde-

TABLE 5: Results of Kinetic Experiments

Temperature: 533 - 536K

Methanol Feed Rate: 1.08×10^{-4} moles/sec

Run No.	Air Feed Rate $\times 10^3$ (moles/sec)	Fractional Conversion X_A	Rate Constants $\times 10^7$		
			k_1 (m/sec)	$k_{1/2}$ (gmoles$^{1/2}$/m$^{1/2}$-sec)	k_0 (m/sec)
		CATALYST 3			
69- 74	1.33	0.45	5.5	6.2	3.0
75- 83	1.86	9	5.7	5.8	2.7
90- 98	2.26	0.36	6.1	5.8	2.6
99-105	2.64	0.36	6.4	6.0	2.6
		CATALYST 6			
226-233	1.30	0.48	6.1	6.9	3.3
216-225	1.60	0.51	7.8	8.1	3.8
213-215	2.27	0.47	8.9	8.3	3.7

hyde analyses.

The data show that the rate function which is ½ order in methanol (Equation 20) describes the data well. This rate function is similar to that proposed by Pomerantsev and Mukhlenov [26] if one considers that, for the conditions used in our experiments, the term $(1 + 0.5p_{CH_2O}/p_{CH_3OH}p_{O_2}^{0.5})^{0.5}$ is approximately constant (< ±5% variation).

In order to determine the temperature dependence of the rate constant several experimental runs were carried out for Catalyst 3. Table 6 summarizes the experimentally obtained values. An Arrhenius plot of these results is shown in Figure 14. It can be seen from this plot that the experimental points lay quite well on a straight line. The activation energy and pre-exponential factor calculated from the slope and intercept of this line, by linear-least-squares, were E = 16.5 kcal/mole and A = 3.51 moles^{½}/m^{½}-sec.

The activation energy of 16.5 kcal/mole agrees well with the values obtained by other workers. Jiru et al. [24], using the same rate function as given by Equation 20 obtained an activation energy of 16 kcal/mole. Pomerantsev and Mukhlenov [26], using a modified half-

TABLE 6: Effect of Temperature o[illegible] Reaction Rate Constant

Catalyst Sample: 3

Methanol Feed Rate: 1.08×10^{-4} moles/sec

Run No.	[illegible]emp. ([illegible])	Air Feed Rate $\times 10^3$ (gmoles/sec)	Fractional Conversion X_A	$k_{\frac{1}{2}} \times 10^7$ (moles$^{\frac{1}{2}}$/m$^{\frac{1}{2}}$-sec)
118-122	504	2.54	0.16	2.48
123-130	513	2.30	0.23	3.45
156-162	519	2.27	0.26	3.92
131-139	524	2.30	0.26	4.05
90- 98	533	2.27	0.36	5.83
140-146	544	2.30	0.52	8.93
106-112	552	2.28	0.57	10.00
152-155	568	2.28	0.80	16.20
113-117	571	2.04	0.81	16.10

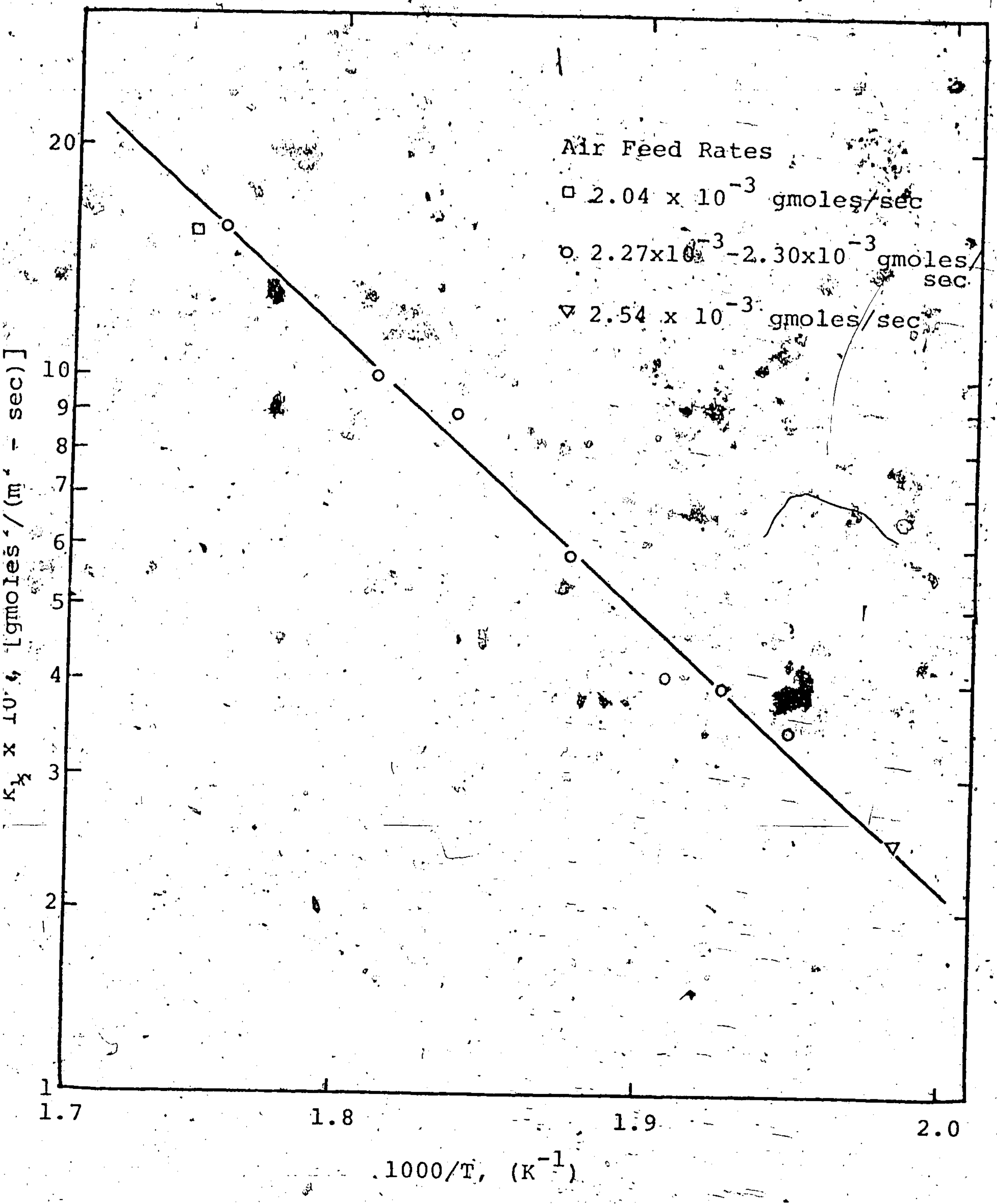


Figure 14: Arrhenius Plot for Methanol Oxidation

order rate function, obtained activation energies of 14 to 20 kcal/mole. The comparison of the pre-exponential factor of 3.51 moles$^{1/2}$/m$^{1/2}$-sec obtained in this work with values obtained by other investigators is difficult since most of the reported rate constants are not based on catalyst surface area. Jiru *et al.* [24], reports the specific surface area of the catalyst employed, and by using the reported values of the half order rate constant at 270°C and the activation energy, a pre-exponential factor of 3.4 moles$^{1/2}$/m$^{1/2}$-sec is obtained. This excellent agreement of the pre-exponential factor reported by Jiru *et al.* [24] and the results of the present study are somewhat surprising since the catalyst used by these authors had a Mo/Fe atomic ratio of 2.6 while the same ratio for the catalyst used in this study was 3.1.

Other factors, besides the composition of the catalyst, which can influence the apparent kinetics are energy and mass transport limitations. The two factors, as applied to the present system, will be discussed in a later section.

(ii) Catalyst Activity Measurements

The kinetic studies to determine the activity of the catalysts were carried out with an air feed rate of

2.20 - 2.27 x 10^{-3} moles/sec (except for the runs with Catalysts 7 and 11 where the air feed rates used were 1.86 x 10^{-3} and 1.59 x 10^{-3} moles/sec, respectively). The methanol feed rate was 1.08 x 10^{-4} moles/sec for all the runs. The average temperature of the catalyst bed, as measured by thermocouples TC1, TC3, TC4, TC5 and TC7 (see Figure [illegible]) ranged from 531 to 536 K. The amount of catalyst charged to the reactor for all catalysts, except Catalyst 11, was 20 to 21 g. For Catalyst 11 only 11.7 g. were used.

Values of the measured fractional conversions and the calculated values of $k_{\frac{1}{2}}$ are listed in Table 7. The reported fractional conversion and rate constant are the average values obtained from methanol, water and formaldehyde analyses. For each experiment several analyses of the feed and product streams were made. The calculated variation was ~ ±5% of the reported value (e.g., if mole % of methanol in product = 2.0%, then the error in this value is ≤ ±0.1). The values of the rate constant $k_{\frac{1}{2}}$ based on methanol, water and formaldehyde analyses varied also within ±5% for $X_A > 0.15$. For Catalyst 1 several experiments were made under similar conditions (cf. Runs 168-176, 177-182, 183-189 and 190-193) and the results obtained show that the value of $k_{\frac{1}{2}}$ based on the

TABLE 7: Results of Activity Measurements

Run No.	Catalyst	Fractional Conversion X_A	$k_{\frac{1}{2}} \times 10^7$ (gmoles$^{\frac{1}{2}}$/m$^{\frac{1}{2}}$-sec)
168-17[illegible]	1	0.48	7.0
9[illegible]3	3	0.36	5.8
198-204	5	0.49	8.1
213-215	6	0.47	8.3
242-250	7	0.39	8.5
255-258	8	0.11	4.7
263-264	9	0.06	1.8
251-254	10	0.84	6.9
270-271	11	~0.01	~2

average value of X_A is reproducible within ±3%. For small fractional conversion, small errors in the measured methanol composition causes large errors in X_A and $k_{\frac{1}{2}}$, since the fractional conversion for this situation is obtained by subtraction using two numbers that are approximately equal in magnitude (see Equation 25). Therefore, for the cases where the fractional conver[illegible] < 0.15 the average values of X_A and $k_{\frac{1}{2}}$ reported in [illegible]re based only in water and formaldehyde analyses. [illegible]e rate constant for Catalyst 11 is approximate since the conversion was too low to be determined accurately.

V - DISCUSSION

The high activity of Fe-Mo oxide catalyst has generally been attributed to the iron molybdate phase containing Mo in a slight excess to the stoichiometric amount given by the formula $Fe_2(MoO_4)_3$ [11, 12, 17, 31]. Kolovertnov _et al._ [9] also report that an Fe-Mo oxide catalyst with atomic Mo/Fe = 1.7 (_i.e._, Mo in excess of the stoichiometric ratio of 1.5) has the highest specific activity. The results obtained in the present work can be interpreted in terms of this Mo rich iron molybdate phase as the active species.

Before the specific activity of various catalysts can be compared on the basis of rate constants, it has to be established that the measured rate of reaction is the intrinsic rate, _i.e._ it is not influenced by mass or energy transfer limitations.

It is difficult to develop a general criterion for determining whether energy transfer within the catalyst pellets influences the measured rates for reactions following half-order kinetics. The results shown in Table 5 and Appendix D show that the present kinetic data can also be described by a first-order rate function (Equation 19). The first-order rate function does not describe the data quite as well as the half-order rate function, but for the qualitative determination of the effects of internal energy and mass transfer on the reaction rates it is adequate.

If the effect of thermal gradients in the interior of the catalyst pellets is to influence the measured rates by less than 5%, then the value of the parameter δ, defined by Equation 28, should be less than 0.3 for exothermic reactions [43].

$$\delta = \frac{-\Delta H \; E \; D_i \; C_o}{R \; T_o^2 \; \lambda} \tag{28}$$

where

ΔH = heat of reaction = -38×10^3 cal/mole [2].

E = activation energy for first-order rate function $= 19 \times 10^3$ cal/mole (obtained by Arrhenius plot of k_1)

D_i = effective diffusivity $\simeq 0.05$ cm^2/sec (see discussion below).

C_o = concentration of methanol on external surface of catalyst pellet ≤ 1.7 moles/m^3.

T_o = temper[illegible]at external surface of catalyst ≥ 504K

λ = effecti[illegible]rmal conductivity of catalyst pellet ≃ 4 x 10[illegible] cal/cm-sec-K. (See discussion below).

The values of D_i and λ given above are estimates, since no values for these parameters are available for the Fe-Mo oxide-methanol system. The value of D_i was estimated from the molecular diffusivity of methanol in air, D_M, by the method described by Petersen [44]. The ratio of the tortuosity factor to constriction factor was assumed to be 2 (it is probably considerably higher, but larger values of this ratio will result in lower values of D_i). D_M at 0^oC is 0.132 cm^2/sec [45]. Since D_M varies as $T^{3/2}$ [46], D_M at 504K is 0.33 cm^2/sec. With a void fraction of the catalyst being approximately 0.3, D_i is estimated to be ≤ 0.05 cm^2/sec. The effective thermal conductivity for oxides catalysts with a void fraction of ~0.3 is of the order of 4×10^{-4} cal/cm-sec-K [47,48].

The value of δ obtained by substituting the above values into Equation 28 is 0.304. This value is very close to the above cited value of 0.3. It should be kept in mind, that the calculated value of 0.304 used values of the parameters which would maximize δ. Hence, it is unlikely that in the present study the kinetics are influenced by temperature gradients inside the catalyst pellets.

Another problem of energy transport exists, i.e. the transfer of energy between the catalyst pellets and the bulk gas phase. Using the method described by Smith [49], temperature differences between the external surface of the catalyst pellets and the bulk gas phase up to 6 to 8°C were calculated. This was the maximum temperature difference and it occurred for Runs 69-74, 113-117, 152-155, and 226-233, i.e. the experiments carried out at low air feed rate (low Reynolds number resulting in low heat transfer coefficients) and the experiments at higher temperatures (high reaction rates accompanied by high rates of energy liberation). For the majority of experiments (air feed rates > 2500 cc (STP)/min and temperature < 550K), the catalyst pellet-bulk gas phase temperature difference was calculated to be $\lesssim 2$°C.

The above results can explain the observed dependence of the rate constant on air flow rate (see Table 5 and Appendix D). The experimental results show that at low air feed rates ($\lesssim 2500$ cc (STP)/min) the determined rate constants are larger than at higher air feed rates. At the low air flow rates, the catalyst temperature can be several degrees above the measured bulk gas temperature, and hence the rate of reaction and the subsequently calculated rate constants are higher than they would be if the catalyst temperature had been equal to the gas phase temperature.

The problem of internal mass transfer limitations (i.e., concentration gradients in the pores of the catalyst), can be examined by the Thiele parameter [50]. The value estimated for the Thiele parameter based on single pores is $\lesssim 2.0$ using a pore length of 0.2 cm (equal to the radius of the pellets) and a pore radius of ~500 Å (estimated minimum radius of pores from micrographs). A similar value is obtained if the Thiele parameter is based on the catalyst pellet characteristics. This value of the Thiele parameter is close to the value of 3 at which internal mass transfer limitations start to be significant and it is greater than the value of 0.4 below which internal mass transfer limitations can be neglected.

The results shown in Figure 14 (Arrhenius plot) suggest that internal mass transfer is not affecting the measured kinetics since no decrease in activation energy with increasing temperature is observed. This discrepancy of the effect of internal mass transfer as predicted by the estimated Thiele parameter and the observed invariance of the activation energy with temperature can be explained by the physical structure of the catalyst pellets. The diffusion length of 0.2 cm used in estimating the Thiele parameter is un[illegible]edly too large (probably by more than an order of magnitude). This is the case because the catalyst pellets contain many large pores (cracks) as observed by SEM (see Figure 3). The presence of these large pores (radii >10^4 Å) will reduce the resistance to mass transfer considerably, and the diffusion [illegible] the small pores is over much shorter distances. It is therefore concluded that the kinetic results obtained are [illegible] influenced by internal mass transfer limitations. If internal mass transfer limitations are not present and the pellet is isothermal, then it is impossible for external mass transfer limitations to occur [51].

