THE OXIDATION OF O-XYLENE IN AN
INTEGRAL PACKED BED REACTOR

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by

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ABSTRACT

The oxidation of o-xylene was investigated in an integral packed bed reactor using a K_2SO_4 promoted vanadium pentoxide catalyst on a TiO_2 support.

Reaction products consisting of nine chemical components were analyzed by a new temperature-programmed gas chromatographic technique using three different columns to effect separation.

A kinetic model based on the REDOX (catalyst reduction and oxidation) mechanism was employed. The statistical method of experimental design for parameter estimation based on M.J. Box's modification [116] of the Draper and Hunter method [47] was used. Statistical analysis based on the eigenvalue-eigenvector method of Box et al. [45] indicated correlation among the responses and this method was used to transform the multiple response data for use in estimating the parameters in the kinetic model.

Since parameter estimates in the model were available from Wainwright's previous work [26], the method of Hoffman and Reilly [124] which is based on Bayes' theorem, was used to transfer this prior information on the parameters to the present experimental system.

The kinetic data obtained from using the new chromatographic technique developed in this study were found to be consistent. The kinetic model of Wainwright [26] for this reaction system was fitted to the multiple response data obtained from this study. The adequacy of this model in representing the data was also tested. The use of the statistical techniques in experimental programs to develop kinetic models was found to be extremely effective. Some of the difficulties in using them are outlined.

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NOTATION

C_i	Concentration of component i in gm mole/liter
C_a	Concentration of oxygen, gm moles/liter
E	Activation Energy, calories/gm mole
E_{as}	Active site parameter, calories/gm mole
k	Reaction rate constant, liters/gm catalyst hr
k_a	Rate constant for oxygen uptake either by reaction or adsorption liters/gm catalyst hr
n	Stoichiometric coefficient gm-mole of oxygen consumed/gas mole of hydrocarbon reacted
R	Gas constant, calories/gm mole °K
r	Rate of reaction, gm mole/gm catalyst hr
r_a	Rate of oxygen uptake either by reaction or adsorption liters/gm catalyst hr
T	Temperature °K
W	Mass of catalyst, grams
θ, ϕ	Fraction of catalyst surface sites in fully oxidized state at steady state.

Subscripts

r	denotes hydrocarbon reactants

Superscripts

$*$	denotes transformation

NOTE: The prime symbol (') is used throughout to denote the transpose of a matrix.

NOTATIONS FOR STATISTICAL TECHNIQUES

n	number of experiments
p	number of parameters
m	number of replicates
y	measured response
$\underline{n}$	an rx1 vector of the expected value of the responses
T^*	temperature at the center of design °K
F_{ox}	flowrate of o-xylene in cc/minute
F_{02}	flowrate of oxygen in cc/minute
FN_2	flowrate of nitrogen in cc/minute
TR	Reactor temperature in °K
$\underline{V}$	Variance-covariance matrix of the responses (Chapter 4)
Det	determinant
$\underline{\alpha}$	the px1 prior parameter estimates
$\underline{\gamma}$	the px1 vector of parameter values at which the model is linearized
γ_i	the value of on the i^{th} iteration
$\underline{\varepsilon}$	the Nx1 vector of errors
$\underline{\theta}^*$	the px1 vector of true parameter values; this
$\underline{\theta}$	any px1 vector of possible values for $\underline{\theta}^*$ (Chapter 7)
$\underline{\hat{\theta}}$	the posterior mean with linearization at the posterior mean
σ	standard deviation
$\underline{V}$	the error covariance matrix equation 7.2.4
n	number of observations
$\underline{x}_u$	vector of independent variables at the u^{th} trial
$\underline{X}$	the nxp matrix of partial derivatives
$\underline{y}_u$	the rx1 vector of values of dependent variables at the u^{th} trial

$\underline{z}$	the nx1 vector of deviations between the measured and the expected values
p	the number of parameters

Subscripts

-	denotes matrix or vector

Abreviations

OX	o-xylene
OTA	o-tolualdehyde
PI	phthalide
PA	phthalic anhydride

CHAPTER 1

INTRODUCTION

1.1

In chemical engineering, the investigation of a chemical reaction generally involves a study of its kinetics and the underlying mechanism. This type of study often involve the formulation or the development of a kinetic or reaction model. A kinetic model can be described, in general terms, as a convenient and reasonable representation of the reaction rates which when used in conjunction with a reactor model will provide an estimate of the concentration of the reactants and products in the exit stream for any given operating conditions. It may not be unique, but should at least be consistent with known data and permit both interpolation and some extrapolation [69]. The form of a kinetic model is often suggested by the reaction mechanism. In heterogeneous catalysis, the mechanism of a solid-catalyzed reaction is often not adequately understood at the molecular level. A direct implication of this is that the mechanism upon which a kinetic model is developed is usually assumed without adequate proof. If the kinetic model fits the experimental data, no claim is made concerning the mechanism of the reaction or even the uniqueness of the model. The agreement may be held to support the assumed reaction mechanism and in addition may further provide some insights as to the direction in which further work is needed in elucidating the true reaction mechanism. Mechanistically based models are to be preferred over the empirical models not only because they can lead to fundamental scientific development, but also because they are more parsimonious and hence provide better estimates of the response for a given experimental effort. A reaction model serves three main purposes:

i) Reactor design.

ii) Elucidation of the reaction network so that conditions and a suitably selective catalyst can be used to control yields of one or more of the intermediates in the reaction.

iii) For providing an understanding of the behaviour of an existing reactor.

Two types of mechanisms have become very popular for describing oxidation of o-xylene on vanadia catalysts.

i) The REDOX mechanism of Mars and Van-Krevelen [12] which assumes that a steady-state is reached in the catalyst when the rate of reaction between the hydrocarbon and the oxygen of the catalyst becomes equal to the rate of reoxidation of the catalyst by the oxygen in the feed.

ii) The Steady-State Adsorption Model [S.S.A.M.] of Shelstad, Downie and Graydon [3] which assumes that the reaction takes place between adsorbed oxygen and the gas phase hydrocarbon.

Both these models yield the same overall rate equations and distinction cannot be made by taking kinetic measurements. Hence support for one model based on kinetic measurements means support for both. In this study, the REDOX mechanism is assumed.

The gas phase catalytic oxidation of o-xylene occurs by a complex mechanism which involves a number of consecutive and parallel steps resulting in the formation of the desired material, phthalic anhydride, which is an intermediate compound. It is well established that the best contacting pattern for this class of reactions, in which the desired product is an intermediate, is one in which the mixing of fluids of different composition is minimum. This normally requires operation in a packed bed reactor in which the flow pattern approximates that of plug flow. Hydrocarbon oxidation reactions are highly exothermic and due to inefficient heat exchange apparent in fixed bed-reactors, the formation of a hot spot is specially favoured. Hot spots are known to lower yield, reduce selectivity and increase hazards of operation. Moreover, due to deactivation of the catalyst, a packed bed is not suitable for long-term continuous operation, and it becomes necessary for the catalyst to be regenerated or a new one installed. The difficulties of heat removal and catalyst deactivation encountered in the operation of a packed bed reactor has been surmounted by the use of a fluidized bed reactor. Hence fluidized bed reactors have become widespread for use in hydrocarbon oxidation [96]. The major disadvantage of this reaction is that large deviation from plug flow exists and there is significant backmixing. Furthermore, the flow patterns are difficult to define and hence it is not possible to predict performance to any degree of certainty [97, 98, 99]. It has also been noted that phthalic anhydride has not been successfully produced from orthoxylene in a fluidized bed reactor. Sherwood [23] and Graham [24] have compared the operation of a fluidized bed reactor with that of a fixed bed in the industrial manufacture of phthalic anhydride from orthoxylene and naphthalene.

The disadvantages of both the packed bed and the fluidized bed reactors may be overcome by the use of a transported bed reactor, in which the reactant and the product gases pneumatically convey the catalyst particles in a vertical tube, by cocurrent transport. Transported bed reactors have been used successfully in catalytic cracking operations [25]. A pilot scale unit of this reactor has been built in this laboratory and previous studies [41, 26] have been carried out towards evaluating its performance for o-xylene oxidation. Furthermore, the studies of Wainwright and Hoffman [100] was the first to be reported in the literature on a pilot scale transported bed reactor in which a reaction was carried out in a reasonably defined condition of dense phase conveying. The following advantages of a transported bed reactor have been noted [26].

i) The flow pattern of the gas and solids approximates to plug flow. This means that the residence times of the reactant and product gases can be better controlled.

ii) The operation is continuous and regenerated solid catalyst is continuously being added while partially deactivated catalyst may be withdrawn.

iii) Good heat transfer rates exist between the particles and the gas and between the solid/gas slurry and the wall. In addition, because the solid is continuously added and removed, it becomes a significant heat sink for the heat of reaction; thus under large solid loadings the reactor is essentially isothermal.

The disadvantages include the following:

i) Since the solid is pneumatically conveyed, operation may be limited to dilute concentration of solids (catalyst). On the other hand Wainwright [26] has been able to demonstrate smooth operation at very high solid loadings (voidage $\sim$0.77). Whether other solid-gas systems on a large scale can operate at these loadings is yet to be demonstrated.

ii) High attrition rates of the catalyst may occur. Also the solids may cause erosion of the reactor internals. These phenomena will be determined by the catalyst and its support.

iii) The equipment is complicated especially the catalyst recovery system.

Any further attempt to evaluate the performance of the transported bed reactor requires that the behaviour of the catalyst be determined under well-defined reactor conditions. This normally requires that a kinetic model be developed for the o-xylene oxidation reaction in a bench-scale packed bed reactor. Although the major problem associated with the packed bed reactor is that of inefficient heat removal, this is not too severe in small scale laboratory work and reactors can be designed to approach isothermal operation [126]. Also, Orlickas [127], Shaw [21] and Wainwright [26] have demonstrated that a small-scale reactor can be operated essentially isothermally and provide good integral data which may be used to estimate kinetic parameters in reaction models.

The present investigation is thus aimed at obtaining an adequate kinetic model for the o-xylene oxidation reaction using a packed bed reactor and it is directed towards providing useful information for further work on the transported bed reactor.

In order to carry out this investigation most efficiently a sequential statistically-designed experimental program was adopted. The sequential design procedure used was similar to that of M.J. Box [116].

In this approach, the operating conditions for a set of experiments having a number of runs equal to the number of parameters in the proposed model are established on the basis that the experimental responses should provide the minimum variance on the parameters. These experiments are carried out; the responses are then used with appropriate statistical techniques to reestimate the parameters in the kinetic model. The entire procedure may be repeated if the more precise parameter estimates are required. Each set of experiments is determined on the basis of the location of all prior experiments and the current parameter estimates from those experiments.

Since preliminary work had been conducted on the reaction system being presently considered [26], the parameters in the model were estimated by using the statistical techniques of Hoffman and Reilly [124]. This technique employs Bayes' theorem to provide a criterion for the 'best' parameter estimates in situations where information on parameter values, together with their inherent uncertainty, are to be transferred from one experiment to another. The mathematical models describing the data in both experiments need only share some common parameters.

1.2 Objectives of the Experimental Program

The main aim of the project was to employ statistical experimental design techniques to develop a kinetic model for the o-xylene reaction, catalyzed by a titania-supported vanadium pentoxide catalyst, using the integral data from a bench-scale packed bed-reactor.

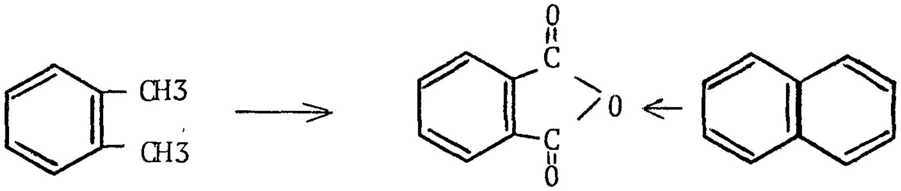
This study is directed towards providing useful information for further work on the pilot scale transported bed reactor.

CHAPTER 2

LITERATURE REVIEW

2.1 General Introduction

Phthalic anhydride production is a process of considerable importance. It is derived by oxidation of o-xylene or naphthalene



o-xylene phthalic anhydride naphthalene

An examination of the stoichiometry of the reaction reveals that in the absolute sense o-xylene is the prefered raw material. The theoretical yields are as follows.

o-xylene (0.72 pounds) → phthalic anhydride (1.0 pound)
Naphthalene (0.86 pounds) → phthalic anhydride (1.0 pound)

Other factors contributing to recent decisions to use o-xylene include availability of feed-stock, low price and low transportation costs. Other raw materials suitable for oxidation to phthalic anhydride are methylated naphthalene and phenanthrene. However, the partial oxidation of these hydrocarbons is accompanied by more heat of reaction than even the conversion of naphthalene and already difficult problems of thermal control are aggravated thereby. Moreover, these materials are not as abundantly available as o-xylene. The traditional outlets for phthalic anhydride include plasticizers, alkyds and saturated polyesters. The specific uses of these products are discussed in [57].

Despite the importance of the o-xylene oxidation reaction, the kinetics and the reaction network have not yet been clearly established. Most of the early work on oxidation of o-xylene has been concentrated on studying the effects of variables such as the reaction temperature, air-to-o-xylene ratio in the feed, contact time, type of catalyst and type of reactor (fluidized bed, or fixed bed) on the yield of phthalic anhydride. These studies were directed towards optimizing the yield of phthalic anhydride [29, 48, 50-55]. Marek and Hahn [48] have reviewed the early studies up to 1931. Most of the references to o-xylene in this review deal mainly with patents. Dixon and Longfield [2] have provided an excellent review of the literature for work carried out in the period between 1931 and 1959. A review of the o-xylene oxidation publications until 1966 is contained in [12].

In spite of the large volume of work that has been published on o-xylene oxidation, a reaction mechanism that completely describes reaction rates and product distribution has not yet appeared in the literature. This can be ascribed to the following:

i) The hydrocarbon-catalyst interaction is very complex.

ii) Little was understood on the influence of the materials used to support the catalyst nor of the promoters used to affect reaction rates and selectivities. It is now well established [9, 10, 11, 15] that the product distribution depends upon the nature of the catalyst support.

The review of some of the papers which have appeared recently in the literature will be presented in the following sections.

2.2 Reaction Mechanism and Kinetics

Two types of mechanisms have been used to evaluate and describe much of the experimental heterogeneous catalytic data in the literature. These are

i) The Langmuir-Hinshelwood Mechanism, in which adsorption equilibrium is assumed to be established reactants and the molecules react while adsorbed.

ii) The Rideal mechanism in which equilibrium adsorption of only one of the reactants is assumed to be established. Reaction then occurs directly on collision of a gas molecule with an adsorbed molecule or atom.

However, these mechanisms have not been successfully applied to describe the o-xylene oxidation reaction. In 1954 Mars and Van Krevelen [12] applied the REDOX mechanism to the catalytic o-xylene oxidation reaction with encouraging results. The REDOX mechanism assumes that adsorption equilibrium is not established but that a steady state is reached in the catalyst when the rate of reaction between the hydrocarbon and the oxygen of the catalyst becomes equal to the rate of reoxidation of the catalyst by the oxygen in the feed stream. Hence the so-called catalyst is not really a catalyst in the chemical sense since in this proposed mechanism it actually enters into the reaction mechanism and does not merely promote the reaction by lowering the required activation energy. This mechanism was also used by Mars and Van-Krevelen [12] in their studies of the oxidation of benzene, toluene, naphthalene, and anthracene in a fluidized bed of 200-300 micron catalyst particles. The reactor was made of pyrex and the catalyst contained 9 weight percent vanadium pentoxide and 21 weight percent potassium sulphate on a silica-gel support. Since the publication of their paper in 1954, the Mars and Van Krevelen approach has enjoyed considerable popularity; the recent paper of Mathur and Viswanath [78] contains many references to its uses.

In a paper published in 1961, Shelstad, Downie and Graydon [3] proposed the Steady State Adsorption Mechanism [S.S.A.M.]. This assumes that a steady state is established in the catalyst when the rate of adsorption of oxygen on the catalyst becomes equal to the rate of removal by reaction with hydrocarbon from the gas phase.

An example of the application of the REDOX mechanism is in the formulation of the basic rate equations involved in the o-xylene oxidation reaction. Here, this formulation is demonstrated by considering the simplest case in which all the reaction products have been lumped together as one. Basically, there are two steps involved in the REDOX mechanism.

Step 1:

Aromatic compound + oxidized catalyst → oxidation product + reduced catalyst.

If the rate of hydrocarbon oxidation is considered to be first order with respect to hydrocarbon concentration and first order with respect to the fraction of active oxygen sites θ,

$$r_r = k_r C_r \theta \qquad 2.2.1$$

Then, if n moles of oxygen are required per mole of hydrocarbon, the rate of oxygen removal from the catalyst surface becomes

$$= n\ k_r\ C_r\ \theta \tag{2.2.2}$$

Step 2:

Reduced catalyst + oxygen → oxidized catalyst.

If the rate of catalyst oxidation is considered to be proportional to the oxygen concentration in the gas phase and to the number of the reduced sites, then

$$r_a = k_a\ C_a\ (1-\theta) \tag{2.2.3}$$

At steady state, the rate of oxygen removal from the catalyst by reaction with the hydrocarbon becomes equal to the rate of oxygen supply to the catalyst from the gas in the reoxidation process.

$$\text{i.e.}\quad n\ k_r\ C_r\ \theta = k_a\ C_a\ (1-\theta)$$

or

$$\theta = \frac{k_a\ C_a}{k_a\ C_a + n\ k_r\ C_r} \tag{2.2.4}$$

and from 2.2.1

$$r_r = \frac{k_a\ k_r\ C_a\ C_r}{k_a\ C_a + n\ k_r\ C_r} \tag{2.2.5}$$

It should be noted that this identical rate equation 2.2.5 can also be derived by applying the S.S.A.M. mechanism of [3]. In fact agreement between the rate equation 2.2.5 and the experimental data would not be a proof of the correctness of the assumed reaction mechanism. It has been established that several postulated mechanisms yielding the Langmuir-Hinshelwood type of rate expression can often be fitted equally well to experimental data. Several examples of this have been considered in [69].

Both the S.S.A.M. and the REDOX mechanisms have become very popular for describing the o-xylene oxidation reaction on vanadia catalysts. It will be of interest to discriminate between these mechanisms using kinetic data. However this is not possible since the rate expression for the overall rate of reaction is identical in both cases. Distinction may be possible in initial rate studies, using 0^{18} in the catalyst or in the feed. If the mechanism is assumed to proceed through the REDOX mechanism, then the chemisorbed oxygen must be removed from the catalyst surface prior to reaction. A major difficulty may be that of removing the chemisorbed oxygen. Support for the S.S.A.M. has come from several studies [6, 17, 7, 3]. This support may be considered weak due to considerable non-catalytic reactions and unstable catalytic activity evident in some of these studies. These can be ascribed to the fact that sulphur dioxide was not present in the feed. Simard et al. [16] studied the oxidation of o-xylene on vanadia catalyst. The feed contained only nitrogen and o-xylene. Their results showed that the amount of oxygen contained in the reaction products was in excess of that which could be obtained if only the chemisorbed oxygen participated in the reaction. It was then concluded that the catalyst oxygen contributes, at least in part, to the oxygen involved in the oxidation. Vrbaski and Mathews [36] also came to the conclusion on the basis of the results they obtained when o-tolualdehyde was oxidized over vanadia catalyst in a stream of nitrogen.

Some of the results of recent studies, especially from Russian workers in this field indicate that both the S.S.A.M. and the REDOX mechanism may be responsible for the oxidation reaction. Andreikov et al. [70] investigated the mechanism of the vapour-phase oxidation of naphthalene on a vanadia catalyst by a pulsed microcatalytic method. The results of their work were explained as follows

i) The initial attack on the aromatic molecule is always produced by the oxygen from the catalyst lattice.

ii) Further oxidation of the labile intermediate compounds can occur with the participation of the lattice oxygen and the participation of adsorbed forms of oxygen in the case when the rate of reoxidation of the catalyst is low.

Blanchard and Louquet [71] also carried out butene oxidation reaction on V_20_5-$Ti0_2$, V_20_5-M_00_3 and Bi_20_3-M_00_3 catalyst systems with 0^{18} enriched oxygen in a circulating apparatus at 300°C. They arrived at the following conclusions:

i) When a highly selective catalyst is employed only the oxide oxygen enters into the oxidation products.

ii) When catalysts are used which exhibit low or medium selectivity, the reoxidation of the reduced surface centers due to migration of oxide ions do not proceed effectively enough and that the adsorbed oxygen, or even the oxygen of the gas phase participates to varying degrees in this oxidation. With less selective catalyst, the participation of the oxygen of the gas phase becomes more significant.

2.3 O-xylene Oxidation Reaction Networks

It is valuable to have available a rate expression for the formation of phthalic anhydride which includes the rates of the individual steps in the reaction network. Most of the early studies on analysis of multistep reaction networks have traditionally been done by subjective interpretation of product distribution data, and there were no supporting rate studies carried out to test the proposed schemes. Hence these studies provide mainly qualitative information. Moreover, confusion existed as to the sequence of steps in the o-xylene oxidation reaction. This confusion can now be understood in view of the fact that different types of support materials were used in these studies. In general, there appears to be three main factors which tend to influence the product distribution in the catalytic o-xylene oxidation reaction. These are:

i) The nature of the catalyst support material. The results of Kakinoki et al. [10, 11] and Wainwright [26] strongly support this view. This will be discussed further in Section 2.7.

   These studies indicate the importance of including all information to describe the catalyst, support and promoters/modifiers since the reaction network and products are determined by the composition and nature of the entire solid material.

ii) The extent of homogeneous oxidation reaction . This is further discussed in Section 2.5.

iii) The oxidation state of the catalyst. It has been shown [16] that the active oxides for partial oxidation are V_2O_5

and $V_2O_{4.34}$. Catalysts having lower oxidation states produce considerable amounts of total oxidation products [5].

Juusola [28] and Paetkau [41] have provided excellent reviews of most of the early literature pertaining to o-xylene reaction networks, covering the period between 1955 and 1966. Some of the more recent papers in the literature will now be discussed. Herten and Froment [4] studied the gas phase oxidation of o-xylene on a V_2O_5 (French synoxy) SiO_2-supported catalyst in a quasi-isothermal laboratory fixed bed reactor. The studies were conducted in the temperature range 325 to 402°C. The following reaction scheme was postulated. In this scheme all

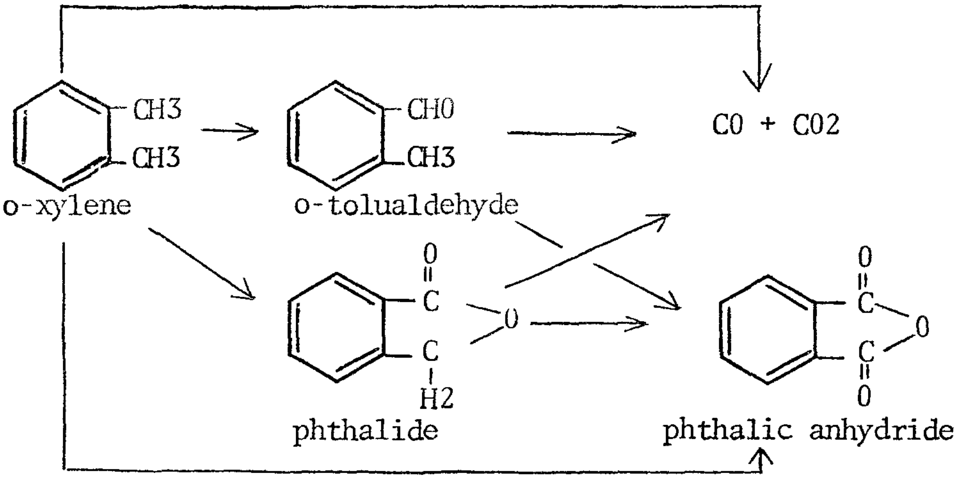


Figure 2.3.1 - Reaction Network of Herten and Froment

products were formed in primary reaction steps, but this conclusion was based on the slopes of selectivity curves extrapolated back to zero conversion from their lowest value of 25 percent. Also their data did not provide any direct support for the secondary reactions included in this scheme.

Juusola [28] proposed the network of Figure 2.3.2. from studies carried out on the oxidation of o-xylene and o-tolualdehyde on a SiO_2-supported catalyst. He concluded that o-tolualdehyde, p-benzoquinone and CO2 were

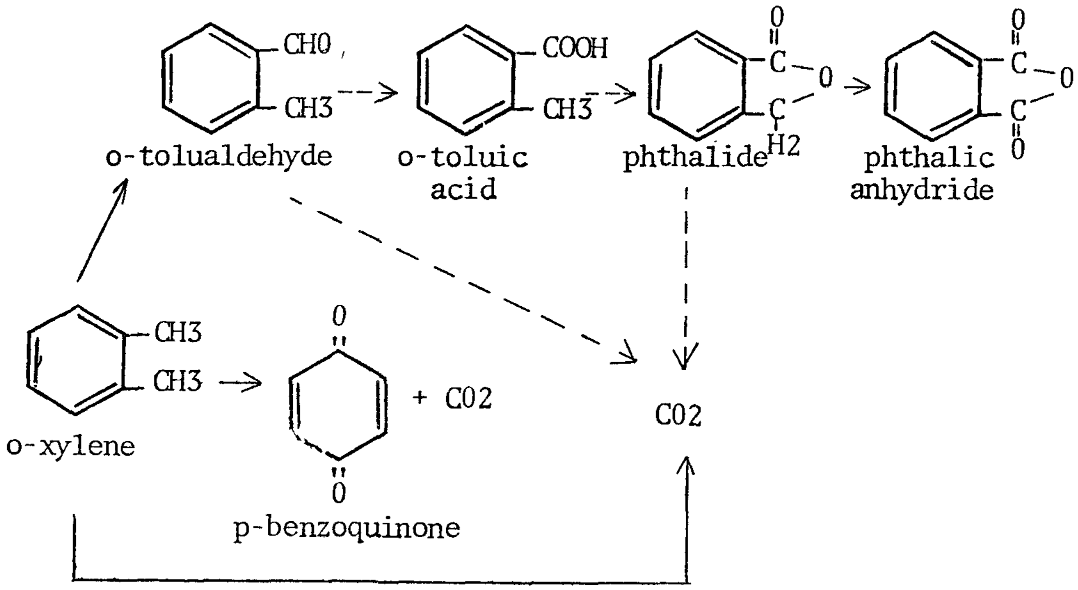


Figure 2.3.2 - Reaction Products of o-tolualdehyde Oxidation Connected in a Plausible Sequence

formed in primary reaction steps. This conclusion was based on data obtained at very low conversions (less than 5 percent) of o-xylene. It should be noted that when reactions are carried out at very low conversions, changes in product distribution may not be noticeable and in addition conclusive identification of stable products cannot be made. Secondary reactions (as shown in Figure 2.3.2) were also considered to be occurring on the basis of studies carried out on the oxidation of o-tolualdehyde. It is to be noted that in view of the interaction effects reported by Luybarskii et al. [76], the processes occurring when o-tolualdehyde is oxidized may not necessarily represent those taking place on the catalyst when the primary reactant together with some intermediates are also competing for catalytic sites.

Wainwright [26] studied o-xylene oxidation over a silica-gel supported catalyst using a fixed bed reactor. The scheme of Figure 2.3.3 was proposed. This scheme was based on a qualitative evaluation of the selectivity data obtained on the catalyst. It retains the main features of the more complex reaction networks proposed by Herten and Froment [4] and Juusola [28]. Phthalic anhydride, phthalide,

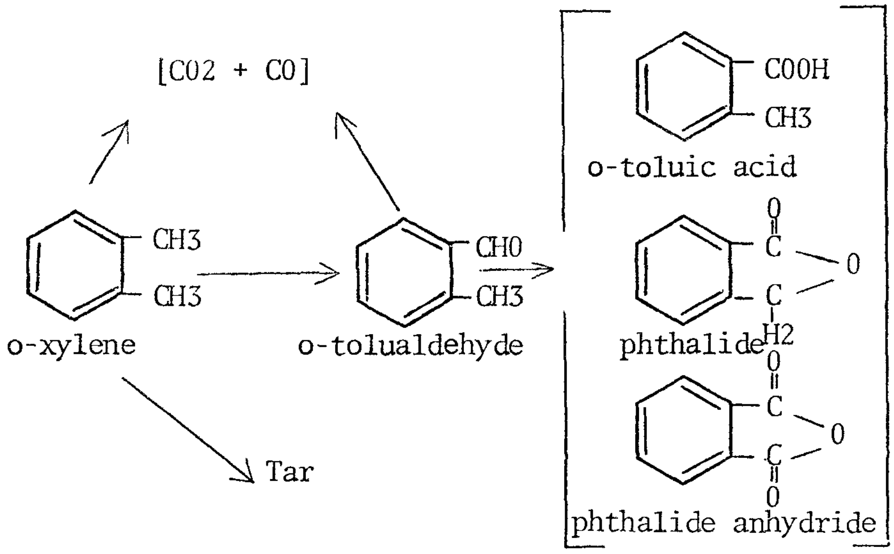


Figure 2.3.3 - Reaction Network of Wainwright for Reaction on Silica gel Catalyst

and o-toluic acid have been lumped together since they were present in small quantities and were formed sequentially from o-tolualdehyde. A step leading to tar formation from o-xylene was also evident in this scheme. The tar formation was considered to occur solely from the cracking of o-xylene. This scheme proposed by Wainwright is simpler and more practical, for reaction modelling purposes, than those of other workers reported earlier, in that it involves fewer parameters to describe it.

Boag et al. [72] applied quantitative modelling techniques to the o-xylene oxidation reaction data gathered in a recirculation reactor. The catalyst employed was vanadium oxide, potassium sulphate promoted, on a silica carrier. The following reaction network was found to be adequate for describing the oxidation process.

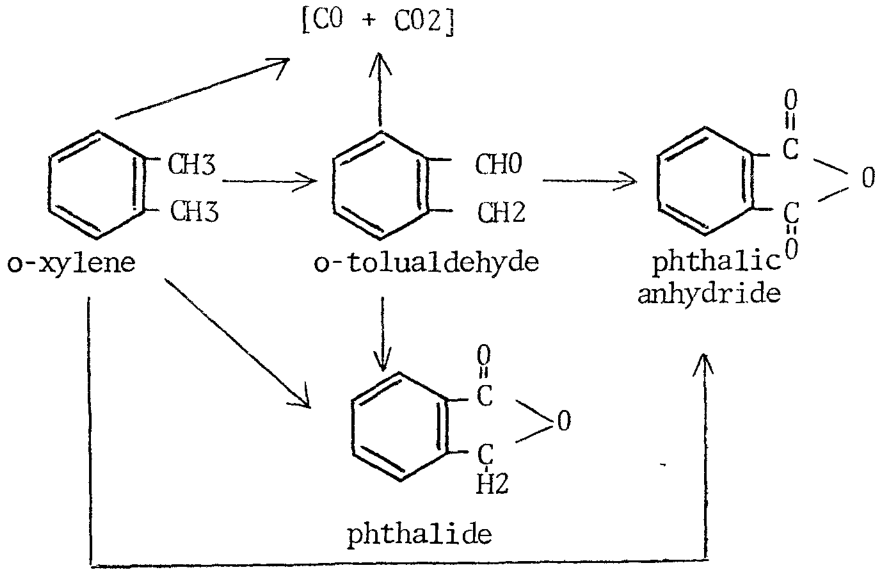


Figure 2.3.4 - Reaction Network of Boag et al.

This scheme is similar to that proposed by Herten and Froment [4]. The component mass balances for such a reactor are algebraic, rather than differential equations. This suggests that the estimation of parameters in the kinetic model is greatly simplified.

Lyubarski et al. [76] also studied the catalytic oxidation of o-xylene and its partial oxidation products in a gradientless reactor by a flow circulation method on a high temperature vanadium silicon carbide catalyst. The following scheme was proposed.

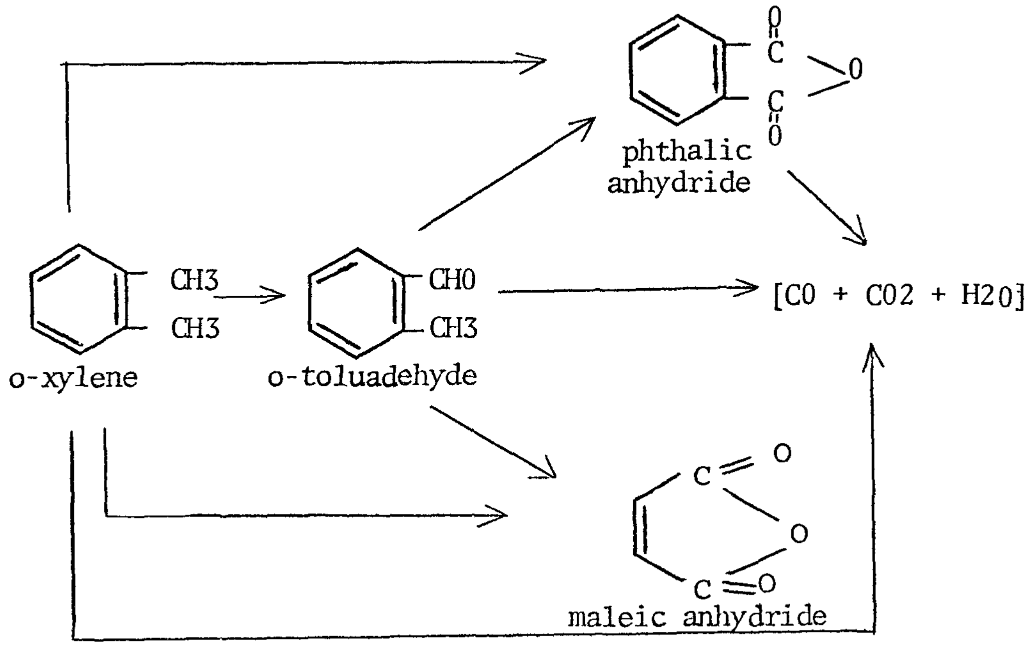


Figure 2.3.5 - Reaction Scheme by Lyubarski et al. [76]

The model was based on a qualitative analysis of the product distribution data. However, in their study, o-xylene together with its oxidation products were used as feed in the oxidation process. In this way the mutual effect of the various components of the reaction mixture on the rate of the separate steps in the process was determined. It was established that the presence of phthalic anhydride in the gaseous mixture lowered the rate of maleic anhydride oxidation. A similar 'interaction effect' has also been reported by Roiter et al. [77].

Few studies have been carried out on o-xylene oxidation on titania-supported vanadia catalyst. This is because titania-supported catalysts have only been developed relatively recently [31].

Vanhove and Blanchard [108] studied o-xylene oxidation at low conversions, on different amounts of vanadium pentoxide on titania from 0 - 100 mole percent. The highest selectivity for phthalic anhydride formation was obtained on a catalyst which consisted of 12.5 mole percent V_2O_5 on TiO_2. Reactions were carried out at 450°C in a reactor made of pyrex. The reaction network of Figure 2.3.6 was developed, based on a qualitative evaluation of the product distribution data. Further in their work [75] the reaction intermediates were then oxidized over this catalyst at 400°C for the purpose of defining the reaction paths of the intermediate compounds. In the case of o-tolualdehyde oxidation, it was observed that both the formation of phthalide and phthalic anhydride occurred with measurable rates, whereas in o-xylene oxidation the initial rates for the formation of these intermediates was found to be negligible. The reaction network of Figure 2.3.6 was proposed.

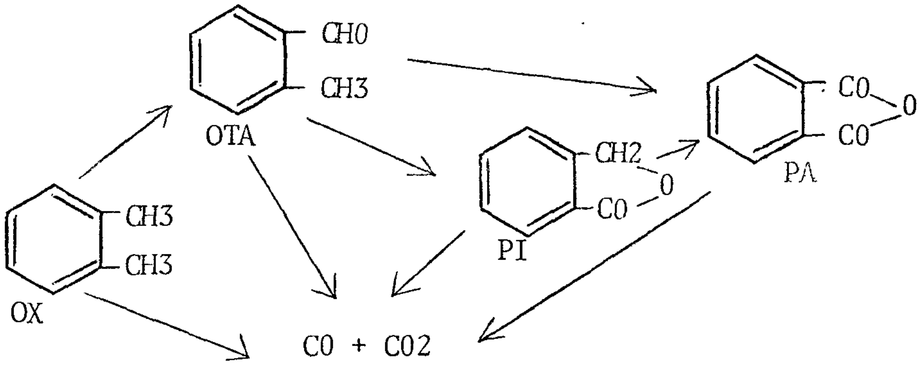


Figure 2.3.6 - Reaction Network of Vanhove and Blanchard for o-Xylene Oxidation and Titania Catalyst

Wainwright's network differs from that of Vanhove and Blanchard in that it does not consider the oxidation of phthalide and phthalic anhydride to carbon oxides to be significant (on the grounds of the more stable ring structure), nor does he consider the direct reaction of o-tolualdehyde to phthalic anhydride without going through the phthalide intermediate. This network will be discussed further in section 7.1.

Allen [123] proposed a reaction network similar to that of Figure 2.3.6 for o-xylene oxidation on titania-catalysts. His network contained, in addition to that of Figure 2.3.6 a route leading the formation of phthalic anhydride directly from o-xylene.

It is important to note that all networks proposed for o-xylene oxidation on titania catalyst so far have been based on only qualitative evaluation of product distribution data; none has been suggested by experiments which were designed specifically to determine the actual mechanistic route.

2.4 Oxidation of the Intermediate Compounds

Besides the studies on o-xylene oxidation, several workers [36, 39, 5, 74, 28, 75, 76] have also oxidized various intermediates for the purposes of defining the secondary reactions.

Two factors must be considered if secondary reactions are to be defined by oxidizing intermediate products (as feed) on o-xylene oxidation catalysts:

i) In view of the 'interaction effects' [76] rate constants observed for the secondary reaction when intermediates are oxidized may not represent those that are actually occurring when the primary reactant (o-xylene) is oxidized.

ii) The catalyst/reactant interaction may be such that the secondary reactions observed to be taking place when intermediates are oxidized may not necessarily represent those occurring when the primary reactant is also competing for catalytic sites.

With these in mind, some of the studies conducted on oxidizing the intermediates will now be discussed.

In the period between 1954 and 1967 some studies were carried out on oxidizing the products of o-xylene oxidation [36, 39, 5, 74], namely the following intermediates: o-methylbenzyl-alcohol, o-tolualdehyde, o-toluic acid, phthalide, and phthalic anhydride. Reaction have been carried out at low conversions using different vanadia concentrations and different support materials; moreover only products formed in significant amount have been included in the reaction schemes. Furthermore, the schemes have been based on qualitative interpretation of the data with a plausible sequence of reactions being guessed for the products. In view of these facts, most of these studies have resulted in different reaction schemes being proposed for the same oxidation reaction. Most of these studies have been reviewed in detail by Juusola [28]. A brief review of some of the more recent studies follows.

Oxidation of o-tolualdehyde

Vanhove and Blanchard [75] studied the oxidation of o-tolualdehyde in a tubular reactor (pyrex) over a V_2O_5-TiO_2 catalyst at 450°C. They concluded that phthalide and phthalic anhydride are formed from o-tolualdehyde according to the scheme of Figure 2.4.1, since the formation of these compounds occurred initially with measurable rates. From the examination of their Figure 1 [75], the distribution curve for phthalic anhydride seems to have been extrapolated from the lowest conversion of 10 percent. The following reaction schemes was proposed.

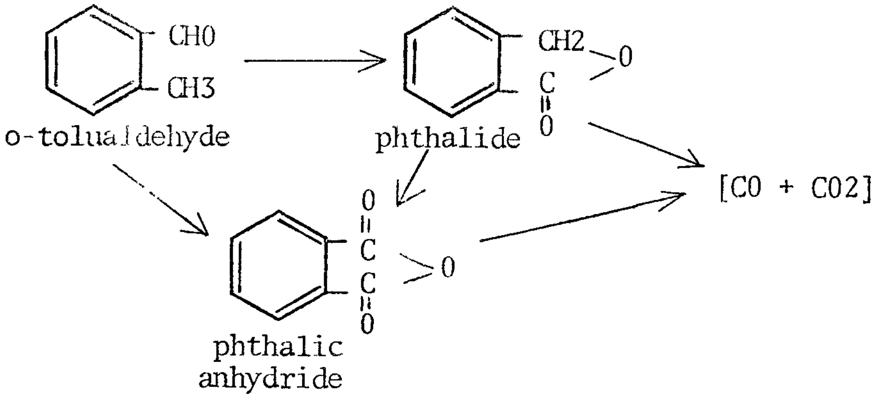


Figure 2.4.1

Lyubarskii et al. [76] studied o-tolualdehyde oxidation using a high temperature vanadium pentoxide catalyst at 400 - 460°C. A Langmuir-Hinshelwood type of rate expression was found to describe the overall rate of o-tolualdehyde oxidation. The proposed scheme is similar to the o-tolualdehyde reaction scheme presented in Figure 2.4.1. The concentration of o-tolualdehyde, oxygen, water-vapour and carbon dioxide was found to affect the rate of o-tolualdehyde oxidation.

Oxidation of o-toluic acid and phthaldialdehyde

Vanhove and Blanchard [75] oxidized solutions of o-toluic acid and phthaldialdehyde in o-xylene (methyl ^{14}C) over V_2O_5-TiO_2 catalyst. (The solution containing 80 to 90 percent of the compound to be oxidized.) 100 percent conversions were achieved in these cases thus suggesting that these intermediates are strongly adsorbed; hence their formation in the gas phase is expected to be negligible under all conditions. In the initial conditions where o-xylene yields only o-tolualdehyde, o-toluic acid yields phthalide together with phthalic anhydride. Phthaldialdehyde yields phthalic anhydride. The results are consistent with the observations reported in the early studies by Bernardini and Ramacci [74].

Oxidation of Phthalic Anhydride

Lyubarskii et al. [76] oxidized phthalic anhydride over a high temperature vanadium pentoxide catalyst in the temperature range (440°C to 500°C). The oxidation was considered to occur by two parallel pathways; one to maleic anhydride and the other to carbon monoxide and carbon dioxide. The rate of phthalic anhydride to the carbon oxides was shown to be independent of the phthalic anhydride concentration. These results are consistent with those of Hughes and Adams [5]. Bernadini and Ramacci [74] also using a high temperature vanadium based catalyst, showed that at temperatures below 380°C only carbon oxides were formed.

Oxidation of Maleic Anhydride and Phthalide

Maleic anhydride is generally considered to be oxidized to extensive oxidation products CO, CO2 [76, 74] while phthalide has been oxidized, over V_2O_5 silica-gel supported catalyst, in the temperature range 420°C to 440°C with 98 percent yields to phthalic anhydride [74].

2.5 Homogeneous Oxidation of o-xylene

The study of homogeneous oxidation of o-xylene (i.e. with no catalyst) is very important, not only because its slow combustion characteristics can be studied, but also because it can influence the results of catalytic reaction studies. Wright [27], Loftus and Satterfield [19] have carried out studies on homogeneous gas phase oxidation of o-xylene in quartz and borosilicate glass flow reactors at 1 atmosphere pressure and at 650°C and 475°C respectively. The results in [19] show that the rate of reaction is first order with respect to o-xylene. The rate constant was given by the following equation

$$\ln k = 10.5 - 20{,}000/RT \qquad 2.5.1$$

where k is the first order rate constant $\sec^{-1}$ and the activation energy is 20,000 cal/gm mole. The results reported in [27, 19] also show that the oxidation reaction is very complex since a wide variety of products are formed which indicates that a large number of reactions are simultaneously taking place. In fact earlier studies [64, 75] were hampered by the lack of an adequate analytical method to analyze the product formed.