The above analyses have [illegible] internal energy transfer and internal and external mass transfer do not affect the reaction rates. External mass and energy transfer was found to influence the reaction rates at temperatures >550°K and air flow rates ≲2500 cc (STP)/min. The experiments to determine the effect of treatment on the catalytic activity were carried out at 536K and air flow rates of >2500 cc (STP)/min; hence the measured rates were intrinsic rates.

The specific activities (i.e., the activity per unit of surface area) are proportional to the rate constants, $k_{\frac{1}{2}}$, listed in Table 7. Treatment of catalyst for ≤ 18 hrs. at temperature ≤ 820K resulted in an increase of up to 30% in the specific catalytic activity. This is probably due to crystallization of the active phase. Longer treatment at elevated temperatures (Catalysts 8, 9 and 11) and very long treatment at lower temperatures (Catalyst 3) results in a decrease in specific activity. This is probably due to the reduction of the excess Mo in the $Fe_2(MoO_4)_3$ phase. This Mo could be incorporated into the MoO_3 crystals or be lost by sublimation.

The scanning electron micrographs show the development of large well defined spheroids attributed to $Fe_2(MoO_4)_3$ for Catalysts 8, 9 and 11. Although these spheroids are not as well developed in Catalyst 3, it is reasonable to assume that the prolonged treatment at 500K would result in the segregation of stoichiometric $Fe_2(MoO_4)_3$ and MoO_3 phases.

Examination of numerous scanning electron micrographs showed spheroids in contact with MoO_3 crystals. The "pitted" structures in these cases indicate that material transport, probably MoO_3, occurs between the $Fe_2(MoO_4)_3$ and MoO_3 phases. This would suggest that as long as sufficient physical contact exists between the two phases an active Mo rich iron molybdate phase will be present. This need of the physical contact in order for the catalyst to be active, would explain the process of reactivation of deactivated catalyst by the addition or redispersion of molybdenum oxide [30].

The results of this work therefore qualitatively support the hypothesis that the loss of activity of Mo-Fe oxide catalysts is due to the removal of Mo from a Mo rich $Fe_2(MoO_4)_3$ phase. This loss occurs by recrystallization into well defined MoO_3 and $Fe_2(MoO_4)_3$ phases (as shown by micrographs), plus the sublimation of MoO_3. Although the XRF analysis of the catalysts pellet did not yield quantitative Mo/Fe ratios, the XRF analysis of the sublimated material showed only Mo. The micrographs of the sublimated material (Figure 9) showed that it consisted of MoO_3 crystals. It is not known whether the sublimation of MoO_3 occurs from the $Fe_2(MoO_4)_3$ crystals rich in Mo or only from MoO_3 crystals . The sublimation process is another possible mechanism by which Mo can be removed from the Mo rich $Fe_2(MoO_4)_3$ phase.

One difficulty arises in the determination of specific activities if one ascribes the catalytic activity to the Mo rich $Fe_2(MoO_4)_3$ phase. In this case one should express the rate constants in terms of $Fe_2(MoO_4)_3$ surface area rather than in terms of the total surface area.

Unfortunately, surface area measurements by the BET method do not enable one to distinguish between MoO_3 and $Fe_2(MoO_4)_3$ surface areas. On the basis of the scanning electron micrographs it is possible to estimate (very approximately) the $Fe_2(MoO_4)_3$ surface area if one assumes that the spheroid particles make up this phase. The approximate estimate of the $Fe_2(MoO_4)_3$ surface areas from the micrographs and the specific activities based on these areas showed the same trends for the specific activity as those based on the total surface area, but the increase in specific activity, based on $Fe_2(MoO_4)_3$ surface area, due to treatment at 820K and 18 hr. was ~70% as compared with 30% when based on the total surface area.

In the case of industrial reactors one is not interested in the specific activity of the catalyst, but in the total activity. Hence the specific activity of the catalyst may increase for an initial period, but the total activity declines due to the decrease in surface area. For prolonged treatment, as it is the case in industrial reactors (assuming that the treatment in air has similar effects as the conditions encountered in the reactor), both specific activity and specific surface area decrease. Hence, the deactivation of Fe-Mo oxides in industrial reactors is believed to occur because of losses in specific activity and specific surface area.

VI - CONCLUSIONS

The treatment at elevated temperatures has the following effects on iron molybdenum oxide catalysts:

1. Loss of Specific Surface Area

Based on the marked decrease in surface areas with thermal treatments observed in this work, it is concluded that one of the reasons for the deactivation of the Fe-Mo oxide catalysts is a loss of surface area.

2. Sublimation of MoO_3

The physical loss of MoO_3 from the Fe-Mo oxide catalysts by sublimation reduces the Mo content in the Mo rich $Fe_2(MoO_4)_3$ phase either directly by sublimation of MoO_3 from this phase or indirectly by reducing the amount of MoO_3 in physical contact with the $Fe_2(MoO_4)_3$.

3. Growth and Segregation of MoO_3 and $Fe_2(MoO_4)_3$ phases

The elevated temperatures, or very long treatment at lower temperatures, produce the redistribution and growth of MoO_3 crystals and also a significant growth of $Fe_2(MoO_4)_3$ spheroids. This segregation apparently separates the $Fe_2(MoO_4)_3$ and MoO_3 phases originally in contact and reduces the transfer of MoO_3 between the two phases which is necessary to maintain the catalytic activity.

The high Mo/Fe (>3) ratio in fresh industrial catalysts is necessary to extend the catalyst life since a lower Mo content would result in a more rapid segregation of the phases and depletion of the excess MoO_3 by sublimation.

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APPENDIX A

CALIBRATION OF ROTAMETER

Calibration of Rotameter

The calibration of a rotameter for compressible fluids requires that the calibration runs be conducted in such a manner so that the density of the fluid in the rotameter is a constant. This is required since the mass flow rate, $\dot{m}$, is related to the rotameter reading by

$$\dot{m} = [(\rho_f-\rho)\rho]^{\frac{1}{2}} f(y) \qquad \text{(A.1)}$$

where

ρ_f = density of the rotameter float

ρ = density of the fluid at the conditions in the rotameter

$f(y)$ = relationship between volumetric flow rate of fluid at conditions in rotameter and the rotameter reading, y. $f(y)$ is not a function of ρ.

In order to calibrate a specific rotameter, it is necessary to determine the relationship between $\dot{m}$ and y at only one value of ρ. The ideal gas law, for gases at low pressures, and Equation A-1 can then be used to determine the mass flow rate at rotameter pressures and temperatures other than the pressure and temperature used for the calibration runs. The procedure to obtain the mass flow rate at conditions other than the calibration conditions is illustrated below.

Let

ρ_c = density at the calibration conditions (T_c and P_c)
ρ = density at any other temperature and pressure (T and P)

Using the ideal gas law we obtain

$$\rho_c = \frac{P_c M}{RT_c} \tag{A.2}$$

and

$$\rho = \frac{PM}{RT} \tag{A.3}$$

where M = molecular weight of gas

Then the ratio of the mass flow at T and P to the mass flow rate at T_c and P_c, $\dot{m}_c$, at a fixed value of y, is given by

$$\frac{\dot{m}'}{\dot{m}_c} = \frac{[(\rho_f-\rho)\rho]^{\frac{1}{2}}}{[(\rho_f-\rho_c)\rho_c]^{\frac{1}{2}}} \tag{A.4}$$

or

$$\dot{m} = \frac{[(\rho_f-\rho)\rho]^{\frac{1}{2}}}{[(\rho_f-\rho_c)\rho_c]^{\frac{1}{2}}}\,\dot{m}_c \qquad (A.5)$$

By knowing the relationship between $\dot{m}_c$ and y, the flow rate at other conditions can be calculated by means of Equation A.5.

In the present work, the calibration runs were carried out at 21.1°C and a pressure in the rotameter of 747 Torr. The volumetric flow rate as a function of rotameter reading was measured by a wet-test meter (0.1 ft^3/revolution). The pressure at the exit of the rotameter was measured by a manometer, and this pressure was kept constant at all flow rates by adjusting a needle valve downstream of the wet-test meter. The results of the calibration are shown in Table A-1. The measured volumetric flow rates were converted to volumetric flow rates at standard conditions $Q_{c,STP}$, (STP, standard temperature, T_o = 0°C; standard pressure, P_o = 760 Torr). The use of flow rates at standard conditions is analogous to using mass flow rate. Hence, a plot of y versus $Q_{c,STP}$ yields the necessary calibration curve. Figures A-1 and A-2 show the calibration curves for the two floats in the Matheson rotameter employed in this work.

For the present application Equation A-5 can be simplified since for all flow rate measurements the temperature was 21°C ±1°C, and the density of the rotameter floats are much larger than the fluid density (ρ_f for glass float $\simeq 3$ g/cc, ρ_f for stainless steel float $\simeq 8$ g/cc, and $\rho_{air} = 1 \times 10^{-3}$ g/cc). With these simplications, Equation A-5 becomes

$$\dot{m} = \left(\frac{P}{P_c}\right)^{\frac{1}{2}} \dot{m}_c \qquad \text{(A.6)}$$

and substituting Q_{STP} for $\dot{m}$ and $Q_{c,STP}$ for $\dot{m}_c$ yields

$$Q_{STP} = \left(\frac{P}{P_c}\right)^{\frac{1}{2}} Q_{c,STP} \qquad \text{(A.7)}$$

Hence, with the aid of the calibration curves, $Q_{c,STP}$ can be found as a function of y, and the flow rate at the measured rotameter pressure P can be calculated by Equation A.7.

TABLE A-1: Experimental Data for Calibration of Rotameter

$$P = P_{atm} + P_{manom} = 707.0 + 40.0 = 747.0 \text{ Torr}$$

$$T = 21.1^{\circ}C$$

y [mm]		Time for 1/10 ft^3 [sec]	Q' at 747.0 Torr & 21.1°C [cc/min]	$Q_{c,STP}$ at S.T.P. [cc(STP)/min]
Float: Glass	Float: Stainless Steel			
-	110	42	4045.3	3689.3
-	85	51	3331.4	3038.2
150	65	65	2613.9	2384.9
125	56	74	2296.0	2094.9
100	47	88	1930.0	1761.6
75	37	113	1503.6	1371.9
50	25	168	1011.3	922.7
25	14	381	445.9	406.8

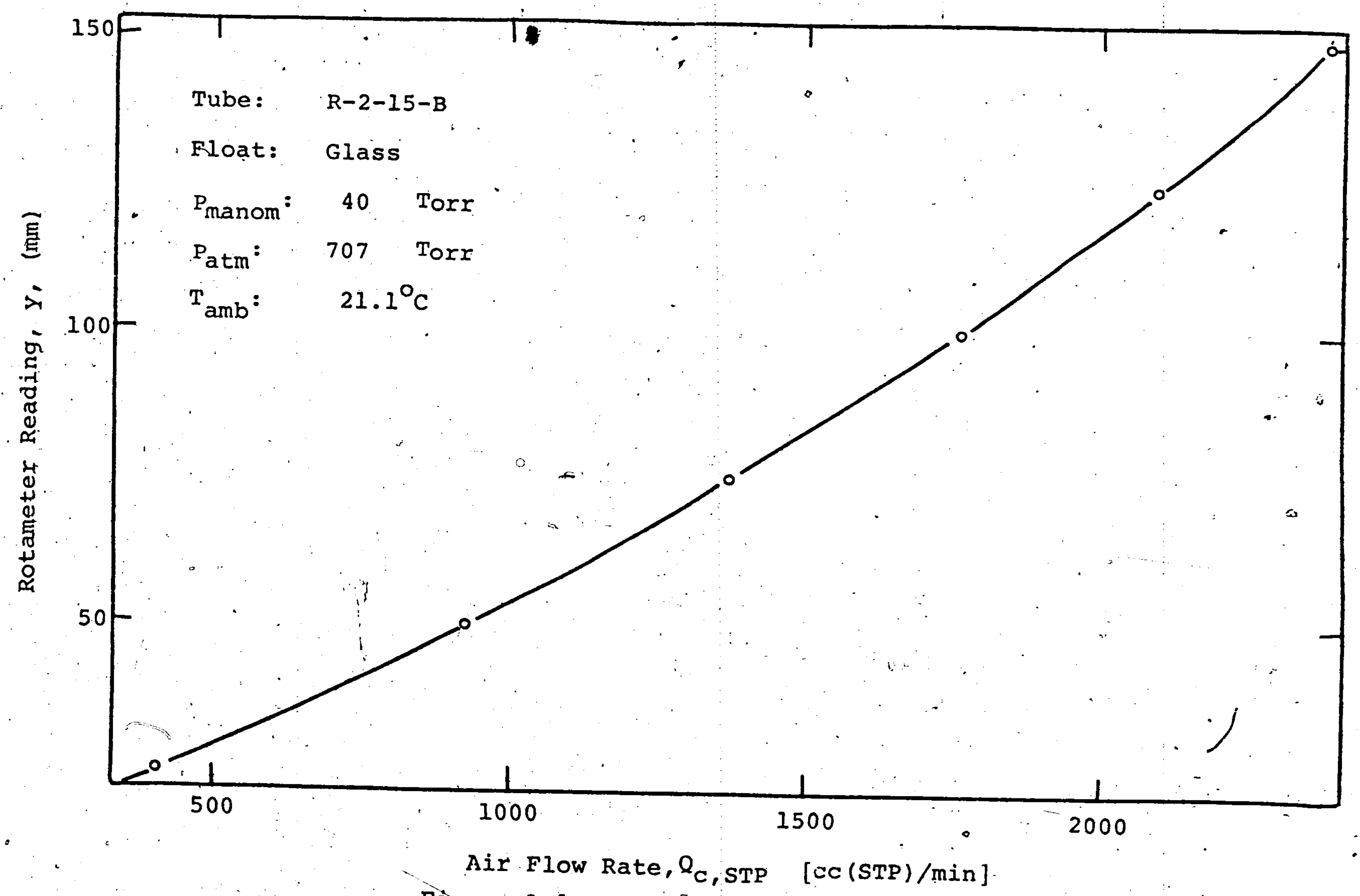

Figure A-1: Rotameter Calibration Curve

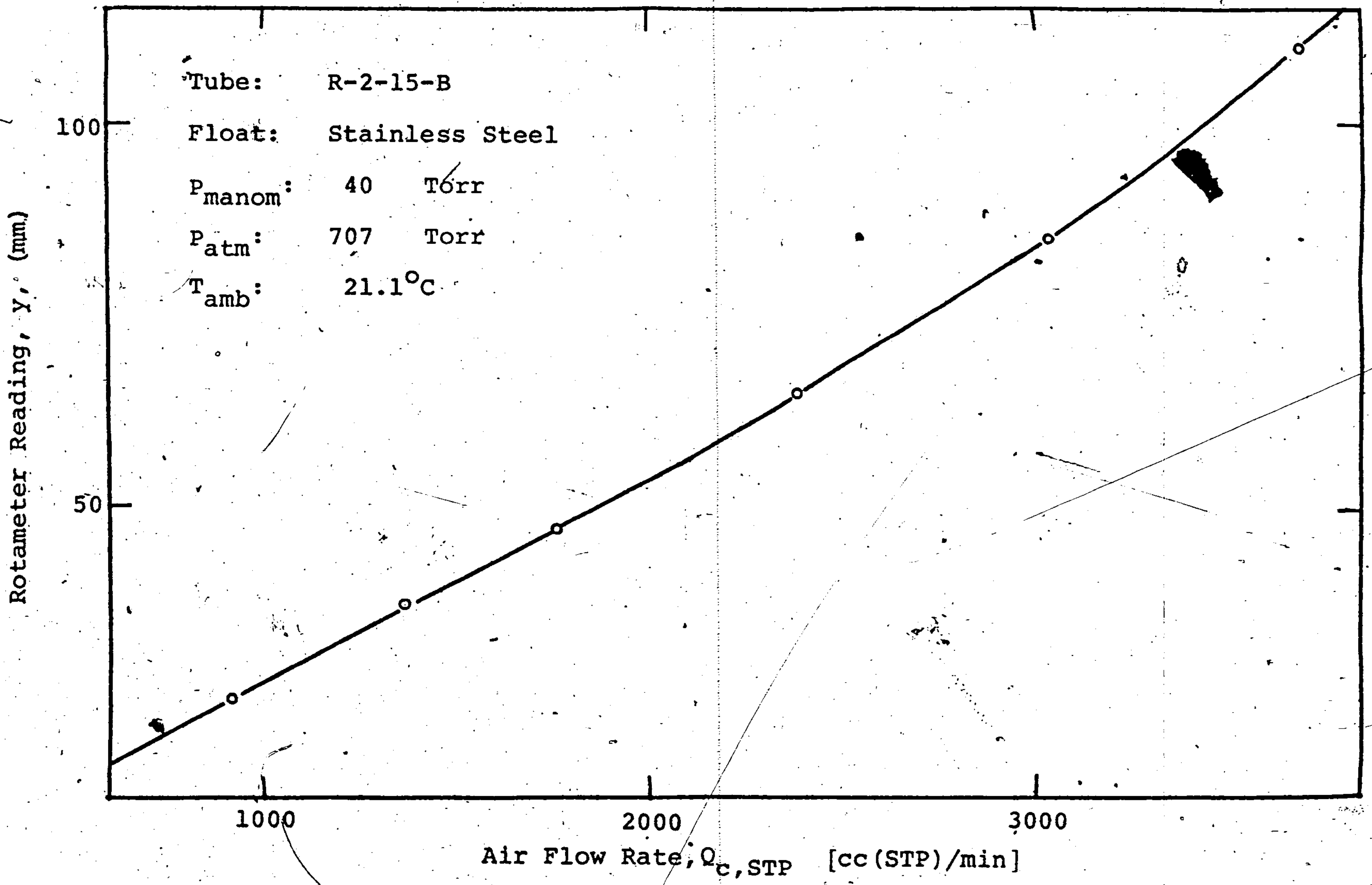

Figure A-2: Rotameter Calibration Curve

APPENDIX B

GAS CHROMATOGRAPHIC ANALYSIS

B-I Calculation of the Correction Factors

By definition the correction factor, F_i, for component i is

$$F_i = F_{ref} \frac{A_{ref} \, x_i}{A_i \, x_{ref}} \qquad \text{(B.1)}$$

where

A_{ref} - area under the peak for the component considered as a reference.

A_i - area under the peak for component i.

x_{ref} - mole fraction of the reference component.

x_i - mole fraction of component i.

If we take methanol as a reference and we assign to this component a correction factor of 1.00 the correction factor is now defined by

$$F_i = \frac{A_{CH_3OH} \, x_i}{A_i \, x_{CH_3OH}} \qquad \text{(B.2)}$$

Samples, of various known compositions containing air, methanol and water, were prepared by introducing liquid mixtures of methanol and water into a hot air stream by means of the syringe pump. The composition of the liquid was known (by mixing measured amounts of methanol and water). The liquid rate of addition to the air stream was known from the calibration of the syringe pump. The air flow rate was measured using the calibrated rotameter. Mixtures having the following range of composition were prepared and analyzed: mole fraction methanol 0.057 to 0.092, mole fraction water 0.010 to 0.036, the remainder of the samples being air. Approximately 20 samples were analyzed in this manner. A set of sample calculations to obtain F_{air} and F_{H_2O} from the peak areas and compositions is shown below. The average values obtained for the correction factors are given in Table B-1.

(i). Example of calculation of the correction factor for air

G_{F,CH_3OH} = 0.2079 g/min, given by syringe pump.

or $G_{F,CH_3OH} = 0.2079/32.04 = 6.49 \times 10^{-3}$ moles/min.

$Q_{F,air}$ = 2050 cc (STP)/min.

or $G_{F,air} = 2050/22410 = 91.48 \times 10^{-3}$ moles/min.

Thus, the mole fractions are:

$$x_{CH_3OH} = \frac{6.49 \times 10^{-3}}{6.49 \times 10^{-3} + 91.48 \times 10^{-3}} = 0.0662$$

and $$x_{air} = \frac{91.48 \times 10^{-3}}{6.49 \times 10^{-3} + 91.48 \times 10^{-3}} = 0.9338$$

From the computer output the following value was obtained

$$\frac{\text{Peak area of methanol}}{\text{Peak area of air}} = \frac{A_{CH_3OH}}{A_{air}} = 0.0746$$

Using these values and Equation B.2 the correction factor for air was calculated as

$$F_{air} = (0.9338/0.0662)(0.0746) = 1.05$$

(ii) Example of calculation of the correction factor for water:

Sample:

Water	9.9571 g	(Density = 1.000)
Methanol	28.8196 g	(Density = 0.792)

Therefore, the fractions in volume are:

Water	0.2148
Methanol	0.7852

The flow rate of syringe pump is $Q_{pump} = 0.2625$ cc/min. Thus,

$$G'_{F,H_2O} = (0.2625)(0.2148)(1.000) = 0.0564 \text{ g/min}$$

$$G'_{F,CH_3OH} = (0.2625)(0.7852)(0.792) = 0.1632 \text{ g/min}$$

and

$$G_{F,H_2O} = 0.0564/18.02 = 3.13 \times 10^{-3} \text{ moles/min}$$

$$G_{F,CH_3OH} = 0.1632/32.04 = 5.09 \times 10^{-3} \text{ moles/min}$$

$$Q_{F,air} = 1760 \text{ cc (STP)/min}$$

and

$$G_{F,air} = 1760/22410 = 78.54 \times 10^{-3} \text{ moles/min}$$

Therefore, the molar fractions are:

$$x_{CH_3OH} = \frac{5.09 \times 10^{-3}}{5.09\text{x}10^{-3} + 3.13\text{x}10^{-3} + 78.54\text{x}10^{-3}} = 0.0587$$

$$x_{H_2O} = \frac{3.13 \times 10^{-3}}{5.09\text{x}10^{-3} + 3.13\text{x}10^{-3} + 78.54\text{x}10^{-3}} = 0.0361$$

From the computer output the following value was obtained

$$\frac{\text{Peak area of methanol}}{\text{Peak area of water}} = \frac{A_{CH_3OH}}{A_{H_2O}} = 2.70$$

Using these values and Equation B.2 the correction factor for water was calculated as

$$F_{H_2O} = (0.0361/0.0587)(2.70) = 1.66$$

(iii) Calculation of the correction factor for formaldehyde

The correction factor for formaldehyde could not be obtained in this fashion since no formaldehyde solution of known composition was available. The value for F_{CH_2O} reported in Table B-1 was obtained from product analyses of methanol-air oxidation experiments. Since the only observed reaction products were formaldehyde and water, the product stream contains equal number of moles of water and formaldehyde (water in feed stream was removed by drying column). Therefore, the correction factor for formaldehyde is given by

$$F_{CH_2O} = \frac{A_{H_2O}}{A_{CH_2O}} F_{H_2O}$$

Over 50 analyses were carried out, and the average value of F_{CH_2O} obtained from these experiments is given in Table B-1.

TABLE B-1: Correction Factors for Chromatographic Analysis

Component	Average Correction Factor F_i
Methanol	1.00
Air	1.02
Water	1.66
Formaldehyde	1.40

B-II Computing Monitoring Program (CMP)

Table B-2 shows the listing of the job defined for chromatographic analysis using the calculated correction factors.

The analysis was started by entering information on a teletype to call the corresponding program. Then the sample was injected and simultaneously the CMP interrupt button was depressed. After the GC data were processed, the corresponding results appeared on the teletype. Figure B-1 shows a typical chromatogram; its corresponding teletype print-out is shown in Table B-3.

TABLE B-2: GC Job Listing

```
     JOB NUMBER  =  81            CALCULATION OPTION =  7
     GC NUMBER   =  8             TOTAL PEAKS        =  8

     FINISH TIME            =      450
     NORMALIZATION CONST.   =      100.

                    * REFERENCE PEAK DATA *
                      ---------------------

     LOW TIME OF REF PEAK              10.
     HIGH TIME OF REF PEAK             50.
     CONCENTRATION OF REF PEAK         0.
     RESPONSE FACTOR OF REF PEAK       0.

                       * TIME-BAND DATA *
                         --------------

 LOW TIME  HIGH TIME  CONC FOR STND   FACTOR   JTYPE  COMPONENT
    10.       72.           0.         102.      1     AIR
    72.      185.           0.         140.      1     FORMALDE
   185.      252.           0.         166.      1     WATER
   252.      448.           0.         100       4     METHANOL

   COMPONENT       SEQNO  IPLUS  INREF  IFCGO  IREST   UNITS
  AIR                1      0      9      0      0     MO.%
  FORMALDEHYDE       2      0      0      0      0     MO.%
  WATER              3      0      0      0      0     MO.%
  METHANOL           4      3      0      0      0     MO.%

           * PARAMETER AND CONTROL ACTION DATA *
             ---------------------------------

 PARAMETER ACTIONS

 ACT.TIME KNDTM ISTS IRATE IHIGH ILOW IHARD ISOFT IEXP1 IEXP2
    0      AB    11  8PPS   150 -150    5     5     1     2
   10      AB     1  8PPS   150 -150    5     5     1     2
   72      RL     0  1PPS    30  -30    4     4     1     2
  448      RL    20  1PPS    30  -30    4     4     1     2
  450      RL    19  1PPS    30  -30    4     4     1     2


 ECO ACTIONS
```

```
        GC JOB LISTING           ...(CONT'D)
     NO ECO ACTIONS SPECIFIED
 JOB COMPLETE
```

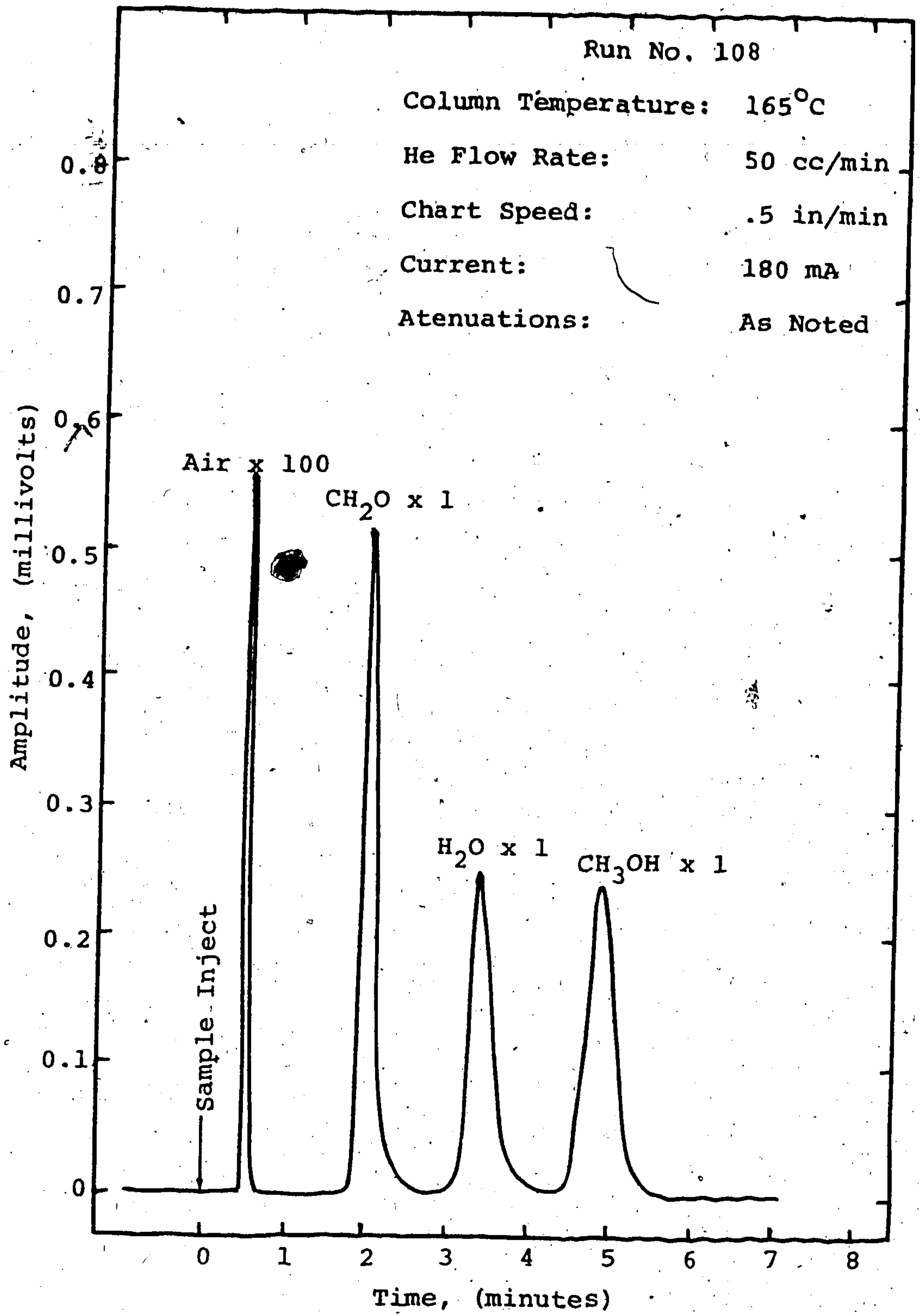

Figure B-1: Representative Chromatogram for Separation of Air, CH_2O, H_2O and CH_3OH.