The mechanism of the homogeneous reaction is quite different from that of the catalytic reaction and it is only in the studies of Wright [60, 61] that a detailed analysis of reaction products arising from the homogeneous reaction was first reported. The major products in the study of Wright [27] are methylvinyl-benzene., toluene, benzene, and o-tolualdehyde while that of Loftus and Satterfield are o-xylene oxide. One cannot tell from these studies whether the material of the reactor internals made any significant contribution to the reaction. For example, Wainwright [26] found that silver solder significantly promoted the complete oxidation of all products from the o-xylene oxidation reaction even at relatively low temperatures.

It has been shown by several workers [60, 61, 62, 63] that the homogeneous reaction does not form phthalic anhydride so that the overall yield of phthalic anhydride in catalytic reactions will be reduced by homogeneous oxidation. Mann [14] has reported an uncommonly high reaction rate on work conducted on the homogeneous reaction in an aluminum reactor. It was stated in the report that the reaction rate was time dependent. However, it has been suggested that the aluminum reactor used might have contributed significantly to the reaction.

Bhalla [1] carried out studies on homogeneous oxidation of o-xylene in a stainless steel flow reactor. o-xylene oxide was the main reaction product. This result agreed with the studies of Loftus and Satterfield [19]. It was suggested that the temperature for the catalytic reaction study, depending on the catalyst, be maintained in the range 380°C to 430°C in order to minimize the contribution of the homogeneous reactions [1].

Juusola [28] also made a thorough examination of the temperature limit at which a non-catalytic or blank reaction becomes significant. It was found that at temperatures below 315°C, in a stainless steel reactor, this reaction would be insignificant. This result does not agree directly with those of Bernardini et al. [104] in which similar studies were conducted in a type 316 stainless steel reactor. It was observed that at temperature lower than 380°C, the blank reaction was apparently insignificant.

These observations suggest that the homogeneous (blank) reaction should be studied in any particular reactor to ascertain the upper working temperature below which the homogeneous reaction may be considered negligible. With careful selection of materials this should not be a constraint on the study of the catalytic reaction.

2.6 Catalyst Properties

The type of catalyst traditionally used mainly for o-xylene oxidation is generally classified as the 'German' catalyst. A typical 'German-type' catalyst contains about 10 percent V_2O_5 and 20-30% K_2SO_4. Silica gel and titanium dioxide are the most common support materials.

Kakinoki et al. [9] has described methods for preparation of these catalyst supported on silica gel, gypsum and titanium dioxide. Vanadium pentoxide results from the oxidation of vanadium. It is a yellowish red powder which is sparingly soluble in water [30].

Recently, a new catalyst was developed [31] for o-xylene oxidation. It is covered by Canadian Patent No. 873904 and has the following properties:

Surface area:	5 m^2/gm
Bulk density:	1.2 gm/cc
Average Particle Size:	65 microns

Probable Composition (based on patent literature)

percent by weight:	V_2O_5	6.0%,	Sb_2O_3	6.0%
	K_2O	2.0%.	TiO_2	84. %
	SO_3	2.0%		

This type of catalyst (with particle size 50/70 mesh) was used in the current study. This was obtained from the research laboratories of W.R. Grace and Co., Baltimore, Maryland [26].

The nature of the support materials has been found to be most important in determining catalyst activity and selectivity [9, 26]. The influence of both the solid support materials (i.e. silica gel, titanium dioxide) and SO_2 will be discussed briefly with reference to the literature.

2.7 Influence of the Support Material on o-xylene Oxidation

For o-xylene oxidation, Simard et al. [16] have suggested that, a catalyst of small surface area and low sensitivity to promoter addition is to be preferred over one that is highly porous. A highly porous catalyst can lead to over-oxidation possibly because the intermediate oxidation products are caught in the pores and are further oxidized to undesirable products before they can diffuse out of the catalyst. The surface areas of silica gel supported catalysts are usually between 5 to 8 orders of magnitude greater than those supported by titanium dioxide. For o-xylene oxidation differences in product distributions exist for SiO_2 and TiO_2 supported catalyst. For instance higher yields of phthalic anhydride have been obtained using the TiO_2 supported catalysts [26, 66, 10]. Several workers have also shown that the SiO_2 supported catalysts are highly selective for o-tolualdehyde formation while those supported on TiO_2 are highly selective for phthalic anhydride formation. The major reasons for this and other differences observed in the product distribution are not completely understood. Kakinoki et al. [10] carried out a series of studies in which oxygen was adsorbed on the following support materials (i) silica gel, (ii) titanium dioxide, (iii) gypsum, (iv) carborundum. Langmuir-type isotherms were obtained for the adsorption of oxygen on all catalysts at 400°C. The oxygen adsorbed, for each support was expressed as the equilibrium volume of oxygen adsorbed per unit area of the catalyst. o-xylene oxidation reactions were carried out on these catalysts at temperatures ranging from 320°C to 430°C. Selectivities for the formation of phthalic anhydride, carbon dioxide and carbon monoxide were measured at these temperatures. The results indicated that the TiO_2 supported catalyst had the highest selectivity for phthalic anhydride and the highest oxygen adsorption. The SiO_2 supported catalyst had the lowest selectivity and the lowest oxygen adsorption. The other catalysts exhibited intermediate adsorptions and selectivities.

Finally, a factor of some significance is the type of interaction set up between the catalyst and the substance undergoing oxidation. High catalyst selectivity requires also that the catalyst system interact favourably with the substance undergoing oxidation. For instance, in naphthalene oxidation, excellent yields of phthalic anhydride have been obtained with catalysts supported on SiO_2 but low yields have resulted when o-xylene was oxidized on the same catalyst system. Another point relating to the catalyst/reactant interaction is that tar formation has been reported when o-xylene was oxidized on silica gel supported catalysts [26] while the formation of tars was not observed using a titania support one.

2.8 The Importance of SO_2 Addition as Catalyst Promoter

The importance of sulphur trioxide as a catalyst addition has been demonstrated by Kakinoki et al. [10]. In their investigation, they prepared catalysts supported on titanium dioxide, silica gel, and gypsum. They noticed that differences in catalyst activity occurred when 'hot press' naphthalene (containing some sulphur impurities) and pure naphthalene were employed as raw materials. The catalyst activity remained constant when 'hot press' naphthalene was fed but a gradual decrease in catalyst activity was observed when pure naphthalene was used as the feed. During this deactivation, which was allowed to continue for 100 days, the phthalic anhydride yield had dropped considerably. Sulphur dioxide was then added to the feed stream and within 48 hours, the original catalyst activity was restored. On the basis of these results, it was concluded that the sulphur level in the feed was important in determining the catalyst activity.

Once this fact was established it became necessary to determine the optimum sulphur level in the feed to maintain the catalyst activity at a particular operating condition. Since vanadium pentoxide is used commercially to oxidize sulphur dioxide, it should be noted that at high sulphur dioxide concentration the sulphur dioxide will be competing with the o-xylene for active oxidation sites. Mizushina et al. [1] investigated the effects of sulphur trioxide levels on the activity of a V_2O_5-TiO_2/K_2SO_4 catalyst. The catalyst contained 0.5 moles of K_2SO_4 per mole of V_2O_5 and a large amount of sulphur trioxide. Several catalyst samples of this type were prepared. A sample was then placed in a reactor and the reactor was immersed in a salt bath. Different sulphur trioxide levels were achieved in the catalyst by varying the salt bath temperature and the duration of heat treatment. The amount of SO_3 contained in the catalysts was observed to decrease with increasing treatment temperature. o-xylene oxidation was then carried out using these catalysts. No SO_2 was added to the reactant feed stream. The results show that an optimum SO_3 level of 5 percent by weight in the catalyst was needed for high selectivity in phthalic anhydride formation. However, Wainwright [26] points out that during the tests with this catalyst when the phthalic anhydride yield was the highest the o-xylene conversion was 100%. This suggests that the o-xylene was fully oxidized near the entrance of the bed; therefore the actual optimum concentration of SO_3 for maximum phthalic anhydride yield may be even higher.

Mizushina et al. [11] have also demonstrated that a certain amount of SO_3 is lost from the catalyst due to temperature effects. The amount of SO_3 'evaporated' from the catalyst was found to increase with increasing temperature. By carrying out naphthalene oxidation using 'hot press' feedstock at 410°C and 435°C, this group observed that the rate of catalyst deactivation was much greater at 435° than at 410°C. The catalyst activity was restored soon after SO_2 was introduced in the feedstream. Wainwright [26] observed a similar behaviour with another silica gel supported catalyst (American Cyanamide Aero PAA). He also observed that repeating an experiment at a lower temperature following reaction at an elevated temperature produced a loss in catalyst activity for a TiO_2 supported catalyst. It is thus apparent that the sulphur dioxide present in the feed was not adequate to restore the amount of SO_3 lost due to thermal decomposition. The relative rates of sulphur trioxide production (and then take-up by the catalyst) or loss from the catalyst appear to be a factor in determining the catalyst activity.

Barishnikov et al. [68] studied the role of sulphur dioxide in the oxidation of naphthalene to phthalic anhydride on a fixed bed of V_2O_5/K_2SO_4 silica gel supported catalyst. SO_2 (0.5 volume per cent) was added to the naphthalene/air feed stream before the catalyst bed; in the form of pulses of one minute duration. This case was then compared with that in which SO_2 was introduced continuously to the feed stream. From their experiments, the following conclusions were drawn

i) Some sulphuric acid was formed in the period when SO_2 was introduced continuously into the naphthalene/air feed stream over a prolonged period.

ii) The sulphuric acid formed was responsible for the marked fall in catalyst activity apparent in their study [Figures 2, 3, of 68]. The acid was active in blocking the active centers of the catalyst.

iii) The poisoning action of the acid was reversible as the catalyst exhibited its enhanced activity after the acid was removed.

In general there has not been agreement as to the optimum quantity of SO_2 required to maintain the catalyst activity for a given reaction condition. This quantity, however, will depend on factors such as

i) The nature of the catalyst support and promoter material.

ii) The reactor temperature and flow conditions.

Considerable experimentation of the type conducted by Kakinoki et al. [10] will be necessary at lower conversions in order to know if there is a narrow optimum SO_3 level.

The mechanism by which SO_2 promotes the catalyst activity has not been completely understood, but recently it is becoming generally accepted that $V_2O_5.SO_3$ is responsible for the catalyst activity. On the basis of studies of Kakinoki et al. [10], the following reaction steps occur when o-xylene reacts with the catalyst in the presence of air.

i) $V_2O_5.SO_3 \rightarrow V_2O_4 + SO_2 + 2O$ [used in hydrocarbon oxidation]

ii) $SO_2 + V_2O_5 \rightarrow V_2O_4 + SO_3$

iii) $V_2O_4 + O_2$ (air) $\rightarrow V_2O_5$

The action of K_2SO_4 in the catalyst is considered to stabilize the amount of free SO_3 in the system, thereby maintaining a constant amount of $V_2O_5.SO_3$. The role of K_2SO_4 as catalyst promoter will be reviewed in the following section.

2.9 The Role of K_2SO_4 as Catalyst Promoter

As early as 1940, Frazer and Kirkpatrick [82] and Kiyoura [83] reported that the promoting action of the alkali metals in vanadium pentoxide catalyst was due to the formation of higher sulphates known as the pyrosulphates. These materials have lower melting points than the corresponding sulphates and may form a eutectic mixture with sulphates. The pyrosulphates also have the ability to dissolve appreciable quantities of vanadium oxides. $V_2O_5/K_2S_2O_7$ on TiO_2 or silica gel supports is a glassy amorphous substance [80]. The melting point of V_2O_5 is generally around 700°C but confusion exists as to the melting point of the potassium pyrosulphate.

It is desirable to determine whether the catalyst exists in the form of solid or melt under reaction conditions, since this may lead to a better understanding of the performance of a K_2SO_4-doped catalysts. For instance, a structural change in the catalyst, which may take place prior to melting can influence significantly the activity and selectivity of the catalyst. Riley [79] stated that the melting point of V_2O_5-$K_2S_2O_7$ occurs at a minimum temperature of 370°C. If this is the case, then the catalyst system would be liquid at reaction temperatures. Various other workers have also determined the melting point to be 210°C, 300°C, 360°C and 414°C [79,78]. In the phase diagram of Kiyoura [83] for the K_2SO_4-V_2O_5 system, the melting point was shown to be 440°C which is far above the normal reaction temperatures. Tandy [84] also examined the systems of alkali metal sulphates in equilibrium with SO_2-SO_3-air mixtures. His experiment covered a temperature range of 380°C to 600°C with V_2O_5 and metal sulphates including K_2SO_4. He stated that in the range between 440°C and 600°C a liquid is produced that is a vanadium compound dissolved in alkali pyrosulphate melt.

More recently, the role of K_2SO_4 in the catalyst is generally considered to be that of supplying SO_3 to V_2O_5 resulting in the formation of $V_2O_5.SO_3$ complex which is thought to be responsible for the catalytic activity. Kakinoki et al. [9] carried out a series of studies from 310°C to 400°C using a V_2O_5-K_2SO_4, TiO_2 supported catalyst and also with a similar catalyst, but containing no K_2SO_4. The results of these studies have led them to conclude that the role of K_2SO_4 is merely to stabilize the free SO_3 content of the catalyst and thus ensure a constant V_2O_5-SO_3 complex.

Various patents suggest that the optimum SO_3 to K_2O molar ratio is approximately 2.

CHAPTER 3

EXPERIMENTATION

3.1 Description of the Apparatus and the Flow System

A diagramatic sketch of the experimental apparatus, is shown in Figure 3.1.1. This system was similar to that used by Wainwright [26] in his packed bed studies. The flows of nitrogen and oxygen from high pressure cylinders (Canadian Liquid Air) were controlled by needle valves and measured by calibrated capillary flow meters. The nitrogen and oxygen flowed through a mixer into a three way ball valve which directed the gas either into the o-xylene saturator and then into the reactor or bypassed the saturator when the catalyst was to be regenerated. The saturator was a jacketted glass vessel, containing a coarse porous frit through which the oxygen-nitrogen mixture was admitted. Water from a constant temperature bath circulated through the jacket to maintain the vapour pressure of o-xylene at a desired level. A manometer was also used to measure the pressure at the exit of the reactor so that the required partial pressure of o-xylene in the feed could be attained by raising or lowering its vapour pressure. The pressure in the measurement section of the gas flow system was maintained at 80 cm of mercury by a back pressure regulator and was measured by a U-tube manometer; this ensured a constant calibration for the gas metering system. A stream of sulphur dioxide was mixed with the main gas stream after the saturator and before the inlet gas sample valve. During all these experiments, the flow of a sulphur dioxide-nitrogen mixture

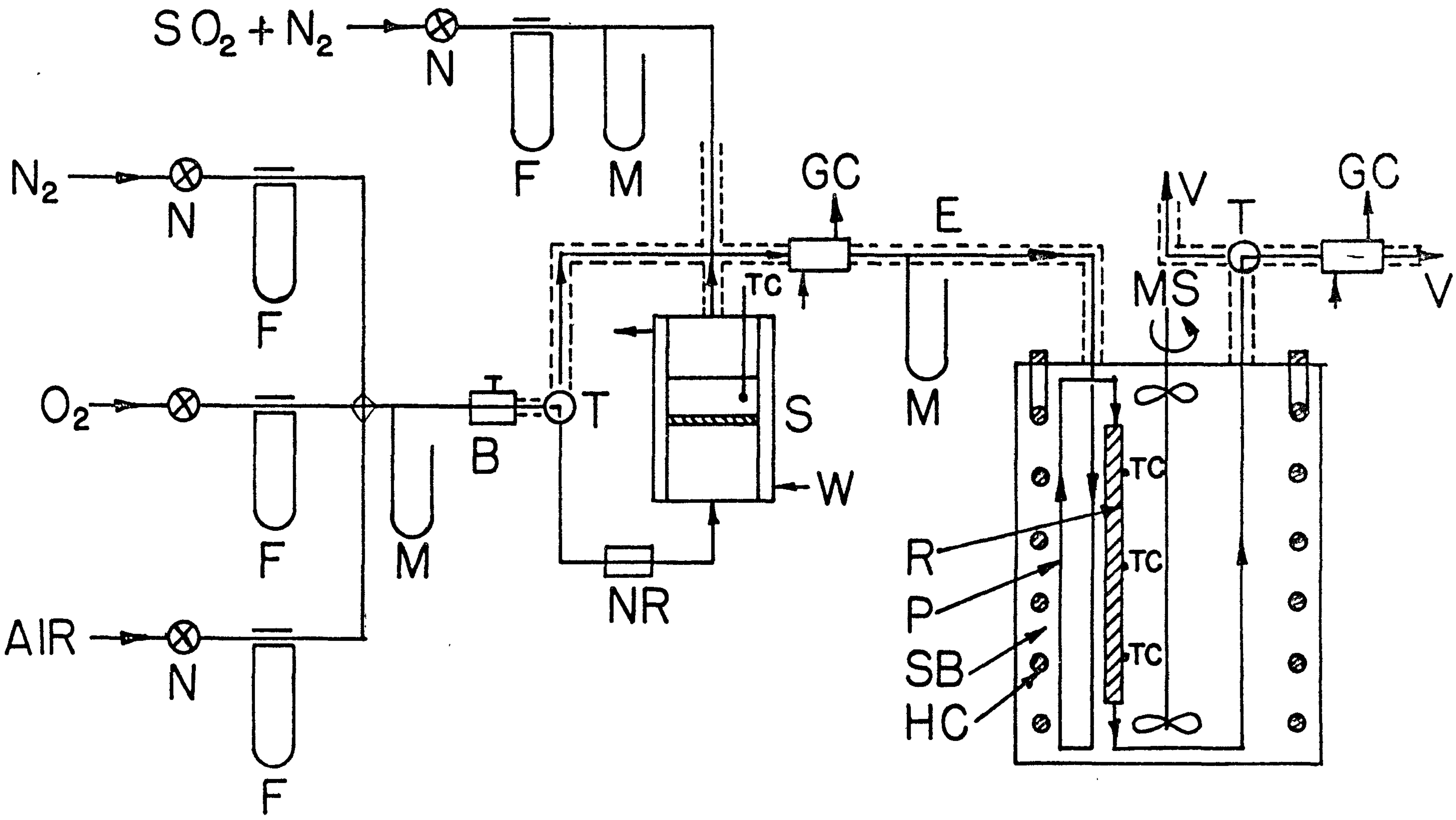


Figure 3.1.1: A Diagramatic Sketch of the Flow System From [26]

Legend for Figure 3.1.1

B	Back pressure regulator
F	Capillary flowmeters
GC	Gas chromatograph
HC	Heater coil
MS	Stirrer
M	Manometer
N	Needle valves
NR	No return valves
P	Preheater
R	Reactor
SB	Salt bath
S	o-xylene Saturator
T	Three way ball valve
TC	Chromel/alumel thermocouple
V	Gas sample valves
W	Water flow through the saturator jacket

(0.502 mole percent SO_2) was adjusted to maintain 0.01 mole percent SO_2 in the feed gas. This flow was measured by a capillary flowmeter. The manometer on this meter contained Meriam fluid having a density of 2.95.

The reactor consisted of a 0.475 cm I.D. by 14 cm long, type 316 stainless steel tube. This tube was immersed in a well-stirred molten salt bath (7% $NaNO_3$, 40% $NaNO_2$, 53% KNO_3 eutectic mixture) which was heated by a coiled 5250 W, 230 V, 330.2 cm long chromalox heating element immersed in the bath (30.48 cm high x 30.48 cm diameter). Reaction temperature was measured by two chromel-alumel thermocouples silver soldered at two axial positions on the outer reactor wall. This temperature was controlled to within ± 0.5°C by adjusting a variable transformer on the heater system. The reactor was fitted with a preheater tube made from a 6 cm length of 1/8 inch O.D. stainless tubing.

The reactor was packed with 1.0 gram of -50/+70 mesh catalyst particles which were sieved from a catalyst sample obtained from W.R. Grace (Baltimore, Md.). The packing depth was about 9 cm; the catalyst was held in place by a loose packing of glass wool.

The pressure in the reactor was measured by a mercury manometer. The gas stream leaving the reactor passed to the gas chromatograph sample valve, via a two way vent valve. In order to prevent the condensation of reactants and products all lines after the saturator through to the reactor exit were maintained at approximately 200°C by two hot air guns (12A, 120V). The reactor exit valve was fitted with a 1/2 inch O.D. diameter, 8.9 cm long stainless steel tubing to direct the product gases into a cold trap, where most of the organic materials were condensed and collected. The stainless steel tubing was heated by an electric heating tape (2.0A, 120V) to prevent the product materials from condensing before the cold trap. A thermocouple was installed in the sample valve compartment so that the temperature of the valves did not exceed 220°C. These valves should not be subjected to temperatures above 250°C.

3.2 Experimental Procedure

1.0 gram of V_2O_5-TiO_2 supported catalyst of the type described in section 2.6.1 was placed in the reactor. The catalyst was conditioned by passing a mixture of nitrogen and oxygen containing 0.01 volume percent sulphur dioxide through the reactor for at least twelve hours. During catalyst oxidation (regeneration), the temperature, oxygen and nitrogen flowrates were set equal to those at which the next experiment was to be conducted.

After the catalyst had been oxidized, o-xylene was then introduced into the gas stream by switching the oxygen/nitrogen mixture to the saturator. At the end of the previous run, the saturator was filled up to 80% its volume with o-xylene to ensure constant o-xylene level in the reactant gases during reaction; also the temperature of the saturator bath was set at a level such that when o-xylene was introduced into the gas stream it was of the desired concentration. Wainwright [26] had shown that the catalyst activity and selectivity decreased monotonically from an initial high value. It was determined in his and these experiments that approximately 24 hours were required to reach steady state activity and selectivity. In general several measurements were taken in the period 24 to 32 hours. It was assumed that the steady-state was reached when three samples taken at one hour intervals had composition that differed by less than 5 percent.

Following the steady state experiments, the nitrogen, oxygen and the SO_2 flowrates, the o-xylene concentration, and the reactor bath temperature, were changed to that desired for the next experimental run (inlet analysis were taken to ensure this). o-xylene flow was stopped and the reoxidation of the catalyst followed for the next twelve hours.

3.3 Reaction Product Analysis

Chemical reaction studies require knowledge of the composition of the feed and product streams entering and leaving the reaction zone. Gas chromatographic methods for the separation and analysis of mixtures containing the fixed gases and other aliphatic hydrocarbons in the literature have been reviewed in [102]. These techniques are often complex and require special equipment to effect complete separation of the components.

The method employed in this study involves the use of a porapak Q (80/100 Mesh) column for the separation of water and the non-condensable products N_2, O_2, CO, CO_2, while the separation of the organic components was achieved by temperature programming a silicone gum rubber column. The basic experimental set up was similar to that used by Wainwright [26] with some modifications.

The chromatographic conditions were as follows:

i) Carrier gas (Helium flowrate) = 85 mls per minute at ambient conditions

ii) Filament current = 250 mA

iii) Temperature of the injection port = 200°C

iv) Temperature of the sample valve compartment = 200°C

A diagram of the gas sampling valve system for feed and reaction product analysis is shown in Figure 3.3.1. To begin an analysis of the product stream, the gas stream leaving the reactor was passed to the gas chromatograph exit analysis sample valve. A sample (approximately 5 cc at S.T.P.) was initially passed to a 12.7 cm length by 1/8 inch O.D. stainless steel column packed with 50/80 mesh porapak Q. The materials passing through this column or retained by it can then be directed either to a 488.0 cm by 1/4 inch O.D. stainless steel column packed with 80/100 mesh porapak Q or to a similar column packed with silicone gum rubber (10% Se 52 on Chromosorb W, high performance, 80/100 mesh) by the use of a Carle Switching valve.

The operating procedure for analysis of the product stream is as follows: A helium stream containing no sample is referred to as the reference gas while that carrying a sample is named the carrier gas.

i) The short porapak column (12.7 cm long) was cooled to near ambient temperature by the use of an air line. The column switching valve was in the position such that the carrier gas stream passed through the 488.0 cm porapak Q column which was immersed in a dry ice-trichloroethylene mixture at -78°C. This mixture was contained in a Thermos flask. The reference gas passed through the silicone gum rubber column which was kept in the oven at 125°C. The sample was then introduced through the exit analysis sample valve.

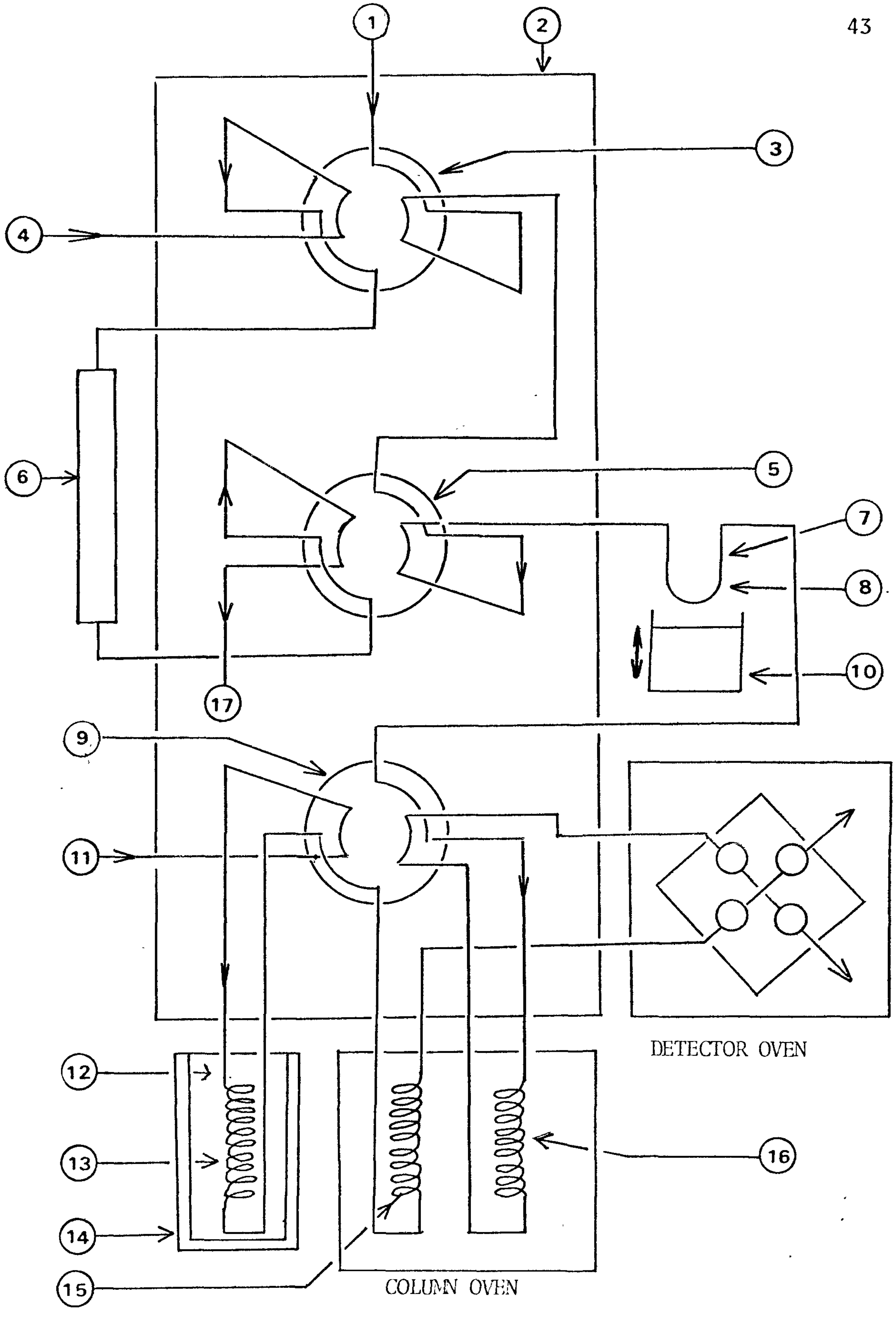


Figure 3.3.1: Flow diagram of analysis systems
in position for the separation of N2, O2, CO.

Figure 3.3.1:

This figure shows the analysis system in position for the separation of N_2, O_2, CO. In order to separate CO_2, H_2O, the Porapak Q Column is transferred into a Thermos flask containing boiling water at 100°C.

For the position corresponding to the separation of the condensable materials, following the elution of H_2O, the column valve is switched and the salt bath at 220°C is raised.

Legend for Figure 3.3.1.

1. Carrier gas Helium
2. Valve compartment must be kept at temperatures around 205°C
3. Inlet gas sample valve
4. Gas from saturator
5. Exit gas sample valve
6. Reactor
7. Porapak Q Column 50/80 Mesh
8. Column at ambient temperature
9. Column switch valve
10. Molten salt bath (lowered)
11. Reference gas Helium
12. Dry-ice trichloroethylene mixture
13. Porapak Q Column 80/100 Mesh
14. Thermos flask
15. Blank column
16. Silicone gum rubber column
17. Vent stream.

The short Porapak column at the ambient temperature trapped all the condensable materials except water while the fixed gases and water passed to the 488 cm Porapak column. The nitrogen, oxygen, and carbon monoxide were eluted in that order from the 488 cm Porapak column.

ii) Following the elution of carbon monoxide, the 488 cm Porapak Q column was transferred into a thermos flask containing boiling water at near 100°C. Carbon dioxide and water were then eluted in that order. A typical chromatogram is shown in Figure 3.3.2.

iii) After the water had been eluted, the column switching valve was turned into its second position such that the carrier gas was switched to the silicone gum rubber column. About five minutes after the switching, the molten salt bath at 220°C was raised such that the short Porapak column (including the fittings) was completely immersed. The condensable products maleic anhydride, o-xylene, o-tolualdehyde, phthalic anhydride and phthalide were driven from the short column into the silicone gum column contained in the oven. The temperature of the oven was then programmed from 125°C at the rate of 6°C per minute for 16 minutes.

Maleic anhydride, o-xylene, o-tolualdehyde, phthalic anhydride and phthalide were eluted in that order. After the elution of phthalide, the salt bath was lowered and the oven was cooled to 125°C. Figure 3.3.3 shows a typical chromatogram and Table 3.4.1 gives a list of the retention times and the elution temperatures of the various components.

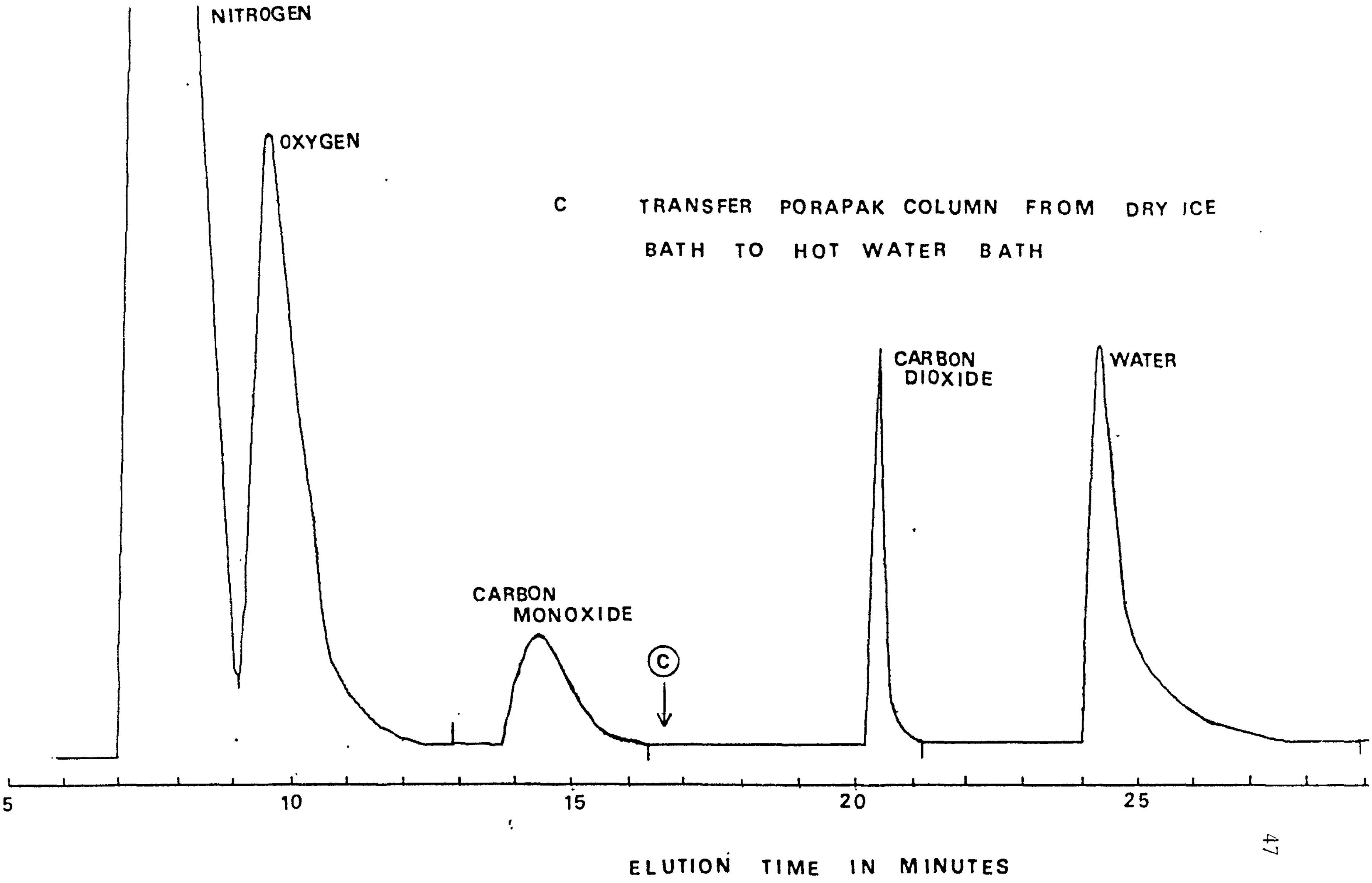


Figure 3.3.2: Typical chromatogram for the fixed gases and water.

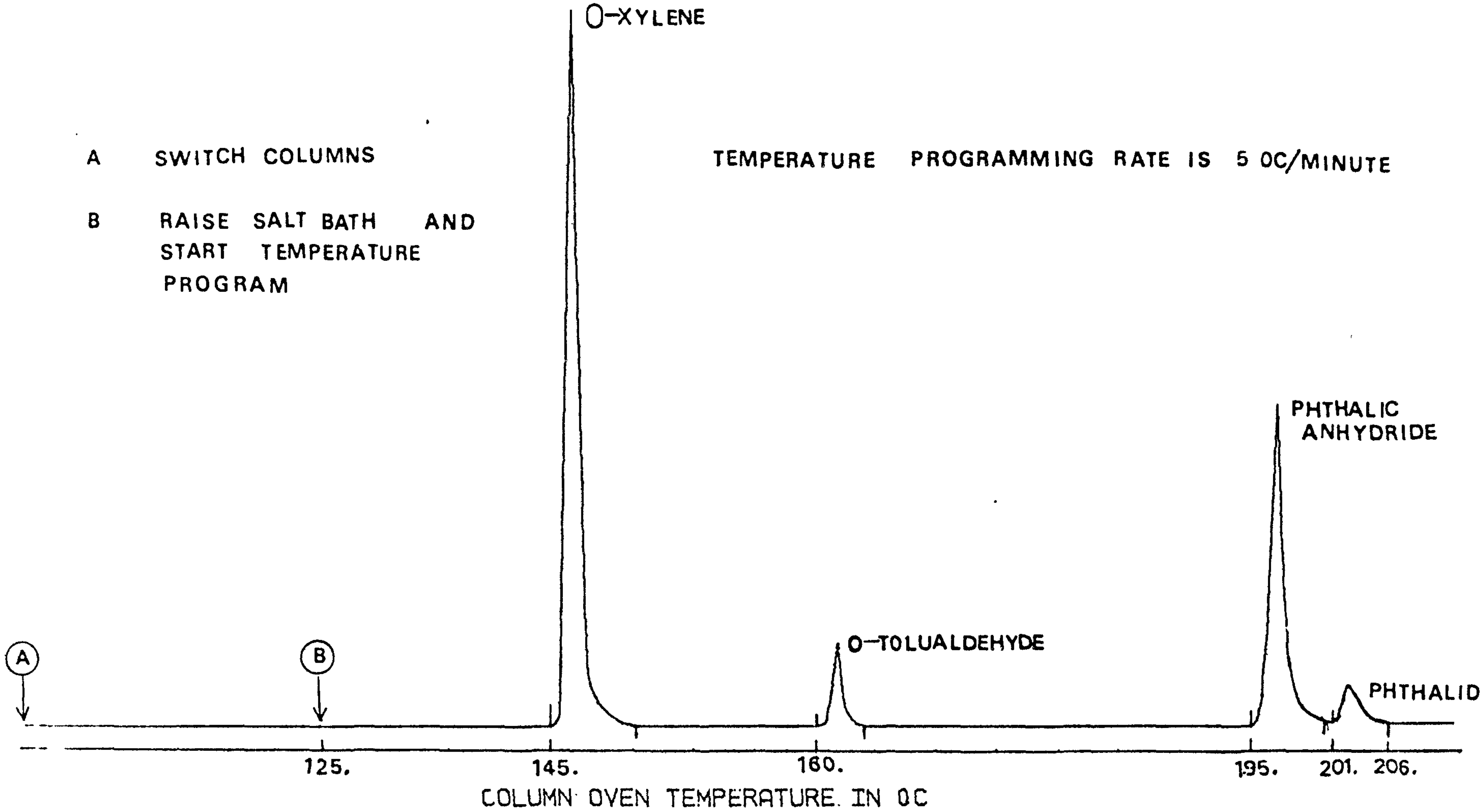


Figure 3.3.3: Typical chromatogram for the organic components.

The whole procedure was then repeated to analyze another reactor sample. The blank column (Figure 3.3.1) was a 488 cm x 1/4 inch outside diameter made of stainless steel. It contained no packing and was installed to control the base line drift due to the temperature programming of the silicone gum rubber column.

3.4 Calibration of Gas Chromatograph

The reaction products analyzed by the gas chromatograph can be grouped as follows

i) The fixed gases - nitrogen, oxygen, carbon dioxide, and carbon monoxide.

ii) Water vapour.

iii) Organic components - o-xylene, o-tolualdehyde, phthalic anhydride and phthalide.

In order to obtain accurate analysis of the reaction products, it was necessary to calibrate the gas chromatograph. An internal standard technique was adopted. The molar response factors (fc) were determined for the product components, relative to nitrogen (internal standard). The molar response factor of nitrogen was taken as equal to one. The molar response factors were calculated from [42].

$$fc = \frac{Ac}{As} \times \frac{Ws}{Wc} \times \frac{Mc}{Ms} \times fs \qquad 3.4.1$$

where As is the area of the internal standard peak, Ac is the area of the component peak, Wc is the weight of the compound, Ws is the weight of the internal standard, Mc and Ms are the molecular weights of the component and standard respectively and fs is the molar response factor of the internal standard.

Procedure

i) Fixed gases

The calibration apparatus is shown in Figure 3.4.1. The sample vessel was flushed (by evacuating and filling) several times with nitrogen to remove any impurities. The sample vessel and the lines leading to it were evacuated by the use of a vacuum pump. About 5 cc of water at room temperature were injected into the vessel through the septum. Enough time was allowed for the water vapour to attain saturation at the temperature of the thermostat. The vessel was then filled to a required partial pressure with each of the fixed gases (02, CO, CO2 and N2). When a particular component had been introduced into the vessel to a required pressure; all the valves were closed and the lines leading to the vessel were evacuated before the next gaseous component was introduced.

The gases in the vessel were then allowed to mix for several hours (in excess of 12 hours) before samples were analyzed by the gas chromatograph. The temperature of the thermostat was kept at or below room temperature, the sample line, the sample valve compartment and the lines leading to and including the short Porapak column were kept above the room temperature. This was necessary to prevent condensation of the water vapour.

Several samples were prepared in this way. The concentrations of components in the samples were varied to cover the ranges that were expected in the experimental program.

Table 3.4.1 includes the relative molar response factors obtained for the fixed components.

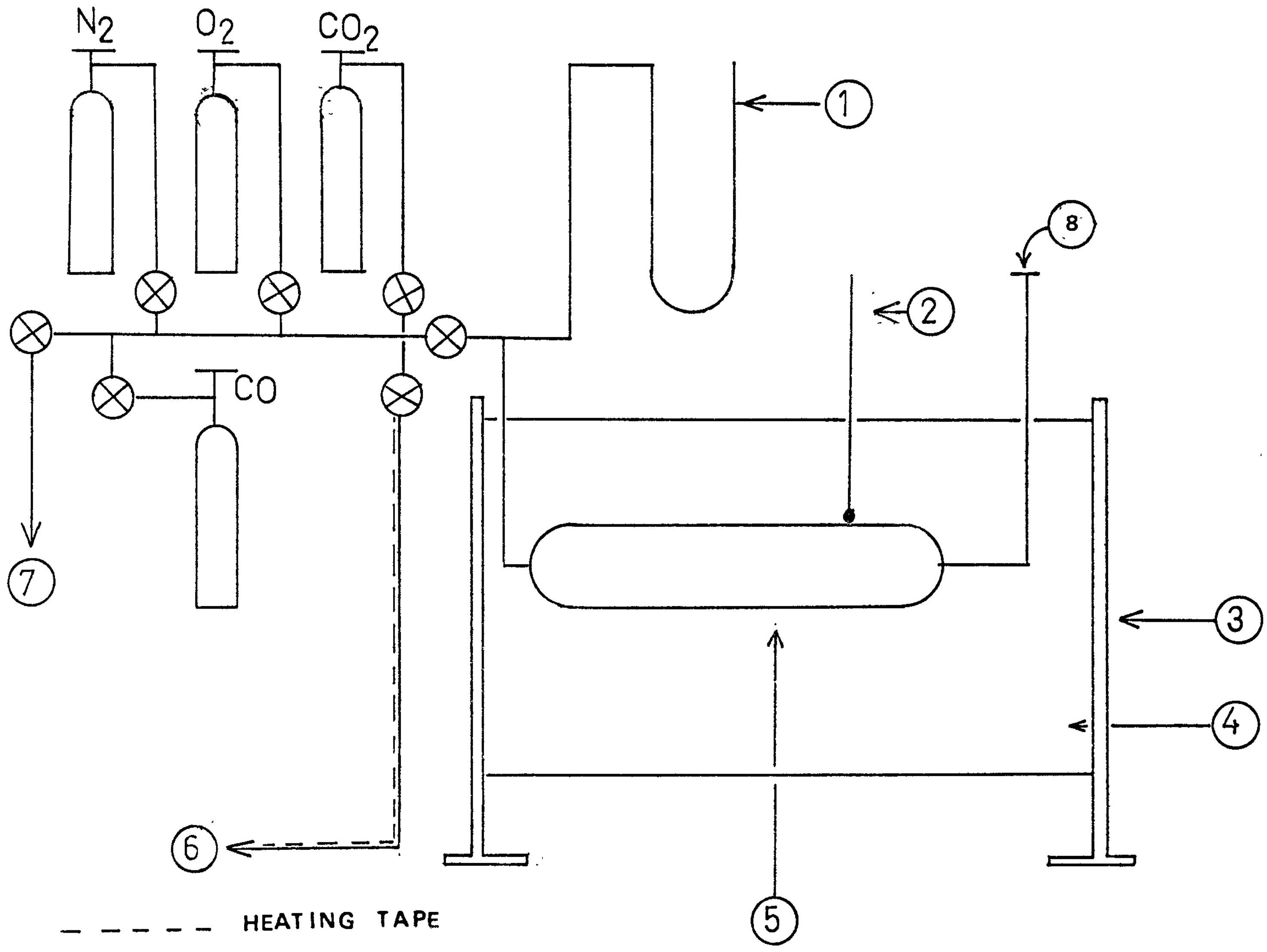


Figure 3.4.1: Apparatus for the Calibration of gas chromatograph

Legend for Figure 3.4.1.