TABLE B-3: Run 108-Teletype Output

```
 OGCJOB

** GC JOB ENTRY **
ENTER
GC. NO., JOBNO., LUN, KALC, CYCLE IND,(-1,0,1)
 8 81 11 7 0
 88111 7
1 IF OK .. 2 IF NOT
 1
 JOB ENTERED


9 MAR 74
12/34 HRS


      ** GC REPORTING JOB 81 **


PERCENT AREA UNKNOWN = 0.00


COMPONENT        RESULTS   UNITS   ELUTION TIME   PEAK AREA


AIR               93.611    MO.%        31       0.4318612E 03

FORMALDEHYDE       2.274    MO.%       127       0.7644201E 01

WATER              2.317    MO.%       210       0.6569401E 01

METHANOL           1.797    MO.%       298       0.8455801E 01


                 JOB COMPLETE
```

APPENDIX C

SURFACE AREA DETERMINATIONS: COMPUTER PROGRAM AND SAMPLE RESULTS

C-I BET Program

```
C
C
C***************************************************
C*****************************************
C
C     THE FOLLOWING PROGRAM CALCULATES THE NITROGEN UPTAKE
C     AS A FUNCTION OF PRESSURE FOR SURFACE AREA AND PORE
C     SIZE DISTRIBUTION DETERMINATIONS
C
C***************************************************
C*****************************************
C
C
C     DATA TO BE READ IN CONSISTS OF THE FOLLOWING
C
C     CARD=1 - NSAM = NUMBER OF SAMPLES (I.E., NO. OF
C     COMPLETE DETERMINATIONS)
C     THE FOLLOWING DATA IS READ IN FOR EACH DETERMINATION
C
C     CARD =2 - T= AVERAGE AMBIENT TEMP (DEG. F)  THIS IS
C     THE BURET TEMP
C             PSAT= AVERAGE SATURATION PRESSURE (TORR)
C             W = WEIGHT OF CATALYST SAMPLE (GRAMS)
C     CARD =3 - RUN = RUN NUMBER
C
C     VOLUME PRESSURE DATA ARE NOW READ IN
C     THE VOLUME-PRESSURE DATA ARE OF FOUR DIFFERENT TYPES.
C     EACH TYPE IS IDENTIFIED BY THE NUMBER 'ID' WHICH
C     ALONG WITH NP, THE NUMBER OF  SETS OF DATA, IS READ
C     IN CARD 4
C
C     ID = 1 - HELIUM CHARGE FOR DEAD VOLUME DETERMINATION
C        = 2 - HELIUM EXPANDED INTO SAMPLE CELL
C        = 3 - NITROGEN CHARGE FOR ADSORPTION MEASUREMENT
C        = 4 - NITROGEN ADSORPTION MEASUREMENTS
C
C     THE VOLUME-PRESSURE DATA ARE READ IN FOR EACH SET OF
C     DATA AS
C     NB2(I) = HG LEVEL IN BURET 2
C     NB3(I) = HG LEVEL IN BURET 3
C     NB4(I) = HG LEVEL IN BURET 4
C     B1V(I) = VOLUME OF GAS IN BURET 1 (CC)
C     R(I) = READING FROM TEXAS INSTRUMENT PRESSURE GAUGE
C     PS(I) = SATURATION PRESSURE AT EACH DATA POINT (TORR)
C
C     THE LEVEL IN EACH BURET IS 7 WHEN THE HG IS AT THE
C     TOP , AND 1 WHEN THE HG IS AT THE BOTTOM. ALL OTHER
C     LEVELS ARE SEQUENCIAL BETWEEN THESE LIMITS
C
```

BET PROGRAM ...(CONT'D)

```
C
      INTEGER RUN
      DIMENSION B1V(30),NB2(30),NB3(30),NB4(30),R(30),P(30),
     *VV(30),AD(30),PR(30),Y(30) ,X(30) ,YC(30),DY(30),
     *PX(30)
      READ(5,1) NSAM
    1 FORMAT(1I2)
      DO 888 IJK=1,NSAM
      READ(5,2) T,PSAT,W
    2 FORMAT(3F10.3)
      READ (5,555) RUN
  555 FORMAT (1I2)
      WRITE (6,444)
  444 FORMAT ('1')
      WRITE (6,556) RUN,W
  556 FORMAT (///////////////,10X,'ADSORPTION MEASUREMENTS',
     *//,10X,'CATALYST SAMPLE NUMBER',3X,I2,//,10X,'WEIGHT
     *OF CATALYST SAMPLE',3X,F10.3,3X,'GRAMS')
      T=(T-32.)/1.8+273.16
    5 READ(5,4) NP,ID
    4 FORMAT (2I2)
      DO 38 I=1,NP
      READ(5,3) NB2(I),NB3(I),NB4(I),B1V(I),R(I),PX(I)
    3  FORMAT(3I2,1F13.3,2F10.3)
      P(I)=3.07*R(I)
      V=B1V(I)+52.7
      N2=NB2(I)
      GO TO (11,12,13,14,15,16,17), N2
   11 V=V+200.09
      GO TO 18
   12 V=V+99.31
      GO TO 18
   13 V=V+59.92
      GO TO 18
   14 V=V+25.19
      GO TO 18
   15 V=V+12.43
      GO TO 18
   16 V=V+5.69
      GO TO 18
   17 V=V+0.
   18 CONTINUE
      N3=NB3(I)
      GO TO (21,22,23,24,25,26,27), N3
   21 V=V+339.81
      GO TO 28
   22 V=V+195.93
      GO TO 28
   23 V=V+108.16
```

```
      GO TO 28
 24   V=V+68.
      GO TO 28
 25   V=V+29.76
      GO TO 28
 26   V=V+15.19
      GO TO 28
 27   V=V+0.
 28   CONTINUE
      N4=NB4(I)
      GO TO (31,32,33,34,35,36,37), N4
 31   V=V+344.95
      GO TO 38
 32   V=V+193.2
      GO TO 38
 33   V=V+105.19
      GO TO 38
 34   V=V+65.07
      GO TO 38
 35   V=V+28.27
      GO TO 38
 36   V=V+14.11
      GO TO 38
 37   V=V+0.
 38   VV(I)=V
      GO TO (50,150,200,250), ID
 50   WRITE(6,51)
      PVS=[illegible]
 51   FORMAT(///,10X,'HELIUM CHARGE - CONSISTENCY CHECK',/,
     *10X,'NUMBER    PRESSURE      VOLUME       PV')
      DO 60 J=1,NP
      PV=P(J)*VV(J)
      WRITE(6,52) J,P(J),VV(J),PV
 52   FORMAT(12X,1I2,3F12.2)
      PVS=PVS+PV
 60   CONTINUE
      FNP=NP
      PVA=PVS/FNP
      WRITE(6,53) PVA
 53   FORMAT(//,10X,'AVERAGE HELIUM CHARGE (PV) =',1F12.2,'
     * TORR-CC')
      GO TO 5
150   WRITE(6,151)
151   FORMAT(///,10X,'DEAD VOLUME OF SAMPLE CELL',/,10X,
     *'NUMBER    PRESSURE      VOLUME        PV         ,DEAD
     *VOLUME')
      DVS=0.
      DO 160 J=1,NP
      DV=PVA/P(J)-VV(J)
      PV=P(J)*(VV(J)+DV)
```

```
      WRITE(6,152) J,P(J),VV(J),PV,DV
  152 FORMAT(12X,1I2,4F12.2)
      DVS=DVS+DV
  160 CONTINUE
      FNP=NP
      DVA=DVS/FNP
      WRITE(6,153) DVA
  153 FORMAT(//,10X,'AVERAGE DEAD VOLUME =',1F10.2,' CC')
      GO TO 5
  200 WRITE (6,201)
  201 FORMAT('1',///////////////,10X,'NITROGEN CHARGE
     *DETERMINATION',/,10X,'NUMBER    PRESSURE      VOLUME   CH
     *ARGE(CC AT STP)')
      SN2=0.
      DO 210 J=1,NP
      VN2=P(J)*VV(J)*273.16/T/760.
      WRITE(6,52) J,P(J),VV(J),VN2
      SN2=SN2+VN2
  210 CONTINUE
      FNP=NP
      VN2A=SN2/FNP
      WRITE(6,203) VN2A
  203 FORMAT(//,10X,'AVERAGE NITROGEN CHARGE =',1F12.2,' CC
     * AT STP')
      GO TO 5
  250 WRITE(6,251)
  251 FORMAT(//,10X,'NITROGEN ADSORPTION UPTAKE',/,10X,
     *'NUMBER   PRESSURE      VOLUME    N2 IN GAS   N2 ADSOR
     *BED')
      DO 260 J=1,NP
      VGP=VV(J)+DVA
      CGP=P(J)*VGP*273.16/T/760.
      ADN2=VN2A-CGP
      WRITE(6,152) J,P(J),VGP,CGP,ADN2
      AD(J)=ADN2/W
      PR(J)=P(J)/PX(J)
      Y(J)=PR(J)/(1.-PR(J))/AD(J)
  260 CONTINUE
      WRITE(6,300) PSAT
  300 FORMAT('1',/////////////////,25X,'BET RESULTS',//,10X,
     *'SATURATION PRESSURE =',1F6.1,' TORR')
      WRITE(6,301)
  301 FORMAT(//,43X,'AMOUNT ADS.',/,10X,'NUMBER',4X,'P/PSAT'
     *,3X,'P/V(PSAT-P)',5X,'(CC/GM)',5X,'PSAT (TORR)')
      DO 350 J=1,NP
      WRITE(6,351) J,PR(J),Y(J),AD(J)   ,PX(J)
  351 FORMAT(12X,1I2,2F12.4,1F12.2,2X,1F12.2)
  350 CONTINUE
      N=0
      DO 400 J=1,NP
```

BET PROGRAM ...(CONT'D)

```
      IF(PR(J)-0.05) 400,401,401
  401 IF(PR(J)-0.35) 402,402,400
  402 N=N+1
      X(N)=PR(J)
      Y(N)=Y(J)
  400 CONTINUE
      SX=0.0
      SXY=0.0
      SY=0.0-
      SXX=0.0
      DO 30 I=1,N
      SX=SX+X(I)
      SY=SY+Y(I)
      SXY=SXY+X(I)*Y(I)
      SXX=SXX+X(I)*X(I)
   30 CONTINUE
      DEM=N*SXX-SX*SX
      A=(SY*SXX-SXY*SX)/DEM
      B=(N*SXY-SX*SY)/DEM
      SY2=0.0
      SSDY=0.0
      SDY=0.0
      DO 40 I=1,N
      YC(I)=A+B*X(I)
      DY(I)=Y(I)-YC(I)
      SDY=SDY+DY(I)
      SSDY=SSDY+DY(I)*DY(I)
      SY2=SY2+Y(I)*Y(I)
   40 CONTINUE
      SDV=SQRT(SSDY/(N-2))
      PSDV=((SDV*N)/SY)*100.
      WRITE(6,100)
      DO 59 I=1,N
      WRITE(6,102)                      X(I),Y(I),YC(I),DY(I)
   59 CONTINUE
      AREA=4.25/(A+B)
      WRITE(6,106) SDV
  106 FORMAT(/,10X,' STANDARD DEVIATION   = ' 2X,E15.5)
      WRITE(6,108) PSDV
  108 FORMAT(/,10X,' PERCENT STANDARD DEVIATION =' 2X,F10.5)
      WRITE(6,107) A,B
  107 FORMAT(/,10X,' Y=A+B*X ',/,10X,'A= ',F10.5,
     1 /,10X 'B= ',F10.5)
  102 FORMAT(1F16.4,3F15.6)
  100 FORMAT('1',////////////////,10X,'LEAST SQUARE FIT OF
     *BET RESULTS',//,10X,'P/PSAT',9X,'YMEAS', 10X,'YCALC',
     *10X,'YM-YC')
      WRITE(6,600) AREA
  600 FORMAT(////,20X,'SURFACE AREA =',1F7.2,' SQ.M/GRAM')
  888 CONTINUE
```

```
      CALL EXIT
      END
```

C-II Computer Output for Catalyst 1

```
ADSORPTION MEASUREMENTS

CATALYST SAMPLE NUMBER      1

WEIGHT OF CATALYST SAMPLE         1.425    GRAMS


HELIUM CHARGE - CONSISTENCY CHECK
NUMBER    PRESSURE       VOLUME       PV
   1       207.25         77.89     16143.14
   2       143.10        112.62     16116.82
   3       105.94        152.01     16104.79
   4        63.57        252.79     16072.30

AVERAGE HELIUM CHARGE (PV) =      16109.26 TORR-CC


DEAD VOLUME OF SAMPLE CELL
NUMBER    PRESSURE       VOLUME       PV          DEAD VOLUME
   1        58.59        252.79     16109.26        22.15
   2        92.45        152.01     16109.26        22.23
   3       119.63        112.62     16109.26        22.03
   4       161.49         77.89     16109.26        21.85

AVERAGE DEAD VOLUME =       22.06 CC
```

```
NITROGEN CHARGE DETERMINATION
NUMBER    PRESSURE      VOLUME     CHARGE(CC AT STP)
   1        87.37       541.14         57.31
   2        73.54       641.92         57.22
   3        60.14       785.80         57.28
   4        50.51       937.55         57.41

AVERAGE NITROGEN CHARGE =          57.31 CC AT STP

NITROGEN ADSORPTION UPTAKE
NUMBER    PRESSURE      VOLUME      N2 IN GAS  N2 ADSORBED
   1        48.26       959.61         56.14         1.17
   2        57.19       807.86         56.01         1.29
   3        69.59       663.98         56.01         1.29
   4        81.95       563.20         55.95         1.35
   5        97.11       475.19         55.94         1.36
   6       118.91       387.42         55.84         1.46
   7       132.40       348.03         55.86         1.44
   8       149.34       307.91         55.74         1.56
   9       171.62       267.75         55.70         1.60
  10       196.83       233.02         55.60         1.70
  11       233.16       196.22         55.46         1.84
  12       288.36       157.98         55.22         2.08
  13       328.41       138.48         55.13         2.17
  14       409.66       110.21         54.73         2.57
```

BET RESULTS

SATURATION PRESSURE = 719.0 TORR

NUMBER	P/PSAT	P/V(PSAT-P)	AMOUNT ADS. (CC/GM)	PSAT (TORR)
1	0.0670	0.0874	0.82	720.00
2	0.0790	0.0941	0.91	723.50
3	0.0966	0.1180	0.90	720.00
4	0.1135	0.1343	0.95	722.00
5	0.1348	0.1627	0.95	720.00
6	0.1653	0.1932	1.02	719.00
7	0.1836	0.2215	1.01	721.00
8	0.2077	0.2383	1.09	719.00
9	0.2377	0.2772	1.12	722.00
10	0.2730	0.3131	1.19	721.00
11	0.3231	0.3684	1.29	721.50
12	0.4021	0.4600	1.46	717.00
13	0.4551	0.5469	1.52	721.50
14	0.5689	0.7302	1.80	720.00

```
LEAST SQUARE FIT OF BET RESULTS

P/PSAT          YMEAS            YCALC            YM-YC
0.0670          0.087443         0.085043         0.002399
0.0790          0.094120         0.098418        -0.004298
0.0966          0.118017         0.118008         0.000008
0.1135          0.134345         0.136749        -0.002403
0.1348          0.162728         0.160531         0.002197
0.1653          0.193200         0.194463        -0.001262
0.1836          0.221500         0.214770         0.006730
0.2077          0.238387         0.241533        -0.003145
0.2377          0.277216         0.274913         0.002303
0.2730          0.313162         0.314167        -0.001005
0.3231          0.368452         0.369975        -0.001522

 STANDARD DEVIATION   =      0.33378E-02

 PERCENT STANDARD DEVIATION =      1.66244

 Y=A+B*X
A=      0.01048
B=      1.11240


          SURFACE AREA =    3.78 SQ.M/GRAM
```

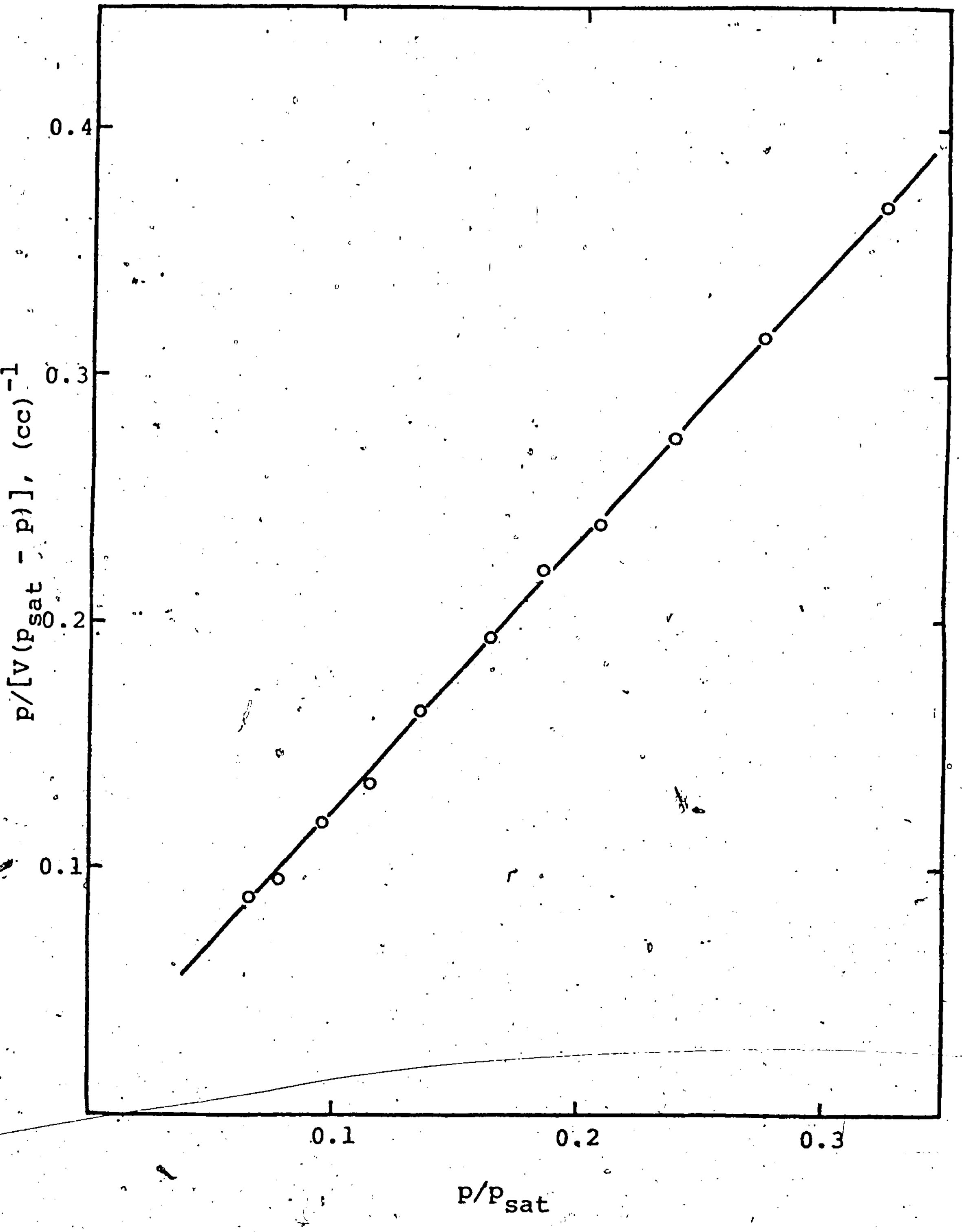

Figure C-1: Plot of Brunauer-Emmett-Teller Equation for Catalyst 1

APPENDIX D

COMPUTER PROGRAM FOR KINETIC DATA ANALYSIS AND RESULTS OF INDIVIDUAL EXPERIMENTS

D-I Computer Program for Activity Measurements

```
C
C****************************************
C***********************************
C
C     THE FOLLOWING PROGRAM CALCULATES THE FRACTIONAL
C     CONVERSIONS AND RATE CONSTANTS FOR THE OXIDATION OF
C     METHANOL TO FORMALDEHYDE
C
C****************************************
C***********************************
C
C
C     DATA INPUT DESCRIPTION
C
C     CARD 1 NGC,ND   FORMAT(2I2)
C             NGC NOT EQUAL TO ZERO THEN NO FEED GC ANAL.
C             ND = 0 CAUSES PROGRAM TO EXIT
C     CARD 2, 3, AND 4 ALPHEMERIC DESCRIPTION OF RUN
C                       UP TO 55 CHARACTERS PER CARD
C                       STARTING IN SPACE 6 ON EACH CARD.
C
C
C     CARD 5 M1,A1,A2,A3,A4,A5,A6   (FORMAT(1I2,,6F10.4))
C             M1=0 MEANS FEED COMPOSITION FROM FLOW RATES
C             A1 = TOTAL AIR FEED RATE IN CC(STP)/MIN
C             A2 = METHANOL FEED RATE IN CC OF LIQUID/MIN
C             A3 = ABSOLUTE PRESSURE IN REACTOR IN TORR
C             A4 = REACTOR TEMPERATURE IN DEGREES KELVIN
C             A5 = CATALYST WEIGHT IN GRAMS
C             A6 = CATALYST SURFACE AREA IN SQ.M/GRAM
C
C     CARD 6 M1,A1,A2,M2        FORMAT(1I2,6F13.4,1I2)
C             M1=1 MEANS FEED ANALYSIS BY GC
C             A1 = PEAK AREA OF AIR IN FEED
C             A2 = PEAK AREA OF METHANOL IN FEED
C             A5 = NUMBER OF SQUARES ON GC CHART FOR WATER
C                  IN FEED (GC JOB DEFINED DOES NOT DETECT
C                  THESE SMALL PEAKS. THESE VALUES ARE
C                  MULTIPLIED BY 0.245 TO CONVERT TO AREA
C                  GIVEN BY GC PEAK)
C             M2 = NUMBER OF GC FEED ANALYSIS
C
C     CARD 7  REPEAT OF GC FEED ANALYSIS DATA (CARD 6)
C
C    CARD 8  M1,A1,A2,A3,A4,A5,A6,M2  FORMAT(1I2,6F10.4,1I2)
C             M1 =2 MEANS PRODUCT GC ANALYSIS
C             A1 = AREA OF AIR PEAK IN PRODUCT
C             A2 = AREA OF FORMALDEHYDE PEAK IN PRODUCT
C             A3 = AREA OF WATER PEAK IN PRODUCT
```

ACTIVITY MEASUREMENTS ...(CONT'D)

```
C              A4 = AREA OF METHANOL PEAK IN PRODUCT
C              A5 AND A6 ARE ZERO
C              M2 = NUMBER OF REPEAT GC PRODUCT ANALYSIS
C
C      CARD 9 REPEAT OF CARD 8 FOR EACH PRODUCT ANALYSIS
C              NEXT CARD IS CARD 1 FOR NEXT RUN
C
C
C      ONLY ONE SET OF FEED FLOW RATES CAN BE GIVEN PER
C      RUN. NEW SET OF DATA CARDS REQUIRED FOR EACH SET
C      OF FEED FLOW RATES.
C
C

       DIMENSION X2FME(5),X2FN(5),X2FO(5),XPH(8),XPC(8),
      1 XPM(8),XPO(8),XPN(8),X1(5),X2(5),X3(5),X2FH2(5)
       DIMENSION XPOA(8)
       FME=1.00
       FAIR=1.02
       FH2O=1.66
       FCH2O=1.4
C      FME,FAIR,FH2O AND FCH2O ARE GC CORRECTION FACTORS
C

   150 CONTINUE
       WRITE(6,11)
    11 FORMAT('1',//////,5X,'KINETICS OF METHANOL OXIDATION'
      1,/)
       READ(5,200) NGC,ND
   200 FORMAT(2I2)
       IF(ND) 250,998,250
   250 CONTINUE
       M3=0
       M4=0
       READ(5,10) Z1,Z2,Z3,Z4,Z5,Z6,Z7,Z8,Z9,ZA,ZB,ZC,ZD,ZE
       WRITE(6,10)Z1,Z2,Z3,Z4,Z5,Z6,Z7,Z8,Z9,ZA,ZB,ZC,ZD,ZE
       READ(5,10) Z1,Z2,Z3,Z4,Z5,Z6,Z7,Z8,Z9,ZA,ZB,ZC,ZD,ZE
       WRITE(6,10)Z1,Z2,Z3,Z4,Z5,Z6,Z7,Z8,Z9,ZA,ZB,ZC,ZD,ZE
       READ(5,10) Z1,Z2,Z3,Z4,Z5,Z6,Z7,Z8,Z9,ZA,ZB,ZC,ZD,ZE
       WRITE(6,10)Z1,Z2,Z3,Z4,Z5,Z6,Z7,Z8,Z9,ZA,ZB,ZC,ZD,ZE
    10 FORMAT(5X,14A4)
     1 READ(5,20) M1,A1,A2,A3,A4,A5,A6,M2
    20 FORMAT(1I2,6F10.4,1I2)
      IF(A1-0.01) 150,150,155
   155 IF(M1-1) 30,40,50
    30 WRITE(6,31) A1,A2,A3,A4,A5,A6
    31 FORMAT(5X,'AIR FEED RATE (CC(STP)/MIN) =',1F7.1,/,5X,
      1'METHANOL FEED RATE (CC(LIQUID)/MIN) =',1F8.5,/,5X,
      2'REACTOR PRESSURE (TORR) =',1F6.1,/,5X,'TEMPERATURE
```

ACTIVITY MEASUREMENTS ...(CONT'D)

```
     3(KELVIN) =',1F6.1,/,5X,'CATALYST CHARGE (GRAMS) =',
     41F6.2,/,5X,'CATALYST SURFACE AREA (SQ.M/G) =',1F5.2)
      QA=A1/22410.

C     QA IS THE FEED RATE OF AIR IN MOLES/MIN

      QM=A2*0.792/32.04

C     QM IS THE FEED RATE OF METHANOL IN MOLES/MIN

      X1FME=QM/(QM+QA)*100.
      X1FO=20.9*QA/(QM+QA)
      X1FN=79.1*QA/(QM+QA)
      AREA=A6*A5

C      AREA IS THE TOTAL AREA OF CATALYST IN REACTOR

      PRES=A3/760.

C      PRES IS THE ABSOLUTE PRESSURE IN REACTOR IN ATM.

      TEMP=A4

C     TEMP IS REAC[illegible]R TEMPERATURE IN DEG. K
C
C     THE ABOVE 3 X1'S ARE THE MOLE PERCENT OF MEOH, O2 AND
C     N2 IN THE FEED AS CALCULATED FROM FEED FLOW RATES
C

      WRITE(6,32)
   32 FORMAT(/,5X,'FEED AND PRODUCT COMPOSITIONS (MOLE PER
     1CENT)',//,5X,'TYPE OF ANALYSIS  NITROGEN OXYGEN METHA
     2NOL WATER CH2O',/)
      WRITE(6,33) X1FN,X1FO,X1FME
   33 FORMAT(5X,'FEED (FLOW RATES)',1F7.2,1F9.2,1F7.2)
      GO TO 1
   40 M3=M3+1
      A2=A2+1.7
      A9=A5*0.245

C     THIS IS TO CONVERT SQUARES TO GC PEAK AREA

      SA = FAIR*A1+A2+A9*FH2O
      X2FME(M3)=A2/SA*100.
      X2FO(M3)=20.9*FAIR*A1/SA
      X2FN(M3)=79.1/20.9*X2FO(M3)
      X2FH2(M3)= FH2O*A9/SA*100.
      WRITE(6,41) X2FN(M3),X2FO(M3),X2FME(M3)   ,X2FH2(M3)
   41 FORMAT(5X,'FEED(G.C.)',8X,1F6.2,1F9.2,1F7.2,1F8.3)
      IF(M2-M3)998,60,1
```

```
   60 M3=0
      FM2=M2
      F1=0.
      F2=0.
      F3=0.
      F4=0.
      DO 65 I=1,M2
      F1=F1+X2FME(I)
      F2=F2+X2FO(I)
      F4=F4+X2FH2(I)
   65 F3=F3+X2FN(I)
      XAMGC=F1/FM2
      XAOGC=F2/FM2
      XANGC=F3/FM2
      XAHGC=F4/FM2
C   ABOVE VALUES ARE AVERAGE FEED COMP, FROM GC
      WRITE(6,61) XANGC,XAOGC,XAMGC ,XAHGC
   61 FORMAT(5X,'AVG. FEED (G.C.)',1F8.2,1F9.2,1F7.2,1F8.3)
      XAFM=(X1FME+XAMGC)/2.
      XAFO=(X1FO+XAOGC)/2.
      XAFN=(X1FN+XANGC)/2.
C  AVERAGE FEED COMP. BY GC PLUS FEED RATES
      WRITE(6,62) XAFN,XAFO,XAFM
   62 FORMAT(/,5X,'AVERAGE FEED',6X,1F6.2,1F9.2,1F7.2,/)
      GO TO 1
   50 M4=M4+1
      A2=A2+1.2
      A3=A3+1.7
      A4=A4+1.7
C       THE ABOVE ARE CORRECTION FACTORS DUE TO DEAD BAND IN
C       GC JOB DEFINITION
      SIGA=FAIR*A1+A4+FCH2O*A2+FH2O*A3
      XPH(M4)=FH2O*A3/SIGA*100.
      XPC(M4)=FCH2O*A2/SIGA*100.
      XPM(M4)=A4/SIGA*100.
C     THE FOLLOWING VALUES OF MOLE PERCENT FOR OXYGEN AND
C     NITROGEN ARE ESTIMATED FROM MEASURED FEED FLOW RATES
C     AND METHANOL FEED COMPOSITION (X1FME) AND METHANOL
C     PRODUCT (XPM(M4)).
      QFT=QA+QM
C       QFT = TOTAL FEED RATE IN MOLES/MIN
```

```
      QPT=QFT*(100.+0.5*XAFM )/(100.+0.5*XPM(M4))
C      QPT = TOTAL PRODUCT FLOW RATE IN MOLES/MIN
      QFN=0.791*QA
C      QFN = NITROGEN FEED RATE IN MOLES/MIN
C          THIS IS EQUAL TO NITROGEN PRODUCT FLOW RATE
      XPN(M4)=QFN/QPT*100.
     XPO(M4)=  - XPN(M4)-XPC(M4)-XPH(M4) -XPM(M4)+100.
      AVM=(QFT*(XAFM-XAHGC)+QPT*(XPH(M4)+XPC(M4)-XPM(M4)))/
     1 6.
      XPOA(M4)= (QFT*XAFO-AVM)/QPT
      WRITE(6,51) XPN(M4),XPO(M4),XPM(M4),XPH(M4),XPC(M4)
   51 FORMAT(   5X,'PRODUCT (G.C.)',4X,1F6.2,1F9.2,1F7.2,
     1 1F7.2,1F7.2)
      IF(M2-M4)998,70,1
   70 M4=0
      P1=0.
      P2=0.
      P3=0.
      P4=0.
      P5=0.
      P6=0.
      DO 75 I=1,M2
      P1=P1+XPM(I)
      P2=P2+XPC(I)
      P3=P3+XPH(I)
      P4=P4+XPO(I)
      P6=P6+XPOA(I)
   75 P5=P5+XPN(I)
      PM2=M2
      XPAM=P1/PM2
      XPAC=P2/PM2
      XPAH=P3/PM2
      XPAO=P4/PM2
      XPAN=P5/PM2
      XPAVO=P6/PM2
C     THE ABOVE VALUES ARE AVERAGE PRODUCT COMP. OBTAINED
C     BY GC
C
      WRITE(6,71) XPAN,XPAO,XPAM,XPAH,XPAC
   71 FORMAT(/,5X,'AVERAGE PRODUCT',3X,1F6.2,3X,1F6.2,3F7.2,
     1/)
C    THE FOLLOWING SECTION CALCULATES FRACTIONAL CONVERSION
C    OF METHANOL BASED ON THE ANALYSIS OF VARIOUS PRODUCTS
```

```
C
      WRITE(6,100)
  100  FORMAT(    5X,'FRACTIONAL CONVERSION',//,5X,'FEED
     1 COMPOSITION',4X,'BASED ON PRODUCT G.C. ANALYSIS OF',/
     2 ,5X,'BASED ON',14X,'METHANOL  WATER  FORMALDEHYDE',/)
       J=1
       XF=X1FME/100.
  101  XP=XPAM/100.
       X1(J)=(1.-XP/XF)/(1.+0.5*XP)
       XPAZ=XPAH/100.
       XFAZ=XAHGC/100.
       X2(J)=(XPAZ-XFAZ)/XF/(1.-0.5*XPAZ)
       XPAY=XPAC/100.
       X3(J)=XPAY/XF/(1.-0.5*XPAY)

C       X1,X2,X3 ARE FRACTIONAL CONVERSIONS BASED ON
C       METHANOL, WATER AND FORMALDEHYDE, RESPECTIVELY.

       IF(J-2)104,103,102
  104  CONTINUE
       WRITE(6,105) X1(J),X2(J),X3(J)
  105  FORMAT(5X,'FEED FLOW RATES',1F13.3, 1F9.3, 1F10.3)
       GO TO 112
  103  WRITE(6,115) X1(J),X2(J),X3(J)
  115  FORMAT(5X,'AVG GC ANALYSIS',1F13.3, 1F9.3, 1F10.3)
       GO TO 130
  102  WRITE (6,125) X1(J),X2(J),X3(J)
  125  FORMAT(5X,'GC + FEED RATES',1F13.3, 1F9.3, 1F10.3)
       GO TO 131
  112  IF(NGC) 151,110,151
  151  XAVGT=(X1(J)+X2(J)+X3(J))/3.
       GO TO 147
  110  XF=XAMGC/100.
       J=J+1
       GO TO 101
  130  XF=XAFM/100.
       J=J+1
       GO TO 101
  131  CONTINUE
       T1=0.
       T2=0.
       T3=0.
       DO 140 I=1,3
       T1=T1+X1(I)
       T2=T2+X2(I)
  140  T3=T3+X3(I)
       X1AV=T1/3.
       X2AV=T2/3.
       X3AV=T3/3.
```

```
      XAVGT=(T1+T2+T3)/9.
  147 WRITE(6,146) XAVGT
  146 FORMAT(/,5X,'AVERAGE FRACTIONAL CONVERSION =',1F6.3)
C        CALCULATION OF FIRST ORDER RATE CONSTANTS BASED ON
C        SURFACE AREA (UNITS ARE M/SEC)
C        FOLLOWED BY HALF-ORDER RATE CONSTANTS BASED ON
C        SURFACE AREA (UNITS ARE (GMOLES/M)**1/2/SEC)
C        FOLLOWED BY RATE CONSTANT BASED ON HALF ORDER IN
C        METHANOL AND HALF ORDER IN OXYGEN
C       RK1 IS BASED ON FRACTIONAL CONVERSION OBTAINED FROM
C       METHANOL
C       RK2 IS BASED ON FRACTIONAL CONVERSION OBTAINED FROM
C       WATER
C       RK3 IS BASED ON FRACTIONAL CONVERSION OBTAINED FROM
C       FORMALDEHYDE
C       RKAV IS BASED ON AVERAGE FRACTIONAL CONVERSION
C

      CT=PRES*1000./TEMP/0.0821
       CT=1./CT
      QOX=QA*0.209
      YYA=SQRT(QM/2.)
      YYB=SQRT(QOX)
      X=X1AV
       RK1 =((-ALOG(1.-X))*(QFT/QM+0.5)-0.5*X)*QM/60./AREA*
     1 CT
      RK4=2./AREA/60.*(1.-(1.-X)**0.5)*(QFT*QM*CT)**0.5
      YYX=SQRT(QOX-0.5*QM*X)
      YYZ=SQRT(QM/2.*(1.-X))
       RK7=2.82843*QFT/AREA*CT*ALOG((YYZ-YYX)/(YYA-YYB))
     1 /60.
      X=X2AV
       RK2 =((-ALOG(1.-X))*(QFT/QM+0.5)-0.5*X)*QM/60./AREA*
     1 CT
      RK5=2./AREA/60.*(1.-(1.-X)**0.5)*(QFT*QM*CT)**0.5
      YYX=SQRT(QOX-0.5*QM*X)
      YYZ=SQRT(QM/2.*(1.-X))
       RK8=2.82843*QFT/AREA*CT*ALOG((YYZ-YYX)/(YYA-YYB))
     1 /60.
      X=X3AV
       RK3 =((-ALOG(1.-X))*(QFT/QM+0.5)-0.5*X)*QM/60./AREA*
     1 CT
      RK6=2./AREA/60.*(1.-(1.-X)**0.5)*(QFT*QM*CT)**0.5
      YYX=SQRT(QOX-0.5*QM*X)
      YYZ=SQRT(QM/2.*(1.-X))
       RK9=2.82843*QFT/AREA*CT*ALOG((YYZ-YYX)/(YYA-YYB))
     1 /60.
      X=XAVGT
      RKAV =((-ALOG(1.-X))*(QFT/QM+0.5)-0.5*X)*QM/60./AREA*
```