1. Manometer
2. Thermometer
3. Thermostat
4. Bath water
5. Sample vessel
6. To gas chromatograph sample valve
7. Vacuum pump
8. Injection septum

ii) Organic components

Calibration mixtures were made·by mixing together known quantities, by weight of o-xylene, o-tolualdehyde, phthalic anhydride and phthalide in a 100 ml volumetric flask. The mixtures were diluted to volume by dioxane or acetone. Analysis of the samples by the gas chromatograph were then obtained by injecting a one micro liter sample into the injection port. The temperature of the column oven was kept at 200°C during the injection period to ensure that no condensation of the organic materials occurred in the lines carrying the sample from the injection port, through the oven to the sample valves. The temperatures of the injection port, the sample valve compartment and that of the lines leading to the short Porapak column were maintained a little above 200°C.

Responses for these components were obtained relative to o-xylene. Absolute calibrations were then made for o-xylene and nitrogen by injecting known quantities of these compounds, as a gas using the calibration apparatus shown in Figure 3.4.1. The molar response factors of all the organic components were then calculated relative to nitrogen.

Table 3.4.1 presents the relative molar response factors, the retention times and the elution temperature of all components.

Component	Retention time	Elution Temperature	Rel. Molar Resp. factors
Nitrogen	7.0	-78°C	1.00
Oxygen	9.1	-78°C	0.97
Carbon monoxide	12.2	-78°C	0.92
Carbon dioxide	19.2	100°C	1.17
Water	23.2	100°C	2.56
o-xylene	3.3*	150°C	3.04
o-tolualdehyde	6.0	165°C	3.19
phthalic anhydride	12.1	202°C	3.34
phthalide	13.0	206°C	3.28

* The retention time for the organic components was taken as the period from the start of the temperature programming to the elution of the component.

Table 3.4.1

The values of the molar response factors, reported in the literature, for these component are given in [101].

CHAPTER 4

DESIGN OF EXPERIMENTS FOR PARAMETER ESTIMATION

If experiments are not carefully designed, the experimental responses may be such that the estimates which can be obtained for the parameters are not only imprecise, but also highly correlated. Statistical design of experiments for mechanistic models relies on expressing objectives mathematically and then optimizing this criterion with respect to the settings of the independent variables. The form of the theoretical model is either known or is 'tentatively entertained'. These designs are then used as a guide to determine where to locate the experimental points in the independent variable space in order to obtain the most precise estimates of the parameters in the model with a given precision in the measurement of the responses.

In this investigation, the criterion recommended by M.J. Box [48] and Draper and Hunter [47] was used. In the case under consideration, this criterion requires that

$$D = \left| \sum_{u=1}^{n} \underline{X}_u' \, \underline{V}^{-1} \, \underline{X}_u \right| \qquad 4.1$$

be maximized over the control variables: o-xylene and oxygen concentration, total flowrate (residence time) and reactor temperature. Here:

$\underline{X}'$ is the matrix transpose of $\underline{X}$;

$$\underset{r\mathrm{x}p}{\underline{X_u}} = \left[\begin{matrix} \dfrac{\partial\eta_1(\underline{\xi}_1)}{\partial\theta_1} & \cdots\cdots, & \dfrac{\partial\underline{\eta}_1(\underline{\xi}_1)}{\partial\theta_p} \\ \vdots & & \vdots \\ \dfrac{\partial\eta_r(\underline{\xi}_1)}{\partial\theta_1} & \cdots\cdots & \dfrac{\partial\underline{\eta}_r(\underline{\xi}_1)}{\partial\theta_p} \end{matrix}\right]_{\underline{\theta} = \underline{\hat{\theta}}}$$

$\underline{V}$ is an estimate of the variance-covariance matrix of
of the responses.

η_i is the expected value as calculated from the model of
the i^{th} response.

This criterion for a non-linear multi-response model is equivalent to minimizing the asymptotic joint confidence region of the estimated parameters. This criterion does not, however, guarantee that the confidence region is spherical. For cases in which it is required that the confidence region be spherical, the above criterion must be modified to provide a compromise design [43, 44, 110].

It is of importance to note that the derivatives $\frac{\partial\eta_i}{\partial\theta}$ can only be independent of the estimates of the parameter values if the response function $\underline{\eta}$ is independent of $\underline{\theta}$. For non-linear response functions, such as the case in this study, the values of the derivatives and hence the efficiency of any particular design will depend upon the current best estimates $(\underline{\hat{\theta}})$ of the parameters. Poor estimates usually result in poor designs. For this reason, the logical sequence would be to use a sequential procedure. In this approach, parameter estimates from preliminary experiments would be used to plan a second set of experiments and the results of this set would then be used to reestimate the parameters and plan a third set of experiments and so on [45, 46]. In this research program, initial parameter estimates of the reaction model were available from several preliminary experiments performed by Wainwright [26]. Initial estimates of the variance-covariance matrix ($\underline{V}$) of the responses (Table 4.3) were also estimated using replicate data from this study, that is $\underline{V}$ was estimated from the following relationship:

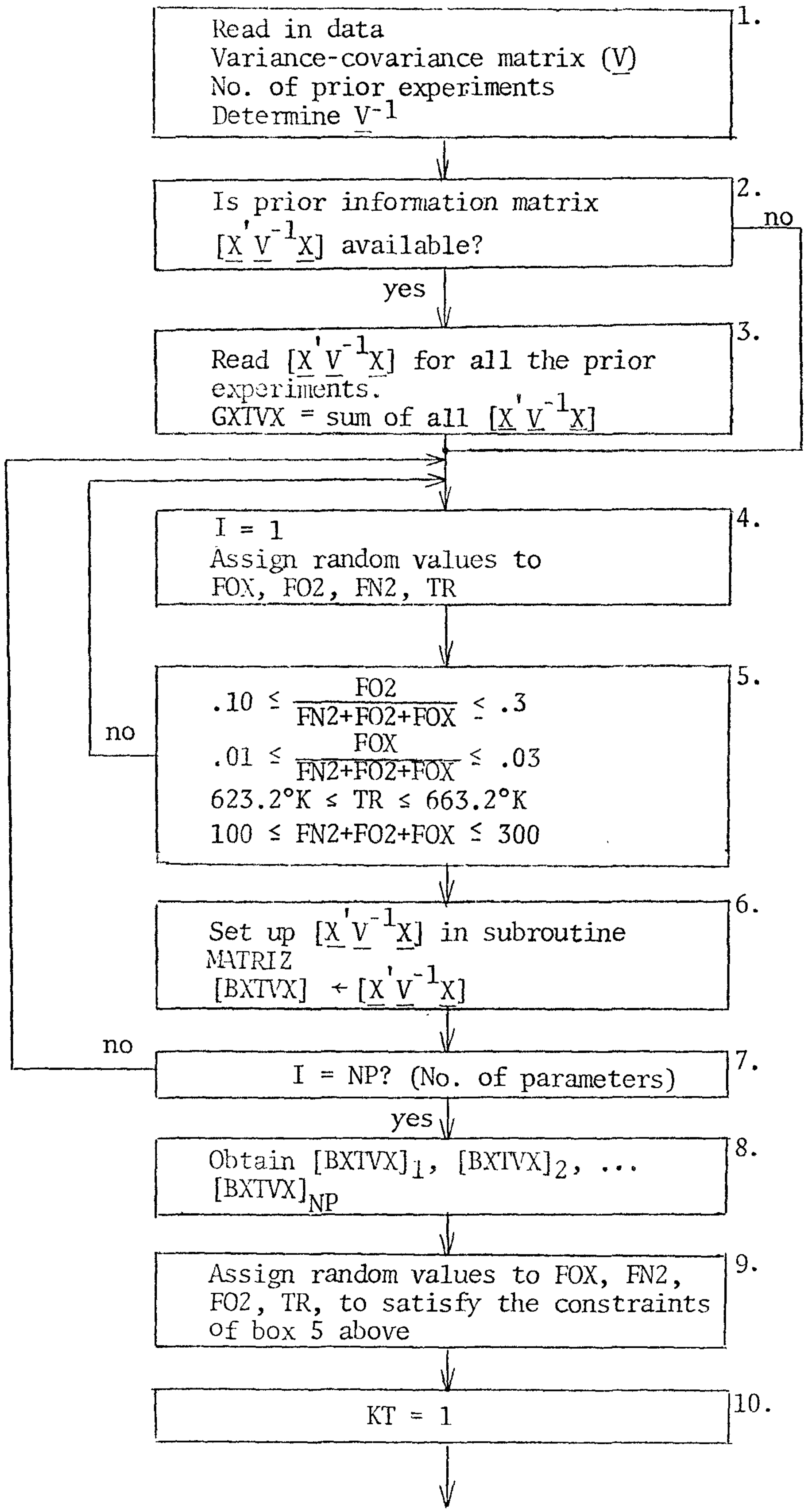
$$V_{ij} = \frac{1}{m-1} \sum_{k=1}^{m} (y_{ik}-\bar{y}_i)(y_{jk}-\bar{y}_j) \qquad 4.2$$

where

m	is the number of replicates
i,j	are number of responses
$\bar{y}_i$	is the arithmetical average value for the i^{th} response

Often, it is more practical from an experimental point of view to design blocks of experiment in a sequential manner. This is only slightly less efficient [47] than the sequential approach of designing only one experiment at a time. If p parameters are to be estimated in a model, a block of experiments will normally consist of at least p experiments.

The determinant D, of equation 4.1 was evaluated over the full range of control variables as indicated in Table 4.1. The experimental program of Table 4.1 is identical to that used by Wainwright [26] for o-xylene oxidation on the titanium dioxide supported catalyst in an integral packed bed reactor. A discussion on the limits of the experimental program is contained in the Ph.D. thesis of Wainwright [26]. Actually, the maximization of this determinant could be achieved by a direct grid search, but because of the high computer time expenditures involved, a Monte Carlo technique was employed [55, 118]. This procedure, together with a criterion which ensured maximum spread in the experimental conditions, was also used by Shaw [21]. An algorithm of this technique is reported in Figure 4.1. A listing of the computer program used is shown in Appendix B. 150 trials were involved before choosing the operating conditions for the first set of experiments. These are presented in Table 4.2.


1.
Read in data
Variance-covariance matrix (V)
No. of prior experiments
Determine V-1
2.
Is prior information matrix
[X'V-1X] available?
no
yes
3.
Read [X'V-1X] for all the prior experiments.
GXTVX = sum of all [X'V-1X]
4.
I = 1
Assign random values to
FOX, FO2, FN2, TR
5.
.10 ≤ FO2 / (FN2+FO2+FOX) ≤ .3
.01 ≤ FOX / (FN2+FO2+FOX) ≤ .03
623.2°K ≤ TR ≤ 663.2°K
100 ≤ FN2+FO2+FOX ≤ 300
no
6.
Set up [X'V-1X] in subroutine MATRIZ
[BXTVX] ← [X'V-1X]
7.
I = NP? (No. of parameters)
no
yes
8.
Obtain [BXTVX]1, [BXTVX]2, ... [BXTVX]NP
9.
Assign random values to FOX, FN2, FO2, TR, to satisfy the constraints of box 5 above
10.
KT = 1

. . ./(cont'd.)

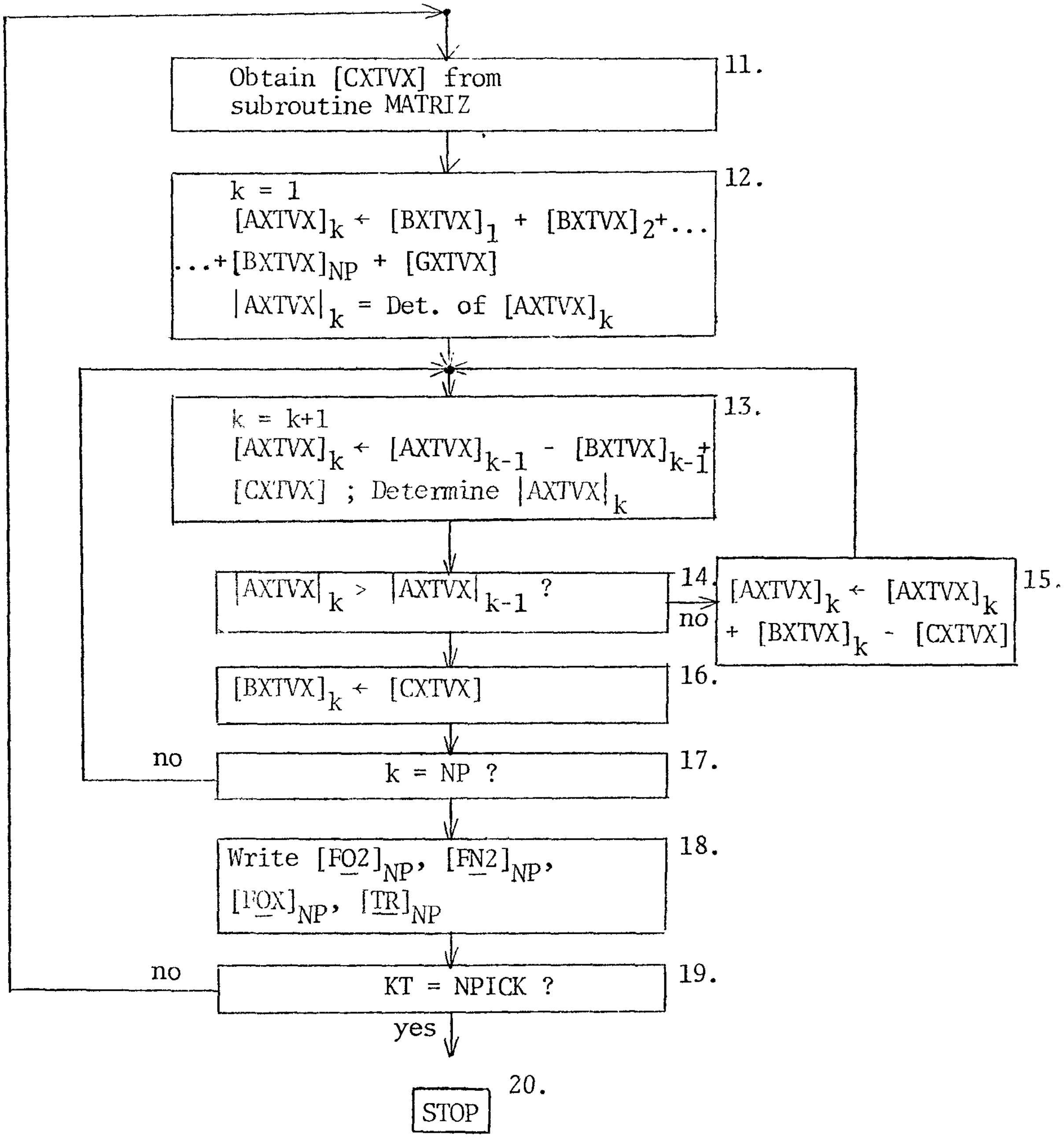


Figure 4.1: A simple algorithm showing steps involved in the experimental design program.

	% o-xylene level	% oxygen level	Reactor temperature	Total gas flow (at N.T.P.)	Catalyst weight
Upper Design Limit	3.0	30.	390.	300.	1.0
Center of Design	1.5	20.	370.	200.	1.0
Lower Design Limit	1.0	10.	350.	100.	1.0

Table 4.1: Experimental Program

	% o-xylene	% oxygen	Reactor temperature °C	Total flow at N.T.P. mLS/min.
1.	2.3	27.3	350	267.6
2.	2.9	14.5	354	186.3
3.	2.8	11.2	383	232.2
4.	2.5	20.3	378	217.2
5.	1.2	26.3	356	118.0
6.	2.8	29.6	372	253.5
7.	3.0	23.6	357	101.9
8.	2.6	14.5	380	117.1
9.	2.9	11.1	371	143.6
10.	2.9	27.4	355	182.6
11.	2.5	27.0	357	185.4

Table 4.2: Experimental Runs Dictated by the Design Program

	OX	OTA	PI	PA	CO/CO2
OX	$.5659\times10^{5}$	$-.1174\times10^{4}$	$.5080\times10^{2}$	$.2383\times10^{4}$	$.3791\times10^{2}$
OTA	$-.1174\times10^{4}$	$.2697\times10^{4}$	$.1926\times10^{3}$	$.8628\times10^{4}$	$.1917\times10^{3}$
PI	$.5080\times10^{2}$	$.1926\times10^{3}$	$.1834\times10^{2}$	$.6688\times10^{3}$	$.1822\times10^{2}$
PA	$.2382\times10^{4}$	$.8628\times10^{4}$	$.6688\times10^{3}$	$.3186\times10^{5}$	$.6639\times10^{3}$
CO/CO2	$.3791\times10^{2}$	$.1917\times10^{3}$	$.1822\times10^{2}$	$.6639\times10^{3}$	$.1816\times10^{2}$

Table 4.3:

Variance-Covariance Matrix of the Responses Evaluated From [26].
This data is used for experimental design.

CHAPTER 5

EXPERIMENTAL RESULTS

5.1 Approach to Steady-State Operation

An application of the REDOX mechanism in formulating the basic rate equations for o-xylene oxidation has been considered in detail in Section 2.2. The rate of hydrocarbon oxidation, considered to be first order with respect to hydrocarbon concentration is given

$$r_r = k_r C_r \phi \qquad 2.2.1$$

The parameter ϕ, representing the fraction of active sites available for oxidation, for a freshly oxidized catalyst is considered to have a value close to unity. When hydrocarbon oxidation is taking place on the catalyst, the value of ϕ decreases until a steady-state value is reached. This value is given by equation 2.2.4,

$$\phi = k_a C_a/(k_a C_a + n k_r C_r)$$

and since the model has been formulated on the basis of ϕ achieving a steady-state value, the experimental responses used for estimating the parameters must pertain to the catalyst when it reaches its steady-state activity. In this study, the steady-state condition was reached by the catalyst after the reactor was on stream for approximately 24 hours at a given condition. Figures 5.1.1 and 5.1.2 show the approach to the steady-state operation on the catalyst.

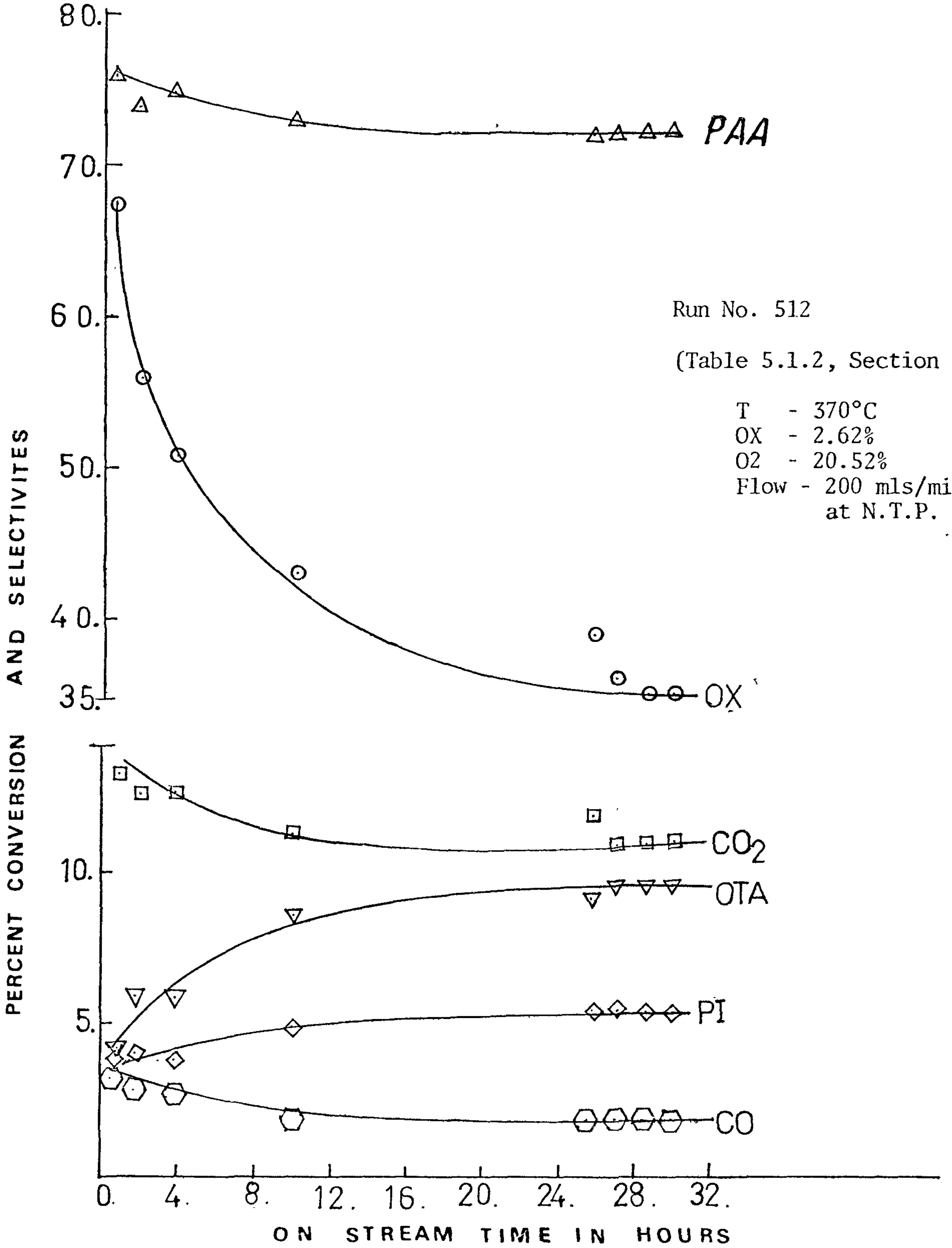
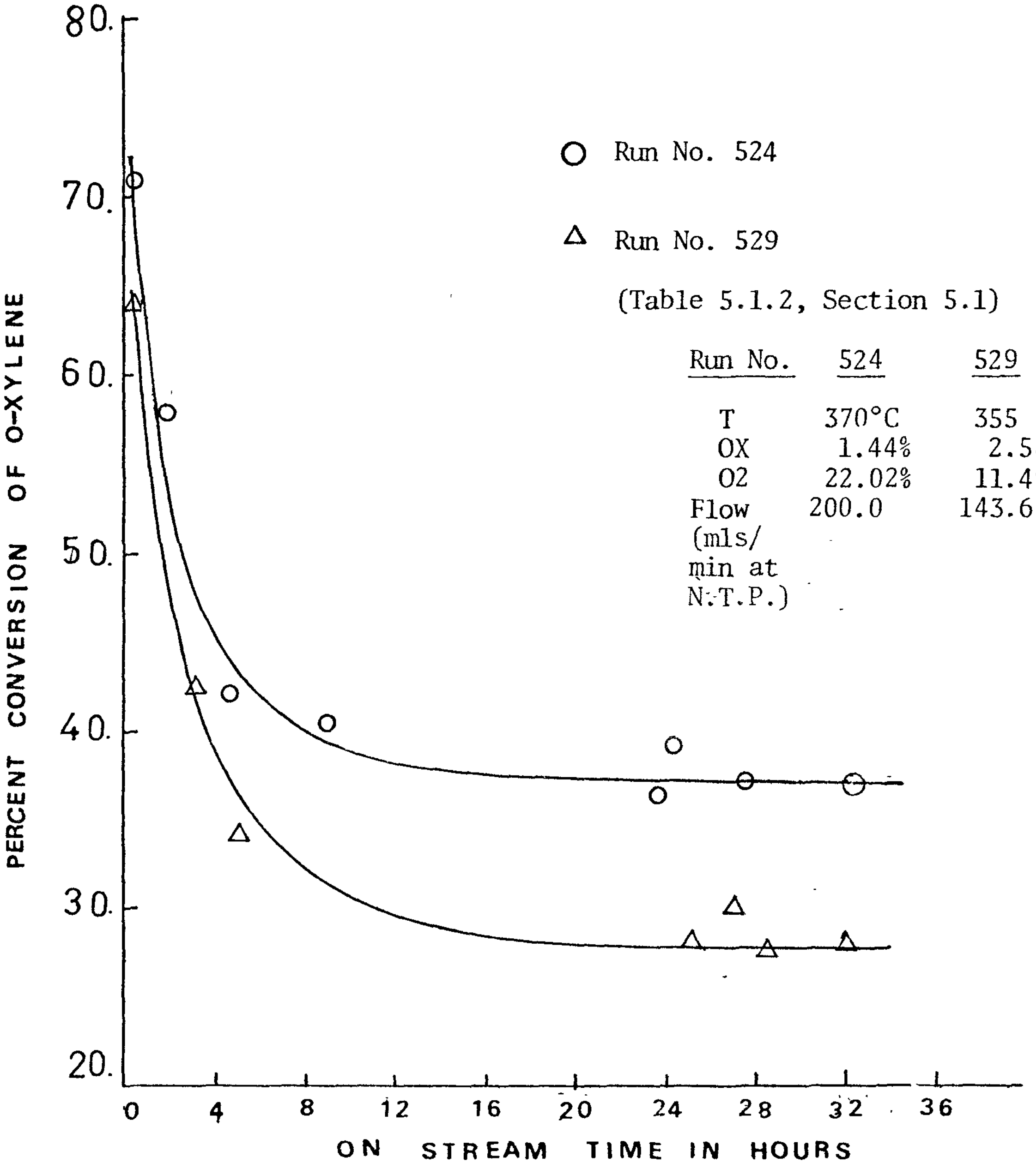


Figure 5.1.1: Approach to steady-state operation (This figure shows the unsteady-state behaviour of the intermediate compounds.)



(Table 5.1.2, Section 5.1)

Run No.	524	529
T	370°C	355
OX	1.44%	2.58%
O2	22.02%	11.49%
Flow (mls/ min at N.T.P.)	200.0	143.6

Figure 5.1.2: Approach to the steady-state operation

In order to obtain a meaningful and consistent set of data on a catalyst, experimental runs should be conducted on a catalyst of constant activity. This implies that standard runs must frequently be carried out to monitor the steady-state catalyst activity. In this study, standard runs were conducted at the set of experimental conditions corresponding to mid-range experimental conditions, (Table 4.1.1). A standard run involved reoxidation of the catalyst and then on-stream oxidation until steady-state was achieved. In some cases this standard run was carried out immediately after another experiment without reoxidizing the catalyst. These latter experiments indicated that:

i) A further 24 hours was required to achieve the steady-state operation following changes in operating conditions.

ii) The final steady-state activity of the catalyst was different from that reached when a standard run was carried out directly following the reoxidation of the catalyst.

Thus each of the steady-state experiments, including the standard runs, reported in this study was carried out after reoxidation of the catalyst following an experimental run according to Section 3.2.

One set of experiments consisting of eleven experimental runs was designed according to the statistical technique described in Section 4.1. A total of nine experimental runs at the different reaction conditions shown in Table 4.1 were carried out as it was not possible to carry out all the eleven experiments within the time allotted for taking experimental measurements. In all a total of 5 standard runs were carried out throughout the steady-state experimental program. It was expected to fit the model using the experimental data obtained from the current study and those available from Wainwright's study [26].

Tables 5.1.1 and 5.1.2 represent the steady-state data obtained in the current study. For an experiment, the steady-state data were taken in the period from 24 to 32 hours as described in Section 3.2.

5.2 Initial Long Term Deactivation

It is important to have a catalyst which did not exhibit any long term decrease in steady-state activity. Wainwright's experience suggested that some initial conditioning of the catalyst is required to stabilize its activity, that is a number of cycles of reduction and reoxidation are required. This deactivation seems to be related to the amount of free sulphur trioxide which is present in the catalyst. In turn, this amount seems to be determined by the amount of sulphur dioxide which is present in the gas stream (feed). Experience suggests that when a new batch of a TiO_2 supported/K_2SO_4 promoted catalyst is first placed in the reactor at a high temperature some of the free SO_3, which is known to exist in the catalyst, is lost due to evaporation (desorption). The addition of SO_2 in the feed stream does compensate for some of the SO_3 which is lost, but an equilibrium must be reestablished; this establishment of the equilibrium level of the free SO_3 also seems to require using the catalyst under reaction conditions. Hence, at the start of the experimental program, fresh catalyst was placed in the reactor and its activity was monitored, for several days by conducting standard runs.

The initial SO_3 level of the fresh catalyst was reported to be 2.0 weight percent (Section 2.6). In this study, the amount of SO_2 introduced in the feedstream was only 0.01 percent of the total gas flow. Under these conditions, the steady-state activity as indicated by the o-xylene reaction

	Reaction Conditions					Exit Concentration gmmoles/liter x 10^6							
Experimental Run Number	Temperature °C	o-Xylene Concentration gm moles/ liter x 10^4	Oxygen Concentration gm moles/ liter x 10^4	Total flow at N.T.P. (cc/min)	Reaction Rate gm mole/hr gm x 10^3	OX	OTA	PI	PA	CO2	CO	Carbon Balance	H2* Bal.
426	350	3.945	74.80	267.	3.55	223.6	12.92	9.543	80.57	111.22	14.38	1.00	1.00
428	370	3.758	51.64	200.	3.18	205.5	12.08	7.652	89.95	118.07	17.83	0.99	1.01
430	354	5.209	36.64	181.	3.57	327.5	15.52	12.04	111.7	155.53	12.77	1.04	0.94
501	370	3.837	51.38	200.	3.08	235.0	12.92	9.849	84.00	98.50	14.60	1.05	0.90
512	370	3.675	51.91	200.	2.93	219.5	11.59	6.514	87.11	105.76	17.45	1.04	1.16
515	378	6.489	50.29	212.	3.714	440.0	23.30	13.45	91.72	127.37	18.43	1.01	1.10
517	356	3.081	60.55	117.	2.68	132.6	6.253	5.286	176.4	240.43	59.77	1.08	0.98
523	357	6.460	50.87	99.	3.91	324.5	16.98	10.71	235.5	284.4	57.00	1.02	0.82
524	370	3.501	53.58	200.	2.98	203.4	10.96	5.758	92.03	110.10	18.40	1.04	1.01
527	380	5.734	30.58	114.	2.644	379.8	18.11	7.443	128.7	159.34	24.95	1.02	0.94
529	355	5.798	25.76	140.	2.842	380.1	16.19	5.895	110.7	129.93	20.27	0.98	0.93
531	355	7.055	75.45	177.	3.568	408.2	18.67	6.956	105.5	139.9	22.20	0.92	0.88
605	370	3.871	52.38	200.	3.150	226.3	11.91	6.573	93.80	120.59	20.01	1.02	1.07
610	383	5.980	26.90	226.	2.708	422.	19.12	4.35	45.60	85.4	50.70	0.94	0.92

* Hydrogen balance is not expected to have the same accuracy as carbon balance since the measurement of the water peak was found to have considerable variance (from replicated calibration runs).

Table 5.1.1:

Steady-state Reaction Data for the Oxidation of o-Xylene on Titania-supported Vanadia (experimental measurements)

	Reaction Conditions					Conversions and Selectivities							
Experimental Run Number	Temperature °C	% O-xylene Level	% Oxygen Level	Total Flow mls/min N.T.P.	$k_2 \times 10^3$ (Reaction Rate)	OX	OTA	PI	PA	CO2	CO	Carbon Balance	H2* Bal.
426	350	1.44	27.27	262.	3.55	34.7	10.9	8.04	67.90	11.70	1.51	1.00	1.00
428	370	1.55	21.33	200.	3.18	39.9	8.94	6.39	71.70	11.20	1.75	0.99	1.01
430	354	2.116	14.92	181.	3.57	32.9	9.68	7.51	69.70	12.1	1.00	1.04	0.94
504	370	1.582	21.25	200.	3.08	33.95	10.75	8.01	69.45	10.29	1.52	1.05	0.90
512	370	1.519	21.44	200.	2.93	35.47	9.61	5.40	69.83	10.93	1.81	1.04	1.16
515	378	2.620	20.52	212.	3.714	24.95	7.95	8.95	62.75	10.90	1.53	1.01	1.10
517	356	1.381	27.08	117.	2.68	62.95	2.78	2.35	78.25	13.35	3.305	1.08	0.98
523	357	2.977	23.45	99.	3.91	49.15	5.42	3.43	75.15	11.35	2.275	1.02	0.82
524	370	1.44	22.02	200.	2.98	38.38	8.693	4.598	74.05	10.80	1.858	1.04	1.01
527	380	2.68	14.303	114.	2.644	31.90	10.303	4.217	72.50	11.233	1.767	1.02	0.94
529	355	2.58	11.49	143.6	2.842	28.47	10.73	3.897	72.97	10.77	1.673	0.98	0.93
531	355	2.765	28.206	177.	3.568	26.0	13.13	4.207	68.60	12.30	1.793	0.92	0.88
605	370	1.583	21.47	200.	3.152	36.5	9.17	5.06	72.20	11.60	1.93	1.02	1.07
610	383	2.48	11.17	226.	2.708	16.8	21.5	5.25	53.30	12.20	7.76	0.94	0.92

* Hydrogen balance is not expected to have the same accuracy as carbon balance since the measurement of the water peak was found to have considerable variance (from replicated calibration runs).

Table 5.1.2:

Steady-State Reaction Data for the Oxidation of o-Xylene on Titania-supported Vanadia (conversion and selectivities) rate was found to decrease as shown in Figure 5.2.1. These results indicate that the catalyst activity declined gradually for a period of approximately five days, but after this time it stabilized.

The experimental program using the experimental conditions suggested by the design procedure was then begun. The catalyst activity was monitored at five times during the fifty day period of this experimental program and as shown in Figure 5.2.2 it remained constant during that time. Hence, it is expected that the catalyst activity was essentially constant during the time that the data was collected for the other experimental conditions employed. It is noted from the examination of the standard runs reported in Tables 5.2.1 and 5.2.2 that the steady state data were quite reproducible and consistent. Also, a comparison of these standard runs with those of Wainwright (Figure 4.9 of [26]) indicates that the activity of the catalyst employed in the current study was higher than that of Wainwright. This information is presented in Table 5.2.3.

	Current study (Figure 5.2.2.)	Wainwright (Figure 4.9 of [26])
Average activity of catalyst as measured by standard runs. gm mole/gm.catalyst·hr	3.18	2.20
Ratio	$\frac{\text{Current study}}{\text{Previous study}} = \frac{3.18}{2.20} = 1.45$	

Table 5.2.3

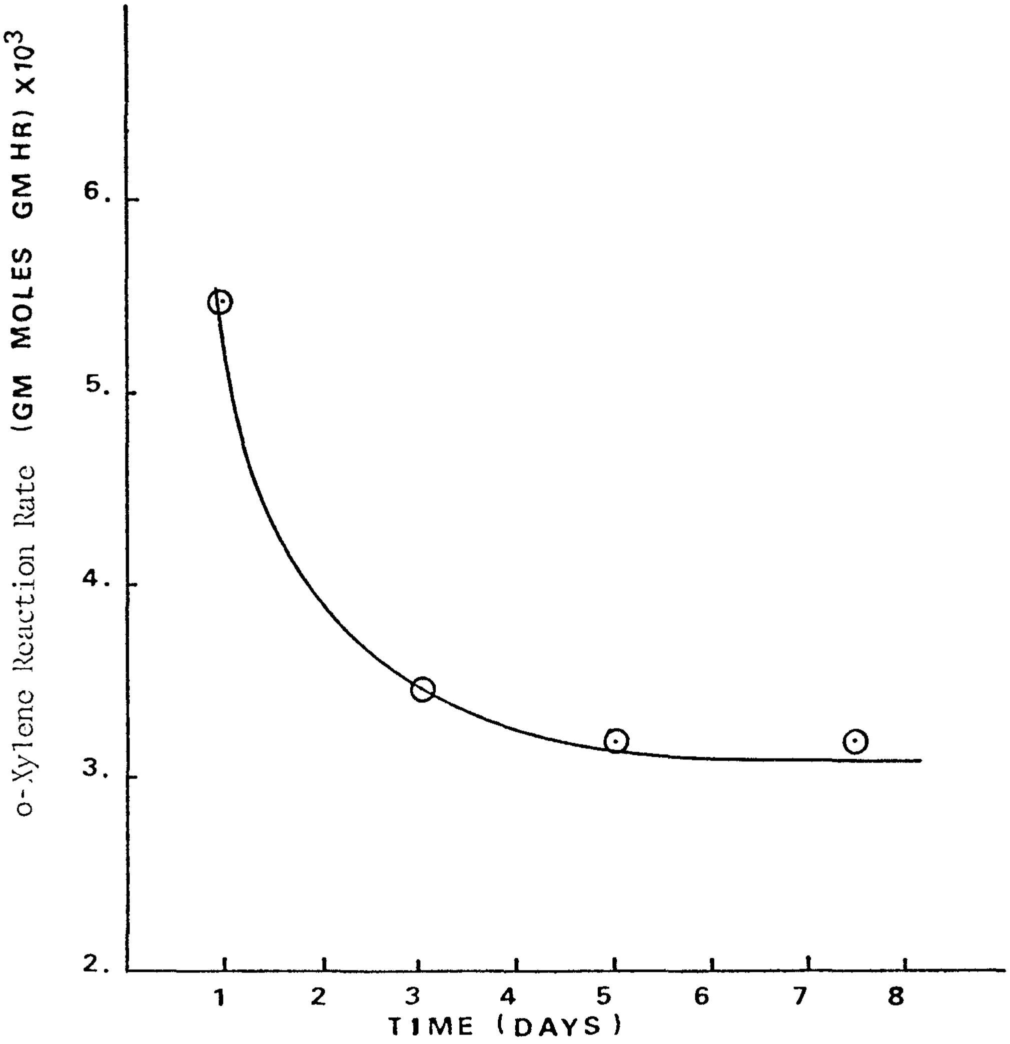


Figure 5.2.1: Initial long term deactivation of the catalyst

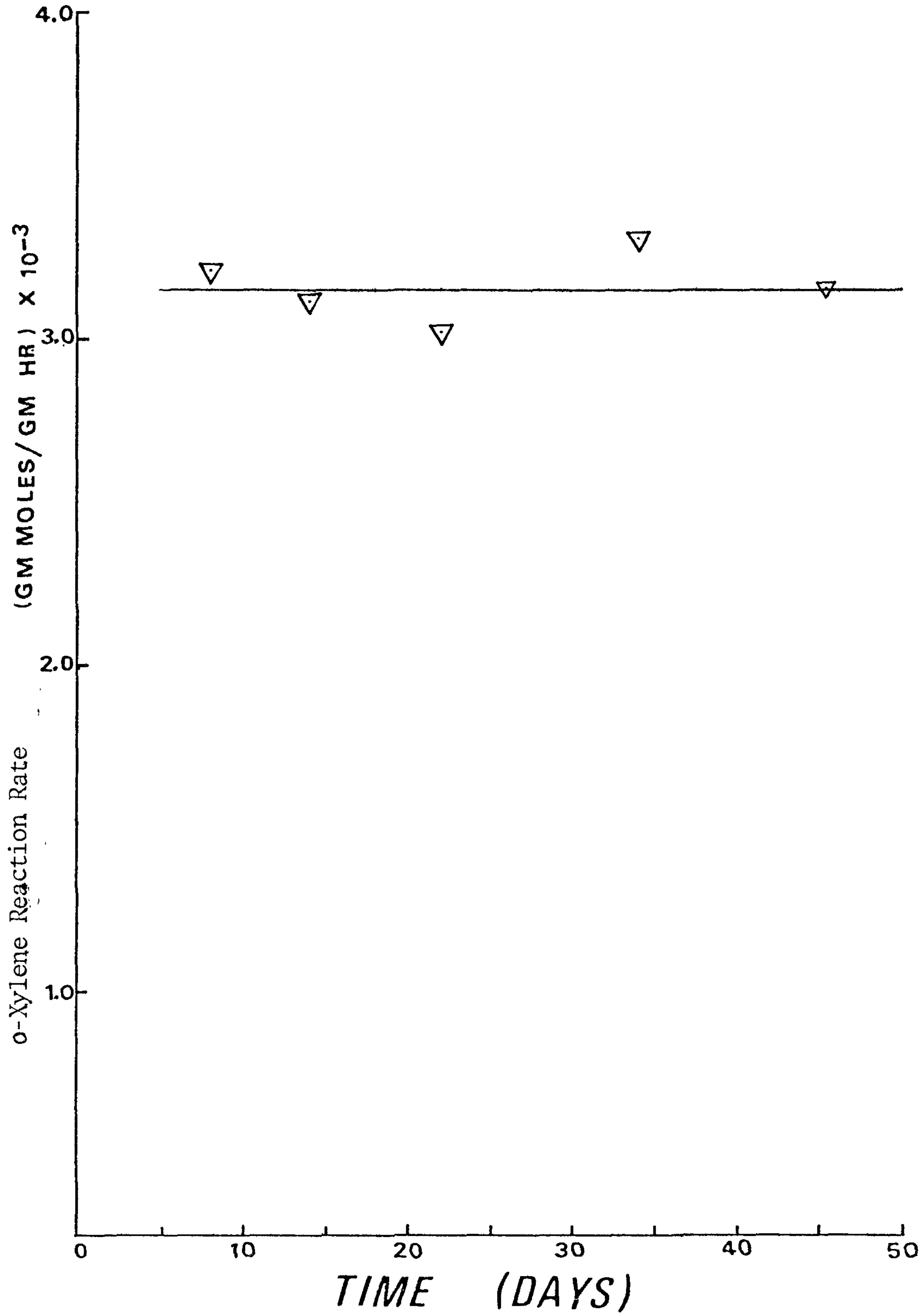


Figure 5.2.2: Shows the activity of the catalyst throughout the experimental program

CHAPTER 6

REACTION MODEL

6.1 Equations for the Reaction Scheme

The reaction model in this study is similar to that proposed by Wainwright [26] for o-xylene oxidation on the TiO_2-supported V_2O_5 catalyst. Figure 6.1.1 represents the reaction network.

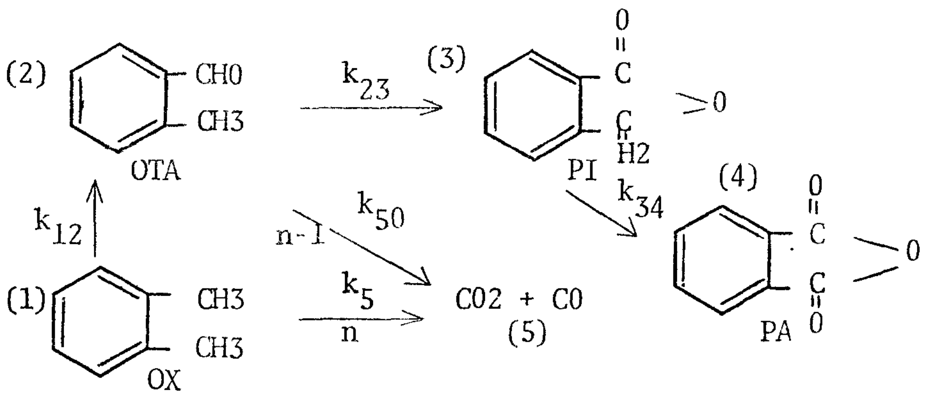


Figure 6.1.1: Reaction Network for o-Xylene Oxidation on TiO_2 Support

Wainwright [26] has demonstrated that the rate of o-xylene conversion had very little, if any, temperature dependence in the temperature range 350-390°C. This was attributed to the loss of SO_3 from the catalyst. This matter has already been discussed in Section 2.8. An active site parameter$(Es/\{R(\frac{1}{T} - \frac{1}{T^*})\})$ was included in the rate expressions to account for the loss of activity. The reaction model, in this study also includes this active site parameter.