ACTIVITY MEASUREMENTS ...(CONT'D)

```
    1  CT
     RKB =2./AREA/60.*(1.-(1.-X)**0.5)*(OFT*QM*CT)**0.5
      YYX=SQRT(QOX-0.5*QM*X)
      YYZ=SQRT(QM/2.*(1.-X))
       RKC=2.82843*OFT/AREA*CT*ALOG((YYZ-YYX)/(YYA-YYB))
    1  /60.
      WRITE(6,149)
      WRITE(6,148)RK1,RK2,RK3,RKAV
      WRITE(6,160) RK4,RK5,RK6,RKB
      WRITE(6,161) RK7,RK8,RK9,RKC
148   FORMAT(/5X,'1ST ORDER', 1E11.3,2E13.3,1E11.3)
160   FORMAT(5X, '1/2 ORDER', 1E11.3,2E13.3,1E11.3)
161   FORMAT(5X, 'OXYGEN   ', 1E11.3,2E13.3,1E11.3)
149   FORMAT(/,5X     ,       'RATE CONSTANTS'          , /,
    1 5X,'BASED ON METHANOL       WATER     FORMALDEHYDE
    2 AVERAGE')
      GO TO 150
998   CALL EXIT
      END
```

D-II Listing of Kinetic Results

```
KINETICS OF METHANOL OXIDATION

RUNS NUMBER 168 TO 176
CATALYST SAMPLE NUMBER  1
FIVE  GC FEED ANALYSES AND THREE GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3029.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 861.5
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 21.06
CATALYST SURFACE AREA (SQ.M/G) = 3.78

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.47    19.94    4.58
FEED(G.C.)         75.34    19.90    4.74    0.000
FEED(G.C.)         75.32    19.90    4.77    0.000
FEED(G.C.)         75.21    19.87    4.90    0.000
FEED(G.C.)         75.44    19.93    4.61    0.000
FEED(G.C.)         75.43    19.93    4.62    0.000
AVG. FEED (G.C.)   75.35    19.91    4.73    0.000

AVERAGE FEED       75.41    19.92    4.65

PRODUCT (G.C.)     74.66    18.35    2.45    2.18    2.34
PRODUCT (G.C.)     74.64    18.38    2.39    2.10    2.46
PRODUCT (G.C.)     74.59    18.99    2.27    1.94    2.19

AVERAGE PRODUCT    74.63    18.57    2.37    2.07    2.33

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON               METHANOL   WATER  FORMALDEHYDE

FEED FLOW RATES       0.475     0.458      0.516
AVG GC ANALYSIS       0.492     0.443      0.499
GC + FEED RATES       0.484     0.450      0.507

AVERAGE FRACTIONAL CONVERSION = 0.480

RATE CONSTANTS
BASED ON    METHANOL       WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.766E-06    0.693E-06    0.821E-06   0.759E-06
1/2 ORDER  0.704E-06    0.647E-06    0.746E-06   0.699E-06
OXYGEN     0.315E-06    0.289E-06    0.334E-06   0.313E-06
```

```
KINETICS OF METHANOL OXIDATION

RUNS NUMBER 177 TO 182
CATALYST SAMPLE NUMBER   1
THREE GC FEED ANALYSES AND THREE GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3051.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 874.2
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 21.06
CATALYST SURFACE AREA (SQ.M/G) = 3.78

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.40     19.94     4.54
FEED(G.C.)         75.63     19.98     4.38    0.000
FEED(G.C.)         75.53     19.95     4.50    0.000
FEED(G.C.)         75.58     19.97     4.43    0.000
AVG. FEED (G.C.)   75.58     19.97     4.44    0.000

AVERAGE FEED       75.54     19.96     4.49

PRODUCT (G.C.)     74.69     18.71     2.31    1.97    2.29
PRODUCT (G.C.)     74.66     18.89     2.23    1.95    2.24
PRODUCT (G.C.)     74.72     18.68     2.38    2.03    2.18

AVERAGE PRODUCT    74.69     18.76     2.31    1.98    2.24

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON              METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES        0.486    0.441    0.498
AVG GC ANALYSIS        0.474    0.451    0.510
GC + FEED RATES        0.480    0.446    0.504

AVERAGE FRACTIONAL CONVERSION = 0.477

RATE CONSTANTS
BASED ON   METHANOL      WATER        FORMALDEHYDE   AVERAGE

1ST ORDER  0.752E-06    0.679E-06    0.806E-06    0.744E-06
1/2 ORDER  0.695E-06    0.637E-06    0.737E-06    0.689E-06
OXYGEN     0.309E-06    0.283E-06    0.327E-06    0.306E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 183 TO 189
CATALYST SAMPLE NUMBER  1
THREE GC FEED ANALYSES AND FOUR  GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3051.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 874.0
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 21.06
CATALYST SURFACE AREA (SQ.M/G) = 3.78

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.50    19.94    4.54
FEED(G.C.)         75.76    20.01    4.21    0.000
FEED(G.C.)         75.58    19.97    4.44    0.000
FEED(G.C.)         75.82    20.03    4.13    0.000
AVG. FEED (G.C.)   75.72    20.00    4.26    0.000

AVERAGE FEED       75.61    19.97    4.40

PRODUCT (G.C.)     74.65    19.51    2.11    1.68    2.03
PRODUCT (G.C.)     74.65    19.40    2.11    1.68    2.13
PRODUCT (G.C.)     74.64    19.48    2.07    1.74    2.05
PRODUCT (G.C.)     74.66    19.22    2.13    1.94    2.02

AVERAGE PRODUCT    74.65    19.40    2.11    1.76    2.06

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON                METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES          0.530    0.391    0.457
AVG GC ANALYSIS          0.499    0.417    0.488
GC + FEED RATES          0.515    0.403    0.472

AVERAGE FRACTIONAL CONVERSION = 0.464

RATE CONSTANTS
BASED ON   METHANOL     WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.832E-06   0.594E-06   0.736E-06   0.716E-06
1/2 ORDER  0.756E-06   0.568E-06   0.682E-06   0.667E-06
OXYGEN     0.336E-06   0.252E-06   0.303E-06   0.296E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 190 TO 193
CATALYST SAMPLE NUMBER  1
TWO   GC FEED ANALYSES AND TWO   GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3048.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 872.7
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 21.06
CATALYST SURFACE AREA (SQ.M/G) = 3.78

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.49     19.94    4.55
FEED(G.C.)         75.55     19.96    4.48    0.000
FEED(G.C.)         75.44     19.93    4.61    0.000
AVG. FEED (G.C.)   75.50     19.94    4.54    0.000

AVERAGE FEED       75.49     19.94    4.55

PRODUCT (G.C.)     74.55     19.45    2.00    1.91    2.07
PRODUCT (G.C.)     74.65     19.18    2.26    1.78    2.11

AVERAGE PRODUCT    74.60     19.31    2.13    1.84    2.09

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON               METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES         0.526    0.410     0.464
AVG GC ANALYSIS         0.525    0.410     0.464
GC + FEED RATES         0.526    0.410     0.464

AVERAGE FRACTIONAL CONVERSION = 0.467

RATE CONSTANTS
BASED ON    METHANOL      WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.859E-06   0.606E-06    0.718E-06   0.723E-06
1/2 ORDER  0.776E-06   0.578E-06    0.668E-06   0.672E-06
OXYGEN     0.345E-06   0.256E-06    0.297E-06   0.299E-06
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KINETICS OF METHANOL OXIDATION

 RUNS NUMBER 69 TO 74
 CATALYST SAMPLE NUMBER 3
 ONE GC FEED ANALYSIS AND FIVE GC PRODUCT ANALYSES
 AIR FEED RATE (CC(STP)/MIN) = 1788.0
 METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
 REACTOR PRESSURE (TORR) = 769.5
 TEMPERATURE (KELVIN) = 533.0
 CATALYST CHARGE (GRAMS) = 20.92
 CATALYST SURFACE AREA (SQ.M/G) = 3.31

 FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

 TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER  CH2O

 FEED (FLOW RATES)  73.15   19.32   7.52
 FEED(G.C.)         73.01   19.29   7.52   0.167
 AVG. FEED (G.C.)   73.01   19.29   7.52   0.167

 AVERAGE FEED       73.08   19.31   7.52

 PRODUCT (G.C.)     72.07   16.87   4.46    3.38    3.19
 PRODUCT (G.C.)     71.90   17.35   3.97    3.45    3.30
 PRODUCT (G.C.)     72.00   16.07   4.28    3.92    3.70
 PRODUCT (G.C.)     72.01   16.41   4.30    3.55    3.71
 PRODUCT (G.C.)     71.95   16.85   4.12    3.76    3.29

 AVERAGE PRODUCT    71.99   16.71   4.23    3.61    3.44

 FRACTIONAL CONVERSION

 FEED COMPOSITION      BASED ON PRODUCT G.C. ANALYSES OF
 BASED ON                METHANOL  WATER  FORMALDEHYDE

 FEED FLOW RATES         0.428    0.467     0.466
 AVG GC ANALYSIS         0.428    0.467     0.466
 GC + FEED RATES         0.428    0.467     0.466

 AVERAGE FRACTIONAL CONVERSION = 0.453

 RATE CONSTANTS
 BASED ON   METHANOL      WATER     FORMALDEHYDE  AVERAGE

 1ST ORDER  0.506E-06   0.570E-06   0.568E-06   0.547E-06
 1/2 ORDER  0.577E-06   0.639E-06   0.637E-06   0.617E-06
 OXYGEN     0.279E-06   0.309E-06   0.309E-06   0.299E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 75 TO 83
CATALYST SAMPLE NUMBER 3
FOUR GC FEED ANALYSES AND FIVE GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 2499.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 821.3
TEMPERATURE (KELVIN) = 533.0
CATALYST CHARGE (GRAMS) = 20.92
CATALYST SURFACE AREA (SQ.M/G) = 3.31

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  74.75     19.75    5.49
FEED(G.C.)         74.42     19.66    5.74    0.162
FEED(G.C.)         74.61     19.71    5.50    0.162
FEED(G.C.)         74.71     19.74    5.38    0.164
FEED(G.C.)         74.54     19.69    5.59    0.167
AVG. FEED (G.C.)   74.57     19.70    5.55    0.164

AVERAGE FEED       74.66     19.72    5.52

PRODUCT (G.C.)     73.88     18.84    3.15    2.24    1.87
PRODUCT (G.C.)     73.99     18.21    3.45    2.35    1.97
PRODUCT (G.C.)     73.91     18.59    3.22    2.14    2.12
PRODUCT (G.C.)     73.95     18.18    3.35    2.45    2.04
PRODUCT (G.C.)     73.93     18.19    3.29    2.36    2.20

AVERAGE PRODUC     73.93     18.40    3.29    2.31    2.04

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON             METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES        0.394    0.395     0.375
AVG GC ANALYSIS        0.400    0.390     0.371
GC + FEED RATES        0.397    0.393     0.373

AVERAGE FRACTIONAL CONVERSION = 0.388

RATE CONSTANTS
BASED ON    METHANOL      WATER      FORMALDEHYDE  AVERAGE

1ST ORDER  0.585E-06    0.577E-06    0.541E-06   0.568E-06
1/2 ORDER  0.599E-06    0.592E-06    0.559E-06   0.583E-06
OXYGEN     0.275E-06    0.272E-06    0.256E-06   0.268E-06
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KINETICS OF METHANOL OXIDATION

RUN NUMBERS 90 TO 98
CATALYST NUMBER 3
FIVE GC FEED ANALYSES AND FOUR GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3046.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 850.0
TEMPERATURE (KELVIN) = 533.0
CATALYST CHARGE (GRAMS) = 20.95
CATALYST SURFACE AREA (SQ.M/G) = 3.31

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT).

TYPE OF ANALYSIS   NITROGEN  OXYGEN  METHANOL  WATER  CH2O

FEED (FLOW RATES)   75.49     19.94    4.55
FEED(G.C.)          75.24     19.88    4.70    0.167
FEED(G.C.)          74.97     19.80    5.05    0.166
FEED(G.C.)          75.45     19.93    4.43    0.165
FEED(G.C.)          75.29     19.89    4.65    0.164
FEED(G.C.)          75.16     19.85    4.81    0.160
AVG. FEED (G.C.)    75.22     19.87    4.73    0.165

AVERAGE FEED        75.36     19.91    4.64

PRODUCT (G.C.)      74.79     18.81    2.75    1.97    1.65
PRODUCT (G.C.)      74.86     18.97    2.92    1.69    1.54
PRODUCT (G.C.)      74.80     18.95    2.76    1.72    1.73
PRODUCT (G.C.)      74.80     19.21    2.77    1.72    1.48

AVERAGE PRODUCT     74.81     18.99    2.80    1.78    1.60

FRACTIONAL CONVERSION

FEED COMPOSITION     BASED ON PRODUCT G.C. ANALYSES OF
BASED ON               METHANOL  WATER   FORMALDEHYDE

FEED FLOW RATES         0.378    0.357    0.354
AVG GC ANALYSIS         0.401    0.344    0.341
GC + FEED RATES         0.390    0.351    0.348

AVERAGE FRACTIONAL CONVERSION = 0.363

RATE CONSTANTS
BASED ON    METHANOL       WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.665E-06    0.581E-06     0.575E-06  0.607E-06
1/2 ORDER  0.633E-06    0.562E-06     0.556E-06  0.583E-06
OXYGEN     0.283E-06    0.251E-06     0.249E-06  0.261E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER  99 TO 105
CATALYST SAMPLE NUMBER  3
FOUR  GC FEED ANALYSES AND THREE GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3546.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 916.3
TEMPERATURE (KELVIN) = 533.0
CATALYST CHARGE (GRAMS) = 20.92
CATALYST SURFACE AREA (SQ.M/G) = 3.31

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS   NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.98     20.07   3.93
FEED(G.C.)         76.19     20.13   3.49     0.179
FEED(G.C.)         75.96     20.07   3.78     0.180
FEED(G.C.)         75.83     20.03   3.94     0.181
FEED(G.C.)         75.91     20.05   3.84     0.181
AVG. FEED (G.C.)   75.97     20.07   3.76     0.180

AVERAGE FEED       75.98     20.07   3.85

PRODUCT (G.C.)     75.35     19.80   2.17     1.41     1.24
PRODUCT (G.C.)     75.43     19.34   2.38     1.55     1.27
PRODUCT (G.C.)     75.41     19.40   2.32     1.44     1.41

AVERAGE PRODUCT    75.40     19.51   2.29     1.47     1.31

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON             METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES      0.412     0.330     0.335
AVG GC ANALYSIS      0.386     0.345     0.350
GC + FEED RATES      0.399     0.337     0.342

AVERAGE FRACTIONAL CONVERSION = 0.360

RATE CONSTANTS
BASED ON   METHANOL      WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.737E-06     0.595E-06   0.605E-06     0.644E-06
1/2 ORDER  0.674E-06     0.558E-06   0.567E-06     0.599E-06
OXYGEN     0.289E-06     0.239E-06   0.[illegible]3E-06    0.257E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 106 TO 112
CATALYST SAMPLE NUMBER  3
FOUR  GC FEED ANALYSES AND THREE GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3061.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 858.8
TEMPERATURE (KELVIN) = 552.0
CATALYST CHARGE (GRAMS) = 20.92
CATALYST SURFACE AREA (SQ.M/G) = 3.31

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.51     19.95    4.53
FEED(G.C.)         75.18     19.86    4.75    0.194
FEED(G.C.)         75.45     19.93    4.40    0.194
FEED(G.C.)         75.54     19.96    4.29    0.198
FEED(G.C.)         75.35     19.91    4.53    0.198
AVG. FEED (G.C.)   75.38     19.91    4.49    0.196

AVERAGE FEED       75.45     19.93    4.51

PRODUCT (G.C.)     74.63     17.76    2.13    2.87    2.59
PRODUCT (G.C.)     74.51     18.62    1.82    2.47    2.55
PRODUCT (G.C.)     74.50     18.58    1.78    2.57    2.55

AVERAGE PRODUCT    74.55     18.32    1.91    2.64    2.56

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON              METHANOL   WATER   FORMALDEHYDE

FEED FLOW RATES        0.572     0.546      0.573
AVG GC ANALYSIS        0.569     0.550      0.578
GC + FEED RATES        0.571     0.548      0.576

AVERAGE FRACTIONAL CONVERSION = 0.565

RATE CONSTANTS
BASED ON    METHANOL       WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.117E-05    0.110E-05    0.119E-05   0.115E-05
1/2 ORDER  0.101E-05    0.963E-06    0.102E-05   0.100E-05
OXYGEN     0.462E-06    0.439E-06    0.468E-06   0.456E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 113 TO 117
CATALYST SAMPLE NUMBER  3
TWO  GC FEED ANALYSES AND THREE GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 2739.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 854.0
TEMPERATURE (KELVIN) = 571.0
CATALYST CHARGE (GRAMS) = 20.92
CATALYST SURFACE AREA (SQ.M/G) = 3.31

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.11     19.84    5.04
FEED(G.C.)         74.69     19.73    5.38    0.188
FEED(G.C.)         74.70     19.73    5.37    0.184
AVG. FEED (G.C.)   74.69     19.73    5.38    0.186

AVERAGE FEED       74.90     19.79    5.21

PRODUCT (G.C.)     73.60     17.36    1.09    4.01    3.92
PRODUCT (G.C.)     73.65     16.24    1.23    4.47    4.39
PRODUCT (G.C.)     73.64     15.84    1.20    4.70    4.60

AVERAGE PRODUCT    73.63     16.48    1.17    4.39    4.30

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON               METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES        0.762    0.853     0.873
AVG GC ANALYSIS        0.776    0.799     0.817
GC + FEED RATES        0.769    0.825     0.844

AVERAGE FRACTIONAL CONVERSION = 0.813

RATE CONSTANTS
BASED ON    METHANOL      WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.191E-05    0.229E-05     0.244E-05  0.219E-05
1/2 ORDER  0.147E-05    0.165E-05     0.172E-05  0.161E-05
OXYGEN     0.696E-06    0.783E-06     0.816E-06  0.763E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 118 TO 122
CATALYST SAMPLE NUMBER  3
THREE GC FEED ANALYSES AND TWO  GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3421.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 884.5
TEMPERATURE (KELVIN) = 504.0
CATALYST CHARGE (GRAMS) = 20.92
CATALYST SURFACE AREA (SQ.M/G) = 3.31

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.87    20.04    4.07
FEED(G.C.)         75.56    19.96    4.30    0.161
FEED(G.C.)         75.61    19.97    4.25    0.157
FEED(G.C.)         75.53    19.95    4.35    0.157
AVG. FEED (G.C.)   75.57    19.96    4.30    0.158

AVERAGE FEED       75.72    20.00    4.19

PRODUCT (G.C.)     75.64    19.17    3.56    0.96    0.65
PRODUCT (G.C.)     75.62    19.35    3.51    0.88    0.62

AVERAGE PRODUCT    75.63    19.26    3.53    0.92    0.63

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON              METHANOL   WATER   FORMALDEHYDE

FEED FLOW RATES        0.130     0.188     0.157
AVG GC ANALYSIS        0.174     0.179     0.148
GC + FEED RATES        0.153     0.183     0.152

AVERAGE FRACTIONAL CONVERSION = 0.163

RATE CONSTANTS
BASED ON   METHANOL     WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.226E-06   0.277E-06    0.226E-06  0.243E-06
1/2 ORDER  0.231E-06   0.281E-06    0.232E-06  0.248E-06
OXYGEN     0.980E-07   0.119E-06    0.982E-07  0.105E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 123 TO 130
CATALYST SAMPLE NUMBER  3
FIVE  GC FEED ANALYSES AND THREE GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3096.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 864.1
TEMPERATURE (KELVIN) = 513.0
CATALYST CHARGE (GRAMS) = 20.92
CATALYST SURFACE AREA (SQ.M/G) = 3.31

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.55     19.96     4.48
FEED(G.C.)         75.48     19.94     4.41     0.159
FEED(G.C.)         75.52     19.95     4.35     0.160
FEED(G.C.)         75.60     19.97     4.26     0.160
FEED(G.C.)         75.29     19.89     4.64     0.159
FEED(G.C.)         75.28     19.89     4.66     0.159
AVG. FEED (G.C.)   75.43     19.93     4.46     0.159

AVERAGE FEED       75.49     19.94     4.47

PRODUCT (G.C.)     75.20     19.10     3.55     1.18     0.95
PRODUCT (G.C.)     75.16     19.12     3.42     1.27     1.01
PRODUCT (G.C.)     75.16     19.15     3.42     1.30     0.94

AVERAGE PRODUCT    75.17     19.13     3.46     1.25     0.96

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON              METHANOL   WATER  FORMALDEHYDE

FEED FLOW RATES        0.223     0.245     0.216
AVG GC ANALYSIS        0.220     0.246     0.217
GC + FEED RATES        0.221     0.246     0.217

AVERAGE FRACTIONAL CONVERSION = 0.228

RATE CONSTANTS
BASED ON   METHANOL      WATER      FORMALDEHYDE  AVERAGE

1ST ORDER  0.324E-06   0.365E-06    0.316E-06   0.335E-06
1/2 ORDER  0.334E-06   0.374E-06    0.327E-06   0.345E-06
OXYGEN     0.145E-06   0.162E-06    0.141E-06   0.149E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 131 TO 139
CATALYST SAMPLE NUMBER  3
FOUR  GC FEED ANALYSES AND FIVE  GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3099.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 864.7
TEMPERATURE (KELVIN) = 524.0
CATALYST CHARGE (GRAMS) = 20.92
CATALYST SURFACE AREA (SQ.M/G) = 3.31

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.55     19.96    4.48
FEED(G.C.)         75.27     19.88    4.67     0.160
FEED(G.C.)         75.38     19.91    4.53     0.159
FEED(G.C.)         75.21     19.87    4.73     0.171
FEED(G.C.)         75.35     19.91    4.56     0.169
AVG. FEED (G.C.)   75.30     19.89    4.62     0.164

AVERAGE FEED       75.43     19.93    4.55

PRODUCT (G.C.)     74.97     19.68    2.99     1.24     1.10
PRODUCT (G.C.)     74.95     19.62    2.92     1.39     1.11
PRODUCT (G.C.)     75.16     18.77    3.50     1.46     1.09
PRODUCT (G.C.)     75.12     19.15    3.39     1.24     1.08
PRODUCT (G.C.)     75.14     18.84    3.44     1.52     1.04

AVERAGE PRODUCT    75.07     19.21    3.25     1.37     1.08

FRACTIONAL CONVERSION

FEED COMPOSITION     BASED ON PRODUCT G.C. ANALYSES OF
BASED ON                METHANOL   WATER   FORMALDEHYDE

FEED FLOW RATES          0.269     0.271      0.243
AVG GC ANALYSIS          0.292     0.262      0.235
GC + FEED RATES          0.281     0.267      0.239

AVERAGE FRACTIONAL CONVERSION = 0.262

RATE CONSTANTS
BASED ON   METHANOL       WATER       FORMALDEHYDE   AVERAGE

1ST ORDER  0.436E-06    0.410E-06     0.362E-06    0.402E-06
1/2 ORDER  0.436E-06    0.412E-06     0.367E-06    0.405E-06
OXYGEN     0.191E-06    0.181E-06     0.161E-06    0.177E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 140 TO 146
CATALYST SAMPLE NUMBER 3
THREE GC FEED ANALYSES AND FOUR GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3087.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 876.4
TEMPERATURE (KELVIN) = 544.0
CATALYST CHARGE (GRAMS) = 20.92
CATALYST SURFACE AREA (SQ.M/G) = 3.31

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS   NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)   75.54    19.95    4.49
FEED(G.C.)          75.33    19.90    4.59    0.159
FEED(G.C.)          75.66    19.99    4.18    0.165
FEED(G.C.)          75.23    19.87    4.71    0.163
AVG. FEED (G.C.)    75.41    19.92    4.49    0.162

AVERAGE FEED        75.47    19.94    4.49

PRODUCT (G.C.)      74.71    17.92    2.26    2.66    2.42
PRODUCT (G.C.)      74.76    17.99    2.39    2.46    2.37
PRODUCT (G.C.)      74.81    17.57    2.53    2.68    2.39
PRODUCT (G.C.)      74.74    17.73    2.33    2.74    2.44

AVERAGE PRODUCT     74.75    17.81    2.38    2.63    2.40

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON              METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES       0.465     0.557     0.542
AVG GC ANALYSIS       0.465     0.557     0.542
GC + FEED RATES       0.465     0.557     0.542

AVERAGE FRACTIONAL CONVERSION = 0.521

RATE CONSTANTS
BASED ON   METHANOL      WATER        FORMALDEHYDE  AVERAGE

1ST ORDER  0.845E-06    0.110E-05    0.105E-05    0.997E-06
1/2 ORDER  0.778E-06    0.971E-06    0.936E-06    0.893E-06
OXYGEN     0.347E-06    0.435E-06    0.419E-06    0.399E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 152 TO 155
CATALYST SAMPLE NUMBER  3
TWO   GC FEED ANALYSES AND TWO   GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3060.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 879.5
TEMPERATURE (KELVIN) = 568.0
CATALYST CHARGE (GRAMS) = 20.92
CATALYST SURFACE AREA (SQ.M/G) = 3.[illegible]

FEED AND PRODUCT COMPOSITIONS (MOL. PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.51    19.95    4.53
FEED(G.C.)         75.18    19.86    4.75    0.184
FEED(G.C.)         75.32    19.90    4.58    0.183
AVG. FEED (G.C.)   75.25    19.88    4.67    0.183

AVERAGE FEED       75.38    19.91    4.60

PRODUCT (G.C.)     74.29    16.69    1.30    3.81    3.89
PRODUCT (G.C.)     74.33    16.19    1.42    4.11    3.91

AVERAGE PRODUCT    74.31    16.44    1.36    3.96    3.90

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON             METHANOL   WATER   FORMALDEHYDE

FEED FLOW RATES       0.694     0.851     0.877
AVG GC ANALYSIS       0.702     0.826     0.852
GC + FEED RATES       0.698     0.838     0.864

AVERAGE FRACTIONAL CONVERSION = 0.800

RATE CONSTANTS
BASED ON   METHANOL      WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.167E-05    0.256E-05    0.281E-05    0.226E-05
1/2 ORDER  0.132E-05    0.176E-05    0.186E-05    0.162E-05
OXYGEN     0.609E-06    0.814E-06    0.861E-06    0.752E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 156 TO 162
CATALYST SAMPLE NUMBER  3
FOUR  GC FEED ANALYSES AND THREE GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3052.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 856.8
TEMPERATURE (KELVIN) = 519.0
CATALYST CHARGE (GRAMS) = 20.92
CATALYST SURFACE AREA (SQ.M/G) = 3.31

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.50     19.94     4.54
FEED(G.C.)         75.65     19.99     4.18    0.162
FEED(G.C.)         75.56     19.96     4.31    0.163
FEED(G.C.)         75.50     19.95     4.37    0.166
FEED(G.C.)         75.60     19.97     4.24    0.165
AVG. FEED (G.C.)   75.58     19.97     4.28    0.164

AVERAGE FEED       75.54     19.96     4.41

PRODUCT (G.C.)     75.06     19.19     3.23    1.31    1.18
PRODUCT (G.C.)     75.12     19.13     3.38    1.22    1.13
PRODUCT (G.C.)     75.07     19.18     3.25    1.31    1.17

AVERAGE PRODUCT    75.08     19.17     3.29    1.28    1.16

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON              METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES       0.271    0.247     0.257
AVG GC ANALYSIS       0.227    0.263     0.273
GC + FEED RATES       0.250    0.255     0.265

AVERAGE FRACTIONAL CONVERSION = 0.256

RATE CONSTANTS
BASED ON   METHANOL     WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.374E-06   0.383E-06   0.402E-06   0.386E-06
1/2 ORDER  0.381E-06   0.390E-06   0.407E-06   0.392E-06
OXYGEN     0.167E-06   0.171E-06   0.178E-06   0.172E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 198 TO 204
CATALYST SAMPLE NUMBER  5
TWO  GC FEED ANALYSES AND TWO  GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3040.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 868.0