The reaction model also includes a relative catalyst activity parameter, k_s. This parameter estimates the activity of a catalyst relative to another. Because Wainwright's catalyst was found to be less active than the one used here, it was found convenient to introduce this additional relative catalyst activity parameter, k_s. This parameter is expected to account for the difference in catalyst activity from one catalyst to another and if correct, should mean that the remaining parameter values are essentially the same from one catalyst batch to another. This would have important ramifications for future studies on this catalyst system.

Equations for the reaction model are established as follows:

Rate of disappearance of o-xylene

$$-\frac{dC_1}{dt} = (k_{12}C_1\theta + k_5C_1\theta)$$

$$= (k_{12} + k_5)\ C_1\theta \qquad 6.1.1$$

Rate of formation of o-tolualdehyde

$$\frac{dC_2}{dt} = (k_{12}C_1\theta - k_5C_2\theta - k_{23}C_2\theta)$$

$$= (k_{12}C_1 - k_5C_2 - k_{23}C_2)\theta \qquad 6.1.2$$

Rate of formation of phthalide

$$\frac{dC_3}{dt} = (k_{23}C_2\theta - k_{34}C_3\theta)$$

$$= (k_{23}C_2 - k_{34}C_3)\theta \qquad 6.1.3$$

Rate of formation of phthalic anhydride

$$\frac{dC_4}{dt} = k_{34}C_3\theta \qquad 6.1.4$$

Rate of formation of CO and CO2

$$\frac{dC_5}{dt} = 8(k_5C_2\theta + k_5C_1\theta)$$

$$= 8k_5(C_2 + C_1)\theta \qquad 6.1.5$$

Rate of oxidation of the catalyst

$$r_a = k_aC_a(1-\theta) \qquad 6.1.6$$

Rate of oxygen consumption (r_a)

o-xylene → o-tolualdehyde

$$r_{a_{12}} = k_{12}C_1\theta \qquad 6.1.7$$

o-xylene → CO/CO2

$$r_{a_{15}} = nk_5C_1\theta \qquad 6.18$$

o-tolualdehyde → CO/CO2

$$r_{a_{25}} = (n-1)k_5C_5\theta \qquad 6.1.9$$

o-tolualdehyde → phthalide

$$r_{a_{23}} = k_{23}C_2\theta \qquad 6.1.10$$

phthalide → phthalic anhydride

$$r_{a_{34}} = k_{34}C_3\theta \qquad 6.1.11$$

$$r_a = r_{a_{12}} + r_{a_{15}} + r_{a_{25}} + r_{a_{23}} + r_{a_{34}} \qquad 6.1.12$$

$$= k_{12}C_1\theta + nk_5C_1\theta + (n-1)k_5C_2\theta + k_{23}C_2\theta + k_{34}C_3\theta$$

$$\therefore \quad k_aC_a(1-\theta) = k_{12}C_1\theta + nk_5C_1\theta + (n-1)k_5C_2\theta + k_{23}C_2\theta + k_{34}C_3\theta$$

$$k_aC_a = (k_aC_a + k_{12}C_1 + nk_5C_1 + (n-1)k_5C_2 + k_{23}C_2 + k_{23}C_2 + k_{34}C_3)\theta$$

$$\text{i.e. } \theta = \frac{k_a\,C_a}{k_aC_a + k_{12}C_1 + nk_5C_1 + (n-1)k_5C_2 + k_{23}C_2 + k_{34}C_3}$$

6.1.13

where n is the stoichiometric coefficient for the formation of carbon oxides. This coefficient is calculated from the experimental selectivity data as follows

$$n = (10.5\ S_{CO_2} + 6.5\ S_{CO})/(S_{CO_2} + S_{CO})$$

The logarithm of the catalyst activity parameter, k_s was used since this procedure would ensure that it remained positive during the parameter estimation procedure.

The reaction model thus becomes

$$\frac{dC_1}{dt} = \frac{-k_aC_a(k_{12}+k_5)C_1 * e^{[k_s+\frac{E_s}{R}(\frac{1}{T}-\frac{1}{T^*})]}}{k_aC_a+(k_{12}+nk_5)C_1 + (k_{23}+(n-1)k_5)C_2 + k_{34}C_3} \qquad 6.1.14$$

$$\frac{dC_2}{dt} = \frac{k_aC_a(k_{12}C_1-k_5C_2-k_{23}C_2) * e^{[k_s+\frac{E_s}{R}(\frac{1}{T}-\frac{1}{T^*})]}}{k_aC_a+(k_{12}+nk_5)C_1 + (k_{23}+(n-1)k_5)C_2+k_{34}C_3} \qquad 6.1.15$$

$$\frac{dC_3}{dt} = \frac{k_aC_a(k_{23}C_2-k_{34}C_3) * e^{[k_s+\frac{E_s}{R}(\frac{1}{T}-\frac{1}{T^*})]}}{k_aC_a(k_{12}+nk_5)C_1 + (k_{23}+(n-1)k_5)C_2 + k_{34}C_3} \qquad 6.1.16$$

$$\frac{dC_4}{dt} = \frac{k_aC_a(k_{34}C_3) * e^{[k_s+\frac{E_s}{R}(\frac{1}{T}-\frac{1}{T^*})]}}{k_aC_a+(k_{12}+nk_5)C_1 + (k_{23}+(n-1)k_5)C_2 + k_{34}C_3} \qquad 6.1.17$$

$$\frac{dC_5}{dt} = \frac{8k_aC_ak_5(C_1+C_2) * e^{[k_s+\frac{E_s}{R}(\frac{1}{T}-\frac{1}{T^*})]}}{k_aC_a+(k_{12}+nk_5)C_1 + (k_{23}+(n-1)k_5)C_2+k_{34}C_3} \qquad 6.1.18$$

6.2 Reparameterization of Pre-exponential Factors

It must be noted that the rate constants were reparameterized according to a base temperature T*. This procedure is the Hunter and Atkinson [129] reparameterization technique. This was necessary here, since we are interested in obtaining uncorrelated parameter estimates, etc.

i.e. $K_a = K_a^* e^{-[\frac{E_a}{R}(\frac{1}{T}-\frac{1}{T^*})]}$

where T* is the base temperature corresponding to the center of design. In this study

$$T^* = (370 + 273)°K = 643°K$$

where

$$K_a^* = K_a e^{-E_a/(643 \times R)}$$

This means that the values of K_a^*, K_{12}^*,... K_5^* were estimated instead of K_a, K_{12}, ... K_5.

CHAPTER 7

PARAMETER ESTIMATION

7.1 Introduction

In many instances in research, previous studies on a particular system have been carried out and reported in the literature. These studies provide prior information either as raw experimental data or as parameter estimates in a mathematical model. It therefore becomes useful to include this prior information or the estimates of parameters in the current analysis or model formulation given the new data from the experimental system at hand. In the present work prior information in the form of experimental data and parameter estimates for the proposed kinetic model were available from Wainwright's experiments on an integral packed bed reactor [26]. Because the experimental information was limited to that from nine runs, which were not designed for parameter estimation, the parameter estimates were not of sufficient precision to really evaluate the adequacy of the model. Hence, it was required to estimate the parameters in the model using this prior information together with the experimental data obtained from the present study.

Before proceeding to estimate the parameters in the multi-response model using conventional methods, it was necessary to examine the two sets of data very carefully to ensure that one set was consistent with the other. That is, for the two sets of data, the following criteria must be satisfied,

i) The responses should be essentially the same from both experimental systems. In particular, it was important that both the catalyst activity as indicated by the o-xylene conversion or reaction rate from the standard runs (center-point experiments) was essentially the same.

ii) The variance-covariance matrix from the experimental responses should be essentially the same in both systems.

If the above conditions were not satisfied, the model predictions based on the resulting parameter estimates would be both biased and uncertain.

It has already been established in Section 5.2 that the catalyst employed for the present study was more active than that used by Wainwright. The problem thus became that of finding an effective and correct method of transferring information from Wainwright's experiments to the current one. Many of the methods used in chemical engineering to transfer information from one experiment to another have been less than satisfactory.

Recently Hoffman and Reilly [124] have developed an efficient statistical technique for transferring information from one experiment to another. This method employs Bayes' theorem in which prior information on the parameters (best prior estimates and the variance-covariance matrix of those parameters) is combined with the current experimental information (multiresponse data and an estimate of the variance-covariance matrix for those responses) to provide posterior parameter estimates and information as to their precision. In this case (as described) the statistical inference is not subjective since this is what might be termed 'hard' information. This procedure also allows the researcher to include estimates of parameters in a model which are not determined from experimental measurements but rather express his 'degree of belief' that a parameter has a certain value. When such estimates of parameter values and their variances are included in the analysis the resulting statistical inference is thus subjective.

Their recent paper considered the application of this technique to the hydrogenolysis of butane reaction. Kinetic parameters were determined from a bench scale, integral packed-bed reactor. These parameters were then transferred to a model for a fluidized-bed reactor in which the same chemical reaction occurred. The parameter estimates were updated and two additional parameters in the fluidized bed model were estimated from the data obtained from the fluidized bed reactor. A useful point about this technique is that the uncertainty in all sources of information is considered. Also a more realistic estimate of the uncertainty in all parameter values is contained in the posterior information of the parameters.

This technique was used in this study and its statistical background is reviewed below.

7.2 Parameter Estimation Technique

Let the mathematical model, for the measured responses obtained in the present study, be represented by the following expression

$$\underline{y}_u = \underline{\eta}(\underline{x}_u, \underline{\theta}^*) + \underline{\varepsilon}_u \qquad 7.2.1$$

$\underline{y}_u$ is the vector of values of the measured r-responses for the uth experiment.

$\underline{\eta}$ is the vector of expected values predicted from the model responses at the u^{th} trial given the vector of parameters $\underline{\theta}^*$ and the vector of independent variables $\underline{x}_u$.

$\underline{\varepsilon}_u$ is the error at the u^{th} trial

By the use of Taylor's series, the model can be linearized in the neighbourhood of some vector $\underline{\gamma}$ of parameter values, that is

$$\underline{z} = \underline{X}(\underline{\theta}^* - \underline{\gamma}) + \underline{\varepsilon} \qquad 7.2.2$$

where

$$\underline{z} = \{\underline{y}_u - \underline{\eta}(\underline{x}_u, \underline{\gamma})\} \qquad u^{th} \text{ element}$$

$$\underline{X} = \frac{\delta_\eta(\underline{x}_u, \underline{\theta})}{\delta\underline{\theta}_j} \qquad u, j \text{ element}$$

$$\underline{\varepsilon} = \{\underline{\varepsilon}_u\} \qquad u \text{ element}$$

There are n observations and p parameters.

The prior information about the parameter is expressed by

$$\underline{\theta}^* : N(\underline{\alpha}, \underline{U}) \qquad 7.2.3$$

$\underline{\theta}^*$ is assumed to have a multivariate normal distribution with mean $\underline{\alpha}$ and covariance matrix $\underline{U}$. The error vector $\underline{\varepsilon}$ is also assumed to be normally distributed with mean $\underline{0}$ and covariance matrix $\underline{V}$

$$\text{i.e. } \underline{\varepsilon} : N(\underline{0} \; ; \underline{V}) \qquad 7.2.4$$

The values of $\underline{\alpha}$, $\underline{U}$ and $\underline{V}$ are known numerically. By applying the Bayes' Theorem, Hoffman and Reilly [124] have shown that the posterior distribution of $\underline{\theta}^*$ is normal and symmetric and is expressed by

$$P(\underline{\theta}^*/\underline{y}) : N\{\underline{\gamma} + (\underline{U}^{-1}+\underline{X}'\underline{V}^{-1}\underline{X})^{-1}[\underline{U}^{-1}(\underline{\alpha}-\underline{\gamma})+\underline{X}'\underline{V}^{-1}\underline{z}];$$

$$(\underline{U}^{-1}+\underline{X}'\underline{V}^{-1}\underline{X})^{-1}\} \qquad 7.2.5$$

It is clear from equation 7.2.5 that the most likely set of parameter value is the posterior mean vector. This vector contains the best choice of $\underline{\gamma}$, the vector of values for $\underline{\theta}^*$ about which the model is linearized. By setting the posterior mean in equation 7.2.5 equal to $\underline{\gamma}$ and simplifying, the following relationship is obtained

$$\underline{U}^{-1}(\underline{\alpha}-\underline{\gamma}) + \underline{X}'\underline{V}^{-1}\underline{z} = \underline{0} \qquad 7.2.6$$

This is the condition for the most recent set of parameter values $\underline{\gamma}$ to become the posterior mean. Equation 7.2.6 becomes difficult to solve as both $\underline{X}$ and $\underline{z}$ are functions of $\underline{\gamma}$. A better approach has been derived from equation 7.2.5 by linearizing the model at the set of parameter values $\underline{\gamma}_i$. The posterior mean on the (i+1) iteration, $\underline{\gamma}_{i+1}$, is given by equation

$$\underline{\gamma}_{i+1} = \underline{\gamma}_i + \underline{T}_i \qquad 7.2.7$$

where $\underline{T}_i = (\underline{V}^{-1}+\underline{X}'\underline{V}^{-1}\underline{X})^{-1}[\underline{U}^{-1}(\underline{\alpha}-\underline{\gamma})+\underline{X}'\underline{V}^{-1}\underline{z}]$

$\underline{X}$ and $\underline{z}$ are calculated using $\underline{\gamma}_i$.

Equation 7.2.7 is solved iteratively until the correction $\underline{T}_i$ between $\underline{\gamma}_{i+1}$ and $\underline{\gamma}_i$ becomes vanishingly small.

The following suggests the iterative method of solution

1) Guess a starting value for $\underline{\gamma}_i$
2) Calculate the correction $\underline{T}_i$
3) Correct $\underline{\gamma}_i$ to the best estimated value for $\underline{\theta}$. That is find γ_{i+1} by adding $\underline{T}_i$ to $\underline{\gamma}_i$.
4) Recalculate $\underline{T}_i$ after using $\underline{\gamma}_{i+1}$
5) Repeat 3 and 4 until the correction $\underline{T}_i$ becomes vanishingly small.

If the converged values of $\underline{\gamma}$ is represented by $\underline{\gamma}$, the posterior mean with the model linearized at those values, the posterior distribution of $\underline{\theta}^*$ is given by (equation 7.2.5)

$$P(\underline{\theta}^*/\underline{y}) \ : \ N\{\underline{\hat{\theta}} \ ; \ (\underline{U}^{-1}+\underline{X}'\underline{V}^{-1}\underline{X})^{-1}\} \qquad 7.2.8$$

7.3 Transformation of the Observed Responses

When several responses are observed, in each experimental run, the use of all the independent responses gives more precise estimates of the parameters $\underline{\theta}$ than just one response.

Box, Hunter, MacGregor and Erjavec [45] have pointed out that difficulties can be experienced in the application of some parameter estimation techniques, if linear relationships exist among the measured responses. Three types of dependencies were considered.

i) Linear dependencies among errors. This situation can occur when the method of multiresponse analysis does not satisfy the assumption that the errors committed in an experimental run are all uncorrelated.

ii) Linear dependencies among expected values of responses. This occurs when the material and energy balances, or the steady-state condition require that certain linear relationships exist among the expected values of the responses.

iii) Linear dependencies in the data. This occurs when the responses are not determined independently. An example of this is the normalization of chromatographic data.

An experimenter should determine each response independently, and having done so should refrain from forcing observed responses to satisfy theoretical relationships that be believes to be true.

In this study, the eigenvalue and eigenvector analysis, presented in their paper, was used to determine whether linear relationships were present among the data. The method considers a matrix

$$\underline{D} = \{y_{iu} - \bar{y}_i\} \qquad i = 1 \ldots r \qquad 7.3.1$$

of deviations from individual averages.

y_{iu} is the value of the originally measured response i at the u^{th} experimental trial

$\bar{y}_i$ is the arithmetical average for response i for all the experimental runs

The eigenvalues λ_k and r-dimensional eigenvectors $\underline{z}_k$ of $\underline{D}\,\underline{D}'$ are such that if there are m_1 independent exact linear relations in the data, there will be m_1 zero eigenvalues. Also the size of the remaining m_2=m-m_1

eigenvalues will depend on the experimental errors, that is,

$$E(\lambda_k) = (n-1)\underline{z}_k' \underline{\Sigma}\, \underline{z}_k \qquad k = m+1, \ldots m_1+m_2 \qquad 7.3.4$$

where $\underline{\Sigma}$ is the rxr covariance matrix for the errors in the r responses. The sample estimate $\hat{\underline{\Sigma}}$ for replicate runs (Table 7.3.1) was substituted in equation 7.3.4 to yield estimates of all the λ_k's.

Table 7.3.2 presents the eigenvectors and eigenvalues of $\underline{D}\,\underline{D}'$. The expected values $E(\lambda_k)$ of these eigenvalues as calculated from equation 7.3.4 are also included on the Table 7.3.2. From Table 7.3.2, it is obvious that the values of λ_2 and λ_3 would have been zero were it not for the round-off errors. Hence there are only 3 independent responses in the data.

Before any meaningful analysis of data can be conducted the two dimensional singularity resulting in λ_2 and λ_3 being equal to zero must be removed. As it was not possible to pinpoint the true singularity relationships, the method of empirical eigenvectors was adopted in this study. Using this approach, the final analysis of data was conducted on three linearly independent combinations of all the five observed responses. Following Box et al. [45], the transformation of the responses was carried out as follows

$$\begin{aligned} y^*_{1u} &= \underline{z}_1\underline{y}_u \\ y^*_{2u} &= \underline{z}_4\underline{y}_u \qquad\qquad 7.3.5 \\ y^*_{3u} &= \underline{z}_5\underline{y}_u \end{aligned}$$

Table 7.3.1

Variance-Covariance Matrix of the Observed Responses

	R1	R2	R3	R4	R5
R1	0.1824E-09	0.7235E-11	0.1356E-10	-0.2600E-10	-0.6462E-10
R2	0.7235E-11	0.5287E-12	0.1106E-11	-0.1822E-11	-0.3217E-11
R3	0.1356E-10	0.1106E-11	0.2535E-11	-0.4757E-11	-0.1020E-10
R4	-0.2600E-10	-0.1822E-11	-0.4757E-11	0.1525E-10	0.3787E-10
R5	-0.6462E-10	-0.3217E-11	-0.1020E-10	0.3787E-10	0.1150E-09

Table 7.3.2

Eigenvectors and the Eigenvalues of $\underline{D}\,\underline{D}'$ Matrix

i	λ_i	$E(\lambda_i)$	Eigenvectors (presented rowise) $\underline{z}_i$				
1	0.1288E-06	0.3041E-07	0.9978E+00	0.4442E-01	-0.4906E-01	0.2041E-02	0.6713E-02
2	0.3621E-23	0.4326E-09	0.6565E-01	-0.5733E+00	0.8162E+00	-0.2652E-01	0.9591E-02
3	-0.8020E-16	0.2168E-07	0.7064E-02	0.1017E-01	0.8227E-02	0.3540E+00	0.9351E+00
4	0.2706E-06	0.4600E-09	0.2687E-02	-0.5376E-01	-0.3479E-02	0.9341E+00	-0.3530E+00
5	0.5991E-07	0.3728E-09	0.7927E-02	0.8163E+00	0.5756E+00	0.3826E-01	-0.2853E-01

where for an experimental run at the uth trial,

$\underline{y}_u' = [y_1, y_2, y_3, y_4, y_5]$

= vector of the original 5 observed responses at the uth set of experimental condition,

and $\underline{y}_i^*$ is the vector of linearly independent responses obtained by carrying out the transformation of equation 7.3.5.

In order to obtain the point estimates of the parameters for a consistent set of experimental data, one should minimize the determinant $|V|$ where

$$|V| = \{(\underline{y}_i^* - E(\underline{y}_i^*))'(\underline{y}_j^* - E(\underline{y}_j^*))\} \quad i,j = 1, 2, 3 \qquad 7.3.6 \quad .$$

and $\qquad E(\underline{y}_i^*) = \underline{z}_i'\underline{\eta}$

where the notation ' denotes the matrix transpose operator.

This could be the case if prior information was not available. It is the Box and Draper [56] criterion and it is used if an estimate of the covariance matrix for the response is not available. Otherwise a least squares (multiresponse) criterion should be used.

i.e. for the least squares criterion (linearizing about parameter set $\underline{\theta}^*$), the best parameter estimates are given by

$$\underline{\hat{\theta}} = (\underline{X}'\underline{V}^{-1}\underline{X})^{-1}\underline{X}'\underline{V}^{-1}\ [\underline{y}_i^*-E(y_i^*)] \qquad 7.3.7$$

The Hoffman and Reilly equation 7.2.7 reduces to this if no prior information was available

i.e. $\underline{\alpha} = \underline{0}$, $\underline{U}^{-1} = \underline{0}$.

Summary of Prior Information

The prior information required in equations 7.2.3, and 7.2.4 comprises the following:

i) The initial parameter estimates ($\underline{\alpha}$)

ii) The covariance matrix on the initial parameter estimates ($\underline{U}$)

iii) The covariance matrix for the errors in the observed responses ($\underline{V}$)

These will be considered in turn.

7.4 Initial Parameter Estimates ($\underline{\alpha}$)

Because the catalyst activity for the current experiments was shown to be higher than that in Wainwright's experiments, it was necessary to introduce a catalyst activity parameter into the model [Section 6.1]. The catalyst used in the previous study was assigned a unit activity, and the activity of the catalyst employed in this study would be estimated relative to this value.

In order to simplify analysis, the initial estimate of the activity parameter for the data gathered in this study was assigned a unit value. Since this parameter was assumed to be normally distributed and was to be estimated with wide variance; it became necessary to work with the logarithm of this parameter rather than the parameter itself to preclude the possibility of negative parameter values. An estimate of the variance on this parameter was based on the maximum and the minimim values that were expected for it. This value was expected to lie between 1/4 and 4 with an expected value of 1.0 ($\ell n\ k_s = 0$). Therefore,

$$\ln 4 = 2 * \sigma = 1.3863$$

$$\text{i.e. } \sigma = 0.69315$$

$$\rightarrow \sigma^2 = 0.48045$$

where σ is its standard deviation. The initial estimate of the covariances between this parameter (α_{12}) and the remaining parameters in the model would be zero since its mean value estimate was independent of the others.

Parameters $\alpha_1, \alpha_2, \ldots \alpha_{11}$ were estimated from the data of Wainwright using the technique of Box and Draper [56] which can be applied in the multi-response situations. The best estimates of the parameters $\alpha_1, \alpha_2, \ldots \alpha_{11}$ are obtained when the posterior density function of the parameters is maximized or when the determinant $|\underline{S}|$ is minimized with respect to the parameters $\alpha_1, \alpha_2, \ldots \alpha_{11}$.

Here $\underline{S}$ is a r x r matrix and its determinant is represented by

$$|\underline{S}| = \left| \sum_{u=1}^{n} \{\underline{y}_u - \underline{\eta}(\underline{x}_u,\underline{\alpha})\} \{\underline{y}_u - \underline{\eta}(\underline{x}_u,\underline{\alpha})\}' \right| \qquad 7.4.1$$

and

$$\eta(\underline{x}_u,\underline{\alpha}) = E(\eta_i(\underline{x}_u,\underline{\alpha}) + \varepsilon_{iu})$$

$i = 1, 2, \ldots r$ response

$u = 1, 2, \ldots n$ experiments

E denotes the expectation operator

For a more detailed presentation of this parameter estimation procedure, the reader is referred to the Ph.D. thesis of Wainwright [26]. Table 7.5.1 Presents the parameter values $\underline{\alpha}$. It must be noted that in view of the linear dependencies found to exist in the data, (section 7.3) the parameter estimates $\alpha_1, \alpha_2, \ldots \alpha_{11}$ must be determined by applying the method of empirical eigenvectors as discussed in Section 7.3. Hence the determinant $|V|$ in the expression 7.3.6 must be minimized. This was not done by Wainwright; however, his parameter estimates were used directly.

7.5 ii) Covariance Matrix of the Parameter Estimates $\{\underline{U}(\underline{\alpha})\}$

In its present form, the Hoffman and Reilly method requires an estimate of the covariance matrix of the parameter estimates as determined by Wainwright. An approximation of this matrix can be obtained as follows.

It is well known [128] that the variance-covariance matrix for the parameters for a linear model can be estimated from:

$$\underline{U}(\underline{\alpha}) = \left(\frac{1}{n-P/n}\right)\left[\sum_{u=1}^{n}\left(\underline{X}_u' \, \underline{V}^{-1} \, \underline{X}_u\right)\right]^{-1} \qquad 7.5.1$$

For a non-linear model, as is the case here, linearization of the model using the best estimates of the parameters can be used to obtain $\underline{X}$, viz:

$$\underline{X}_u = \left[\frac{\delta\underline{\eta}(\underline{x}_u,\underline{\theta})}{\delta\underline{\theta}}\right]_{\underline{\theta}=\underline{\alpha}} \; ; \; \frac{\underline{V}}{r x r} = \sum_{u=1}^{n}[\underline{Y}_u-\underline{\eta}_u(\underline{x}_u,\underline{\theta})][\underline{Y}_u-\underline{\eta}_u(\underline{x}_u,\underline{\theta})]'$$

where $\underline{\alpha}' = \{\alpha_1, \alpha_2, \ldots \alpha_{11}\}$ and $\underline{x}_u$ refers to the u^{th} trial. The use of equation 7.2.7 requires knowledge of the variance-covariance matrix of the experimental responses. This method assumes that the model $\underline{\eta}$ is correct. Hence $\underline{U}(\underline{\alpha})$ represents the total uncertainty due to the kinetic model and the estimated parameters $(\alpha_1, \alpha_2, \ldots \alpha_{11})$. Again, the covariances between α_{12} and all the other parameters in the model are zero.

The resultant 12 x 12 covariance matrix was evaluated and is presented in Table 7.5.1. It must be noted that in view of the dependencies

Table 7.5.1

Prior Parameter Distribution

Prior Mean $(\underline{\hat{\theta}})$

0.223E+01	0.185E+02	0.350E+03	0.839E+03	0.245E+01	-0.207E+05	-0.255E+05	-0.234E+05	-0.280E+05	-0.230E+05	0.180E+05	0.000E+0

Prior Covariance Matrix $\{V(\theta^*)\}$

0.721E-02	0.201E-02	-0.490E-01	-0.887E+00	-0.228E+01	0.980E+08	-0.980E+08	-0.980E+08	-0.980E+08	0.980E+08	0.980E+08	0.000E+0
0.201E-02	0.251E-02	-0.381E-02	-0.852E-01	-0.441E+00	0.179E+08	-0.179E+08	0.179E+08	-0.179E+08	0.179E+08	0.179E+08	0.000E+0
-0.490E-01	-0.381E-02	0.534E+00	0.112E+02	0.285E+02	-0.225E+09	0.225E+09	-0.255E+09	0.255E+09	-0.255E+09	-0.255E+09	0.000E+0
-0.887E+00	-0.852E-01	0.112E+02	0.260E+03	0.571E+03	0.925E+09	-0.925E+09	0.925E+09	-0.925E+09	0.925E+09	0.925E+09	0.000E+0
-0.228E+02	-0.441E+00	0.285E+02	0.571E+03	0.231E+04	0.272E+10	-0.272E+10	0.272E+10	-0.272E+10	0.272E+10	0.272E+10	0.000E+0
0.980E+08	0.179E+08	-0.225E+09	0.925E+09	0.272E+10	0.439E+19	-0.439E+19	0.439E+19	-0.439E+19	0.439E+19	0.439E+19	0.000E+0
-0.980E+08	-0.179E+08	0.225E+09	-0.925E+09	-0.272E+10	-0.439E+19	0.439E+19	-0.439E+19	0.439E+19	-0.439E+19	-0.439E+19	0.000E+0
0.980E+08	0.179E+08	-0.225E+09	0.925E+09	0.272E+10	0.439E+19	-0.439E+19	0.439E+19	-0.439E+19	0.439E+19	0.439E+19	0.000E+0
-0.980E+08	-0.179E+08	0.225E+09	-0.925E+09	-0.272E+10	-0.439E+19	0.439E+19	-0.439E+19	0.439E+19	-0.439E+10	-0.439E+19	0.000E+0
0.980E+08	0.179E+08	-0.225E+09	0.925E+09	0.272E+10	0.439E+19	-0.439E+19	0.439E+19	-0.439E+19	0.439E+19	0.439E+10	0.000E+0
0.980E+08	0.179E+08	-0.225E+09	0.925E+09	0.272E+10	-0.439E+19	-0.439E+19	0.439E+19	-0.439E+19	0.439E+19	0.439E+19	0.000E+0
0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+19	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+0

in data discussed in Section 7.3 $\underline{n}_u$ and $\underline{y}_u$ must be transformed using the method of empirical eigenvectors. Also the parameters $\alpha_1, \alpha_2, \ldots \alpha_{11}$ used in estimating $\underline{U}(\underline{\alpha})$ must be those obtained by minimizing the determinant $|V|$ of equation 7.3.6. This was not done in obtaining the data presented in Table 7.5.1. This together with fact that the method used, in this section, for obtaining the $\underline{V}(\underline{\alpha})$ matrix assumes that the model is adequate may have resulted in very wide variances being associated with the activation energy parameters.

7.6 iii) The Covariance Matrix of the Observations

The five replicated data obtained in this study were used to estimate the covariance matrix $\underline{\Sigma}$. The linear dependencies in the data were removed by transforming the observed responses according to the techniques discussed in Section 7.3 as follows:

$$\underset{r\times r}{\hat{\underline{\Sigma}}} = \frac{1}{m-1} (\underline{y}_i^* - \bar{\underline{y}}_i^*)'(\underline{y}_i^* - \bar{\underline{y}}_i^*) \qquad 7.6.1$$

where $\underline{y}_i^* = \underline{z}_k \underline{y}_i$ $\quad k = 1, 4, 5$ for all the replicate data (m=5) and $\underline{y}_i'$ is a vector of the originally measured responses given by

$$\underline{y}_i' = \{y_1, y_2, y_3, y_4, y_5\}$$

$\underline{y}_i^*$ is a mxr matrix of the transformed responses;

r is the number of linearly independent responses (r=3);

$\underline{z}_k$ is a 1x5 eigenvector (k = 1, 4, 5) of Table 7.3.1.

$\underline{\Sigma}$ was estimated and the matrix is presented in Table 7.6.1.

In the statistical technique of Hoffman and Reilley [124], the use of the coveriance matrix $\underline{\hat{\Sigma}}$ was simplified by factoring it into two triangular pairs of matrices.

$$\text{i.e.}\quad \underline{\hat{\Sigma}} = \underline{T}' \, \underline{T} \qquad 7.6.2$$

and equation 7.2.1 was rewritten as

$$\underline{T}'^{-1} \, \underline{y}_u = \underline{T}'^{-1} \, \underline{\eta}(\underline{x}_u, \underline{\theta}^*) + \underline{T}'^{-1} \, \underline{\varepsilon}_i \qquad i = 1, 2, \ldots \ldots n \qquad 7.6.3$$

The covariance matrix of the error term in this equation can be shown to be the identity matrix [125]. Hence, the model in the form of equation 7.6.3 becomes easy to apply.

The computer program for obtaining the inverse of the upper triangular matrix $\underline{T}'^{-1}$ from the covariance matrix $\underline{\Sigma}$ of the transformed observations is presented in Appendix B. Table 7.6.2 presents the $\underline{T}'^{-1}$ matrix.

7.7 Analysis and Results

The parameters in the model were estimated using the iterative technique of equation 7.2.7. The computer program employed for the parameter estimation was developed by Hoffman and Reilly and was modified so that it could be used in this study. A listing of this program as applied to the present study is contained in Appendix B.

A total of 6 iterations were required before convergence was achieved. This required less than 4 minutes on the CDC 6400 computer.

Table 7.6.1

Variance-Covariance Matrix of the Transformed Responses $(\underline{\hat{\Sigma}})$

	1	2	3
1.	0.17993E-09	-0.14315E-11	0.15807E-10
2.	-0.14315E-11	0.27167E-11	-0.80452E-12
3.	0.15807E-10	-0.80452E-12	0.26676E-11

Table 7.6.2

Inverse Upper Triangular Matrix T'^{-1}

	1	2	3
1.	0.74550E+05	0.48370E+04	-0.81540E+05
2.	0.000E+00	0.60798E+06	0.23829E+06
3.	0.000E+00	0.000E+00	0.94970E+06

The final parameter estimates together with information as to their precision are presented in Table 7.7.1.

Table 6.8.3 indicates that the correlation coefficients of $\hat{\theta}_{12}$ with the remaining parameters are reasonable, considering the fact that the model was inadequate (Section 8.2). Also the normalized change in the activation energy parameters appear to be very small (Table 7.7.2). It is important to note that the prior covariance matrix of these parameters had very large variances (see Section 7.5).

Table 7.7.1

Posterior Parameter Distribution

Posterior Means $(\hat{\theta})$

0.283E 02	0.185E 02	0.349E 03	0.822E 03	0.241E 01	-0.156E 05	-0.280E 05	-0.202E 05	-0.339E 05	-0.197E 05	0.237E 05	0.350E 0

Posterior Covariance Matrix $\{V(\theta^*)\}$

0.237E-02	0.111E-02	-0.130E-01	-0.287E+00	0.240E-03	0.539E+00	0.393E+00	-0.909E+01	-0.518E+01	0.740E+01	0.134E+02	-0.637E-0
0.111E-02	0.299E-02	0.310E-02	0.387E-01	0.654E-03	-0.130E+02	-0.517E+01	-0.370E+01	0.730E+01	-0.137E+02	0.206E+01	-0.205E-0
-0.130E-01	0.310E-02	0.148E+00	0.366E+01	0.496E-03	-0.785E+02	-0.299E+03	0.377E+02	0.937E+02	-0.106E+03	-0.823E+02	0.349E-0
-0.287E+00	0.387E+01	0.366E+01	0.105E+03	-0.252E-01	-0.149E+04	-0.300E+03	0.344E+03	0.189E+04	-0.131E+04	-0.114E+04	0.623E-0
0.240E+03	0.654E-03	0.496E-03	-0.252E-01	0.404E-02	-0.241E+02	0.191E+02	-0.156E+02	0.232E+02	-0.331E+02	-0.239E+02	0.152E-0
0.539E+00	-0.130E+02	-0.785E+02	-0.149E+04	-0.241E+02	0.820E+06	-0.226E+06	0.436E+06	-0.106E+07	0.500E+06	0.294E+06	-0.916E+0
0.393E+00	-0.517E+01	-0.230E+02	-0.300E+03	0.191E+02	-0.226E+06	0.297E+06	-0.278E+06	0.252E+06	-0.190E+06	-0.274E+06	0.738E+0
-0.909E+01	-0.370E+01	0.377E+02	0.344E+03	-0.156E+02	0.436E+06	-0.278E+06	0.554E+06	-0.506E+06	0.614E+05	0.986E+04	-0.347E+0
-0.518E+01	0.730E+01	0.937E+02	0.189E+04	0.232E+02	-0.106E+07	0.252E+06	-0.506E+06	0.1584E+07	-0.152E+06	-0.219E+06	0.103E+0
0.740E+01	-0.137E+02	-0.106E+03	-0.131E+04	-0.331E+02	0.500E+06	-0.190E+06	0.614E+05	-0.512E+06	0.754E+06	0.619E+06	-0.137E+0
0.134E+02	0.206E+01	-0.823E+02	-0.114E+04	-0.239E+02	0.294E+06	-0.274E+06	0.986E+04	-0.219E+06	0.619E+06	0.971E+06	-0.147E+0
-0.637E-03	-0.205E-03	0.349E-02	0.623E-01	0.152E-02	-0.916E+01	0.738E+01	-0.347E+01	0.130E+02	-0.137E+02	-0.147E+02	0.880E+0

Table 7.7.2

Normalized Change in Parameter Estimates

Parameter	Prior Mean	Prior Standard Deviation	Posterior Mean	Posterior Standard Deviation	Movement
i	α_i	$\sqrt{V_{ii}}$	$\hat{\theta}_i$	$[V(\theta^*)]_{ii}^{1/2}$	$(\alpha_i-\hat{\theta}_i)/\sqrt{V_{ii}}$
1	0.223E+01	0.8490E-03	0.238E+01	0.486E-01	-0.1767E+02
2	0.185E+02	0.5008E-03	0.185E+02	0.478E-01	0.000 E+00
3	0.350E+03	0.7309E-02	0.349E+03	0.384E+00	0.1368E+03
4	0.839E+03	0.1613E+02	0.822E+02	0.102E+02	0.1054E+01
5	0.285E+01	0.4803E+02	0.241E+01	0.636E-01	0.9161E-02
6	-0.207E+05	0.2095E+10	-0.156E+05	0.905E+03	-0.2434E-05
7	-0.255E+05	0.2095E+10	-0.280E+05	0.545E+03	0.1193E-05
8	-0.235E+05	0.2095E+10	-0.202E+05	0.744E+03	-0.1575E-05
9	-0.280E+05	0.2095E+10	-0.339E+05	0.126E+04	0.2816E-05
10	-0.230E+05	0.2095E+10	-0.197E+05	0.869E+03	-0.1575E-05
11	0.180E+05	0.2095E+10	0.237E+05	0.985E+03	-0.2721E-05
12	0.000E+00	0.2095E+10	0.350E+00	0.297E-01	-0.1671E-09

Table 7.7.3

Correlation Coefficient Between $\hat{\theta}_{12}$ and the Remaining Parameters of the Model

i	j	$\hat{\rho}_{ij}$
1	12	-0.44
2	12	-0.15
3	12	0.31
4	12	0.21
5	12	0.81
6	12	-0.34
7	12	0.46
8	12	-0.16
9	12	0.28
10	12	-0.53
11	12	-0.50
12	12	1

$\hat{\rho}_{ij}$ is the estimate of the correlation coefficient between the parameters i and j.

CHAPTER 8

EVALUATION OF THE REACTION MODEL

Once a model has been proposed and the parameters in it have been estimated from experimental data, there still remains the problem of testing its validity.

The following points are considered in the evaluation of the model:

i) It is important that the values of the parameter estimates bear some relationship to those obtained by other researchers on similar systems. In particular, the activation energies must be positive and approximately what have been found for this particular type of reaction with the catalyst used. In the literature, very few studies, if any, have published results of parameter estimation of o-xylene oxidation in tubular reactors using the TiO_2 supported catalyst.

ii) Test for lack of fit:

To test for lack of fit the mean square lack of fit for each of the transformed responses was compared, through an appropriate F-test with the mean square pure error as determined from replicate experimental runs. This test was conducted using the expected values of the transformed responses, $\underline{y}_i^*$ as calculated by the model at the experimental conditions for each experimental measurement. These data are presented in Table 8.1. The test for lack of fit is shown in Table 8.2. The model was found to be inadequate as the mean square lack of fit (MSLF) was too large compared to the experimental error variance (MSPE).

The values of the observed responses along with their predicted values are plotted and presented in Figures 8.1 to 8.5. An examination of these plots indicates that o-xylene conversion was predicted fairly well (within 5%) but considerable error existed on o-tolualdehyde, phthalide, phthalic anhydride, and the carbon oxides (within 25%).

iii) The plot of the residuals (the observed response-minus the expected value of the response) versus the independent variables and the run numbers are shown in Figures 8.6 to 8.9. It is demonstrated by these plots that the residuals do not show any appreciable correlation with the run numbers or with the independent variables.