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 20.08
CATALYST SURFACE AREA (SQ.M/G) = 3.53

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)   75.48     19.94   4.56
FEED(G.C.)          75.35     19.90   4.53    0.203
FEED(G.C.)          75.45     19.93   4.40    0.202
AVG. FEED (G.C.)    75.40     19.92   4.46    0.203

AVERAGE FEED        75.44     19.93   4.51

PRODUCT (G.C.)      74.68     18.34   2.34    2.31    2.30
PRODUCT (G.C.)      74.66     18.37   2.27    2.44    2.24

AVERAGE PRODUCT     74.67     18.36   2.30    2.38    2.27

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON              METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES        0.488    0.483     0.503
AVG GC ANALYSIS        0.477    0.493     0.514
GC + FEED RATES        0.483    0.488     0.509

AVERAGE FRACTIONAL CONVERSION = 0.493

RATE CONSTANTS
BASED ON  METHANOL     WATER     FORMALDEHYDE  AVERAGE

1ST ORDER 0.855E-06   0.868E-06   0.922E-06  0.881E-06
1/2 ORDER 0.788E-06   0.798E-06   0.839E-06  0.808E-06
OXYGEN    0.351E-06   0.356E-06   0.374E-06  0.360E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 213 TO 215
CATALYST SAMPLE NUMBER  6
ONE   GC FEED ANALYSES AND TWO   GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3051.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 870.7
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 20.08
CATALYST SURFACE AREA (SQ.M/G) = 3.22

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  75.50    19.94    4.54
FEED(G.C.)         75.53    19.95    4.35    0.157
AVG. FEED (G.C.)   75.53    19.95    4.35    0.157

AVERAGE FEED       75.51    19.95    4.45

PRODUCT (G.C.)     74.70    18.85    2.30    2.12    2.00
PRODUCT (G.C.)     74.72    18.59    2.34    2.25    2.07

AVERAGE PRODUCT    74.71    18.72    2.32    2.19    2.04

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON                METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES          0.483    0.452    0.453
AVG GC ANALYSIS          0.460    0.472    0.473
GC + FEED RATES          0.472    0.462    0.463

AVERAGE FRACTIONAL CONVERSION = 0.466

RATE CONSTANTS
BASED ON   METHANOL       WATER       FORMALDEHYDE  AVERAGE)

1ST ORDER  0.907E-06   0.881E-06   0.883E-06   0.890E-06
1/2 ORDER  0.840E-06   0.819E-06   0.821E-06   0.827E-06
OXYGEN     0.374E-06   0.364E-06   0.365E-06   0.368E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 216 TO 225
CATALYST SAMPLE NUMBER  6
THREE GC FEED ANALYSES AND FOUR  GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 2153.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 823.2
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 20.08
CATALYST SURFACE AREA (SQ.M/G) = 3.22

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)   74.09     19.57    6.32
FEED(G.C.)          74.00     19.55    6.43    0.000
FEED(G.C.)          74.16     19.59    6.23    0.000
FEED(G.C.)          74.15     19.59    6.24    0.000
AVG. FEED (G.C.)    74.11     19.58    6.30    0.000

AVERAGE FEED        74.10     19.57    6.31

PRODUCT (G.C.)      72.85     18.13    2.86    3.06    3.07
PRODUCT (G.C.)      72.83     18.15    2.81    3.11    3.07
PRODUCT (G.C.)      72.80     17.93    2.72    3.24    3.28
PRODUCT (G.C.)      72.89     18.15    2.97    2.92    3.05

AVERAGE PRODUCT     72.84     18.09    2.84    3.08    3.12

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON               METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES         0.542     0.495     0.501
AVG GC ANALYSIS         0.541     0.497     0.503
GC + FEED RATES         0.541     0.496     0.502

AVERAGE FRACTIONAL CONVERSION = 0.513

RATE CONSTANTS
BASED ON   METHANOL      WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.846E-06   0.742E-06   0.756E-06   0.780E-06
1/2 ORDER  0.865E-06   0.778E-06   0.789E-06   0.810E-06
OXYGEN     0.404E-06   0.362E-06   0.367E-06   0.377E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 226 TO 233
CATALYST SAMPLE NUMBER  6
FOUR  GC FEED ANALYSES AND THREE GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 1753.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 799.0
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 20.08
CATALYST SURFACE AREA (SQ.M/G) = 3.22

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  73.04    19.29   7.65
FEED(G.C.)         72.72    19.21   7.83   0.232
FEED(G.C.)         72.89    19.28   7.60   0.232
FEED(G.C.)         72.42    19.13   8.20   0.232
FEED(G.C.)         72.65    19.19   7.92   0.233
AVG. FEED (G.C.)   72.67    19.20   7.88   0.232

AVERAGE FEED       72.85    19.25   7.77

PRODUCT (G.C.)     71.66    16.90   3.85   3.90    3.67
PRODUCT (G.C.)     71.66    17.21   3.85   3.55    3.72
PRODUCT (G.C.)     71.69    16.61   3.94   3.94    3.80

AVERAGE PRODUCT    71.67    16.90   3.88   3.80    3.73

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON               METHANOL   WATER   FORMALDEHYDE

FEED FLOW RATES         0.483     0.474     0.497
AVG GC ANALYSIS         0.498     0.460     0.482
GC + FEED RATES         0.491     0.467     0.489

AVERAGE FRACTIONAL CONVERSION = 0.482

RATE CONSTANTS
BASED ON    METHANOL       WATER        FORMALDEHYDE  AVERAGE

1ST ORDER   0.623E-06    0.582E-06      0.621E-06   0.608E-06
1/2 ORDER   0.708E-06    0.668E-06      0.706E-06   0.694E-06
OXYGEN      0.338E-06    0.319E-06      0.337E-06   0.331E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 242 TO 250
CATALYST SAMPLE NUMBER  7
FIVE  GC FEED ANALYSES AND FOUR  GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 2506.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 814.7
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 20.08
CATALYST SURFACE AREA (SQ.M/G) = 2.42

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)   74.78     19.75    5.48
FEED(G.C.)          74.91     19.79    5.29    0.000
FEED(G.C.)          75.04     19.82    5.12    0.000
FEED(G.C.)          74.71     19.74    5.54    0.000
FEED(G.C.)          74.76     19.75    5.48    0.000
FEED(G.C.)          75.03     19.82    5.14    0.000
AVG. FEED (G.C.)    74.89     19.78    5.31    0.000

AVERAGE FEED        74.82     19.77    5.40

PRODUCT (G.C.)      73.87     19.14    2.95    1.98    2.03
PRODUCT (G.C.)      73.81     19.72    2.79    1.68    1.98
PRODUCT (G.C.)      73.93     18.92    3.13    1.89    2.10
PRODUCT (G.C.)      73.88     19.12    2.98    1.89    2.11

AVERAGE PRODUCT     73.87     19.22    2.96    1.86    2.06

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON              METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES        0.452    0.343     0.379
AVG GC ANALYSIS        0.435    0.354     0.391
GC + FEED RATES        0.444    0.348     0.385

AVERAGE FRACTIONAL CONVERSION = 0.392

RATE CONSTANTS
BASED ON   METHANOL      WATER        FORMALDEHYDE  AVERAGE

1ST ORDER  0.983E-06     0.718E-06    0.815E-06    0.835E-06
1[illegible] ORDER  0.979E-06     0.743E-06    0.831E-06    0.849E-06
OXYGEN     0.453E-06     0.343E-06    0.384E-06    0.393E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 255 TO 258
CATALYST SAMPLE NUMBER  8
TWO   GC FEED ANALYSES AND TWO   GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 2957.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 839.7
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 20.05
CATALYST SURFACE AREA (SQ.M/G) = 1.21

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)   75.39     19.92    4.68
FEED(G.C.)          75.22     19.87    4.74    0.150
FEED(G.C.)          75.22     19.87    4.74    0.149
AVG. FEED (G.C.)    75.22     19.87    4.74    0.149

AVERAGE FEED        75.31     19.89    4.71

PRODUCT (G.C.)      75.08     19.83    3.87    0.70    0.50
PRODUCT (G.C.)      75.09     19.80    3.90    0.71    0.48

AVERAGE PRODUCT     75.08     19.81    3.89    0.71    0.49

FRACTIONAL CONVERSION

FEED COMPOSITION    BASED ON PRODUCT G.C. ANALYSES OF
BASED ON               METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES        0.166    0.120     0.105
AVG GC ANALYSIS        0.176    0.118     0.103
GC + FEED RATES        0.171    0.119     0.104

AVERAGE FRACTIONAL CONVERSION = 0.131

RATE CONSTANTS
BASED ON   METHANOL      WATER        FORMALDEHYDE  AVERAGE

1ST ORDER  0.714E-06    0.481E-06    0.417E-06  0.535E-06
1/2 ORDER  0.737E-06    0.505E-06    0.440E-06  0.560E-06
OXYGEN     0.331E-06    0.226E-06    0.197E-06  0.251E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 263 TO 264
CATALYST SAMPLE NUMBER  9
ONE   GC FEED ANALYSES AND ONE   GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 3002.0
METHANOL FEED RATE,(CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 858.5
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 20.04
CATALYST SURFACE AREA (SQ.M/G) = 1.66

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES) 75.44    19.93   4.62
FEED(G.C.)        75.65    19.98   4.12    0.234
AVG. FEED (G.C.)  75.65    19.98   4.12    0.234

AVERAGE FEED      75.54    19.96   4.37

PRODUCT (G.C.)    75.25    20.15   3.84    0.51     0.23

AVERAGE PRODUCT   75.25    20.15   3.84    0.51     0.23

FRACTIONAL CONVERSION

FEED COMPOSITION   BASED ON PRODUCT G.C. ANALYSES OF
BASED ON             METHANOL   WATER   FORMALDEHYDE

FEED FLOW RATES       0.164     0.060      0.050
AVG GC ANALYSIS       0.066     0.067      0.056
GC + FEED RATES       0.118     0.064      0.052

AVERAGE FRACTIONAL CONVERSION = 0.077

RATE CONSTANTS
BASED ON   METHANOL       WATER        FORMALDEHYDE  AVERAGE

1ST ORDER  0.338E-06    0.181E-06     0.149E-06   0.222E-06
1/2 ORDER  0.357E-06    0.194E-06     0.160E-06   0.236E-06
OXYGEN     0.158E-06    0.862E-07     0.710E-07   0.104E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 251 TO 254
CATALYST SAMPLE NUMBER 10
TWO   GC FEED ANALYSES AND TWO   GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 2971.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 816.8
TEMPERATURE (KELVIN) = 536.0
CATALYST CHARGE (GRAMS) = 20.05
CATALYST SURFACE AREA (SQ.M/G) = 8.70

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS   NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)   75.40     19.92    4.66
FEED(G.C.)          75.39     19.92    4.52     0.160
FEED(G.C.)          75.34     19.90    4.58     0.160
AVG. FEED (G.C.)    75.36     19.91    4.55     0.160

AVERAGE FEED        75.38     19.91    4.61

PRODUCT (G.C.)      74.04     17.19    0.89     4.46     3.40
PRODUCT (G.C.)      74.04     17.09    0.90     4.48     3.46

AVERAGE PRODUCT     74.04     17.14    0.90     4.47     3.43

FRACTIONAL CONVERSION

FEED COMPOSITION     BASED ON PRODUCT G.C. ANALYSES OF
BASED ON               METHANOL  WATER  FORMALDEHYDE

FEED FLOW RATES       0.[illegible]2   0.945     0.749
AVG GC ANALYSIS       0.797     0.968     0.767
GC + FEED RATES       0.800     0.956     0.758

AVERAGE FRACTIONAL CONVERSION = 0.838

RATE CONSTANTS
BASED ON    METHANOL      WATER       FORMALDEHYDE  AVERAGE

1ST ORDER   0.886E-06    0.173E-05    0.781E-06   0.100E-05
1/2 ORDER   0.642E-06    0.920E-06    0.590E-06   0.694E-06
OXYGEN      0.299E-06    0.432E-06    0.274E-06   0.324E-06
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KINETICS OF METHANOL OXIDATION

RUNS NUMBER 270 TO 271   (USED DISC INTEGRATOR)
CATALYST SAMPLE NUMBER 11
ONE   GC FEED ANALYSES AND ONE   GC PRODUCT ANALYSES
AIR FEED RATE (CC(STP)/MIN) = 2134.0
METHANOL FEED RATE (CC(LIQUID)/MIN) = 0.26250
REACTOR PRESSURE (TORR) = 794.0
TEMPERATURE (KELVIN) = 531.0
CATALYST CHARGE (GRAMS) = 11.67
CATALYST SURFACE AREA (SQ.M/G) = 0.25

FEED AND PRODUCT COMPOSITIONS (MOLE PER CENT)

TYPE OF ANALYSIS  NITROGEN OXYGEN METHANOL WATER CH2O

FEED (FLOW RATES)  74.05     19.56    6.37
FEED(G.C.)         74.08     19.57    6.25    0.089
AVG. FEED (G.C.)   74.08     19.57    6.25    0.089

AVERAGE FEED       74.06     19.57    6.31

PRODUCT (G.C.)     73.97     19.73    6.10    0.13     0.04

AVERAGE PRODUCT    73.97     19.73    6.10    0.13     0.04

FRACTIONAL CONVERSION

FEED COMPOSITION      BASED ON PRODUCT G.C. ANALYSES OF
BASED ON                METHANOL   WATER   FORMALDEHYDE

FEED FLOW RATES          0.041     0.007    -0.006
AVG GC ANALYSIS          0.022     0.007     0.006
GC + FEED RATES          0.032     0.007     0.006

AVERAGE FRACTIONAL CONVERSION = 0.015

RATE CONSTANTS
BASED ON   METHANOL      WATER       FORMALDEHYDE  AVERAGE

1ST ORDER  0.787E-06    0.177E-06    0.166E-06   0.375E-06
1/2 ORDER  0.965E-06    0.218E-06    0.205E-06   0.462E-06
OXYGEN     0.446E-06    0.101E-06    0.949E-07   0.213E-06
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