Table 8.1

Observed and Predicted Values of
the Transformed Responses

RUN	RESPONSE 1		RESPONSE 2		RESPONSE 3	
No.	OBSERVED	PREDICTED	OBSERVED	PREDICTED	OBSERVED	PREDICTED
426	0.224E-03	0.211E-03	0.308E-04	0.360E-04	0.173E-04	0.123E-04
428	0.206E-03	0.216E-03	0.359E-04	0.400E-04	0.155E-05	0.146E-04
430	0.328E-03	0.347E-03	0.449E-04	0.256E-04	0.217E-04	0.207E-04
504	0.235E-03	0.222E-03	0.384E-04	0.399E-04	0.181E-04	0.150E-04
512	0.220E-03	0.213E-03	0.379E-04	0.406E-04	0.148E-04	0.145E-04
515	0.441E-03	0.452E-03	0.341E-04	0.339E-04	0.296E-04	0.310E-04
517	0.135E-03	0.107E-03	0.588E-04	0.692E-04	0.740E-04	0.673E-05
523	0.327E-03	0.351E-03	0.994E-04	0.875E-04	0.219E-04	0.218E-04
524	0.204E-03	0.198E-03	0.405E-04	0.422E-04	0.137E-04	0.135E-04
527	0.381E-03	0.397E-03	0.547E-04	0.418E-04	0.217E-04	0.280E-04
529	0.381E-03	0.419E-03	0.505E-04	0.204E-04	0.196E-04	0.250E-04
531	0.409E-03	0.407E-03	0.414E-04	0.665E-04	0.219E-04	0.247E-04
605	0.227E-03	0.230E-03	0.379E-04	0.423E-04	0.149E-04	0.156E-04
610	0.423E-03	0.416E-03	0.269E-05	0.812E-05	0.197E-04	0.292E-04

Table 8.2

Analysis for Lack of Fit

	Degrees of freedom	y_1^*	y_2^*	y_3^*
S.S.R.	42	0.559E-08	0.224E-08	0.206E-09
SSPE	12	0.884E-09	0.486E-10	0.110E-10
SSLF	30	0.471E-08	0.239E-08	0.195E-09
$\frac{MSLF}{MSPE}$	$\frac{30}{12}$	5.68	18.2	19.7
$F_{(30,12,0.95)}$		2.47	2.47	2.47

Table 8.3

Final Parameter Estimates

i	Parameter Symbol	$\hat{\theta}_i$ (95% confidence interval)
1	k_a	0.4889E+06 ± 0.2009E+05
2	k_{12}	0.5966E+11 ± 0.3086E+09
3	k_{23}	0.2519E+10 ± 0.5543E+07
4	k_{34}	0.2601E+15 ± 0.6477E+12
5	k_5	0.1177E+08 ± 0.6212E+06
6	E_a	15637. ± 1810.
7	E_{12}	27983. ± 1090.
8	E_{23}	20187. ± 1488.
9	E_{34}	33846. ± 2520.
10	E_5	19684. ± 1738.
11	E_{AS}	23671.99 ± 1970
12	k_s	1.4195 ± 0.0600

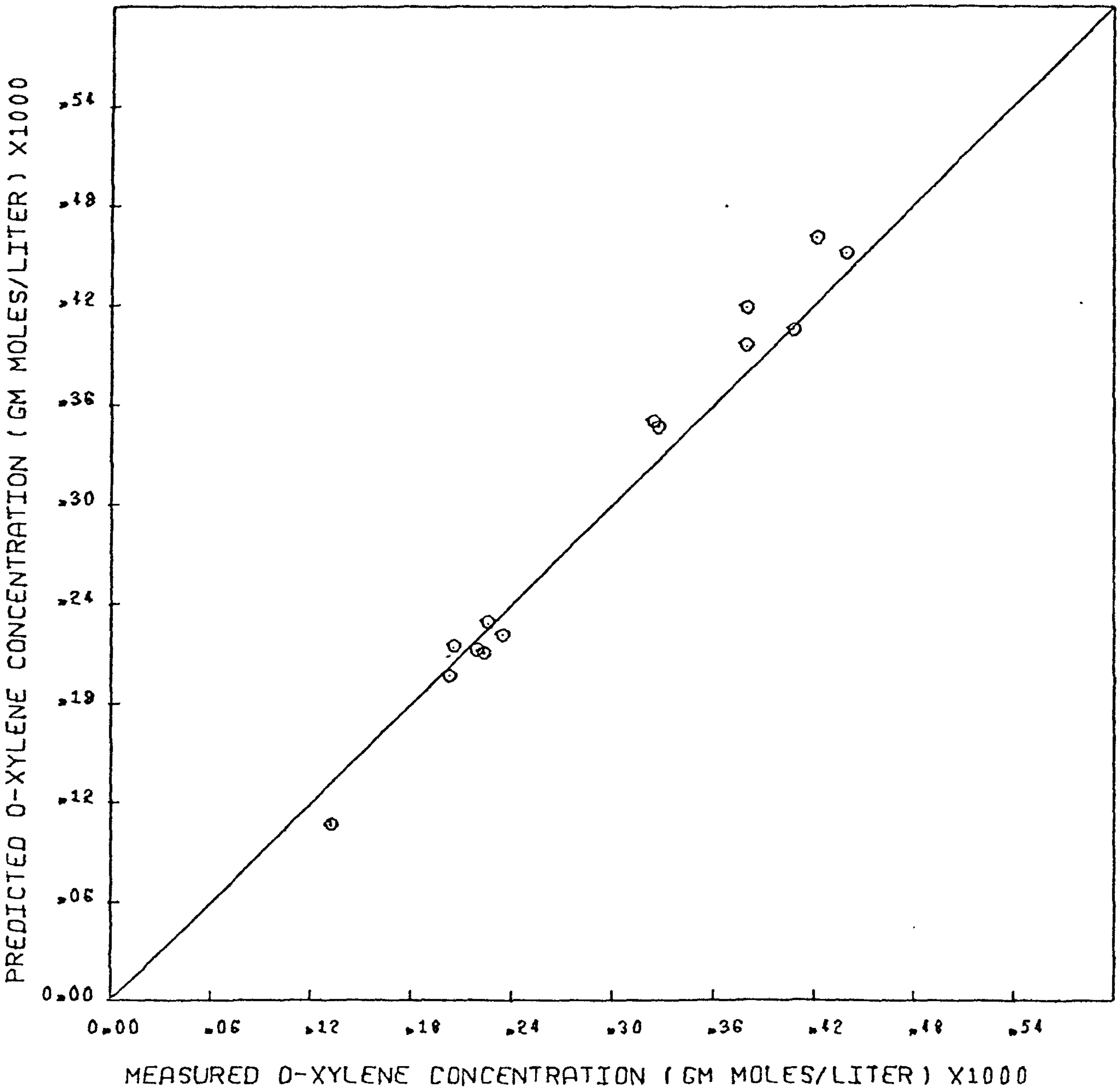

PREDICTED O-XYLENE CONCENTRATION (GM MOLES/LITER) X1000
.54
.48
.42
.36
.30
.24
.18
.12
.06
0.00
0.00
.06
.12
.18
.24
.30
.36
.42
.48
.54
MEASURED O-XYLENE CONCENTRATION (GM MOLES/LITER) X1000

Figure 8.1

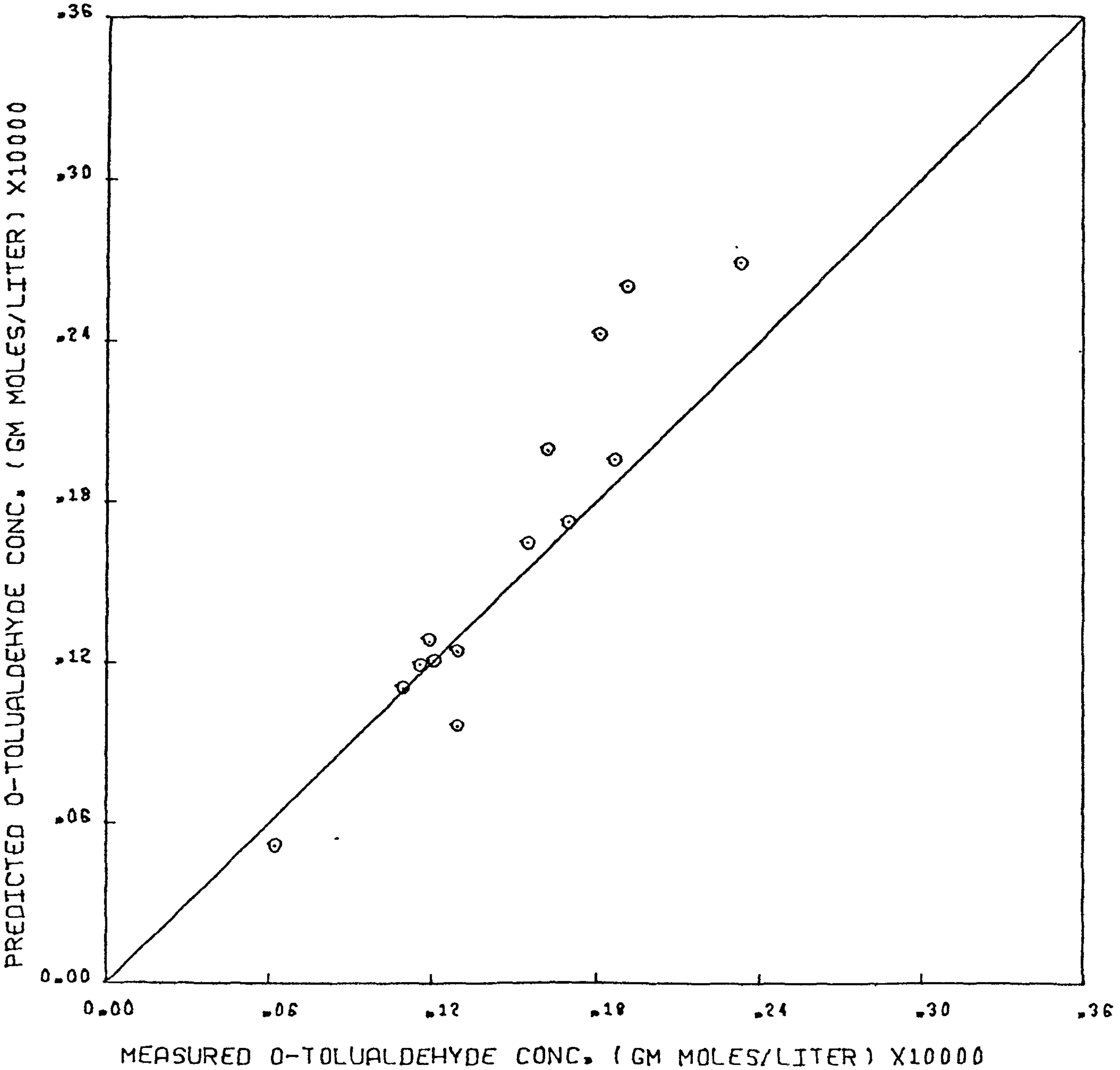
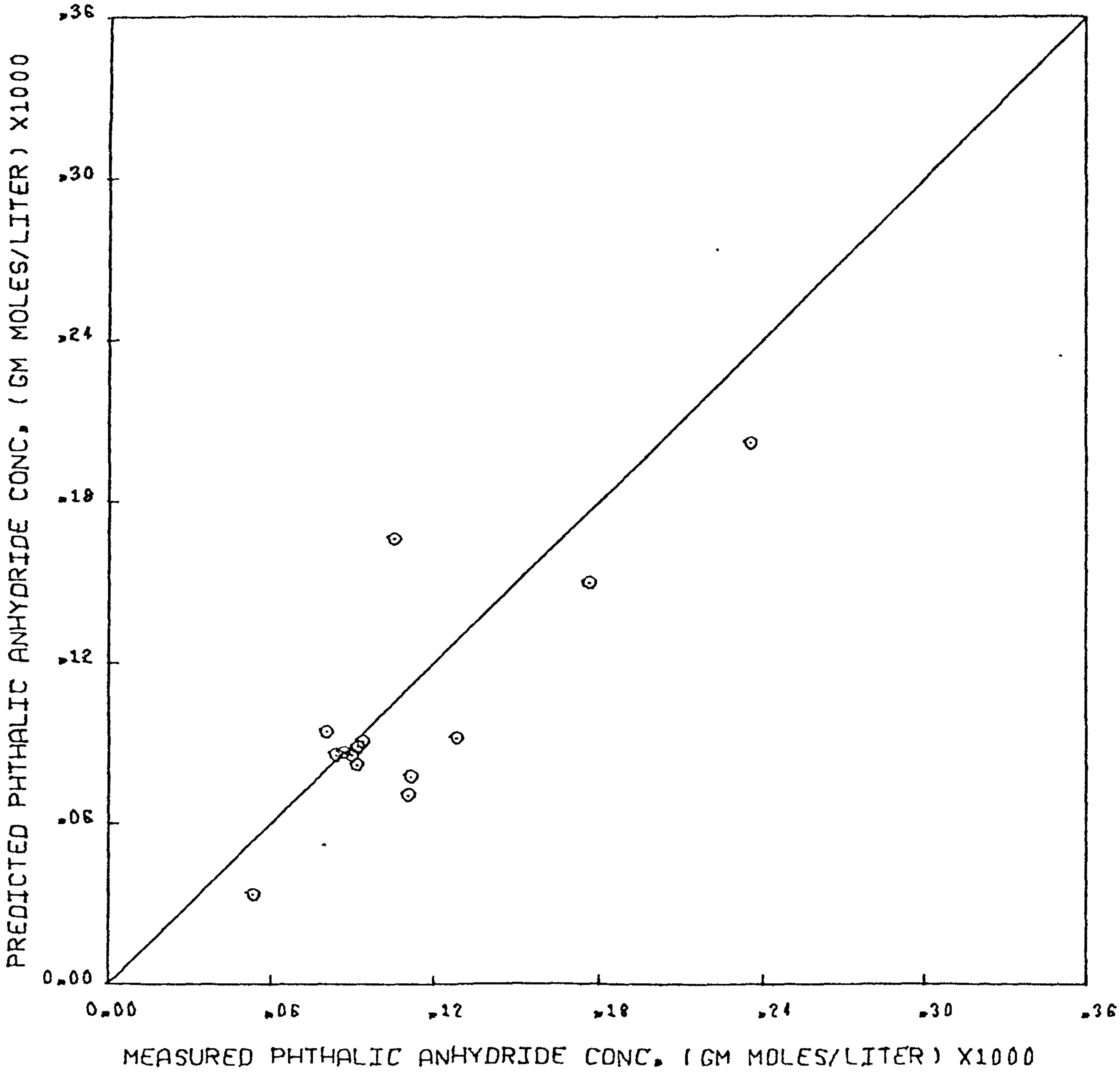

.36
.30
.24
.18
.12
.06
0.00
0.00
.06
.12
.18
.24
.30
.36
PREDICTED O-TOLUALDEHYDE CONC. (GM MOLES/LITER) X10000
MEASURED O-TOLUALDEHYDE CONC. (GM MOLES/LITER) X10000

Figure 8.2



.36
.30
.24
.18
.12
.06
0.00
0.00
.06
.12
.18
.24
.30
.36
PREDICTED PHTHALIC ANHYDRIDE CONC. (GM MOLES/LITER) X1000
MEASURED PHTHALIC ANHYDRIDE CONC. (GM MOLES/LITER) X1000

Figure 8.3

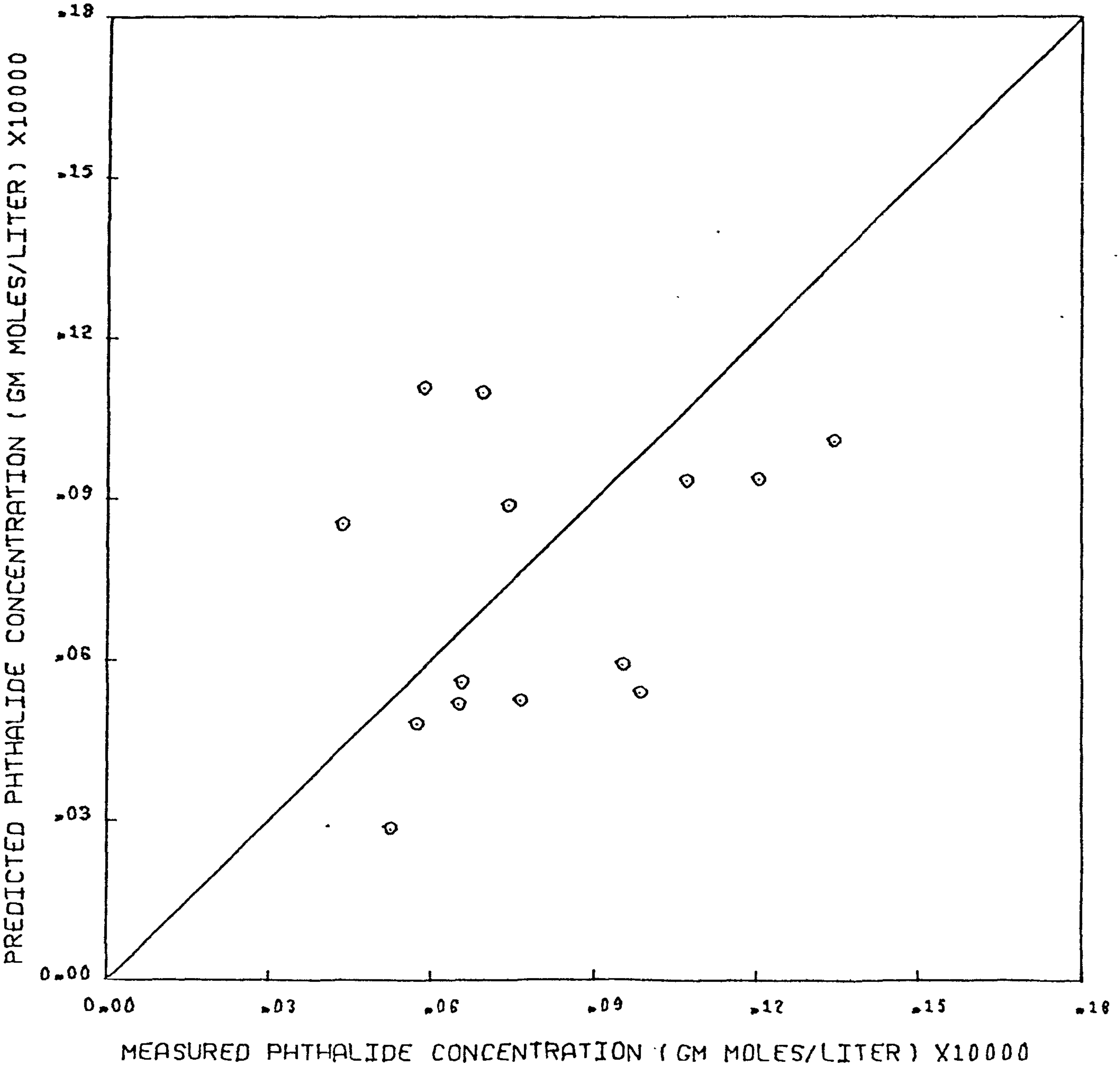

PREDICTED PHTHALIDE CONCENTRATION (GM MOLES/LITER) X10000
MEASURED PHTHALIDE CONCENTRATION (GM MOLES/LITER) X10000
.18
.15
.12
.09
.06
.03
0.00
0.00
.03
.06
.09
.12
.15
.18

Figure 8.4

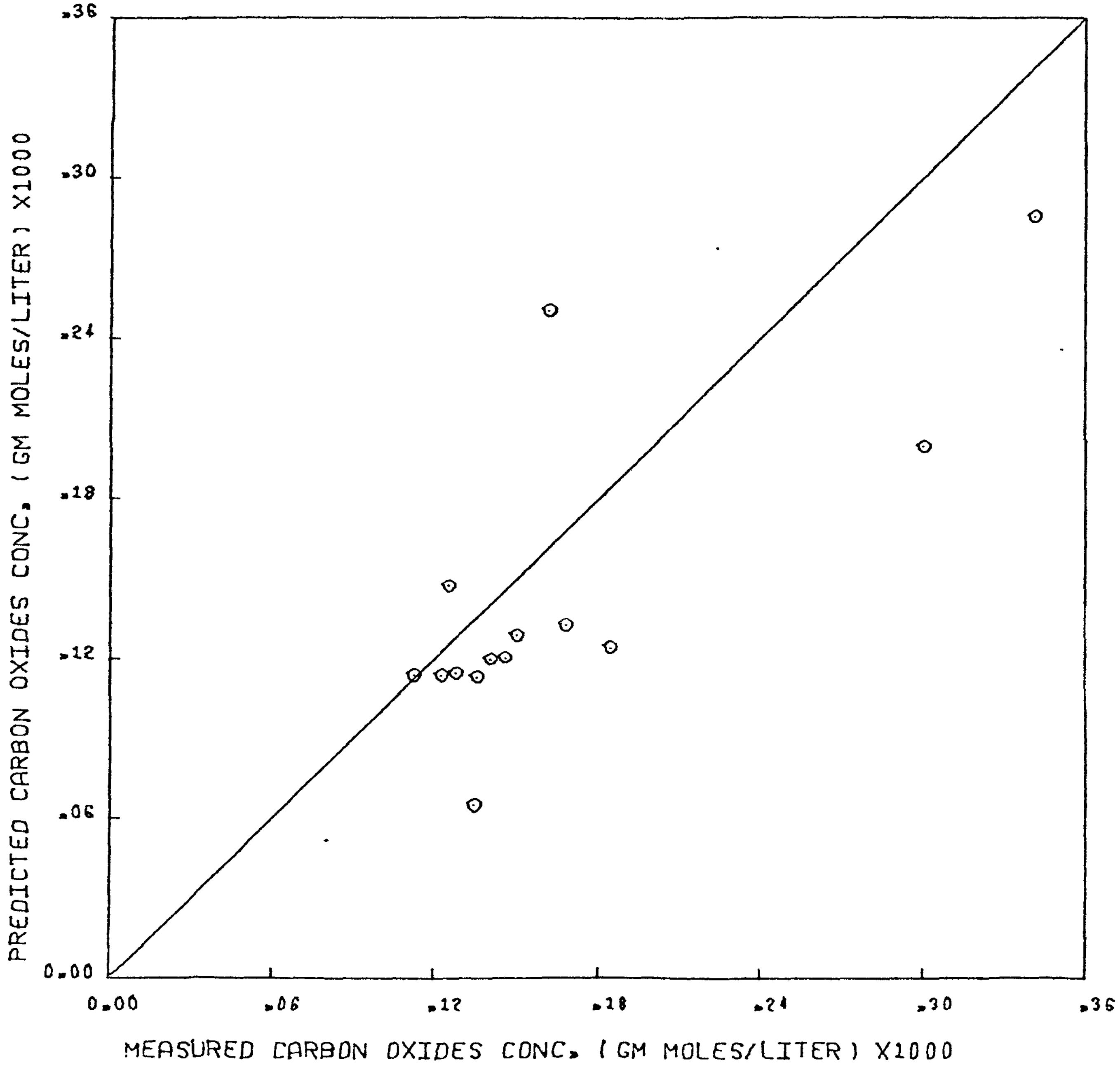

.36
.30
.24
.18
.12
.06
0.00
PREDICTED CARBON OXIDES CONC. (GM MOLES/LITER) X1000
0.00
.06
.12
.18
.24
.30
.36
MEASURED CARBON OXIDES CONC. (GM MOLES/LITER) X1000

Figure 8.5

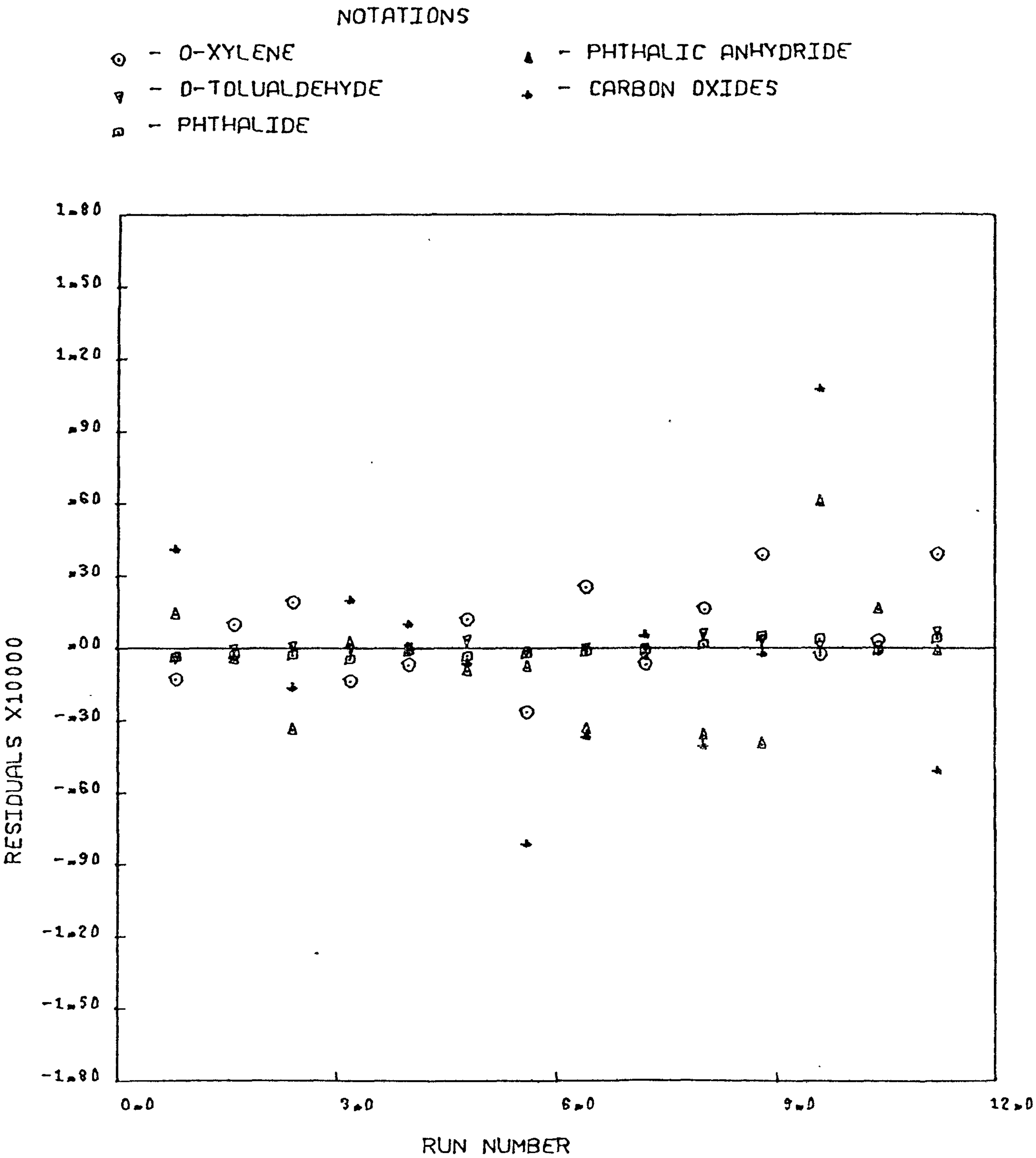

NOTATIONS
⊙ - O-XYLENE
▽ - O-TOLUALDEHYDE
⊡ - PHTHALIDE
▲ - PHTHALIC ANHYDRIDE
+ - CARBON OXIDES
1.80
1.50
1.20
.90
.60
.30
.00
-.30
-.60
-.90
-1.20
-1.50
-1.80
RESIDUALS X10000
0.0
3.0
6.0
9.0
12.0
RUN NUMBER

Figure 8.6

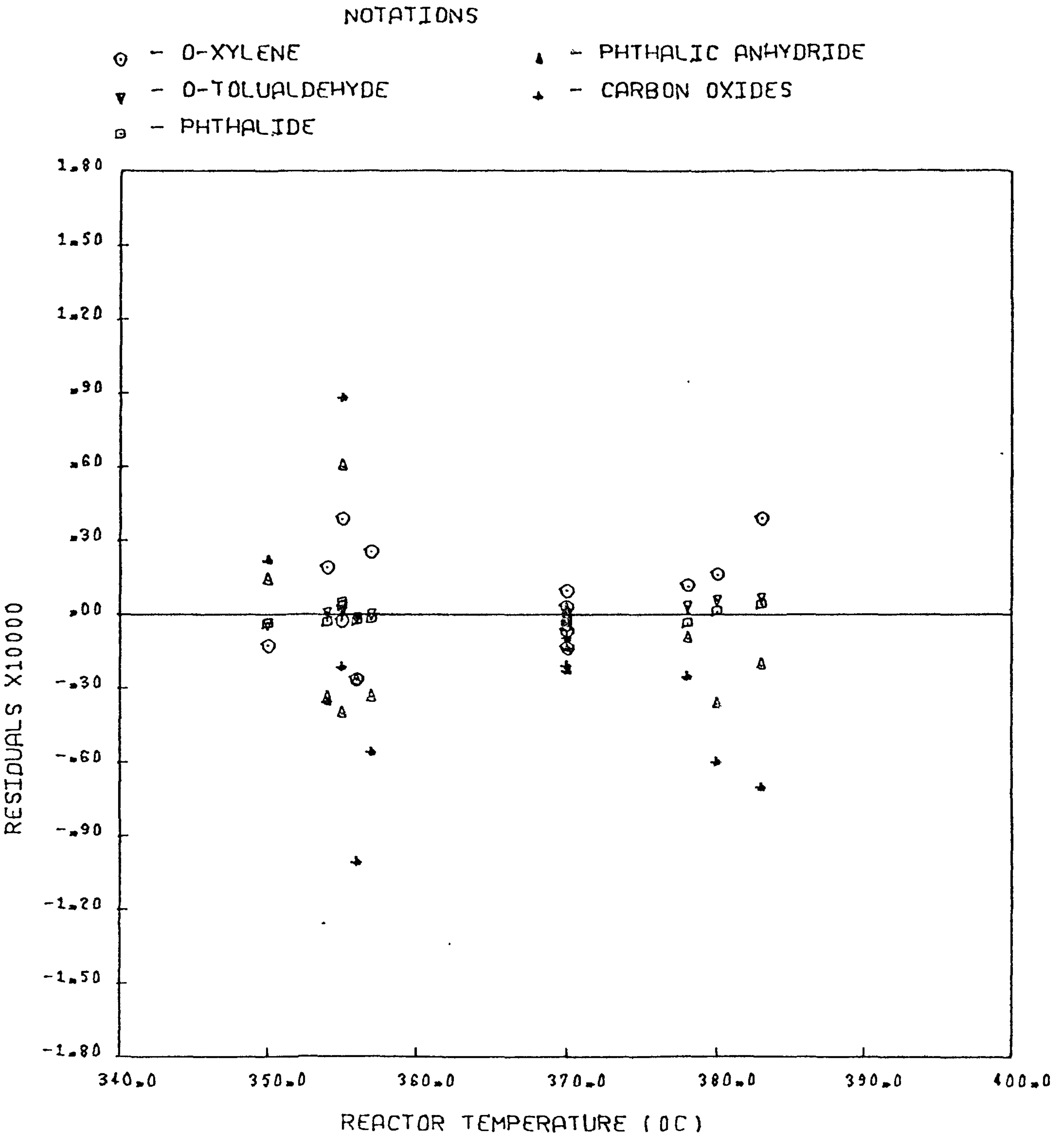

NOTATIONS
⊙ - O-XYLENE
▼ - O-TOLUALDEHYDE
⊡ - PHTHALIDE
▲ - PHTHALIC ANHYDRIDE
+ - CARBON OXIDES
1.80
1.50
1.20
.90
.60
.30
.00
-.30
-.60
-.90
-1.20
-1.50
-1.80
RESIDUALS X10000
340.0
350.0
360.0
370.0
380.0
390.0
400.0
REACTOR TEMPERATURE (OC)

Figure 8.7

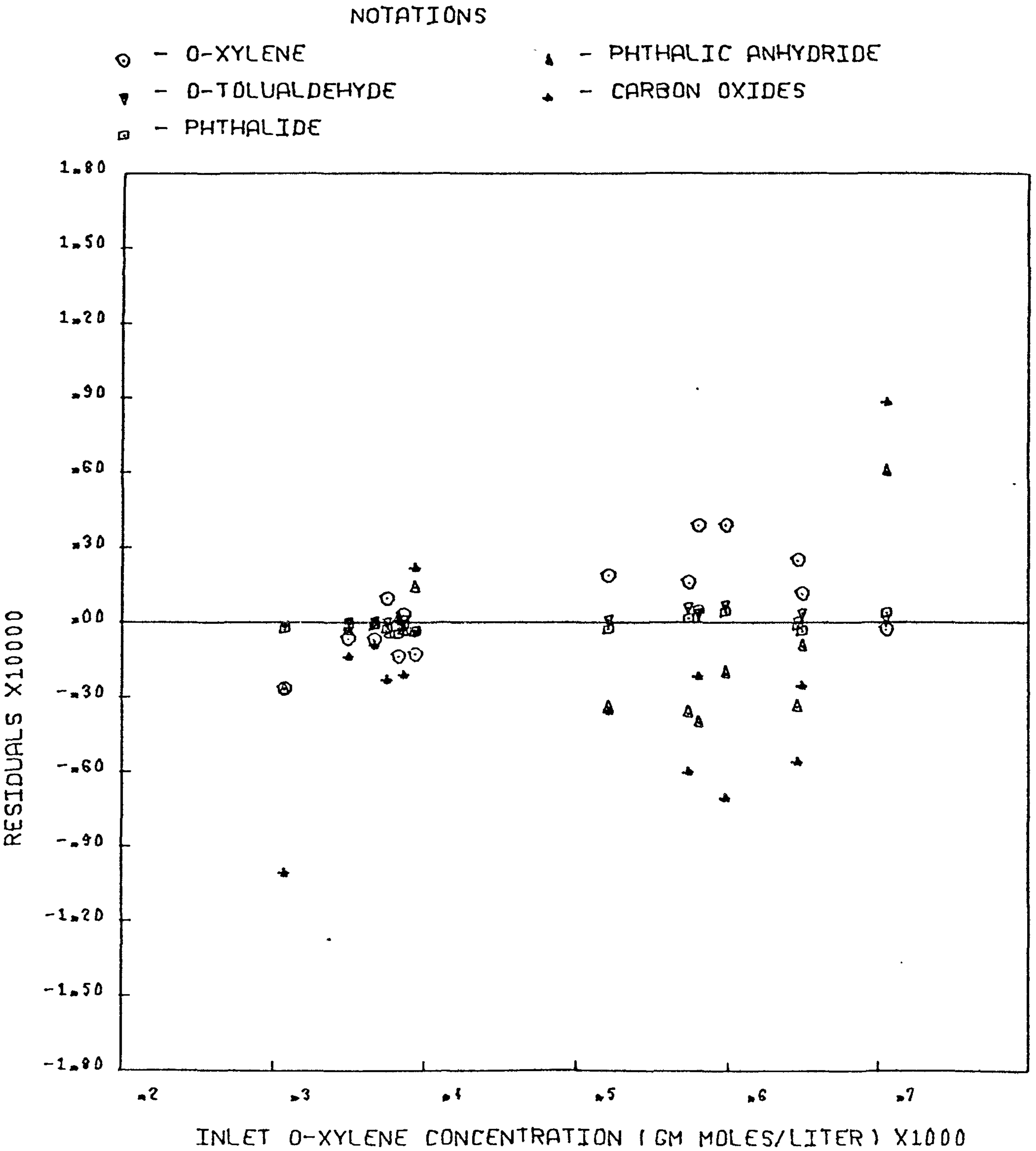

NOTATIONS
⊙ - O-XYLENE
▼ - O-TOLUALDEHYDE
▫ - PHTHALIDE
▲ - PHTHALIC ANHYDRIDE
+ - CARBON OXIDES
1.80
1.50
1.20
.90
.60
.30
.00
-.30
-.60
-.90
-1.20
-1.50
-1.80
.2
.3
.4
.5
.6
.7
RESIDUALS X10000
INLET O-XYLENE CONCENTRATION (GM MOLES/LITER) X1000

Figure 8.8

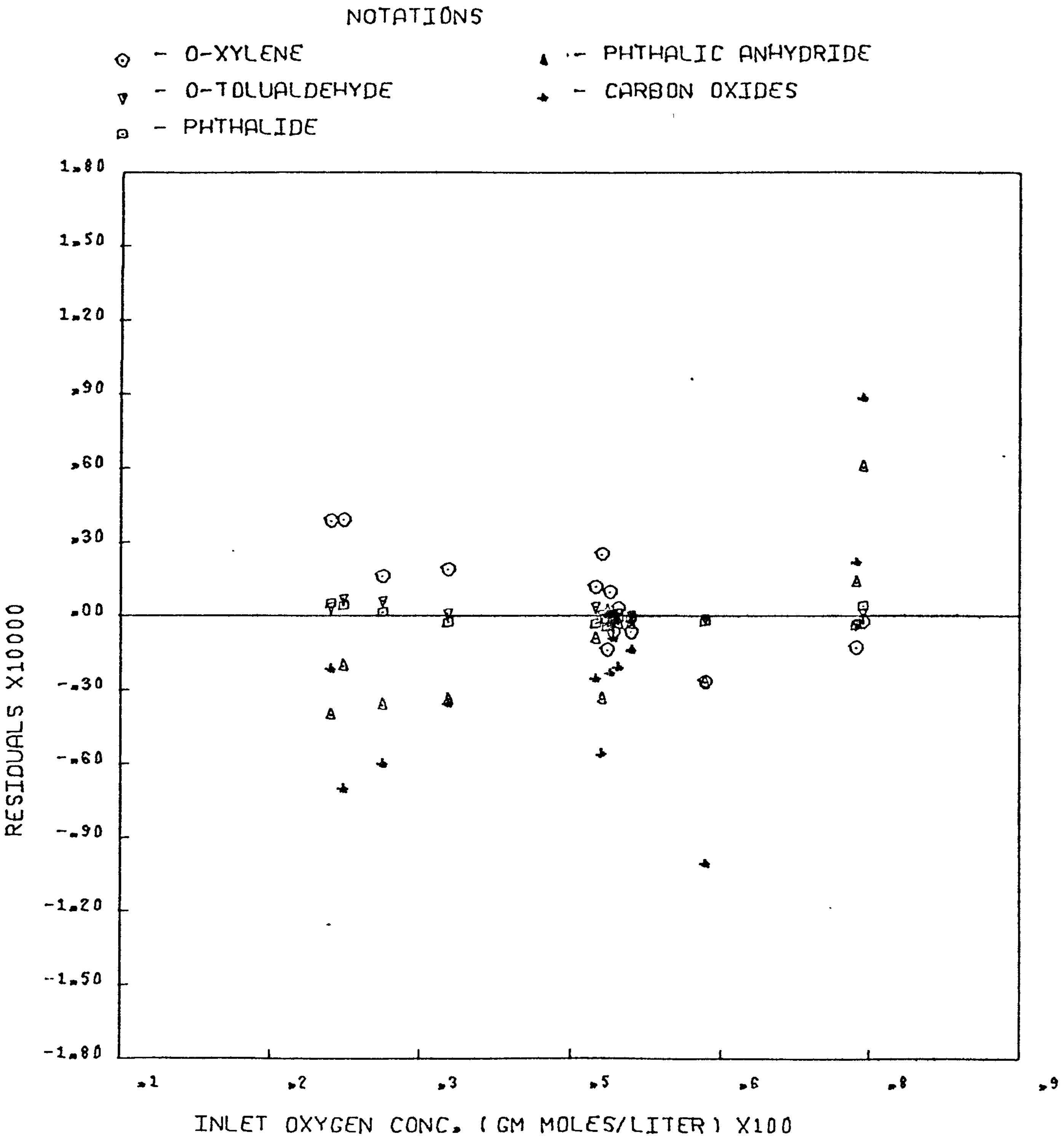

NOTATIONS
⊙ - O-XYLENE
▽ - O-TOLUALDEHYDE
⊡ - PHTHALIDE
▲ - PHTHALIC ANHYDRIDE
+ - CARBON OXIDES
1.80
1.50
1.20
.90
.60
.30
.00
-.30
-.60
-.90
-1.20
-1.50
-1.80
RESIDUALS X10000
.1
.2
.3
.5
.6
.8
.9
INLET OXYGEN CONC. (GM MOLES/LITER) X100

Figure 8.9

CHAPTER 9

DISCUSSION OF RESULTS

An active site parameter was included in the model to account for the loss of activity with temperature probably due to loss of SO_3 in the catalyst. This parameter was assumed to obey an exponential temperature dependency, as discussed in Section 7.1, and it may not model the thermal deactivation behaviour of the catalyst very accurately. It must be noted that precise estimates of the kinetic parameters can be obtained for the TiO_2 catalyst model only when the catalyst has been adequately modelled. It will be necessary, in the future, to design experiments primarily to model the thermal deactivation behaviour of the catalyst.

The paper of Vanhove and Blanchard (discussed in Section 2.3) represent the report of very few studies, in the literature, in which radioactive tracers have been used for defining the reaction paths involved in o-xylene oxidation on vanadium pentoxide catalyst supported on titanium dioxide. It is important to note that of the sophisticated approaches that have been applied to the establishing of reaction networks (or mechanisms) for complex reactions such as the one considered in the present study, the use of isotropic tracer techniques has been most useful in providing unambiguous answers. It was demonstrated in their work that phthalic anhydride is formed directly from o-tolualdehyde and phthalide. In the present study, phthalic anhydride was considered to be formed only from phthalide. In addition the assumption made that the formation of CO and CO_2 directly from the phthalic anhydride and phthalide was insignificant, may not be valid. It may be necessary to oxidize o-tolualdehyde, phthalide and phthalic anhydride independently, to determine the significance of several of the reaction steps not included in the model of section 6.1. The most probable models can be set up and the information derived from oxidizing these intermediates, for instance, the relative rate of formation of carbon oxides from o-tolualdehyde, phthalic anhydride and phthalide, the rate constants and the activation energies of the significant steps will be useful in planning future experiments for o-xylene oxidation, designed to discriminate among postulated models.

In addition Hughes and Adams [5] have observed that a lower oxidation catalyst increased the rate of oxidation of phthalic anhydride to CO_2 and CO and maleic anhydride. This suggests that sites of lower oxidation state in the catalyst, produced by partial oxidation of the aromatic compound, may be active for total oxidation. Perhaps, the rate of oxidation of o-xylene and o-tolualdehyde to CO/CO_2 is not dependent on ϕ(the oxygen active sites) but on $(1-\phi)$.

The results of the center point experiments conducted in this study demonstrates that no long term deactivation was apparent in the catalyst, within the period of steady experimentation lasting a total of fifty days. This finding suggests that even when experimental design techniques are applied to this catalyst, consistent data can be obtained. It must be noted that it has been demonstrated in [26] and [28] that some vanadia catalysts supported on silica gel exhibited long term decays that were dependent on the past temperature histories of the catalysts.

The temperature during the reoxidation period of the catalyst appears to determine the catalyst activity for the steady-state experiments. Wainwright[26] had attempted to stabilize the catalyst activity by reoxidizing the catalyst at temperatures of at least 20°C higher than that at which the steady-state experiments were to be conducted. In the present work, the reoxidation temperature of the catalyst was set equal to that at which the steady-state experiments were to be conducted. The resulting catalyst was higher in activity and more stable than that of Wainwright. It has also been demonstrated elsewhere [26, 28] that catalysts of different stability and activity can be produced depending on the heat treatment or the reoxidation temperature of the catalyst.

It has been demonstrated in this study (Section 5.3) that the amount of SO_2 introduced in the feedstream may not have been enough to maintain the original activity of the fresh catalyst. This suggests that the SO_2 in the feedstream may be increased to a level such that the SO_2 content of the catalyst during operation becomes equal to that of the original fresh catalyst. In this case, it is expected that a suitable catalyst of higher activity would result.

The ratio of the activity of the catalyst employed in the present study to that of the previous study was calculated to be 1.45 (see Section 5.2) as determined from the relative rates of reaction of the center point experiments. A value of 1.42 was estimated for the relative activity parameter, k_s by employing the statistical technique of Hoffman and Reilly [124] to transfer information from the previous experiment to that considered in this study. This demonstrates the effectiveness of this technique.

At a constant o-xylene saturator bath temperature and gas flowrate, the o-xylene concentration in the feed was observed to vary. This variation did not enable accurate control of the o-xylene concentrations in the feed.

Thus true replicate measurements could not be obtained and this resulted in an inflated estimate of the covariance matrix of the responses. It is important to note that true replicates are necessary for the accurate estimation of the covariance matrix which is necessary for testing for lack of fit in the model under consideration.

CHAPTER 10

CONCLUSIONS AND CONTRIBUTION TO KNOWLEDGE

10.1 Contribution to Knowledge

1) A new chromatographic technique has been developed and applied successfully in this work.
2) This study has demonstrated the use of statistical techniques in reaction kinetics, - the following were demonstrated:
    i) Design of experiments for parameter estimation;
    ii) The use of Box et al. [45] technique for determining the existence of linear relationships among the data;
    iii) The application of the Hoffman and Reilley [124] technique for transferring information to a catalytic system when catalyst activity changes.
3) Useful information concerning the reaction model and the catalyst activity have been obtained in this study.
4) The proposed reaction model (Wainwright's model) discussed in Chapter 5 was found inadequate and recommendation for future work is discussed in Section 10.3.

10.2 Conclusions

This study has demonstrated that the reaction model, for o-xylene oxidation on vanadium pentoxide catalyst supported on titanium dioxide, considered in this study is inadequate.

However, useful information has been obtained in this study and recommendations have also been made that will be helpful in planning future studies to develop more suitable reaction models.

10.3 Recommendation for Future Work

Further attempt to elucidate the reaction network should include the oxidation of the intermediate compounds as discussed in Chapter 9. Probable reaction models should be set up and the statistical techniques of experimental design for model discrimination should be employed to develop a suitable kinetic model. The use of the Hoffman and Reilly [124] parameter estimation technique has been applied successfully in this work; also suitable computer programs for applying this technique in the current work have been developed. These together with the data gathered in this study may be of some use in obtaining precise parameter estimates when a suitable model has been developed.

Further studies need to be conducted to contribute more understanding to the catalyst behaviour. In particular, experiments should be designed primarily to model the thermal deactivation of the catalyst.

Further work on the development of a suitable reaction model will require accurate control of o-xylene in the feed. Results of tests carried out on the o-xylene saturator indicated that the reactant gas was not saturated with o-xylene at the operating bath temperature. It is suggested that the height of the saturator be increased to allow saturation of the gas with o-xylene.

The hot air guns (12A, 120V) used for heating the sample valve compartment to prevent the condensation of the product material were not suitable for continuous operation as required in this study. These heaters often developed electrical noises which interfered with the voltage signals from the gas chromatograph. Accurate interpretation of peak areas from the chromatograph by the integrator could not be made under such conditions. Hence these heaters had to be replaced very often. It is important that future work employs stronger, industrial type air guns.

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APPENDIX A

Equipment Specification

Gas chromatographic technique

1. Gas chromatograph

Manufacturer : Varian Aerograph
Model : 1520
Features : Matrix temperature programmer
Detector : Thermal Conductivity
Filaments : Rhenium Tungsten (WX)

2. Integrator

Manufacturer : Hewlett Packard
Model : 3370B

3. Recorder

Manufacturer : Johns Scientific
Model : 291/MM

4. Gas Sample Valves

Manufacturer : Carle Instrument Inc.
Type : Micro volume switching valve with zero dead volume
Catalogue No. : 2014

Chemicals-Liquid and Solid Components

1. Orthoxylene
Analytical and packed bed reactor

Manufacturer : Matheson, Coleman and Bell
Catalogue No. : XX17
Grade : Chromatographic quality purity: 99+%

2. Orthotolualdehyde

Manufacturer : Aldrich Chem. Co.
Catalogue No. : 11,755-2
Purity : Gas chromatographic

3. Phthalic Anhydride

Manufacturer : J.T. Baker and Co.
Catalogue No. : 0272
Purity : Analytical

4. Phthalide

Manufacturer : Fisher Scientific Co.
Catalogue No. : 17827
Purity : Laboratory grade

5. Dioxane

Manufacturer : Fisher Scientific Co.
Catalogue No. : D-111
Purity : Laboratory grade

6. Trichloro-ethylene

Manufacturer : J.T. Baker

Electric heaters

1. Air gun heater

Manufacturer : W.J. West Away Co. Ltd.
Catalogue No. : HAS-018K

2. Immersion heater

Manufacturer : VYCOR (120V, 500W)
Catalogue No. : 745601-7950

3. Refractory heater

Manufacturer : Fisher Scientific Co. Ltd.
Catalogue No. : 11-463-0100B

4. Reactor salt bath heater

Manufacturer : Canadian Chromalox Co. Ltd.
Catalogue No. : 13045

5. Reactor exit block heater

Manufacturer : Canadian Chromalox Co. Ltd.
Catalogue No. : C-202

6. Electrothermal heating tape

   Manufacturer : Fisher Scientific Co. Ltd.
   Catalogue No. : HT 351

Gases

1. Helium: Canadian Liquid Air Limited
2. High Purity Nitrogen: Canadian Liquid Air Limited
3. Oxygen: Canadian Liquid Air Limited
4. Carbon dioxide: Canadian Liquid Air Limited
5. Carbon monoxide: Canadian Liquid Air Limited
6. Sulphur dioxide (0.5%), Nitrogen (99.5%) - Calibrated standard. Matheson of Canada.

APPENDIX B

LISTINGS OF COMPUTER PROGRAMS

PROGRAM NO 1:

The following program converts raw chromatographic peak area data into experimental inlet and outlet concentration and to punch data for parameter estimation programs.

```
      PROGRAM TST(INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C      FOLLOWING IS A PROGRAM TO CONVERT RAW DATA INTO EXPERIMENTAL
C      INLET AND OUTLET CONCENTRATIONS AND TO PUNCH DATA FOR PARAMETER
C      ESTIMATION AND EXPERIMENTAL DESIGN PROGRAMS.
C      ****************************************************************
C                    PHTHALIC ANHYDRIDE REACTOR MODEL.
C                   STEADY STATE ADSORPTION MODEL.
C                    O-XYLENE OXIDATION REACTION DATA
C      *****************************************************************
C      TOXA-ABSOLUTE TEMP (K)
C      TOX-TEMPERATURE OF O-XYLENE SATURATOR (C)
C      FO2-FLOWRATE OF OXYGEN CC/MIN.
C      FN2- FLOWRATE OF NITROGEN CC/MIN.
C      TA-TAMB+273.2
C      PAMB-ABSOLUTE PRESSURE AT WHICH FO2,FN2, ARE MEASURED, MM.HG.
C      TAMB-TEMPERATURE AT WHICH  FO2, FN2 ARE MEASURED
C      KRUN-EXPERIMENT RUN NUMBER
C      A,B-CONSTANTS IN OXYLENE VAPOUR PRESSURE CORRELATION
C      VPOX-VAPOUR PRESSURE OF OXYLENE
C      O2,N2,OX,-FLOWRATES IN MOLES /MIN.
C      YO2,YN2,YOX-MOLE FRACTIONS
C      TR,PR,-TEMP(C),ABSOLUTE PRESSURE AT REACTOR INLET
C      COX,CO2,CN2-CONCENTRATIONS OF COMPONENTS (GM MOLES/LITER)
C      Y-CONCENTRATIONS IN MERSON SUBROUTINE (GM.MOLE/LITER)
C       FR-MOLE FRACTION OF EXIT
C       YE-EXPERIMENTAL EXIT CONCENTRATION (GM. MOLES/LITER)
C       AI-AREA OF INLET ANALYSIS
C       AO-AREA OF OUTLET ANALYSIS
C       RM-RELATIVE RESPONSE
C       RA-RATIO
C      1,2,3,4,5,6,7,8,9-OX,OTA,PI,PA,CO2,O2,N2,H2O,CO RESPECTIVELY
C      10 IS MAA FOR  TIO2-SUPPORTED CATALYST
C      W-WEIGHT OF CATALYST, GRAMS
C      DELP-PRESSURE DROP ACROSS REACTOR ,MM. HG.
C      PT- TOTAL ABSOLUTE PRESSURE IN REACTOR,MM.HG.
C      NN IS STOICHIOMETRIC COEFFICIENT FOR CARBON OXIDE FORMATION
C      MODIFY THIS EXPRESSION ACCORDINLY IF OTHER COMPOUNDS ARE TO BE  LUMPED
C
C
C
C
C      *****************************************************************
       DIMENSION Y(10)
       DIMENSION ARRAY(25,25)
       DIMENSION RM(10),AI(10),AO(10),RA(10),YE(10),FR(10)
C
       REAL NN,N2
C      RELATIVE MOLAR  RESPONSES FOR ALL COMPONENTS
C
       DATA RM/3.04,3.19,3.28,3.34,1.20,0.97,1.0,2.57,1.06,1.6/
C      NNEXP-EXPERIMENT SET NUMBER.
C      NSET IS THE NUMBER OF DIFFERENT REACTION CONDITIONS
       READ(5,997) NNEXP
       READ(5,997)NSETS
       DO 5000 KKK=1,NSETS
C
C
```

```
C       ZERO STORAGE ARRAY -ARRAY(I,J)
        DO 11 I=1,25
        DO 11  J=1,25
        ARRAY(I,J)=0.
     11 CONTINUE
C
        READ(5,997) KRUN
        READ(5,800) TAMB,PAMB,TOX,FO2,FN2,TR,PR,DELP,W
        READ(5,800) AI(1),AI(6),AI(7)
C       READ ANALYSIS DATA
C       CALCULATE CONCENTRATIONS AND VOLUMETRIC FLOWRATE INTO REACTOR
C       FLOWS IN MOLES /UNIT TIME
        TA=TAMB+273.2
        DEN=22400.*TA*760./(273.2*PAMB)
        O2=FO2/DEN
        N2=FN2/DEN
C       REACTOR EXPERIMENTAL CONDITIONS
        GRADP=DELP/W
        PT=PR
C       CALCULATE MOLE FRACTION OF O-XYLENE
        RA(1)=(AI(1)/AI(7))*(RM(7)/RM(1))
        RA(6)=(AI(6)/AI(7))*(RM(7)/RM(6))
        YOX=RA(1)/(1.+RA(1)+RA(6))
        RAA=RA(1)
        RAD=RA(6)
        OX=(O2+N2)*YOX/(1.-YOX)
        T=TR+273.2
        FGAS=(O2+N2+OX)*22400.*T*760./(273.2*PR)

C       CALCULATE CONCENTRATIONS IN REACTOR  IN MOLES/CC.
        COX=OX/FGAS
        CO2=O2/FGAS
        CN2=N2/FGAS
        WRITE(6,998) NNEXP,KRUN
        WRITE(6,554)
        WRITE(6,558)
        WRITE(6,555) AI(1),AI(6),AI(7)
        WRITE(6,988) TOX,FO2,FN2,TAMB,PAMB,FGAS
        WRITE(6,996)TR,PR,W,DELP
        FAC=OX*60.
        WFAO=W/FAC
        A=9998.5
        B=8.147551
        VPOX =10.0**(((-0.2185*A)/(273.2 +TOX))+B)
C       NDA IS THE NUMBER OF EXIT ANALYSIS CONDUCTED AT EACH EXPERIMENTAL COND.
        READ(5,997)NDA
        DO 300 III=1,NDA
        READ(5,240) TIME
        READ(5,800) (AO(I),I=1,10)
        WRITE(6,557)
        WRITE(6,560)
        WRITE(6,556) (AO(I),I=1,10)
    556 FORMAT(10F12.2)
C       CALCULATE EXPERIMENTAL EXIT CONCENTRATION
        DO 801 I=1,10
    801 RA(I)=(AO(I)/AO(7))*(RM(7)/RM(I))
C       CALCULATE WATER RESPONSE
```

```
      RH20=RA(2)+RA(3)*2. +RA(4)*3. +(RA(5)+RA(9))*5./8.+RA(10)*1.5
C     CALCULATE OXYGEN RESPONSE
      RAC=RA(2)+RA(3)*2.+RA(4)*3. +RA(5)*10.5/8.0+RA(9)*6.5/8.0 +RA(10)*
     11.5
C     CALCULATE OVERALL STOICHIOMETRIC COEFFICIENT
      CSN=(RAD-RA(6))/(RAA-RA(1))
C     CALCULATE OXYGEN BALANCE (STOICHIOMETRIC O2 OUT-MEASURED O2 OUT)
      OB=(RAD-RAC)/RA(6)
      COU=(RAD-RA(6))/RAC
C     CALCULATE STOICHIOMETRIC NUMBER FOR CARBON OXIDES FORMED
      NN=((RA(5)*10.5)+(RA(9)*6.5))/(RA(5)+RA(9))
C     WATER RESPONSE RATIO (OBSERVED VALUE/CALCULATED VALUE)
      WRR=RA(8)/RH20
C     CARBON BALANCE
      RAB=RA(1)+RA(2)+RA(3)+RA(4)+(RA(5)+RA(9))/8.+RA(10)
     1*0.5
      CBR=RAB/RAA
C     HYDROGEN BALANCE
      RHB=RA(1)+RA(2)*4.0/5.0 +RA(3)*3.0/5.0 +RA(4)*2.0/5.0 +RA(8)/4.0 +
     1RA(10)/4.0
      HBR=RHB/RAA
C     CALCULATE CONVERSION AND SELECTIVITIES
      CONV=RAB-RA(1)
      YIELD=CONV/RAB
      SOTA=RA(2)/CONV
      SPI=RA(3)/CONV
      SPAA=RA(4)/CONV
      SCO2=RA(5)/(CONV*8.)
      SCO =RA(9)/(CONV*8.)
      SMAA=RA(10)/CONV
      SUM=0.0
C
C
      DO 820 I=1,10
  820 SUM=SUM+RA(I)
      POUT=PR-DELP
      CONS=273.2*POUT/(22.400*760.*T)
      DO 803 I=1,10
      FR(I)=RA(I)/SUM
  803 YE(I)=FR(I)*CONS
C     SET CONCENTRATIONS FOR INTERGRATION
C     CONCENTRATIONS IN GM-MOLES/LITER
C
C
      FGASS=FGAS*1.0E-03
      WRITE(6,975) VFOX,YOX
      Y(1)=COX*1.0E 03
      Y(2)=0.
      Y(3)=0.
      Y(4)=0.
      Y(5)=0.
      Y(6)=CO2*1.0E 03
      Y(7)=CN2*1.0E 03
      Y(8)=0.
      Y(9)=0.
      Y(10)=0.
C     GAS FLOWRATE (LITERS/SEC)
```

```
      FGASS=FGASS/60.
      WRITE(6,976) Y(1),Y(6),Y(7)
      DO 5 I=1,9
      ARRAY(I,J)=Y(I)
    5 CONTINUE
      DO 6 K=10,18
      II=K-9
      ARRAY(K,J)=YE(II)
    6 CONTINUE
C     ADD CO AND CO2 CONCENTRATIONS FOR USE IN PARAMETER ESTIMATION
      ARRAY(14,J)=ARRAY(14,J)+ARRAY(18,J)
      ARRAY(19,J)=T
      ARRAY(20,J)=DELP
      ARRAY(21,J)=W
      ARRAY(22,J)=PT
      ARRAY(23,J)=FGASS
      ARRAY(24,J)=GRADP
      WRITE(6,222)
      WRITE(6,231)
      WRITE(6,811) YIELD,SOTA,SPI,SPAA,SCO2,SCO,SMAA
      WRITE(6,226)WFAO
      WRITE(6,812)CBR
      WRITE(6,913) WRR
      WRITE(6,912) HBR
      WRITE(6,223)
      WRITE(6,999) OB,NN,CSN,COU
      WRITE(6,810)
      WRITE(6,230)
      WRITE(6,811)(YE(I),I=1,10)
      WRITE(6,224)
      WRITE(6,230)
      WRITE(6,811)  (FR(I),I=1,10)
      WRITE(6,232)
      WRITE(6,233)  (ARRAY(I,J),I=1,24)
      RRATE=YIELD/WFAO
      WRITE(6,261)  RRATE
C     PUNCH DATA FOR PARAMETER ESTIMATION AND EXPERIMENTAL DESIGN PROGRAMS
      WRITE(7,234)  KRUN,NN
      WRITE(6,432)  KRUN,NN
      WRITE(7,233)  (ARRAY(I,J),I=1,24)
      WRITE(6,77) TIME
    4 CONTINUE
    8 CONTINUE
    3 CONTINUE
      WRITE(6,291)
  300 CONTINUE
 5000 CONTINUE
  997 FORMAT(I3)
  240 FORMAT(F10.5)
  998 FORMAT(1H1,10X, *EXPT. SET NO. * I3, 10X,*RUN NUMBER *I3//)
  988 FORMAT( *  TEMPERATURE OF C-XYLENE  SATURATOR = *F6.1*DEG.C.*//
     1 * OXYGEN  FLOWRATE = *  F6.2 *CC/MIN.*/
     2 * NITROGEN FLOWRATE = * F6.2 * CC/MIN*//
     3 * AMBIENT TEMPERATURE = * F6.1 * DEG.C.*/
     4 * AMBIENT PRESSURE=* F7.1 *MM.HG.*//
     5 * TOTAL FLOWRATE AT REACTOR TEMPERATURE AND PRESSURE = *F7.2
     6 * CC/MIN *)
```

```
         996 FORMAT(* REACTOR TEMPERATURE = *F8.2 * DEG.C.*/
            1 * REACTOR PRESSURE = * F8.2 * MM.HG.*/
            2 * WEIGHT OF CATALYST = * F8.2                  /
            3 * PRESSURE DROP ACROSS REACTOR = * F6.1 * MM.HG.*/)
         975 FORMAT(/ * VAPCUR PRESSURE OF  O-XYLENE = *F5.2 *MM.HG.*/
            1 * MCLE FRACTICN OF O-XYLENE = *F7.5 /)
         976 FORMAT( * INLET CONCENTRATION =*/,10X*O-XYLENE= *E9.3*GM.MOLE /
            1CC.*   /  10X * OXYGEN   = * E9.3 * GM.MOLE/CC.* / 10X
            2  *NITROGEN = * E9.3  * GM.MOLE/CC.*/)
         810 FORMAT(* EXPERIMENTAL EXIT CONCENTRATION (GM.MCLES/LITER) */)
         230 FORMAT(8X,*OX*, 10X,*OTA*, 11X,*PI*, 11X,*PA*,10X,*CO2*,11X,*O2*,
            111X,*N2*,10X,*H2O*,11X,*CO*,11X,*MAA*)
         231 FORMAT(8X,*OX*,10X,*OTA*,11X,*PI*,11X,*PA*,6X,*CO2*,11X,*CO*,11X,*
            1MAA*)
         232 FORMAT(/,*  ARRAY(I,J)-DATA FOR ESTIMATICN AND DESIGN PROGRAMS*/)
         233 FORMAT(8E10.4)
         234 FORMAT(I3,5X,3F8.4)
         999 FORMAT(5F15.5)
         800 FORMAT(10F8.0)
         811 FORMAT(10E13.3)
         222 FORMAT(1X,*CONVERSION AN( SELECTIVITIES *)
         223 FORMAT(1X,*OXYGEN BALANCES*)
         224 FORMAT(1X,*EXPERIMENTAL EXIT MOLE FRACTIONS*)
         995 FORMAT(5E15.5)
         812 FORMAT(/* CARBCN BALANCE RATIO = * E10.3/)
         597 FORMAT(/,20X,* NUMBER OF PARAMETERS * I3)
         599 FORMAT(1H1,20X,* NUMBER CF EXPERIMENTS *I3//)
         912 FORMAT(/,*  HYCROGEN BALANCE RATIO= *E10.3)
         913 FORMAT(/,*  WATER RESPCNSE RATIO=* E10.3)
         226 FORMAT(1X,*W/FAO = *,F8.3)
         261 FORMAT(1X,*RATE OF XYLENE CONVERSION = *,E10.4,1X,*GM MOLE /GM HR
            1*)
          77 FORMAT (6X,/,*  ON  STREAM  TIME  =*F10.2 *SECS.*)
         432 FORMAT(/,6X,*KRUN=*I3,5X,*NN=*F8.4)
         291 FORMAT(*1*)
         557 FORMAT(2X, * OUTLET PEAK AREAS ARE /*)
         560 FORMAT(3X,*OX*,13X,*OTA*,12X,*PI*,10X,*PAA*,9X,*CO2*,9X,*O2*,10X,*
            1N2*,10X,*H2O*,10X,*CO*,10X,*MAA*)
         555 FORMAT(3F12.2)
         554 FORMAT(2X,*INLET PEAK AREAS ARE /*)
         558 FORMAT(3X,*OX*,13X,*O2*,13X,*N2*)
           7 CALL EXIT
             END

ITS--

    3B   INPUT=                43B   OUTPUT=                103B   PUNCH=                3B   TAPE5=
   43B   TAPE6=               103B   TAPE7=                 154B   TST

--

       END.     EXIT     FTNRPV.    INPCI.    INPCR.    OUTCI.    OUTCR.    XTOY.
```

PROGRAM NO. 2:

Program for the statistical design of experiments for parameter estimation.

```
ATTACH,IMSLIB.
ATTACH,MACLIB.
ATTACH,SSPLIB.
FTN(ROUND=*/+-,OPT=2,T,R=3)
LDSET(LIB=IMSLIB)
LDSET(LIB=MACLIB)
LDSET(LIB=SSPLIE)
LGO(PL=8000)
      PROGRAM TST(INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C     **********PROGRAM  FOR  THE  EXPERIMENTAL  DESIGN  *********≠

C     *********TIO2  SUPPORTEC CATALYST -REACTION  MODEL***************C
C                -----------------------------------------------
C
C     ****USING THE MONTE-CARLO SEARCH TECHNIQUES  *********************
C
C
C     FIVE INDEPENDENT VARIABLES -FOX,FC2,FN2,TR,W
C     FCX-FLOWRATE OF OXYLENE IN CC/MIN
C     FO2 -FLCWRATE OF OXYGEN IN CC/MIN
C     FN2 -FLCWRATE OF NITROGEN IN CC/MIN
C     TR -TEMPERATURE  AT REACTOR INLET IN DEG. CENTIGRADE
C     TAMB,PAMB  -AMBIENT TEMPERATURE AND ABSOLUTE PRESSURE  AT WHICH
C     FO2,FN2 ARE MEASURED IN MM HG.
C     NP- NUMBER OF PARAMETERS
C     NEXP- NUMBEF OF EXPERIMENTS
C     THERE NF  NO. OF RUNS IN ONE EXPERIMENT
C     NR -NO OF INDEPENDENT  RESPONSES.
C     TBASE -BASE TEMPERATURE USED FOR REPARAMETERIZATION BY
C     HUNTER /ATKINSON  METHOD.
C     FGAS -TOTAL GAS FLOW  IN CC/MIN.
C     DELP -PRESSURE DROP IN REACTOR IN MM HG
C     SIGMA -ELEMENTS OF THE VARIANCE-COVARIANCE MATRIX.
C     O2, N2, OX -FLOWRATES IN MOLES /MIN.
C     COX, CO2, CN2 -CONCENTRATION  OF COMPONENTS IN GM MOLE /LITER.
C     DELF-PRESSURE DROP ACROSS REACTOR  IN  MM HG
C     PT -TOTAL ABSOLUTE PRESSURE  IN REACTOR IN  MM HG.
C     C0 ,C1 -ARE  CORRELATICN  COEFFICIENTS  OF  GRADP  EXPRESSED
C     AS  A  FUNCTION  OF  TOTAL  GAS  FLOWRATE  (FGAS)
C     NPRICR -NC OF PRIOR EXPERIMENTS AVAILABLE FCR DESIGN .
C
C
C
C
C
      COMMON/ PARA1/KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5
      COMMCN /PARA 3/EAS
      COMMON/ MER/ T,W,PT,GRADP
      COMMON/CONSTA/ PAMB,C0,C1,TAMB
      COMMON /CONST/NN,R,NEX,NP,NC
      DIMENSICN G(11,11)
      DIMENSICN AXTVX(11,11),BXTVX(11,11,11),CXTVX(11,11)
      DIMENSICN GVM(5),HVM(5)
      DIMENSICN SIGMA(5,5)
      CIMENSICN PP(11,11),PM(11,11)
      CIMENSICN SXTVX(11,11)
      DIMENSICN DXTVX(11,11,11)
      DIMENSION GXTVX(11,11)
```

```
      DIMENSICN ASYM(66),ALU(66)
      DIMENSICN FOX(11),FO2(11),FN2(11),TR(11)
      DIMENSICN SX1(11),SX2(11),SX3(11),SX4(11)
C
C
C
      REAL KAI,KR12I,KR34I,NN,KR5I,KR23I
C     READ INITIAL PARAMETER ESTIMATES -INITIAL ESTIMATES OF PRE
C     -EXPONENTIAL FACTORS ARE ALREADY REPARAMETERIZED BY HUNTER/
C     ATKINSON METHOD.
      REAC(5,13) NPICK
      READ(5,13) NPRIOR
      READ(5,35) C0,C1
      READ(5,1) KAI,KF12I,KR23I,KR34I,KR5I
      READ(5,2) EA,E12,E23,E34,E5,EAS
      READ(5,36)PT
      NR=5
      NF=11
      NEXP=11
      NSIG=5
C
C     READ  IN  EXPERIMENTAL  DATA
      READ(5,2) NN,TAMB,PAMB
      WRITE (6,17)
      READ(5,7) ((SIGMA(I,J),J=1,5),I=1,5)
      WRITE(6,77) ((SIGMA(I,J),J=1,5),I=1,5)
C
C     INVERT  THE  VARIANCE-COVARIANCE MATRIX.
      CALL MINV (SIGMA,NSIG,DISIG,GVM,HVM)
      WRITE(6,118)
      WRITE(6,77) ((SIGMA(I,J),J=1,5),I=1,5)
C
C
C     USE AVAILABLE PRIOR INFCRMATICN -IF ANY
      IF (NPRIOR .LT. 1) GO TO 50
      DO  49  K=1,NP
      CO  49 L=1,NP
      FP(K,L)=0.
   49 CONTINUE
      CO 39 I=1,NFRIOR
      WRITE (6,134) I
      WRITE(6,218) NPRIOR
      DO 39  M=1,NP
      READ(5,390) (PM(M,N),N=1,NP)
      WRITE(6,755)
      WRITE(6,570) (PM(M,N),N=1,NP)
      CO  39 K=1,NP
      PP(M,K)=PP(M,K)+PM(M,K)
   39 CONTINUE
      WRITE(6,2239)
      DO 812 M=1,NP
      WRITE(6,755)
      WRITE(6,570) (PP(M,N),N=1,NP)
  812 CONTINUE
   50 CONTINUE
C
C
      WRITE(6,51)
      WRITE(6,52) KAI,EA,KR12I,E12,KR23I,E23,KR34I,E34,KR5I,E5
      WRITE(6,81)EAS
```

```
      WRITE(6,681) PY
      WRITE(6,446) NPICK
      WRITE(6,731)
      WRITE(6,888)
C
      DO 131 LS=1,NP
      DO 131 KS=1,NP
      AXTVX(KS,LS) =0.
      GXTVX(KS,LS)=0.
  131 CONTINUE
C
C
C
C
      DO 61 I=1,NP
  101 CONTINUE
      FOX(I)=RANF(A)
      FO2(I)=RANF(A)
      FN2(I)=RANF(A)
      TR(I)=RANF(A)
      W=1.0
      FOX(I)=FOX(I)*11.0 +1.0
      FO2(I)=FO2(I)*110. +10.
      FN2(I)=FN2(I)*200. +(100. -(FOX(I)+FO2(I)))
      TR(I)=TR(I)*40.0  +350.0
      Z1=FOX(I)/(FN2(I)+FO2(I)+FOX(I))
      Z2=FO2(I)/(FN2(I)+FO2(I)+FOX(I))
      IF(Z1 .LT. 0.01 .OR . Z1 .GT. 0.03 ) GO TO 101
      IF(Z2 .LT. 0.10 .OR. Z2  .GT. 0.30 )GO TO 101
C     STORE THE INITIAL GUESS OF THE DESIGN EXPERIMENTS.
      SX1(I)=FOX(I)
      SX2(I)=FO2(I)
      SX3(I)=FN2(I)
      SX4(I)=TR(I)
      WRITE(6,470) I,SX1(I),SX2(I),SX3(I),SX4(I),W
      CALL MATRIZ(FOX,FO2,FN2,TR,    BXTVX(1,1,I),SIGMA,I)
   61 CONTINUE
C
C
C     USE AVAILABLE PRIOR INFORMATION -IF ANY
      IF (NPRIOR .LT. 1) GO TO 216
      DO   314 . IA=1,NP
      DO   314  JA=1,NP
      AXTVX(IA,JA)=AXTVX(IA,JA)+PP(IA,JA)
      GXTVX(IA,JA)=AXTVX(IA,JA)
  314 CONTINUE
  216 CONTINUE
C
C
C
      ZOMAX=0.
      DOMAX=0.
      DO 999  KT=1, NPICK
      MO=1
      MM=0
  100 CONTINUE
C     GENERATE EXPERIMENTAL RUNS BY THE USE OF RANDOM
C     NUMBERS IN THE RANGE 0.0 TO 1.0
      FOX(1)=RANF(A)
      FO2(1)=RANF(A)
```

```
      FN2(1)=RANF(A)
      TR(1)=RANF(A)
      FOX(1)=FOX(1)*11.0 +1.0
      FC2(1)=FO2(1)*110.0 +10.0
      FN2(1)=FN2(1)*200. +(100.-(FCX(1)+FO2(1)))
      TR(1)=TR(1)*40. +350.
      Z1=FOX(1)/(FN2(1)+FO2(1)+FOX(1))
      Z2=FC2(1)/(FN2(1)+FO2(1)+FOX(1))
      IF(Z1 .LT. 0.01 .OR . Z1 .GT. 0.03 ) GO TO 100
      IF(Z2 .LT. 0.10 .OR. Z2  .GT. 0.30 )GO TO 100
      CALL MATRIZ(FOX,FO2,FN2,TR, CXTVX,SIGMA,1)
      DO  14  M=1,NEXP
      DO 3 J=1,NP
      DO 3 K=1,NP
      DXTVX(J,K,MC)=BXTVX(J,K,MC)
      BXTVX(J,K,MC)=CXTVX(J,K)
      AXTVX(J,K)=GXTVX(J,K)
    3 CCNTINUE
C
      DC 339 I=1,NEXP
      DO 339 J=1,NP
      CC 339 K=1,NP
      AXTVX(J,K)=AXTVX(J,K)+BXTVX(J,K,I)
  339 CONTINUE
C
C     VCVTFS-STORAGE MODE CONVERSICN OF MATRICES
C     -FULL TO SYMMETRIC ,IMSL-LIBRARY.
      CALL VCVTFS(AXTVX,11,11,ASYM)
C     LUDECP-CALCULATES THE DETERMINANT OF A POSITIVE DEFINITE MATRIX
C     IN SYMMETRIC ST-RAGE MODE ,ISML-LIBRARY.
      CALL LUDECP(ASYM,ALU,11,D1,D2,IER)
      DET=D1*2**D2
      WRITE(6,2009) DET
 2009 FORMAT(6X,*D E T = * E15.5 )
      IF (DET.LE. DDMAX) GC TO 144
      DDMAX= DET
      MM=M
  144 CCNTINUE
      DC 4 J=1,NP
      DO 4 K=1,NP
      BXTVX(J,K,MC)=DXTVX(J,K,MC)
    4 CCNTINUE
      MC=MC+1
   14 CONTINUE
      WRITE(6,401) KT,MM,DDMAX
  401 FORMAT(≠0≠,6X,*KT=* I3,6X,*MM=* I3,6X, *DDMAX=*,E15.5 )
      IF (DDMAX .GT. ZDMAX) GO TO 34
      GC TO 999
   34 CCNTINUE
      ZDMAX=DDMAX
      SX1(MM)=FCX(1)
      SX2(MM)=FC2(1)
      SX3(MM)=FN2(1)
      SX4(MM)=TR(1)
      DC 388 I=1,NP
      DO 388 J=1,NP
      BXTVX(I,J,MM)=CXTVX(I,J)
  388 CCNTINUE
      DC 58 I=1,NP
      DO 58 J=1,NP
```

```
      SXTVX(I,J)=AXTVX(I,J)
   58 CONTINUE
      PRINT*,≠A  SET  OF  EXPERIMENT  HAS  BEEN  REPLACED  ≠
  999 CONTINUE
C
C
C
C
      WRITE(6,607)
  607 FORMAT(≠1≠,6X, *THE  BEST  SETTINGS  OF  THE  INDEPENDENT  */
     16X,*VARIABLES  ARE  AS  FOLLOW- *///)
      WRITE(6,888)
  888 FORMAT(14X,*FOX*8X*FO2*8X*FN2*8X*TR*10X * W* /)
      DO  474  I=1,NEXP
      WRITE(6,470)  I,SX1(I),SX2(I),SX3(I),SX4(I),W
  474 CONTINUE
  470 FORMAT(2X,I2,4X,5F12.5//)
      WRITE(6,569)
  569 FORMAT(≠1≠,6X, *THE  CRITERION  MATRIX  IS  *///)
      PRINT*,≠END≠
      DO 599 K=1,NP
      WRITE(6,755)
  755 FORMAT(/,15X, *-----------------------------------------------*)
      WRITE(6,1201)  (SXTVX(K,L),L=1,NP)
      WRITE(7,1201)  (SXTVX(K,L),L=1,NP)
 599  CONTINUE
  570 FORMAT(/,6X,5E15.5//)
      WRITE(6,579) ZDMAX
  579 FORMAT(//6X,*THE DETERMINANT OF THE -D MATRIX IS * E15.5 )
  118 FORMAT(///,20X, *THE  INVERSE VARIANCE -COVARIANCE MATRIX * ///)
    1 FORMAT(6E10.4)
    2 FORMAT(6F10.5)
    7 FORMAT(5E15.4)
   77 FORMAT(5E15.5//)
  9   FORMAT(7F10.5)
   13 FORMAT(I3)
   17 FORMAT(≠1≠,20X,* VARIANCE-COVARIANCE MATRIX*///)
   35 FORMAT(2F10.5)
   36 FORMAT(F10.5)
  390 FORMAT(5E15.5)
  134 FORMAT(≠1≠, 6X, *N P R I O R  =  * I3 //)
  681 FORMAT(///2X,*THE TOTAL PRESSURE IN THE REACTOR IS  * F12.5 )
 2239 FORMAT(///,6X,* PRIOR MATRIX FOR ALL THE  SETS OF EXPTS PERFORMED*
     1)
  218 FORMAT(//,6X, * PRIOR MATRIX FOR EXPT NO. * I2)
  731 FORMAT(≠1≠,////,6X, *THIS EXPERIMENT WILL BE REPLACED BY THE *//6X
     1*DESIGN EXPERIMENT THAT MAXIMIZES THE  -D MATRIX *///)
   81 FORMAT(6X, * ACTIVE SITE PARAMETER = *6X, E13.4)
   51 FORMAT(////////21X,*FREGUENCY FACTORS*6X* ACTIVATION ENERGIES*//)
   52 FORMAT(*   ADSORPTION      *,5X,*  KAI= *,E11.4,7X,* EA= *,F14.4//
     1*   OXYLENE-OTA   *6X,*KR12I= *,E11.4,7X,*E12= *,F14.4//
     2*   OTA-PI        *6X,*KR23I= *,E11.4,7X,*E23= *,F14.4//
     5*     PI- PA      *6X,*KR34I= *,E11.4, 7X, *E34= *,F14.4 //
     4*   ORGANICS-CO2 *6X,* KR5I= *,E11.4 ,7X,* E5= *,F14.4//)
  446 FORMAT(////,6X,*NPICK=*,I3)
 1200 FORMAT(6X, *AXTVX  *)
 1201 FORMAT(4X,11E12.4)
 1203 FORMAT(6X,*ZDMAX=* E15.5 )
      STOP
      END
```

```
      SUBROUTINE MATRIZ (FOX,FO2,FN2,TR,BXTVX,SIGMA,KK)
      COMMON/ PARA1/KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5
      COMMON /PARA 3/FAS
      COMMON/CONSTA/ PAMB,C0,C1,TAMB
      COMMON/CONST/NN,R,NEX,NF,NC
      COMMON/STRAY/ARRAY
      COMMON/REFAR/TBASE,RT
      COMMON/ DER/ FGAS
      COMMON/DEP/YY
      COMMON /MER/T,WWW,PT,GRACP
      DIMENSION  ARRAY(25,50),Y0(10),P0(15),Y(10),YY(10)
      DIMENSION XTVX(11,11),XTSIG(11,5),BXTVX(11,11),SIGMA(5,5)
      DIMENSION DELTA(11,11)
      DIMENSION FOX(11),FO2(11),FN2(11),TR(11)
      DIMENSION XT(11,5),XM(5,11)
      REAL  KAI,KR12I,KR34I,NN,KR5I,KR23I,N2
C
C
C
C
C
      NEXP=11
      NR=5
      W=WWW
C
C     CALCULATE FLOWRATE OF C2 AND N2 ALSO GAS FLOWRATE AT REACTOR
C     CONDITIONS IN CC/MIN
      PR=PT
      TA=TAMB+273.2
      DEN=22400.* TA*760./(273.2*PAMB)
      O2=FO2(KK)/DEN
      N2=FN2(KK)/DEN
      T=TR(KK)+273.2
      YOX=FOX(KK)/(FN2(KK)+FO2(KK)+FOX(KK))
      OX=(O2+N2)*YOX/(1-YOX)
      FGAS=(O2+N2+OX)*22400. *T*760./(273.2*PR)
C     CALCULATE CONCENTRATIONS IN REACTOR IN MOLES/CC
      COX=OX/FGAS
      CO2=O2/FGAS
      CN2=N2/FGAS
C     SET CONCENTRATIONS IN GM -MOLES/LITER
      FGAS=FGAS*1.0E-03
      Y(1)=COX*1.0E 03
      Y(2)=0.0
      Y(3)=0.
      Y(4)=0.
      Y(5)=0.
      Y(6)=CO2*1.0E 03
      Y(7)=CN2*1.0E 03
      Y(8)=0.
      Y(9)=0.
      Y(10)=0.
C     EXPRESS  GAS FLOWRATE IN LITERS /SEC
C
      FGAS=FGAS/60.
      GRADP=C0+FGAS*C1
C
      TBASE=370.0
```

```
      TBASE=TBASE+273.2
      R=-1.9872
      TSTAR=(TBASE-T)/(TBASE*T)
      RT=TSTAR/R
C     SET UP TCLERANCES,STEF LENGTH,BOUNDARY CONDITIONS
C     FOR  INTERGRATION.
      X=0.
      DX=0.005
      TOLKM=1.0E-08
      DXMIN=0.0C01
      N=5
      CELX=W
      P0(1)=KAI
      P0(2)=KR12I
      P0(3)=KR23I
      P0(4)=KR34I
      P0(5)=KR5I
      P0(6)=EA
      P0(7)=E12
      P0(8)=E23
      P0(9)=E34
      P0(10)=E5
      P0(11)=EAS
      CO 182 I=1,10
  182 YY(I)=Y(I)
      CALL MERSCN(X,DELX,DX,DXMIN,TOLKM,N,P0)
      Y0(1)=YY(1)
      Y0(2)=YY(2)
      Y0(3)=YY(3)
      Y0(4)=YY(4)
      Y0(5)=YY(5)
C
C
C
C     SET UP THE  (DIFFERENTIAL )  X-MATRIX
      DELTAP=1.0 E-05
      DO   18   J=1,NP
      PS=P0(J)
      P0(J)=P0(J)+DELTAP*P0(J)
      CC 172 I=1,10
  172 YY(I)=Y(I)
      CX=0.005
      X=0.
      CALL MERSCN(X,DELX,DX,DXMIN,TOLKM,N,P0)
      Y(1)=YY(1)
      Y(2)=YY(2)
      Y(3)=YY(3)
      Y(4)=YY(4)
      Y(5)=YY(5)
      DC   18   K=1,NR
      DELTA(K,J)=(YY(K)-Y((K))/(DELTAP*PS)
      P0(J)=PS
   18 CONTINUE
C
C
C
C     SET UP CETERMINANT FOR EXPTAL DESIGN CRITERION.
      DO   91   J=1,NR
      CO   16   K=1,NP
      XT(K,J)=DELTA(J,K)
```

```
      XM(J,K)=DELTA(J,K)
   16 CONTINUE
   91 CONTINUE
C     GMPRD -GENERAL MATRIX PRODUCT ROUTINE -  SSP LIBRARY
      CALL GMPRD(XT,SIGMA,XTSIG,NP,NR,NR)
      CALL  GMPRD(XTSIG,XM,XTVX,NP,NR,NP)
C     COMPUTE THE XTVX- MATRIX FOR ONE EXPERIMENTS.
      DO 151 IA=1,NP
      DO 151 JA=1,NP
      BXTVX(IA,JA)=XTVX(IA,JA)
  151 CONTINUE
      RETURN
      END


      SUBROUTINE MERSON (X,DELX,DX,DXMIN,TOLKM,N,P0)
C     INTEGRATES FROM X TO (X+DELX)
C     DX IS ESTIMATE FOR INTEGRATION STEP NECESSARY
C     DXMIN IS MINIMUM STEP LENGTH TO BE PERMITTED
C     TOLKM IS REQUIRED ACCURACY
C     N IS NUMBER OF DEPENDENT VARIABLES
C     CONTROL TRANSFERRED TO FIRST LABEL IF INTEGRATION FALLS,X AND Y(I)
C     THEN CONTAIN NEW VALUES
C     CONTROL TRANSFERRED TO SECOND LABEL IF INTEGRATION FAILS, X AND
C     Y(I) THEN CONTAIN MOST RECENT CORRECT VALUES
C     IN EITHER CASE, DX CONTAINS CURRENT STEP LENGTH
      COMMON/ PARA1/KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5
      COMMON /PARA 3/EAS
      COMMON/CEP/Y
      COMMON/GRAD/DY
      COMMON/CONST/NN,R,NEX,NP,NC
      COMMON/MER/ T,W,PPTT,GRADP
      COMMON/ DER/ FFGAS
      COMMON/ERROR/ERR
      COMMON/REPAR/TBASE,RT
      DIMENSION Y(10),YOLD(10),FK(5,10),DY(10)
      DIMENSION P0(12)
      REAL  KAI,KR12I,KR34I,NN,KR5I,KR23I,N2
C
C
      FGAS=FFGAS
      PT=PPTT
      KAI=P0(1)
      KR12I=P0(2)
      KR23I=P0(3)
      KR34I=P0(4)
      KR5I=P0(5)
      EA=P0(6)
      E12=P0(7)
      E23=P0(8)
      E34=P0(9)
      E5=P0(10)
      EAS=P0(11)
      ISW=0
      XMAX=W
      TOLA=5.*TOLKM
      FINTS=DELX/DX+0.5
      TOLB=TOLA/32.
      INTS=FINTS
      IF(INTS.LT.1)INTS=1
```

```
      DX=DELX/INTS
      FMULT=DX/3.
      GO TO 4
C     ERROR CHECK
    1 IF(ERR.GT.TOLA) GO TO 20
      IF(ERR.LT.TOLB) GO TO 21
C     INTEGRATION SATISFACTORY, CALCULATE NEW POINTS
C     ----------------------------------------------------------------------
C     *****THE NEXT 17 CARDS ARE NOT PART OF THE STANDARD MERSON  *******
C     ***** THEY CALCULATE THE VOLUME CHANGE DUE TO REACTION ****************
    3 DO 2 I=1,N
    2 Y(I)=YOLD(I)+0.5*FK(1,I)+2.0*FK(4,I) +0.5*FK(5,I)
      IF(Y(1) .LE. 0.0 ) Y(1)=0.0
      IF(Y(2) .LE. 0.0 ) Y(2)=0.0
C     OXYGEN BALANCE-- OXYGEN TO CO2 AND  H2O
      Y(6)=YOLD(6)-(Y(2)-YOLD(2))-(Y(3)-YOLD(3))*2. -(Y(4)-YOLD(4))*3.0-
     1(Y(5)-YOLD(5))*10.5/8.0
      Y(8)=YOLD(8)+(Y(2)-YOLD(2))+(Y(3)-YOLD(3))*2.0 +(Y(4)-YOLD(4))*3.
     1+(Y(5)-YOLD(5))*5./8.
C     CORRECT CONCENTRATIONS FOR INCREASED FLOW AND DECREASED PRESSURE
      PTN=PT -GRADP*DX
      YOLD(7)=Y(7)
      VOLPLUS=0.
      DO 200 KK=1,8
  200 VOLPLUS=VOLPLUS +FGAS*(Y(KK)-YOLD(KK))
      VMOLE=22.400*760.*T/(273.2*PTN)
      VOLPLUS=VOLPLUS*VMOLE
      FGASN=(FGAS*PT/PTN)+VOLPLUS
      RATIO=FGAS/FGASN
C     ----------------------------------------------------------------------
      DO 210 KK=1,8
  210 Y(KK)=Y(KK)*RATIO
      FGAS=FGASN
      PT=PTN
      IF(ISW.LT.1) GO TO 101
      RETURN
  101 IF(XMAX.GT.X+DX) GO TO 160
      DX = XMAX-X
      ISW=1
  160 CONTINUE
      IF(INTS.EQ.1) RETURN
    6 INTS=INTS-1
C     PRESERVE CURRENT VALUES
    4 XOLD=X
C     IN THE NORMAL RUNGE KUTTA MERSON THE 8 WOULD BE REPLACED BY N
      DO 5 I=1,8
    5 YOLD(I)=Y(I)
      IF(Y(1) .LE. 0.0 ) YOLD(1)=0.0
      IF(Y(2) .LE. 0.0) YOLD(2)=0.0
C    SKIP STEP ADJUSTMENT IF DX IS LAST STEP
      IF (ISW.EQ.1) GO TO 510
      IHALF=0
      GO TO 9
C     ERROR EXCESSIVE, HALVE STEP
   20 DX=0.5*DX
      IF(DX.LT.DXMIN) GO TO 19
      INTS=INTS+INTS
      IHALF=1
      GO TO 8
C     STEP LENGTH TOO SMALL, INTEGRATION FAILS
```

```
   19 X=XOLD
      DO 23 I=1,8
   23 Y(I)=YOLD(I)
      RETURN
C     ERROR SMALL, STEP LENGTH MAY BE INCREASED IF POSSIBLE
C     CHECK IF STEP PREVIOUSLY HALVED (PREVENTS CYCLING)
   21 IF(IHALF.EQ.1) GO TO 3
C     CHECK IF INTS EVEN
      IDOUBLE=INTS/2
      IF((IDOUBLE*2).EQ.INTS) GO TO 22
C     NOT POSSIBLE, INTS ODD
      GO TO 3
C     DOUBLE STEP LENGTH
   22 INTS=IDOUBLE
      DX=2.*DX
C     GO BACK TO LAST POINT, AND INTEGRATE WITH NEW DX
    8 FMULT=DX/3.
      DO 7 I=1,8
    7 Y(I)=YOLD(I)
      X=XOLD
  510 CONTINUE
C     MAIN INTEGRATION PROCESS STARTS HERE ****
C     ADVANCE X BY DX
    9 CALL DERIVS(X,N)
      DO 18 IS=1,5
      GO TO (31,30,32,33,30),IS
   31 X=X+FMULT
      GO TO 30
   32 X=X+0.5*FMULT
      GO TO 30
   33 X=XOLD+DX
C     UPDATE Y(I)
   30 DO 10 I=1,N
      FK(IS,I)=FMULT*DY(I)
      GO TO (11,12,13,14,10),IS
C     PREDICTOR AT (X+DX/3.)
   11 Y(I)=YOLD(I)+FK(1,I)
      IF(Y(1) .LE. 0.0 ) Y(1)=0.0
      GO TO 10
C     CORRECTOR FOR (X+DX/3.)
   12 Y(I)=YOLD(I)+0.5*(FK(1,I)+FK(2,I))
      IF(Y(2) .LE. 0.0 ) Y(2)=0.0
      GO TO 10
C     ADVANCE TO (X+DX/2.)
   13 Y(I)=YOLD(I)+0.375*FK(1,I)+1.125*FK(3,I)
      GO TO 10
C     ADVANCE TO (X+DX)
   14 Y(I)=YOLD(I)+1.5*FK(1,I)-4.5*FK(3,I)+6.0*FK(4,I)
   10 CONTINUE
      IF(IS.EQ.5) GO TO 16
C     EVALUATE DERIVATIVES
      CALL DERIVS(X,N)
      GO TO 18
C     ON LAST INTEGRATION, EVALUATE ERROR
   16 ERR=0.0
      DO 17 I=1,N
      EI=ABS(FK(1,I)-4.5*FK(3,I)+4.0*FK(4,I)-0.5*FK(5,I))
      IF(ERR.LT.EI) ERR=EI
   17 CONTINUE
   18 CONTINUE
```

```
      GO TO 1
      END

      SUBROUTINE DERIVS(X,N)
      COMMON/GRAD/DY
      COMMON/ PARA1/KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5
      COMMON /PARA 3/EAS
      COMMON/DEP/Y
      COMMON/DER/FGAS
      COMMON/CONST/NN,R,NEX,NF,NC
      COMMON/REFAP/TBASE,RT
      DIMENSION Y(10),DY(10)
      REAL  KAI,KR12I,KR34I,NN,KR5I,KR23I,N2
      REAL KA,KR12,KR23,KR34,KR5
C     ****THIS SUBROUTINE CALCALATES  THE RATES OF ALL REACTIONS AT EACH STEP CW
C
C     CALCULATE RATE CONSTANTS  FROM PRE-EXPONENTIAL FACTORS AND
C     ACTIVATION ENERGIES
      KA=KAI*EXP(EA*RT)
      KR12=KR12I*EXP(E12*RT)
      KR23=KR23I*EXP(E23*RT)
      KR5=KR5I*EXP(E5*RT)
      KR34=KR34I*EXP(E34*RT)
C   *** V IS RECIPROCAL GAS FLOW (HOURS / LITRE) ********
      ASF=EXP(EAS*RT)
      V=1./(FGAS*3600.)
      DEN=(KA*Y(6)+(KR12+NN*KR5)*Y(1)  +(KR23+(NN-1)*KR5)*Y(2)+KR34*Y(3))
      DY(1)=(-V*KA*Y(6)*(KR12+KR5)*Y(1))*ASF/DEN
      DY(2)=(V*KA*Y(6)*(KR12*Y(1)-(KR5+KR23)*Y(2)))*ASF/DEN
      DY(3)=(V*KA*Y(6)*(KR23*Y(2)-KR34*Y(3)))*ASF/DEN
      DY(4)=(V*KA*Y(6)*KR34*Y(3))*ASF/DEN
      DY(5)=(8.0*V*KA*Y(6)*KR5*(Y(1)+Y(2)))*ASF/DEN
      RETURN
      END
150
  0
-13.7130    34307.828
0.2200E+010.1894E+020.3519E+030.8320E+030.2946E+01
-30848.     -27307.    -26018.    -29392.    -24426.    12351.
1000.
 9.5242   20.00       760.00
     0.5559E+05    -0.1174E+04      0.5080E+02      0.2383E+04      0.3791E+02
    -0.1174E+04     0.2697E+04      0.1926E+03      0.8628E+04      0.1917E+03
     0.5080E+02     0.1926E+03      0.1834E+02      0.6688E+03      0.1822E+02
     0.2383E+04     0.8628E+04      0.6688E+03      0.3186E+05      0.6639E+03
     0.3791E+02     0.1917E+03      0.1822E+02      0.6639E+03      0.1816E+02
≠       6400 END OF RECORD
≠       6400 END OF RECORD
≠       6400 END OF RECORD
```

CDTOT   650

PROGRAM NO. 3:

This program was used to estimate the (prior) variance-covariance matrix of the parameter estimates ($\underline{U}$).

```
      PROGRAM TST(INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C     **********VAR-COVAR MATRIX FOR PARAMETER ESTIMATES***************
C     **********METHOD ASSUMES MODEL IS ADEQUATE ***********************
C
C     *********TIO2  SUPPORTED CATALYST -REACTION  MODEL****************C
C              -----------------------------------------
C
C
C
C
C     NP- NUMBER OF PARAMETERS
C     NEXP- NUMBER OF EXPERIMENTS
C     NR -NO OF INDEPENDENT  RESPONSES.
C     TBASE -BASE TEMPERATURE USED FOR REPARAMETERIZATION BY
C     HUNTER /ATKINSON  METHOD.
C     FGAS -TOTAL GAS FLOW  IN CC/MIN.
C     DELF -PRESSURE DROP IN REACTOR IN MM HG
C     SIGMA -ELEMENTS OF THE VARIANCE-COVARIANCE MATRIX.
C     CCX, CO2, CN2 -CONCENTRATION  OF COMPONENTS IN GM MOLE /LITER.
C     DELP-PRESSURE DROP ACROSS REACTOR  IN  MM HG
C     PT -TOTAL ABSOLUTE PRESSURE  IN REACTOR IN  MM HG.
C
C
C
C
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE NN
      DOUBLE  KAI,KR12I,KR23I,KR34I,KR5I
      COMMON/ PARA1/KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5
      COMMON /PARA 3/EAS
      COMMON/CAT/T,DELP,W,PT,FGAS,GRADP
      COMMON/FACTOR/FACT
      COMMON /CONST/NN,R,NEX,NP,NC
      DIMENSION BXTVX(11,11),UTHE(12,12),ARRAY(25,25)
      DIMENSION SIGMA(5,5),TRES(5,1),VV(5,5),RES(5),RRES(1,5)
      DIMENSION   GVM(5), HVM(5)
      DIMENSION G1VM(12),H1VM(12)
      DIMENSION G2VM(12),H2VM(12)
      DIMENSION XV(5),YV(5)
C
C
C
      READ(5,1202) KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5,EAS
      WRITE(6,51)
      WRITE(6,52) KAI,EA,KR12I,E12,KR23I,E23,KR34I,E34,KR5I,E5
      WRITE(6,81)EAS
      NR=5
      NP=11
      NEXP=9
      KR=1
      L=1
      DO 50 I=1,NR
      DO 50 J=1,NR
      SIGMA(I,J)=0.D0
 50   CONTINUE
      WRITE(6,62)
      DO 60  I=1,NEXP
      DO 71 J=1,NR
      READ(5,61) XV(J),YV(J)
      RES(J)=XV(J)-YV(J)
```

```
      RRES(L,J)=RES(J)
      TRES(J,L)=RRES(L,J)
      WRITE(6,63) XV(J),YV(J),RES(J)
 71   CONTINUE
      CALL DGMPRD(TRES,RRES,VV,NR,KR,NR)
      FACT=5.0D0/(9.0D0*5.0D0-11.0D0)
      DO 80 II=1,NR
      DO  80  JJ=1,NR
      SIGMA(II,JJ)=SIGMA(II,JJ)+VV(II,JJ)*FACT
 80   CONTINUE
 60   CONTINUE
      PRINT*,≠VAR-COVAR MATRIX OF OBSERV.≠
      WRITE(6,77) ((SIGMA(I,J), J=1,5),I=1,5)
C     TAKE THE INVERSE OF SIGMA
      NSIG=5
      CALL DMINV(SIGMA,NSIG,DISIG, GVM, HVM)
      WRITE(6,118)
      WRITE(6,77) ((SIGMA(I,J),J=1,5),I=1,5)
      DO  103  IU=1, 12
      DO  103  JU=1,12
      UTHE(IU,JU)=0.
 103  CONTINUE
      DO 97  MM=1,NEXP
      READ(5,98)  KRUN,NN
      READ(5,1202) (ARRAY(I,J),I=1,24)
      WRITE(6,1202) (ARRAY(I,J),I=1,24)
      COX=ARRAY(1,J)
      CO2=ARRAY(6,J)
      CN2=ARRAY(7,J)
      T=ARRAY(19,J)
      DELP=ARRAY(20,J)
      W=ARRAY(21,J)
      PT=ARRAY(22,J)
      FGAS=ARRAY(23,J)
      GRADP=ARRAY(24,J)
      CALL MATRIZ(COX,CO2,CN2,BXTVX,SIGMA)
      DO 101 IU=1,NP
      DO  101  JU=1,NP
      UTHE(IU,JU)=UTHE(IU,JU)+BXTVX(IU,JU)
 101  CONTINUE
 97   CONTINUE
      PRINT*, ≠INVERSE VAR-COVAR ESTIMATES FOR PARAMETER ESTIMATES≠
      N1SIG=12
      CALL  DMINV(UTHE,N1SIG,D1SIG,G1VM,H1VM)
      N2SIG=12
      UTHE(12,12)=0.480500
      CALL DMINV(UTHE,N2SIG,D2SIG,G2VM,H2VM)
      WRITE(6,1202)  ((UTHE(KP,JP),JP=1,12),KP=1,12)
      WRITE(7,1202)  ((UTHE(KP,JP),JP=1,12),KP=1,12)
1202  FORMAT(4D20.12)
77    FORMAT(5D15.5//)
   81 FORMAT(6X, * ACTIVE SITE PARAMETER = *6X, D13.4)
   51 FORMAT(////////21X,*FREQUENCY FACTORS*6X* ACTIVATION ENERGIES*//)
   52 FORMAT(*  ADSORPTION     *,5X,*  KAI= *,D11.4,7X,* EA= *,F14.4//
     1*  OXYLENE-OTA  *6X,*KR12I= *,D11.4,7X,*E12= *,F14.4//
     2*  OTA-PI       *6X,*KR23I= *,D11.4,7X,*E23= *,F14.4//
     5*   PI- PA      *6X,*KR34I= *,D11.4, 7X, *E34= *,F14.4 //
     4*  ORGANICS-CO2 *6X,* KR5I= *,D11.4 ,7X,* E5= *,F14.4//)
 333  FORMAT(5X,9D12.4)
61    FORMAT(2D20.12)
```

```
 62   FORMAT(≠1≠,20X,*OBSERVED*,5X,*CALCULATED*)
63    FORMAT(16X, 3(D12.4,4X))
66    FORMAT(2D20.12)
 118  FORMAT(≠1≠,20X,*INVERSE VARIANCE-COVARIANCE MATRIX OF THE OBSERVAT
     1IONS *)
98    FORMAT(I3, D20.12)
 99   FORMAT(8E10.4)
 981  FORMAT(10X,*KRUN=*I4,5X,*NN=*F10.4)
991   FORMAT(10X,8E13.4)
 1201 FORMAT(4X,11E12.4)
      STOP
      END

      SUBROUTINE MATRIZ (COX,CO2,CN2,BXTVX,SIGMA)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLE PRECISION KAI,KR12I,KR23I,KR34I,KR5I ,NN
      DOUBLE PRECISION  N2
      COMMON/ PARA1/KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5
      COMMON /PARA 3/EAS
      COMMON/CONST/NN,R,NEX,NF,NC
      COMMON/REPAR/TBASE,RT
      COMMON/CAT/T,DELP,WWW,PT,FGAS,GRADP
      COMMON/FACTOR/FACT
      COMMON/DEP/YY
      DIMENSION  ARRAY(25,50),Y0(10),P0(15),Y(10),YY(10)
      DIMENSION XTVX(11,11),XTSIG(11,5),BXTVX(11,11),SIGMA(5,5)
      DIMENSION XT(11,5),XM(5,11)
      DIMENSION DELTA(11,11)
      DIMENSION DDYY(5,11)
C
C
C
C
C
      NEXP=9
      NR=5
      W=WWW
C
      Y(1)=COX
      Y(2)=0.D0
      Y(3)=0.D0
      Y(4)=0.D0
      Y(5)=0.D0
      Y(6 )=CO2
      Y(7)=CN2
      Y(8)=0.D0
      Y(9)=0.D0
      Y(10)=0.D0
      TBASE=370.0
      TBASE=TBASE+273.2
      R=-1.9872
      TSTAR=(TBASE-T)/(TBASE*T)
      RT=TSTAR/R
C     SET UP TOLERANCES,STEP LENGTH,BOUNDARY CONDITIONS
C     FOR  INTERGRATION.
      X=0.D0
      DX=0.005D0
      TOLKM=1.0D-08
      DXMIN=0.0001D0
```

```
      N=5
      DELX=W
      P0(1)=KAI
      P0(2)=KR12I
      P0(3)=KR23I
      P0(4)=KR34I
      P0(5)=KR5I
      P0(6)=EA
      P0(7)=E12
      P0(8)=E23
      P0(9)=E34
      P0(10)=E5
      P0(11)=EAS
      DO 182 I=1,10
  182 YY(I)=Y(I)
      CALL MERSON(X,DELX,DX,DXMIN,TOLKM,N,P0)
      Y0(1)=YY(1)
      Y0(2)=YY(2)
      Y0(3)=YY(3)
      Y0(4)=YY(4)
      Y0(5)=YY(5)
C
C
C
C     SET UP THE  (DIFFERENTIAL )  X-MATRIX
      DELTAP=1.0 E-07
      DO  18   J=1,NP
      PS=P0(J)
      P0(J)=P0(J)+DELTAP*P0(J)
      DO 172 I=1,10
  172 YY(I)=Y(I)
      DX=0.005
      X=0.
      CALL MERSON(X,DELX,DX,DXMIN,TOLKM,N,P0)
      DO  18   K=1,NR
      P0(J)=PS
      CDYY(K,J)=YY(K)-Y0(K)
      DELTA(K,J)=(YY(K)-Y0(K))/(DELTAP*PS)
   18 CONTINUE
C
C
C
      DO  91   J=1,NR
      DO  16   K=1,NP
      XT(K,J)=DELTA(J,K)
      XM(J,K)=DELTA(J,K)
   16 CONTINUE
   91 CONTINUE
      PRINT*, ≠XM≠
C     COMPUTE THE XTVX- MATRIX FOR ONE EXPERIMENTS.
C     GMPRD -GENERAL MATRIX PRODUCT ROUTINE -  SSF LIBRARY
      FAINV=1.0/FACT
      CALL DGMPRD(XT,SIGMA,XTSIG,NP,NR,NR)
      CALL DGMPRD(XTSIG,XM,XTVX,NP,NR,NP)
      DO 151 IA=1,NP
      DO 151 JA=1,NP
      RXTVX(IA,JA)=XTVX(IA,JA)*FAINV
  151 CONTINUE
710   FORMAT(2X,11D10.4)
711   FORMAT(5X, *Y*,5D13.4)
```

```
712   FORMAT(5X,11D10.4)
714   FORMAT(5X,11D10.4)
      RETURN
      END


      SUBROUTINE MERSON (X,DELX,DX,DXMIN,TOLKM,N,P0)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLE PRECISION KAI,KR12I,KR23I,KR34I,KR5I ,NN
C     INTEGRATES FROM X TO (X+DELX)
C     DX IS ESTIMATE FOR INTEGRATION STEP NECESSARY
C     DXMIN IS MINIMUM STEP LENGTH TO BE PERMITTED
C     TOLKM IS REQUIRED ACCURACY
C     N IS NUMBER OF DEPENDENT VARIABLES
C     CONTROL TRANSFERRED TO FIRST LABEL IF INTEGRATION FALLS,X AND Y(I)
C     THEN CONTAIN NEW VALUES
C     CONTROL TRANSFERRED TO SECOND LABEL IF INTEGRATION FAILS, X AND
C     Y(I) THEN CONTAIN MOST RECENT CORRECT VALUES
C     IN EITHER CASE, DX CONTAINS CURRENT STEP LENGTH
      COMMON/ PARA1/KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5
      COMMON /PARA 3/EAS
      COMMON/DEP/Y
      COMMON/GRAD/DY
      COMMON/CONST/NN,R,NEX,NF,NC
      COMMON/DAT/T,DELP,W,PPTT,FFGAS,GRADP
      COMMON/ERROR/ERR
      COMMON/REFAR/TBASE,RT
      DIMENSION Y(10),YOLD(10),FK(5,10),DY(10)
      DIMENSION P0(12)
C
C
      FGAS=FFGAS
      PT=PPTT
      KAI=P0(1)
      KR12I=P0(2)
      KR23I=P0(3)
      KR34I=P0(4)
      KR5I=P0(5)
      EA=P0(6)
      E12=P0(7)
      E23=P0(8)
      E34=P0(9)
      E5=P0(10)
      EAS=P0(11)
      ISW=0
      XMAX=W
      TOLA=5.*TOLKM
      FINTS=DELX/DX+0.5
      TOLB=TOLA/32.
      INTS=FINTS
      IF(INTS.LT.1)INTS=1
      DX=DELX/INTS
      FMULT=DX/3.
      GO TO 4
C     ERROR CHECK
    1 IF(ERR.GT.TOLA) GO TO 20
      IF(ERR.LT.TOLB) GO TO 21
C     INTEGRATION SATISFACTORY, CALCULATE NEW POINTS
C     -------------------------------------------------------------------
C     *****THE NEXT 17 CARDS ARE NOT PART OF THE STANDARD MERSON  *******
```

```
C       ***** THEY CALCULATE THE VOLUME CHANGE DUE TO REACTION *****************
      3 DO 2 I=1,N
      2 Y(I)=YOLD(I)+0.5*FK(1,I)+2.0*FK(4,I)+0.5*FK(5,I)
        IF(Y(1) .LE. 0.0 ) Y(1)=0.0
        IF(Y(2) .LE. 0.0 ) Y(2)=0.0
C       OXYGEN BALANCE-- OXYGEN TO CO2 AND  H2O
        Y(6)=YOLD(6)-(Y(2)-YOLD(2))-(Y(3)-YOLD(3))*2. -(Y(4)-YOLD(4))*3.0-
       1(Y(5)-YOLD(5))*10.5/8.0
        Y(8)=YOLD(8)+(Y(2)-YOLD(2))+(Y(3)-YOLD(3))*2.0 +(Y(4)-YOLD(4))*3.
       1+(Y(5)-YOLD(5))*5./8.
C       CORRECT CONCENTRATIONS FOR INCREASED FLOW AND DECREASED PRESSURE
        PTN=PT -GRADP*DX
        YOLD(7)=Y(7)
        VOLPLUS=0.
        DO 200 KK=1,8
    200 VOLPLUS=VOLPLUS +FGAS*(Y(KK)-YOLD(KK))
        VMOLE=22.400*760.*T/(273.2*PTN)
        VOLPLUS=VOLPLUS*VMOLE
        FGASN=(FGAS*PT/PTN)+VOLPLUS
        RATIO=FGAS/FGASN
C        ------------------------------------------------------------------
        DO 210 KK=1,8
    210 Y(KK)=Y(KK)*RATIO
        FGAS=FGASN
        PT=PTN
        IF(ISW.LT.1) GO TO 101
        RETURN
    101 IF(XMAX.GT.X+DX) GO TO 160
        DX = XMAX-X
        ISW=1
    160 CONTINUE
        IF(INTS.EQ.1) RETURN
      6 INTS=INTS-1
C       PRESERVE CURRENT VALUES
      4 XOLD=X
C       IN THE NORMAL RUNGE KUTTA MERSON THE 8 WOULD BE REPLACED BY N
        DO 5 I=1,8
      5 YOLD(I)=Y(I)
        IF(Y(1) .LE. 0.0 ) YOLD(1)=0.0
        IF(Y(2) .LE. 0.0) YOLD(2)=0.0
C      SKIP STEP ADJUSTMENT IF DX IS LAST STEP
        IF (ISW.EQ.1) GO TO 510
        IHALF=0
        GO TO 9
C       ERROR EXCESSIVE, HALVE STEP
     20 DX=0.5*DX
        IF(DX.LT.DXMIN) GO TO 19
        INTS=INTS+INTS
        IHALF=1
        GO TO 8
C       STEP LENGTH TOO SMALL, INTEGRATION FAILS
     19 X=XOLD
        DO 23 I=1,8
     23 Y(I)=YOLD(I)
        RETURN
C       ERROR SMALL, STEP LENGTH MAY BE INCREASED IF POSSIBLE
C       CHECK IF STEP PREVIOUSLY HALVED (PREVENTS CYCLING)
     21 IF(IHALF.EQ.1) GO TO 3
C       CHECK IF INTS EVEN
        IDOUBLE=INTS/2
```

```
      IF((IDOUBLE*2).EQ.INTS) GO TO 22
C     NOT POSSIBLE, INTS ODD
      GO TO 3
C     DOUBLE STEP LENGTH
   22 INTS=IDOUBLE
      DX=2.*DX
C     GO BACK TO LAST POINT, AND INTEGRATE WITH NEW DX
    8 FMULT=DX/3.
      DO 7 I=1,8
    7 Y(I)=YOLD(I)
      X=XOLD
  510 CONTINUE
C     MAIN INTEGRATION PROCESS STARTS HERE ****
C     ADVANCE X BY DX
    9 CALL DERIVS(X,N)
      DO 18 IS=1,5
      GO TO (31,30,32,33,30),IS
   31 X=X+FMULT
      GO TO 30
   32 X=X+0.5*FMULT
      GO TO 30
   33 X=XOLD+DX
C     UPDATE Y(I)
   30 DO 10 I=1,N
      FK(IS,I)=FMULT*DY(I)
      GO TO (11,12,13,14,10),IS
C     PREDICTOR AT (X+DX/3.)
   11 Y(I)=YOLD(I)+FK(1,I)
      IF(Y(1) .LE. 0.0 ) Y(1)=0.0
      GO TO 10
C     CORRECTOR FOR (X+DX/3.)
   12 Y(I)=YOLD(I)+0.5*(FK(1,I)+FK(2,I))
      IF(Y(2) .LE. 0.0 ) Y(2)=0.0
      GO TO 10
C     ADVANCE TO (X+DX/2.)
   13 Y(I)=YOLD(I)+0.375*FK(1,I)+1.125*FK(3,I)
      GO TO 10
C     ADVANCE TO (X+DX)
   14 Y(I)=YOLD(I)+1.5*FK(1,I)-4.5*FK(3,I)+6.0*FK(4,I)
   10 CONTINUE
      IF(IS.EQ.5) GO TO 16
C     EVALUATE DERIVATIVES
      CALL DERIVS(X,N)
      GO TO 18
C     ON LAST INTEGRATION, EVALUATE ERROR
   16 ERR=0.0
      DO 17 I=1,N
      EI=DABS(FK(1,I)-4.5*FK(3,I)+4.0*FK(4,I)-0.5*FK(5,I))
      IF(ERR.LT.EI) ERR=EI
   17 CONTINUE
   18 CONTINUE
      GO TO 1
      END

      SUBROUTINE DERIVS(X,N)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLE PRECISION KAI,KR12I,KR23I,KR34I,KR5I ,NN
      DOUBLE PRECISION KA,KR12,KR23,KR5,KR34
      COMMON/GRAD/DY
```

```
      COMMON/ PARA1/KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5
      COMMON /PARA 3/EAS
      COMMON/DEP/Y
      COMMON/DAT/T,DELP,W,PT,FGAS,GRADP
      COMMON/CONST/NN,R,NEX,NF,NC
      COMMON/REPAR/TBASE,RT
      DIMENSION Y(10),DY(10)
C     ****THIS SUBPOUTINE CALCALATES  THE RATES OF ALL REACTIONS AT EACH STEP DW
C
C     CALCULATE RATE CONSTANTS  FROM PRE-EXPONENTIAL FACTORS AND
C     ACTIVATION ENERGIES
      KA=KAI*DEXP(EA*RT)
      KR12=KR12I*DEXP(E12*RT)
      KR23=KR23I*DEXP(E23*RT)
      KR5=KR5I*DEXP(E5*RT)
      KR34=KR34I*DEXP(E34*RT)
      ASF=DEXP(EAS*RT)
      V=1./(FGAS*3600.)
      DEN=(KA*Y(6)+(KR12+NN*KR5)*Y(1)  +(KR23+(NN-1)*KR5)*Y(2)+KR34*Y(3))
      DY(1)=(-V*KA*Y(6)*(KR12+KR5)*Y(1))*ASF/DEN
      DY(2)=(V*KA*Y(6)*(KR12*Y(1)-(KR5+KR23)*Y(2)))*ASF/DEN
      DY(3)=(V*KA*Y(6)*(KR23*Y(2)-KR34*Y(3)))*ASF/DEN
      DY(4)=(V*KA*Y(6)*KR34*Y(3))*ASF/DEN
      DY(5)=(8.0*V*KA*Y(6)*KR5*(Y(1)+Y(2)))*ASF/DEN
      RETURN
      END
      SUBROUTINE  DGMPRD(A,B,R,N,M,L)
      IMPLICIT  DOUBLE  PRECISION (A-H,O-Z)
      DIMENSION A(1),B(1),R(1)
      IR=0
      IK=-M
      DO  10   K=1,L
      IK=IK+M
      DO  10  J=1,N
      IR=IR+1
      JI=J-N
      IB=IK
      R(IR)=0
      DO  10  I=1,M
      JI=JI+N
      IB=IB+1
10    R(IR)=R(IR)+A(JI)*B(IB)
      RETURN
      END
      SUBROUTINE  DMINV(A,N,D,L,M)
      DOUBLE PRECISION A,D,BIGA,HOLD
      DIMENSION A(1),L(1),M(1)
C
C        ...............................................................
C
C        IF A DOUBLE PRECISION VERSION OF THIS ROUTINE IS DESIRED, THE
C
C        THE C MUST ALSO BE REMOVED FROM DOUBLE PRECISION STATEMENTS
C        APPEARING IN OTHER ROUTINES USED IN CONJUNCTION WITH THIS
C        ROUTINE.
C
C
C        ...............................................................
C
C        SEARCH FOR LARGEST ELEMENT
```

```
C
      D=1.0
      NK=-N
      DO 80 K=1,N
      NK=NK+N
      L(K)=K
      M(K)=K
      KK=NK+K
      BIGA=A(KK)
      DO 20 J=K,N
      IZ=N*(J-1)
      DO 20 I=K,N
      IJ=IZ+I
10    IF(DABS(BIGA)-DABS(A(IJ)))  15,20,20
   15 BIGA=A(IJ)
      L(K)=I
      M(K)=J
   20 CONTINUE
C
C        INTERCHANGE ROWS
C
      J=L(K)
      IF(J-K) 35,35,25
   25 KI=K-N
      DO 30 I=1,N
      KI=KI+N
      HOLD=-A(KI)
      JI=KI-K+J
      A(KI)=A(JI)
   30 A(JI) =HOLD
C
C        INTERCHANGE COLUMNS
C
   35 I=M(K)
      IF(I-K) 45,45,38
   38 JP=N*(I-1)
      DO 40 J=1,N
      JK=NK+J
      JI=JP+J
      HOLD=-A(JK)
      A(JK)=A(JI)
   40 A(JI) =HOLD
C
C        DIVIDE COLUMN BY MINUS PIVOT (VALUE OF PIVOT ELEMENT IS
C        CONTAINED IN BIGA)
C
   45 IF(BIGA) 48,46,48
   46 D=0.0
      RETURN
   48 DO 55 I=1,N
      IF(I-K) 50,55,50
   50 IK=NK+I
      A(IK)=A(IK)/(-BIGA)
   55 CONTINUE
C
C        REDUCE MATRIX
C
      DO 65 I=1,N
      IK=NK+I
      IJ=I-N
```

```
      DO 65 J=1,N
      IJ=IJ+N
      IF(I-K) 60,65,60
   60 IF(J-K) 62,65,62
   62 KJ=IJ-I+K
      A(IJ)=A(IK)*A(KJ)+A(IJ)
   65 CONTINUE
C
C        DIVIDE ROW BY PIVOT
C
      KJ=K-N
      DO 75 J=1,N
      KJ=KJ+N
      IF(J-K) 70,75,70
   70 A(KJ)=A(KJ)/BIGA
   75 CONTINUE
C
C        PRODUCT OF PIVOTS
C
      D=D*BIGA
C
C        REPLACE PIVOT BY RECIPROCAL
C
      A(KK)=1.0/BIGA
   80 CONTINUE
C
C        FINAL ROW AND COLUMN INTERCHANGE
C
      K=N
  100 K=(K-1)
      IF(K) 150,150,105
  105 I=L(K)
      IF(I-K) 120,120,108
  108 JQ=N*(K-1)
      JR=N*(I-1)
      DO 110 J=1,N
      JK=JQ+J
      HOLD=A(JK)
      JI=JR+J
      A(JK)=-A(JI)
  110 A(JI) =HOLD
  120 J=M(K)
      IF(J-K) 100,100,125
  125 KI=K-N
      DO 130 I=1,N
      KI=KI+N
      HOLD=A(KI)
      JI=KI-K+J
      A(KI)=-A(JI)
  130 A(JI) =HOLD
      GO TO 100
  150 RETURN
      E N D
   .223200000000D+01   .184900000000D+02   .349500000000D+03   .838900000000D+03
   .284800000000D+01  -.206990000000D+05  -.255270000000D+05  -.234080000000D+05
  -.280120000000D+05  -.229600000000D+05   .180124759000D+05
   .204300000000D-03   .214654868045D-03
   .115500000000D-04   .119206683932D-04
   .459200000000D-05   .507491979460D-05
   .665800000000D-04   .551011304997D-04
```

```
   .887700000000D-04   .933671352635D-04
   .153200000000D-03   .163311810233D-03
   .956600000000D-05   .860091524210D-05
   .410100000000D-05   .412498492463D-05
   .495000000000D-04   .467154858496D-04
   .802200000000D-04   .820245530973D-04
   .310300000000D-03   .313663693958D-03
   .201900000000D-04   .181350887116D-04
   .553200000000D-05   .686889346049D-05
   .581600000000D-04   .593302942305D-04
   .106500000000D-03   .102701668008D-03
   .273500000000D-03   .264518340059D-03
   .135200000000D-04   .153871107058D-04
   .546600000000D-05   .584883771378D-05
   .460800000000D-04   .579614258861D-04
   .649300000000D-04   .965673580706D-04
   .603200000000D-04   .642754926634D-04
   .503100000000D-05   .378529136008D-05
   .553000000000D-05   .144865815597D-05
   .101900000000D-03   .106347458751D-03
   .165200000000D-03   .137375592217D-03
   .165300000000D-03   .174503252605D-03
   .891400000000D-05   .986370657274D-05
   .391600000000D-05   .368648430977D-05
   .271600000000D-04   .231252059098D-04
   .266000000000D-04   .445170097313D-04
   .130500000000D-03   .163527341829D-03
   .650000000000D-05   .862609104559D-05
   .481100000000D-05   .414295379208D-05
   .929500000000D-04   .539969839002D-04
   .109400000000D-03   .922113052627D-04
   .226900000000D-03   .228428470406D-03
   .126500000000D-04   .120629986734D-04
   .697800000000D-05   .580088957651D-05
   .144700000000D-03   .136299646550D-03
   .245900000000D-03   .213519892321D-03
   .417100000000D-03   .427580278203D-03
   .149300000000D-04   .186400508987D-04
   .521000000000D-05   .756946451278D-05
   .364900000000D-04   .152174126497D-04
   .357700000000D-04   .551952435995D-04
306    .964540000000D+01
   .348900000000D-03  0.                  0.                  0.
  0.                   .498800000000D-02   .199600000000D-01  0.
  0.                   .204300000000D-03   .115500000000D-04   .469200000000D-05
   .655800000000D-04   .887700000000D-04   .393200000000D-02   .170700000000D-01
   .276200000000D-03   .189600000000D-04   .643200000000D+03   .146000000000D+03
   .100000000000D+01   .101400000000D+04   .545400000000D-02   .146000000000D+03
307    .948340000000D+01
   .283700000000D-03  0.                  0.                  0.
  0.                   .877500000000D-02   .204300000000D-01  0.
  0.                   .153800000000D-03   .956600000000D-05   .410100000000D-05
   .495000000000D-04   .802200000000D-04   .669700000000D-02   .170200000000D-01
   .216400000000D-03   .203900000000D-04   .623200000000D+03   .204000000000D+03
   .100000000000D+01   .114500000000D+04   .692000000000D-02   .204000000000D+03
308    .962480000000D+01
   .511100000000D-03  0.                  0.                  0.
  0.                   .790100000000D-02   .194400000000D-01  0.
  0.                   .310300000000D-03   .201900000000D-04   .553200000000D-05
   .581600000000D-04   .106500000000D-03   .581600000000D-02   .158200000000D-01
```

```
   .272300000000D-03   .233000000000D-04   .663200000000D+03   .225000000000D+03
   .100000000000D+01   .115100000000D+04   .768000000000D-02   .225000000000D+03
309   .979230000000D+01
   .391200000000D-03  0.                  0.                  0.
  0.                   .220800000000D-02   .189900000000D-01  0.
  0.                   .273500000000D-03   .135200000000D-04   .546600000000D-05
   .460800000000D-04   .649300000000D-04   .178900000000D-02   .172500000000D-01
   .203300000000D-03   .114900000000D-04   .663200000000D+03   .800000000000D+02
   .100000000000D+01   .892000000000D+03   .321800000000D-02   .800000000000D+02
310   .948130000000D+01
   .211400000000D-03  0.                  0.                  0.
  0.                   .651800000000D-02   .149500000000D-01  0.
  0.                   .603200000000D-04   .503100000000D-05   .563000000000D-05
   .101900000000D-03   .165200000000D-03   .523000000000D-02   .137500000000D-01
   .425400000000D-03   .420700000000D-04   .663200000000D+03   .800000000000D+02
   .100000000000D+01   .896000000000D+03   .321300000000D-02   .800000000000D+02
311   .956700000000D+01
   .267500000000D-03  0.                  0.                  0.
  0.                   .288400000000D-02   .248200000000D-01  0.
  0.                   .165300000000D-03   .891400000000D-05   .391600000000D-05
   .271600000000D-04   .266000000000D-04   .212300000000D-02   .202000000000D-01
   .114900000000D-03   .620600000000D-05   .663200000000D+03   .219000000000D+03
   .100000000000D+01   .115600000000D+04   .744500000000D-02   .219000000000D+03
313   .956460000000D+01
   .263400000000D-03  0.                  0.                  0.
  0.                   .241900000000D-02   .201600000000D-01  0.
  0.                   .130500000000D-03   .650000000000D-05   .481100000000D-35
   .929500000000D-04   .109400000000D-03   .164600000000D-02   .186300000000D-01
   .363400000000D-03   .256000000000D-04   .623200000000D+03   .720000000000D+02
   .100000000000D+01   .887000000000D+03   .304000000000D-02   .720000000000D+02
314   .964020000000D+01
   .446200000000D-03  0.                  0.                  0.
  0.                   .681200000000D-02   .156300000000D-01  0.
  0.                   .226900000000D-03   .126500000000D-04   .697800000000D-05
   .144700000000D-03   .245900000000D-03   .519600000000D-02   .145900000000D-01
   .614300000000D-03   .528500000000D-04   .623200000000D+03   .720000000000D+02
   .100000000000D+01   .889000000000D+03   .302600000000D-02   .720000000000D+02
315   .961870000000D+01
   .565000000000D-03  0.                  0.                  0.
  0.                   .283500000000D-02   .257800000000D-01  0.
  0.                   .417100000000D-03   .149300000000D-04   .521000000000D-05
   .364900000000D-04   .357700000000D-04   .209000000000D-02   .218400000000D-01
   .157200000000D-03   .738100000000D-05   .623200000000D+03   .178000000000D+03
   .100000000000D+01   .113300000000D+04   .717300000000D-02   .178000000000D+03
      ENDLISTING
≠       6400 ENC OF RECORD
≠       6400 END OF RECORD
≠       6400 END OF RECORD
```

CDTOT   708

PROGRAM NO. 4:

This program was used to estimate the inverse of the upper triangular matrix from the steady state replicate data obtained in the current study. The upper triangular matrix was formed by factoring the variance-covariance matrix on the observations into two triangular pairs.

```
ATTACH,IMSLIB.
ATTACH,SSPLIB.
FTN(ROUND=*/+ -, OPT=2,T, R=3)
LDSET(LIB=IMSLIB)
LDSET(LIB=SSPLIB)
LGO.
      PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C     THIS PROGRAM  FACTORS A POSITIVE DEFINITE MATRIX INTO TWO TRIANGULAR PAIRS
C     THE FOLLOWING SUBROUTINES ARE USED FROM MACMASTER  UNIVERSITY
C     COMPUTING CENTER LIBRARY.
C     -VCVTFS,LUDECP,LINV2F,MPRD.
C     MATRIX  CC IS THE COVARIANCE MATRIX ON THE  TRANSFORMED RESPONSES.
      DIMENSION CC(3,3),AA(6),DD(3,3)
      DIMENSION  A(3,3),AI(3,3),WKK(18)
      DIMENSION W(3),Z(3,3),WK(3),BB(6),UL(6)
      DIMENSION  S(3,3)
      DIMENSION  AII(3,3),  SIGMA(3,3)
      N=3
      READ(5,60)  ((CC(I,J),I=1,3),J=1,3)
      DO   33 I=1,N
      DO   33 J=1,N
33    CONTINUE
      WRITE(6,60)  ((CC(I,J),I=1,3),J=1,3)
      DO   50  I=1,3
      DO   50  J=1,3
      DD(I,J)=CC(I,J)
 50   CONTINUE
      CALL  VCVTFS(CC,N,N,AA)
      CALL  LUDECP(AA,UL,N,D1,D2,IER)
      PRINT*, ≠TRIANGULAR MATRIX ELEMENTS≠
      WRITE(6,66)  (UL(I),    I=1,6)
      K=0
      DO 2001 I=1,N
      DO 2000 J=1,I
      K=K+1
2000  A(I,J)=UL(K)
 2001 CONTINUE
      NK=N-1
      DO 2003 I=1,NK
      II=I+1
      DO 2002 J=II,N
 2002 A(I,J)=0.
 2003 CONTINUE
      DO   2004  I=1,N
2004  A(I,I)=1./A(I,I)
      PRINT*, ≠LOWER TRIANGULAR≠
      WRITE(6,60)  ((A(I,J),J=1,N),I=1,N)
      PRINT*, ≠UPPER TRIANGULAR≠
      DO   500   I=1,N
      DO   500   J=1,N
500   S(J,I)=A(I,J)
      WRITE(6,60)  ((S(I,J),J=1,N),I=1,N)
      IDIGT=0
      CALL  LINV2F(S,N,N,AI,IDIGT,WKK,IER)
      PRINT*, ≠INVERSE  OF  UPPER TRIANGULAR≠
      WRITE(6,70)  ((AI(I,J),J=1,N),I=1,N)
      IDIGT=0
      CALL  LINV2F(AI,N,N,AII,IDIGT,WKK,IER)
```

```
      WRITE(6,70)   ((AII(I,J),J=1,N),I=1,N)
      DO 800   I=1,N
      DO  800   J=1,N
800   S(J,I)=AII(I,J)
      MSA=0
      CALL  MPRD (AII,S,SIGMA,N,N,MSA,MSA,N)
      PRINT*, ≠SIGMA≠
      WRITE(6, 70) ((SIGMA(I,J) ,J=1,N) ,I=1,N)
60    FORMAT(3E15.5)
 70   FORMAT(3E12.5)
66    FORMAT(20X,E12.5)
      STOP
      END
   0.17993E-09   -0.14315E-11    0.15807E-10
  -0.14315E-11    0.27167E-11   -0.80452E-12
   0.15807E-10   -0.80452E-12    0.26676E-11
      ENDLISTING
≠        6400 END OF RECORD
≠        6400 END OF RECORD
≠        6400 END OF RECORD

                                   CDTOT      80
```

PROGRAM NO. 5:

This program provides information relating to linear dependencies in the measured multiresponse data.

```
FTN.
LGO(PL=2000)
      PROGRAM TST(INPUT,CUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OU]PUT,TAPE7=PUNC
     1H)
C     THIS PROGRAM  PROVIDES INFORMATION RELATING TO CEPENDENCIES IN THE
C     MULTIRESPCNSE  ANALYSIS
C     SEE TECHNOMETRICS VOL. 15, NC. 1, FEBRUARY 1973 , (PAGE 33 )
C     NEX IS THE NUMBER OF EXPERIMENTAL RUNS
C     NR IS THE NUMBER OF MEASURED RESPONSESOF THE MODEL.
      IMPLICIT COUBLE PRECISICN (A-H,O-Z)
      COUBLE PRECISION NN
      CIMENSICN ARRAY(25,50),Y(14,5)
      CIMENSION  YSUM(5),YBAR(5)
      OIMENSICN  DT(14,5),D(5,14)
      OIMENSICN DDT(5,5)
      OIMENSICN EVECT(5,5)
      OIMENSION VECT(1,5),SIGMA(5,5),VSIG(1,5),VECTT(5,1)
C     DEFINE  DATA CONSTANTS
      NEX=14
      NR=5
      READ(5,555)  ((SIGMA(I,J),I=1,5),J=1,5)
      READ(5,101)  NEX
      DO  10  J=1,NEX
      READ(5,102) KRUN,NN
      READ(5,103)  (ARRAY(I,J),I=1,24)
      WRITE(6,104)
      WRITE(6,105)  KRUN,NN
      WRITE(6,103) (ARRAY(I,J),I=1,24)
10    CONTINUE
C     *******************************************************************
C
      CO  1  J=1,NEX
      DO  1  I=1,NR
      II=I+9
1     Y(J,I)=ARFAY(II,J)
      DO  2  J=1,NP
2     YSUM(J)=0.0D0
      DO  3  J=1,NR
      CC  4  K=1,NEX
4     YSUM(J)=YSUM(J)+Y(K,J)
3     YBAR(J)=YSUM(J)/14.0D0
      DO  5  L=1,5
      CO  5  M=1,NEX
      CT(M,L)=Y(M,L)-YBAR(L)
      D(L,M)=DT(M,L)
5     CONTINUE
      CALL  DGMPRD(D,DT,DDT,NR,NEX,NR)
      MV=0
      CALL  DEIGEN(DDT,EVECT,NR,MV)
      WFITE(6,290)
      WRITE(6,299) ((EVECT(I,J),I=1,NR),J=1,NR)
      WRITE(6,291)
      WRITE(6,299) (DDT(I,I),I=1,NR)
      KV=1
      KS=5
      FACT=14.0D0-1.0D0
      WRITE(6,144)
      CO  6  J=1,NF
      DO  7  I=1,NF
      VECT(1,I)=EVECT(I,J)
```

```
      VECT(1,I)=VECT(1,I)*FACT
      VECTT(I,1)=VECT(1,I)
    7 CONTINUE
      CALL DGMPRD(VECT,SIGMA,VSIG,KV,KS,KS)
      CALL  DGMPRD(VSIG,VECTT,EXVAL,KV,KS,KV)
      WRITE(6,103)  EXVAL
    6 CONTINUE
C     *****************************************************************
  144 FORMAT(5X, *EXPECTED VALUES OF THE EIGENVALUES*)
  101 FORMAT(I3)
  102 FORMAT(I3,D20.12)
  103 FORMAT(4 D20.12)
  104 FORMAT(2X, * EXPERIMENTAL DATA-ARRAY(I,J) *)
  105 FORMAT(2X,*RUN NUMBER= *,I3,/,1X, *NN= *,F10.5)
  299 FORMAT(2X,5(D11.5,3X))
  291 FORMAT(//,5X,*EIGENVALUES OF DDT*)
  290 FORMAT(//,5X,*EIGENVECTORS OF DDT*)
  555 FORMAT(5D12.4)
      STOP
      END
      SUBROUTINE DEIGEN(A,R,N,MV)
C
C     ..................................................................
C
C        SUBROUTINE EIGEN
C
C        PURPOSE
C           COMPUTE EIGENVALUES AND EIGENVECTORS OF A REAL SYMMETRIC
C           MATRIX
C
C        USAGE
C           CALL EIGEN(A,R,N,MV)
C
C        DESCRIPTION OF PARAMETERS
C           A - ORIGINAL MATRIX (SYMMETRIC), DESTROYED IN COMPUTATION.
C               RESULTANT EIGENVALUES ARE DEVELOPED IN DIAGONAL OF
C               MATRIX A IN DESCENDING ORDER.
C           R - RESULTANT MATRIX OF EIGENVECTORS (STORED COLUMNWISE,
C               IN SAME SEQUENCE AS EIGENVALUES)
C           N - ORDER OF MATRICES A AND R
C           MV- INPUT CODE
C                   0   COMPUTE EIGENVALUES AND EIGENVECTORS
C                   1   COMPUTE EIGENVALUES ONLY (R NEED NOT BE
C                       DIMENSIONED BUT MUST STILL APPEAR IN CALLING
C                       SEQUENCE)
C
C        REMARKS
C           ORIGINAL MATRIX A MUST BE REAL SYMMETRIC (STORAGE MODE=1)
C           MATRIX A CANNOT BE IN THE SAME LOCATION AS MATRIX R
C
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C           NONE
C
C        METHOD
C           DIAGONALIZATION METHOD ORIGINATED BY JACOBI AND ADAPTED
C           BY VON NEUMANN FOR LARGE COMPUTERS AS FOUND IN ≠MATHEMATICA
C           METHODS FOR DIGITAL COMPUTERS≠, EDITED BY A. RALSTON AND
C           H.S. WILF, JOHN WILEY AND SONS, NEW YORK, 1962, CHAPTER 7
C
C     ..................................................................
```

```
C
      DIMENSION A(1),R(1)
C
C        ...............................................................
C
C        IF A DOUBLE PRECISION VERSION OF THIS ROUTINE IS DESIRED, THE
C        C IN COLUMN 1 SHOULD BE REMOVED FROM THE DOUBLE PRECISION
C        STATEMENT WHICH FOLLOWS.
C
C     DOUBLE PRECISION A,R,ANORM,ANRMX,THR,X,Y,SINX,SINX2,COSX,
C    1                 COSX2,SINCS
      DOUBLE PRECISION A,R,ANORM,ANRMX,THR,X,Y,SINX,SINX2,COSX,
     1                 COSX2,SINCS
C
C        THE C MUST ALSO BE REMOVED FROM DOUBLE PRECISION STATEMENTS
C        APPEARING IN OTHER ROUTINES USED IN CONJUNCTION WITH THIS
C        ROUTINE.
C
C        THE DOUBLE PRECISION VERSION OF THIS SUBROUTINE MUST ALSO
C        CONTAIN DOUBLE PRECISION FORTRAN FUNCTIONS.  SQRT IN STATEMENT
C        40, 68, 75, AND 78 MUST BE CHANGED TO DSQRT.  ABS IN STATEMENT
C        62 MUST BE CHANGED TO DABS.
C
C        ...............................................................
C
C        GENERATE IDENTITY MATRIX
C
      IF(MV-1) 10,25,10
   10 IQ=-N
      DO 20 J=1,N
      IQ=IQ+N
      DO 20 I=1,N
      IJ=IQ+I
      R(IJ)=0.0
      IF(I-J) 20,15,20
   15 R(IJ)=1.0
   20 CONTINUE
C
C        COMPUTE INITIAL AND FINAL NORMS (ANORM AND ANORMX)
C
   25 ANORM=0.0
      DO 35 I=1,N
      DO 35 J=I,N
      IF(I-J) 30,35,30
   30 IA=I+(J*J-J)/2
      ANORM=ANORM+A(IA)*A(IA)
   35 CONTINUE
      IF(ANORM) 165,165,40
   40 ANORM=1.414*DSQRT(ANORM)
      ANRMX=ANORM*1.0E-6/FLOAT(N)
C
C        INITIALIZE INDICATORS AND COMPUTE THRESHOLD, THR
C
      IND=0
      THR=ANORM
   45 THR=THR/FLOAT(N)
   50 L=1
   55 M=L+1
C
C        COMPUTE SIN AND COS
```

```
C
   60 MQ=(M*M-M)/2
      LQ=(L*L-L)/2
      LM=L+MQ
   62 IF(DABS(A(LM))-THR) 130,65,65
   65 IND=1
      LL=L+LQ
      MM=M+MQ
      X=0.5*(A(LL)-A(MM))
   68 Y=-A(LM)/ DSQRT(A(LM)*A(LM)+X*X)
      IF(X) 70,75,75
   70 Y=-Y
   75 SINX=Y/DSQRT(2.0*(1.0+(DSQRT(1.0-Y*Y))))
      SINX2=SINX*SINX
   78 COSX=DSQRT(1.0-SINX2)
      COSX2=COSX*COSX
      SINCS =SINX*COSX
C
C        ROTATE L AND M COLUMNS
C
      ILQ=N*(L-1)
      IMQ=N*(M-1)
      DO 125 I=1,N
      IQ=(I*I-I)/2
      IF(I-L) 80,115,80
   80 IF(I-M) 85,115,90
   85 IM=I+MQ
      GO TO 95
   90 IM=M+IQ
   95 IF(I-L) 100,105,105
  100 IL=I+LQ
      GO TO 110
  105 IL=L+IQ
  110 X=A(IL)*COSX-A(IM)*SINX
      A(IM)=A(IL)*SINX+A(IM)*COSX
      A(IL)=X
  115 IF(MV-1) 120,125,120
  120 ILR=ILQ+I
      IMR=IMQ+I
      X=R(ILR)*COSX-R(IMR)*SINX
      R(IMR)=R(ILR)*SINX+R(IMR)*COSX
      R(ILR)=X
  125 CONTINUE
      X=2.0*A(LM)*SINCS
      Y=A(LL)*COSX2+A(MM)*SINX2-X
      X=A(LL)*SINX2+A(MM)*COSX2+X
      A(LM)=(A(LL)-A(MM))*SINCS+A(LM)*(COSX2-SINX2)
      A(LL)=Y
      A(MM)=X
C
C        TESTS FOR COMPLETION
C
C        TEST FOR M = LAST COLUMN
C
  130 IF(M-N) 135,140,135
  135 M=M+1
      GO TO 60
C
C        TEST FOR L = SECOND FROM LAST COLUMN
C
```

```
  140 IF(L-(N-1)) 145,150,145
  145 L=L+1
      GO TO 55
  150 IF(IND-1) 160,155,160
  155 IND=0
      GO TO 50
C
C        COMPARE THRESHOLD WITH FINAL NORM
C
  160 IF(THR-ANRMX) 165,165,45
C
C        SORT EIGENVALUES AND EIGENVECTORS
C
  165 IQ=-N
      DO 185 I=1,N
      IQ=IQ+N
      LL=I+(I*I-I)/2
      JQ=N*(I-2)
      DO 185 J=I,N
      JQ=JQ+N
      MM=J+(J*J-J)/2
      IF(A(LL)-A(MM)) 170,185,185
  170 X=A(LL)
      A(LL)=A(MM)
      A(MM)=X
      IF(MV-1) 175,185,175
  175 DO 180 K=1,N
      ILR=IQ+K
      IMR=JQ+K
      X=R(ILR)
      R(ILR)=R(IMR)
  180 R(IMR)=X
  185 CONTINUE
      RETURN
      E N D
      SUBROUTINE  DGMPRD(A,B,R,N,M,L)
C     DGMPRD  -MATRIX PRODUCT ROUTINE
C     DOUBLE PRECISION VERSION OF GMPRD
C     SSP -LIBRARY ROUTINE -MACMASTER UNIVERSITY COMPUTING CENTER.
      IMPLICIT  DOUBLE PRECISION  (A-H,O-Z)
      DIMENSION A(1),B(1),R(1)
C
      IR=0
      IK=-M
      DO 10 K=1,L
      IK=IK+M
      DO 10 J=1,N
      IR=IR+1
      JI=J-N
      IB=IK
      R(IR)=0
      DO 10 I=1,M
      JI=JI+N
      IB=IB+1
   10 R(IR)=R(IR)+A(JI)*B(IB)
      RETURN
      END
   .18240D-09    .72350D-11    .13560D-10   -.26000D-10   -.64620D-10
   .72350D-11    .52870D-12    .11060D-11   -.18220D-11   -.32170D-11
   .13560D-10    .11060D-11    .25350D-11   -.47570D-11   -.10200D-10
```

```
 -.2600D-10  -.1822D-11  -.4757D-11   .1525D-10   .3787D-10
 -.6462D-10  -.3217D-11  -.1020D-10   .3787D-10   .1150D-09
  14
426   .100438000000D+02
  .394500000000D-03  0.                 0.                 0.
  0.                 .748000000000D-02  .195400000000D-01  0.
  0.                 .223600000000D-03  .129200000000D-04  .954300000000D-05
  .805900000000D-04  .125600000000D-03  .576600000000D-02  .171100000000D-01
  .244500000000D-03  .143200000000D-04  .623200000000D+03  .154000000000D+03
  .100000000000D+01  .109900000000D+04  .719400000000D-02  .154000000000D+03
428   .998030000000D+01
  .375800000000D-03  0.                 0.                 0.
  0.                 .516400000000D-02  .276200000000D-01  0.
  0.                 .205500000000D-03  .120800000000D-04  .765200000000D-05
  .899500000000D-04  .135900000000D-03  .396000000000D-02  .166700000000D-01
  .384500000000D-03  .178300000000D-04  .643200000000D+03  .112000000000D+03
  .100000000000D+01  .972000000000D+03  .615800000000D-02  .112000000000D+03
430   .101963000000D+02
  .520900000000D-03  0.                 0.                 0.
  0.                 .366400000000D-02  .204200000000D-01  0.
  0.                 .327500000000D-03  .155200000000D-04  .120400000000D-04
  .111700000000D-03  .198300000000D-03  .279200000000D-02  .184400000000D-01
  .191700000000D-03  .127700000000D-04  .627200000000D+03  .100000000000D+03
  .100000000000D+01  .962000000000D+03  .578800000000D-02  .100000000000D+03
504   .998400000000D+01
  .383700000000D-03  0.                 0.                 0.
  0.                 .513800000000D-02  .187300000000D-01  0.
  0.                 .235000000000D-03  .129200000000D-04  .984900000000D-05
  .840000000000D-04  .113100000000D-03  .409000000000D-02  .168300000000D-01
  .924900000000D-04  .146000000000D-04  .643200000000D+03  .112000000000D+03
  .100000000000D+01  .972000000000D+03  .615100000000D-02  .112000000000D+03
512   .993260000000D+01
  .367500000000D-03  0.                 0.                 0.
  0.                 .519100000000D-02  .186500000000D-01  0.
  0.                 .219500000000D-03  .115900000000D-04  .651400000000D-05
  .871100000000D-04  .123100000000D-03  .415000000000D-02  .166900000000D-01
  .498600000000D-03  .174500000000D-04  .643200000000D+03  .970000000000D+02
  .100000000000D+01  .970000000000D+03  .622000000000D-02  .970000000000D+02
515   .100051000000D+02
  .648900000000D-03  0.                 0.                 0.
  0.                 .502900000000D-02  .190900000000D-01  0.
  0.                 .440000000000D-03  .233000000000D-04  .134500000000D-04
  .917200000000D-04  .145800000000D-03  .412200000000D-02  .171400000000D-01
  .414800000000D-03  .184300000000D-04  .651200000000D+03  .970000000000D+02
  .100000000000D+01  .100500000000D+04  .654100000000D-02  .970000000000D+02
523   .983230000000D+01
  .646000000000D-03  0.                 0.                 0.
  0.                 .508700000000D-02  .159700000000D-01  0.
  0.                 .324500000000D-03  .169800000000D-04  .107100000000D-04
  .235500000000D-03  .341400000000D-03  .390800000000D-02  .156100000000D-01
  .290400000000D-03  .570000000000D-04  .630200000000D+03  .410000000000D+02
  .100000000000D+01  .852000000000D+03  .344200000000D-02  .410000000000D+02
524   .992710000000D+01
  .350100000000D-03  0.                 0.                 0.
  0.                 .535800000000D-02  .186700000000D-01  0.
  0.                 .203400000000D-03  .109600000000D-04  .575800000000D-05
  .920300000000D-04  .128500000000D-03  .405300000000D-02  .172500000000D-01
  .263100000000D-03  .184000000000D-04  .643200000000D+03  .950000000000D+02
  .100000000000D+01  .977000000000D+03  .617100000000D-02  .950000000000D+02
527   .995480000000D+01
```

```
   .573400000000D-03   0.                  0.                  0.
  0.                   .305800000000D-02   .177900000000D-01   0.
  0.                   .379800000000D-03   .181100000000D-04   .744300000000D-05
   .128200000000D-03   .184300000000D-03   .256000000000D-02   .165500000000D-01
   .247300000000D-03   .249600000000D-04   .653200000000D+03   .550000000000D+02
   .100000000000D+01   .872000000000D+03   .401500000000D-02   .550000000000D+02
529   .996160000000D+01
   .579800000000D-03   0.                  0.                  0.
  0.                   .257600000000D-02   .193000000000D-01   0.
  0.                   .380100000000D-03   .161900000000D-04   .589500000000D-05
   .110700000000D-03   .150200000000D-03   .239000000000D-02   .175300000000D-01
   .223200000000D-03   .202700000000D-04   .628200000000D+03   .650000000000D+02
   .100000000000D+01   .879000000000D+03   .478100000000D-02   .650000000000D+02
531   .995080000000D+01
   .705500000000D-03   0.                  0.                  0.
  0.                   .754500000000D-02   .175000000000D-01   0.
  0.                   .408200000000D-03   .186700000000D-04   .695600000000D-05
   .105500000000D-03   .162100000000D-03   .469100000000D-02   .160000000000D-01
   .254600000000D-03   .222000000000D-04   .628200000000D+03   .100000000000D+03
   .100000000000D+01   .992000000000D+03   .534400000000D-02   .100000000000D+03
605   .993050000000D+01
   .387100000000D-03   0.                  0.                  0.
  0.                   .523800000000D-02   .188200000000D-01   0.
  0.                   .226300000000D-03   .119100000000D-04   .657300000000D-05
   .938000000000D-04   .140600000000D-03   .422300000000D-02   .170400000000D-01
   .587400000000D-03   .200100000000D-04   .643200000000D+03   .850000000000D+02
   .100000000000D+01   .980000000000D+03   .620000000000D-02   .850000000000D+02
610   .896880000000D+01
   .598000000000D-03   0.                  0.                  0.
  0.                   .269000000000D-02   .208000000000D-01   0.
  0.                   .422000000000D-03   .191000000000D-04   .440000000000D-05
   .538000000000D-04   .135000000000D-03   .217000000000D-02   .186000000000D-01
   .152900000000D-03   .506000000000D-04   .656200000000D+03   .100000000000D+03
   .100000000000D+01   .985000000000D+03   .721400000000D-02   .100000000000D+03
517   .970440000000D+01
   .308100000000D-03   0.                  0.                  0.
  0.                   .605500000000D-02   .159500000000D-01   0.
  0.                   .132600000000D-03   .625300000000D-05   .528600000000D-05
   .176400000000D-03   .300200000000D-03   .544600000000D-02   .172800000000D-01
   .442400000000D-03   .597700000000D-04   .629200000000D+03   .550000000000D+02
   .100000000000D+01   .875000000000D+03   .387600000000D-02   .550000000000D+02
       ENDLISTING
≠         6400 END OF RECORD
≠         6400 END OF RECORD
≠         6400 END OF RECORD
```

CDTOT   405

PROGRAM NO. 6:

This program was employed to estimate the parameters in the model using the statistical technique of Hoffman and Reilley [124].

```
      PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C      *****FIVE INDEPENDENT RESPONSES-OX,OTA,PA,PI,CO2/CO
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLE  NN
      COMMON /STOIC/NN
      COMMON/EIGVT/Z
      DIMENSION ARRAY (25,50)
      DIMENSION X(14,15), Y(14,3),GAM(12),ALPH(12),UM1(12,12),VM1(12,12)
      DIMENSION  VM2(12,12),T(12),W1(12),XDROW(15),F(3),D(3,12),FD(3)
      DIMENSION IR(12),IC(12)
      DIMENSION YYY(3)
      DIMENSION  Z(3,5)
C
C
C     *************        READ IN EXPERIMENTAL DATA      *************
      READ(5,101)NEX
      DO 10 J=1,NEX
      READ(5,102)KRUN,NN
      READ(5,103) (ARRAY(I,J),I=1,24)
      WRITE(6,104)
      WRITE(6,105)KRUN,NN
      WRITE(6,103) (ARRAY(I,J),I=1,24)
   10 CONTINUE
C
C     READ  IN  PARAMETER VALUES
      READ(5,20) ALPH
      PRINT*, ≠     ALPH≠
      WRITE(6,20) ALPH
      READ(5,20) UM1
      PRINT*,    ≠      UM1≠
      WRITE(6,20) UM1
      READ(5,20) GAM
      PRINT*, ≠      GAM≠
      WRITE(6,20) GAM
      READ(5,*) START, END
      ISTART=START+0.001
      IEND=END+0.001
      NR=5
      NRT=3
      READ(5,666)   ((Z(I,J),J=1,NR ),I=1,NRT)
      PRINT*, ≠INDEPENDENT ORTHORGONAL EIGENVECTORS≠
      WRITE(6,666)  ((Z(I,J),J=1,NR ),I=1,NRT)
      DO   201   J=1,NEX
      DO   2 I=1,9
 2    X(J,I)=ARRAY(I,J)
      DO   3   I=10,15
      II=I+9
 3    X(J,I)=ARRAY(II,J)
      YYY(1)= ARRAY(10,J)*Z(1,1)+ARRAY(11,J)*Z(1,2)+ARRAY(12,J)*Z(1,3)+
     1ARRAY(13,J)*Z(1,4)+ARRAY(14,J)*Z(1,5)
      YYY(2)=ARRAY(10,J)*Z(2,1)+ARRAY(11,J)*Z(2,2)+ARRAY(12,J)*Z(2,3)+
     1ARRAY(13,J)*Z(2,4)+ARRAY(14,J)*Z(2,5)
      YYY(3)=ARRAY(10,J)*Z(3,1)+ARRAY(11,J)*Z(3,2)+ARRAY(12,J)*Z(3,3)+
     1ARRAY(13,J)*Z(3,4)+ARRAY(14,J)*Z(3,5)
      CALL  TRANS(YYY)
      DO   44 I=1,NRT
```

```
   44     Y(J,I)=YYY(I)
  201     CONTINUE
          NPAR=12
          NIND=15
          NDEP=3
          FACT=1.0D-06
          DO  1    I=ISTART,IEND
          CALL  NEWALG(NEX,NPAR,NIND,NDEP,X,Y,GAM,FACT,ALPH,UM1,VM1,VM2,T,W1
         1,XORCW,F,Q,FD,IR,IC)
          PRINT*,≠          I≠
          WRITE(6,22) I
          PRINT*,≠          T≠
          WRITE(6,20) T
          PRINT*,≠          I≠
          WRITE(6,22) I
          PRINT*,≠                  W1≠
          WRITE(6,20) W1
          PRINT*,≠          I≠
          WRITE(6,22) I
          PRINT*, ≠            GAM≠
          WRITE(6,20)   GAM
          IF(I .LT. IEND ) GO TO 400
          WRITE(7,20) GAM
  400     CONTINUE
  1       CONTINUE
          PRINT*,   ≠INITIAL VM2  MATRIX≠
          WRITE(6,222)VM2
          CALL  MINVRD(VM2,NPAR,NPAR,END,I,IR,IC)
          PRINT*,≠           VM2≠
          WRITE(6,222) VM2
  222     FORMAT(1X,12D11.4)
          PRINT*,    ≠DETERMINANT OF  FINAL VM2  MATRIX≠
          WRITE(6,20)  END
  C          **********     FORMAT STATEMENTS     ******
  20      FORMAT(4D20.12)
  21      FORMAT(2F20.5)
  666     FORMAT(5D15.5)
   1004 FORMAT(1X,*----------*,/)
   1001 FORMAT(D20.6)
  22      FORMAT(I10)                                                       TER00220
     108 FORMAT(6X, * ACTIVE SITE PARAMETER = *, F10.5)
     101 FORMAT(I3)
  102     FORMAT(I3,D20.12)
  103     FORMAT(4D20.12)
     104 FORMAT(2X,* EXPERIMENTAL DATA - ARRAY(I,J) *)
     105 FORMAT(2X, * RUN NUMBER = *,I3,/,1X, *NN= *,F10.5)
     106 FORMAT(8F10.0)
          STOP
          END

CKS--

  36B  /EIGVT/                     2B  /STCIC/
```

```
      SUBROUTINE TRANS(F)                                               TER00270
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION F(3)
      DIMENSION TR(6)
      DATA TR/0.745500+05,0.483700+04,-0.815400+05,0.607980+06,
     10.238290+06,0.949740+06/
      F(1)=TR(1)*F(1)+TR(2)*F(2)+TR(3)*F(3)
      F(2)=TR(4)*F(2)+TR(5)*F(3)
      F(3)=TR(6)*F(3)
      RETURN
      END
```

```
      SUBROUTINE MODEL(XI,TH,F)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLEKA,KAI,KR12,KR12I,KR23,KR23I,KR34,KR34I,KR5,KR5I
      COMMON /EIGVT/Z
      COMMON/PARA1/KA,KR12,KR23,KR34,KR5,ASITES
      COMMON/DEP/Y
      COMMON/CONST/RT
      COMMON/DER/FGAS
      COMMON/MER/T,DELP,W,PT,GRACP
      COMMON/ERROR/ERR
      COMMON/REPAR/TBASE
      DIMENSION  XI(15),TH(12),F(3),Y(10)
      DIMENSION  Z(3,5)
      R=1.9872000
      DO 2 I=1,9
2     Y(I)=XI(I)
      T=XI(10)
      DELP=XI(11)
      W=XI(12)
      PT=XI(13)
      FGAS=XI(14)
      GRACP=XI(15)
      TBASE=273.2 +370.
      TSTAR=(TBASE-T)/(TBASE*T)
      RT=TSTAR/R
      KA=TH(1)*DEXP(TH(6)*RT)
      KR12=TH(2)*DEXP(TH(7)*RT)
      KR23=TH(3)*DEXP(TH(8)*RT)
      KR34=TH(4)*DEXP(TH(9)*RT)
      KR5=TH(5)*DEXP(TH(10)*RT)
      ASITES=DEXP(TH(12))*DEXP(TH(11)*RT)
      X=0.
      DX=0.005
      TOLKM=1.0D-08
      DXMIN=0.0001
      N=5
      DELX=W
      CALL  MERSON (X,DELX,DX,DXMIN,TOLKM,N)
      F(1)=Y(1)*Z(1,1)+Y(2)*Z(1,2)+Y(3)*Z(1,3)+Y(4)*Z(1,4)+Y(5)*Z(1,5)
      F(2)=Y(1)*Z(2,1)+Y(2)*Z(2,2)+Y(3)*Z(2,3)+Y(4)*Z(2,4)+Y(5)*Z(2,5)
      F(3)=Y(1)*Z(3,1)+Y(2)*Z(3,2)+Y(3)*Z(3,3)+Y(4)*Z(3,4)+Y(5)*Z(3,5)
      CALL TRANS(F)                                                     TER01700
      RETURN                                                            TER01710
      END                                                               TER01720

CKS--

   2B  /CONST/                  24B  /DEP/                  2B  /DER/
```

```
      SUBROUTINE NEWALG(N,P,NIND,NDEP,XDATA,YDATA,GAM,FACT,ALPH,UM1,VM1,TER00010
     2VM2,T,W1,XDROW,F,D,FD,IR,IC)                                      TER00020
C     SEE XXII P153 FOR WRITEUP                                         TER00030
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION XDATA(N,NIND),YDATA(N,NDEP),GAM(P),ALPH(P),UM1(P,P),VM1 TER00060
     2(P,P),T(P),W1(P),XDROW(NIND),F(NDEP),D(NDEP,P),IR(P),IC(P),FD(NDEPTER00070
     3),VM2(P,P)                                                        TER00080
      INTEGER P                                                         TER00050
C     INITIALIZE VM1 AND T                                              TER00090
      DO 1 IP1=1,P                                                      TER00100
      W1(IP1)=ALPH(IP1)-GAM(IP1)                                        TER00110
      DO 1 IP2=IP1,P                                                    TER00120
1     VM1(IP1,IP2)=UM1(IP1,IP2)                                         TER00130
      CALL VCMPYD(UM1,P,P,P,P,W1,T)                                     TER00140
C     GO THROUGH DATA ONCE ACCUMULATING CONTRIBUTIONS TO VM1 AND T      TER00150
      DO 3 IN1=1,N                                                      TER00160
C     EVALUATE MODEL AND ITS DERIVATIVES                                TER00170
      DO 2 IIND1=1,NIND                                                 TER00180
2     XDROW(IIND1)=XDATA(IN1,IIND1)                                     TER00190
      CALL VALUES(P,NIND,NDEP,FACT,XDROW,GAM,F,D,W1,FD)                 TER00200
C     ADD CONTRIBUTIONS                                                 TER00210
      DO 3 IDEP1=1,NDEP                                                 TER00220
      Z=YDATA(IN1,IDEP1)-F(IDEP1)                                       TER00230
      DO 3 IP1=1,P                                                      TER00240
      X=D(IDEP1,IP1)                                                    TER00250
      T(IP1)=T(IP1)+X*Z                                                 TER00260
      DO 3 IP2=IP1,P                                                    TER00270
3     VM1(IP1,IP2)=VM1(IP1,IP2)+X*D(IDEP1,IP2)                          TER00280
C     FILL IN LOWER TRIANGLE OF VM1 AND GENERATE VM2 AND W1             TER00290
      DO 4 IP1=1,P                                                      TER00300
      W1(IP1)=T(IP1)                                                    TER00310
      DO 4 IP2=IP1,P                                                    TER00320
      Z=VM1(IP1,IP2)                                                    TER00330
      VM1(IP2,IP1)=Z                                                    TER00340
      VM2(IP1,IP2)=Z                                                    TER00350
      VM2(IP2,IP1)=Z
4     CONTINUE
C     CALCULATE CORRECTION AND APPLY IT                                 TER00370
      CALL LNEQND(VM1,P,P,P,T,IR,IC,IER)                                TER00380
      DO 5 IP1=1,P                                                      TER00390
5     GAM(IP1)=GAM(IP1)+T(IP1)                                          TER00400
      RETURN                                                            TER00410
      END                                                               TER00420

--

          LNEQND     VALUES     VCMPYD

 LABELS--

.1     ID          0B               .2     ID         0B               .3     ID          0B               .4     ID          0
.5     ID          0B
```

```
      SUBROUTINE MINVRD(A,IA,MA,DETA,IER,IR,IC)                         TER00610
      DOUBLE A(IA,IA),DETA,PIV,PIV1,TEMP
      DIMENSIONIR(MA),IC(MA)                                            TER00630
      IER=0                                                             TER00640
      DO1I=1,MA                                                         TER00650
      IR(I)=0                                                           TER00660
1     IC(I)=0                                                           TER00670
      DETA=1.0D0                                                        TER00680
      DO123IJKL=1,MA                                                    TER00690
2     CALLSUBMXD(A,IA,IA,MA,MA,IR,IC,I,J)                               TER00700
      PIV=A(I,J)                                                        TER00710
      DETA=PIV*DETA                                                     TER00720
      IF(PIV.EQ.0.D0)GOTO17                                             TER00730
      IR(I)=J                                                           TER00740
      IC(J)=I                                                           TER00750
      PIV=1.D0/PIV                                                      TER00760
      DO5K=1,MA                                                         TER00770
5     A(I,K)=A(I,K)*PIV                                                 TER00780
      A(I,J)=PIV                                                        TER00790
      DO9K=1,MA                                                         TER00800
      IF(K.EQ.I)GOTO9                                                   TER00810
      PIV1=A(K,J)                                                       TER00820
6     DO8L=1,MA                                                         TER00830
8     A(K,L)=A(K,L)-PIV1*A(I,L)                                         TER00840
      A(K,J)=PIV1                                                       TER00850
9     CONTINUE                                                          TER00860
      PIV1=A(I,J)                                                       TER00870
      DO11K=1,MA                                                        TER00880
11    A(K,J)=-PIV*A(K,J)                                                TER00890
      A(I,J)=PIV1                                                       TER00900
123   CONTINUE                                                          TER00910
12    DO16I=1,MA                                                        TER00920
      K=IC(I)                                                           TER00930
      M=IR(I)                                                           TER00940
      IF(K.EQ.I)GOTO16                                                  TER00950
      DETA=-DETA                                                        TER00960
      DO14L=1,MA                                                        TER00970
      TEMP=A(K,L)                                                       TER00980
      A(K,L)=A(I,L)                                                     TER00990
14    A(I,L)=TEMP                                                       TER01000
      DO15L=1,MA                                                        TER01010
      TEMP=A(L,M)                                                       TER01020
      A(L,M)=A(L,I)                                                     TER01030
15    A(L,I)=TEMP                                                       TER01040
      IC(M)=K                                                           TER01050
      IR(K)=M                                                           TER01060
16    CONTINUE                                                          TER01070
      RETURN                                                            TER01080
17    IER=1                                                             TER01090
      RETURN                                                            TER01100
      END                                                               TER01110
```

```
          SUBROUTINEVCMPVD(A,IA,JA,MA,NA,W,X)                                            TER01120
          DOUBLE  A(IA,JA),W(NA),SUMK,X(MA)
          DO3K=1,MA                                                                      TER01140
          SUMK=0.0D0                                                                     TER01150
          DO1L=1,NA                                                                      TER01160
    1     SUMK=SUMK+A(K,L)*W(L)                                                          TER01170
    3     X(K)=SUMK                                                                      TER01180
          RETURN                                                                         TER01190
          END                                                                            TER01200
```

```
          SUBROUTINE VALUES(P,NIND,NDEP,FACT,X,GAM,F,D,THETA,FD)                         TER00430
          IMPLICIT DOUBLE PRECISION (A-H,O-Z)
          INTEGER P                                                                      TER00450
          DIMENSION X(NIND),GAM(P),F(NDEP),D(NDEP,P),THETA(P),FD(NDEP)                   TER00460
    C     MODEL IS EVALUATED UNDER GIVEN CONDITIONS                                      TER00470
          DO 1 IP1=1,P                                                                   TER00480
    1     THETA(IP1)=GAM(IP1)                                                            TER00490
          CALL MODEL(X,THETA,F)                                                          TER00500
    C     DERIVATIVES ARE CALCULATED                                                     TER00510
          DO 2 IP1=1,P                                                                   TER00520
          DELTA=FACT*GAM(IP1)                                                            TER00530
          IF(IP1 .EQ.  12) DELTA=FACT
          THETA(IP1)=THETA(IP1)+DELTA                                                    TER00540
          CALL MODEL(X,THETA,FD)                                                         TER00550
          THETA(IP1)=GAM(IP1)                                                            TER00560
          DO 2 IDEP=1,NDEP                                                               TER00570
    2     D(IDEP,IP1)=(FD(IDEP)-F(IDEP))/DELTA                                           TER00580
          RETURN                                                                         TER00590
          END                                                                            TER00600
```

```
        MODEL

LABELS--

1     ID          0B               .2     ID          0B

AP--

    D A       0B           VAR-DIM           DELTA      D         167B
    D A       0B           VAR-DIM           FACT       D  AU       0B
    D A       0B           VAR-DIM           GAM        D  AU       0B           VAR-DIM
    I  U    172B                             IP1        I   U     171B
    I               SUBROUTINE               NDEP       I  AU       0B
    I AU      0B                             P          I  AU       0B
    D A       0B           VAR-DIM           VALUES     -         153B ENTRY
    D A       0B           VAR-DIM


GRAM-UNIT LENGTH        . 17 SYMBOLS

 STORAGE USED           .195 SECONDS
```

```
      SUBROUTINELNEQND(A,IA,JA,MA,W,IR,IC,IER)                          TER01400
      DOUBLE A(IA,JA),W(MA),DET,PIV,PIV1,PIV2,TEMP                      TER0160
      DOUBLE SMALL,BIG,DET1,FACTOR                                       TER0161
      DIMENSIONIR(MA),IC(MA)                                            TER01430
      R=MA                                                              TER01440
      S=0.                                                              TER01450
      IER=0                                                             TER01460
      DET=1.0D0                                                         TER01470
      DET1=1.0D0                                                        TER01480
      DO2K=1,MA                                                         TER01490
      IR(K)=0                                                           TER01500
2     IC(K)=0                                                           TER01510
      DO20K=1,MA                                                        TER01520
      BIG=DABS(A(K,1))                                                  TER01530
MULTIPLY BY 1 -- IGNORED
      SMALL=BIG                                                         TER01540
      DO21J=2,MA                                                        TER01550
      TEMP=DABS(A(K,J))                                                 TER01560
      IF(TEMP.GT.BIG)BIG=TEMP                                           TER01570
21    IF(TEMP.LT.SMALL)SMALL=TEMP                                       TER01580
      TEMP=DABS(W(K))                                                   TER01590
      IF(TEMP.GT.BIG)BIG=TEMP                                           TER01600
      IF(TEMP.LT.SMALL)SMALL=TEMP                                       TER01610
      IF(SMALL.EQ.0.0D0)SMALL=1.0D0                                     TER01620
      IF(BIG.EQ.0.0D0)GOTO20                                            TER01630
      FACTOR=1.0D0/DSQRT(BIG*SMALL)                                     TER01640
      DET1=DET1/FACTOR                                                  TER01650
      DO22J=1,MA                                                        TER01660
22    A(K,J)=A(K,J)*FACTOR                                              TER01670
      W(K)=W(K)*FACTOR                                                  TER01680
20    CONTINUE                                                          TER01690
3     CALLSUBMXD(A,IA,JA,MA,MA,IR,IC,I,J)                               TER01700
      PIV=A(I,J)                                                        TER01710
      DET=PIV*DET                                                       TER01720
      IF(DABS(PIV).LT.1.0D-10)GOTO16                                    TER01730
      IR(I)=J                                                           TER01740
      IC(J)=I                                                           TER01750
      PIV=1.D0/PIV                                                      TER01760
      DO6K=1,MA                                                         TER01770
6     A(I,K)=A(I,K)*PIV                                                 TER01780
      W(I)=W(I)*PIV                                                     TER01790
      DO10L=1,MA                                                        TER01800
      IF(IC(L).NE.0)GOTO10                                              TER01810
      PIV1=A(I,L)                                                       TER01820
      DO9K=1,MA                                                         TER01830
9     IF(K.NE.I)A(K,L)=A(K,L)-PIV1*A(K,J)                               TER01840
10    CONTINUE                                                          TER01850
      PIV2=W(I)                                                         TER01860
      DO12K=1,MA                                                        TER01870
12    IF(K.NE.I)W(K)=W(K)-PIV2*A(K,J)                                   TER01880
      S=S+1.                                                            TER01890
      IF(S.LT.R)GOTO3                                                   TER01900
      DO15J=1,MA                                                        TER01910
      K=IC(J)                                                           TER01920
      L=IR(J)                                                           TER01930
      IF(K.EQ.J)GOTO15                                                  TER01940
      TEMP=W(J)                                                         TER01950
```

```
              W(J)=W(K)                                                         TER01960
              W(K)=TEMP                                                         TER01970
              IC(L)=K                                                           TER01980
              IR(K)=L                                                           TER01990
              DET=-DET                                                          TER02000
        15    CONTINUE                                                          TER02010
        16    A(1,1)=DET*DET1                                                   TER02020
        MULTIPLY BY 1 -- IGNORED
              IF(DABS(DET).LT.1.0D-09)IER=1                                     TER02030
              RETURN                                                            TER02040
              END                                                               TER02050

              SUBROUTINESUBMXD(A,IA,JA,MA,NA,IR,IC,I,J)                         TER01210
              DOUBLE A(IA,JA),TEST,X
              DIMENSIONIR(MA),IC(NA)                                            TER01230
              I=0                                                               TER01240
              J=0                                                               TER01250
              TEST=0.0D0                                                        TER01260
              DO5K=1,MA                                                         TER01270
              IF(IR(K).NE.0)GOTO5                                               TER01280
              DO4L=1,NA                                                         TER01290
              IF(IC(L).NE.0)GOTO4                                               TER01300
              X=DABS(A(K,L))                                                    TER01310
              IF(X.LT.TEST)GOTO4                                                TER01320
              I=K                                                               TER01330
              J=L                                                               TER01340
              TEST=X                                                            TER01350
        4     CONTINUE                                                          TER01360
        5     CONTINUE                                                          TER01370
              RETURN                                                            TER01380
              END                                                               TER01390

 LABELS--

.4      D        60B              .5      D        64B

MAP--

     D AU      0B            VAR-DIM          DABS      D                INTRINSIC
     I A       0B                             IA        I AU      0B
     I AU      0B            VAR-DIM          IR        I AU      0B              VAR-DIM
     I A       0B                             JA        I AU      0B
     I  U    106B                             L         I  U    107B
     I AU      0B                             NA        I AU      0B
D    -        72B ENTRY                       TEST      D       112B
     C       110B

OGRAM-UNIT LENGTH         17 SYMBOLS

M STORAGE USED          .129 SECONDS
```

```
      SUBROUTINE DEIGEN(A,R,N,MV)
C
C        ..................................................................
C
C           SUBROUTINE EIGEN
C
C           PURPOSE
C              COMPUTE EIGENVALUES AND EIGENVECTORS OF A REAL SYMMETRIC
C              MATRIX
C
C           USAGE
C              CALL EIGEN(A,R,N,MV)
C
C           DESCRIPTION OF PARAMETERS
C              A - ORIGINAL MATRIX (SYMMETRIC), DESTROYED IN COMPUTATION.
C                  RESULTANT EIGENVALUES ARE DEVELOPED IN DIAGONAL OF
C                  MATRIX A IN DESCENDING ORDER.
C              R - RESULTANT MATRIX OF EIGENVECTORS (STORED COLUMNWISE,
C                  IN SAME SEQUENCE AS EIGENVALUES)
C              N - ORDER OF MATRICES A AND R
C              MV- INPUT CODE
C                      0   COMPUTE EIGENVALUES AND EIGENVECTORS
C                      1   COMPUTE EIGENVALUES ONLY (R NEED NOT BE
C                          DIMENSIONED BUT MUST STILL APPEAR IN CALLING
C                          SEQUENCE)
C
C           REMARKS
C              ORIGINAL MATRIX A MUST BE REAL SYMMETRIC (STORAGE MODE=1)
C              MATRIX A CANNOT BE IN THE SAME LOCATION AS MATRIX R
C
C           SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C              NONE
C
C           METHOD
C              DIAGONALIZATION METHOD ORIGINATED BY JACOBI AND ADAPTED
C              BY VON NEUMANN FOR LARGE COMPUTERS AS FOUND IN ≠MATHEMATICA
C              METHODS FOR DIGITAL COMPUTERS≠, EDITED BY A. RALSTON AND
C              H.S. WILF, JOHN WILEY AND SONS, NEW YORK, 1962, CHAPTER 7
C
C        ..................................................................
C
      DIMENSION A(1),R(1)
C
C        ..................................................................
C
C           IF A DOUBLE PRECISION VERSION OF THIS ROUTINE IS DESIRED, THE
C           C IN COLUMN 1 SHOULD BE REMOVED FROM THE DOUBLE PRECISION
C           STATEMENT WHICH FOLLOWS.
C
C     DOUBLE PRECISION A,R,ANORM,ANRMX,THR,X,Y,SINX,SINX2,COSX,
C    1                 COSX2,SINCS
      DOUBLE PRECISION A,R,ANORM,ANRMX,THR,X,Y,SINX,SINX2,COSX,
     1                 COSX2,SINCS
C
C        THE C MUST ALSO BE REMOVED FROM DOUBLE PRECISION STATEMENTS
C        APPEARING IN OTHER ROUTINES USED IN CONJUNCTION WITH THIS
C        ROUTINE.
```

```
C
C        THE DOUBLE PRECISION VERSION OF THIS SUBROUTINE MUST ALSO
C        CONTAIN DOUBLE PRECISION FORTRAN FUNCTIONS.  SQRT IN STATEMENT
C        40, 68, 75, AND 78 MUST BE CHANGED TO DSQRT.  ABS IN STATEMENT
C        62 MUST BE CHANGED TO DABS.
C
C        ..............................................................
C
C        GENERATE IDENTITY MATRIX
C
      IF(MV-1) 10,25,10
   10 IQ=-N
      DO 20 J=1,N
      IQ=IQ+N
      DO 20 I=1,N
      IJ=IQ+I
      R(IJ)=0.0
      IF(I-J) 20,15,20
   15 R(IJ)=1.0
   20 CONTINUE
C
C        COMPUTE INITIAL AND FINAL NORMS (ANORM AND ANORMX)
C
   25 ANORM=0.0
      DO 35 I=1,N
      DO 35 J=I,N
      IF(I-J) 30,35,30
   30 IA=I+(J*J-J)/2
      ANORM=ANORM+A(IA)*A(IA)
   35 CONTINUE
      IF(ANORM) 165,165,40
   40 ANORM=1.414*DSQRT(ANORM)
      ANRMX=ANORM*1.0E-6/FLOAT(N)
C
C        INITIALIZE INDICATORS AND COMPUTE THRESHOLD, THR
C
      IND=0
      THR=ANORM
   45 THR=THR/FLOAT(N)
   50 L=1
   55 M=L+1
C
C        COMPUTE SIN AND COS
C
   60 MQ=(M*M-M)/2
      LQ=(L*L-L)/2
      LM=L+MQ
   62 IF(DABS(A(LM))-THR) 130,65,65
   65 IND=1
      LL=L+LQ
      MM=M+MQ
      X=0.5*(A(LL)-A(MM))
   68 Y=-A(LM)/ DSQRT(A(LM)*A(LM)+X*X)
      IF(X) 70,75,75
   70 Y=-Y
   75 SINX=Y/DSQRT(2.0*(1.0+(DSQRT(1.0-Y*Y))))
      SINX2=SINX*SINX
```

```
   78 COSX=CSQRT(1.0-SINX2)
      COSX2=COSX*COSX
      SINCS =SINX*COSX
C
C        ROTATE L AND M COLUMNS
C
      ILQ=N*(L-1)
      IMQ=N*(M-1)
      DO 125 I=1,N
      IQ=(I*I-I)/2
      IF(I-L) 80,115,80
   80 IF(I-M) 85,115,90
   85 IM=I+MQ
      GO TO 95
   90 IM=M+IQ
   95 IF(I-L) 100,105,105
  100 IL=I+LQ
      GO TO 110
  105 IL=L+IQ
  110 X=A(IL)*COSX-A(IM)*SINX
      A(IM)=A(IL)*SINX+A(IM)*COSX
      A(IL)=X
  115 IF(MV-1) 120,125,120
  120 ILR=ILQ+I
      IMR=IMQ+I
      X=R(ILR)*COSX-R(IMR)*SINX
      R(IMR)=R(ILR)*SINX+R(IMR)*COSX
      R(ILR)=X
  125 CONTINUE
      X=2.0*A(LM)*SINCS
      Y=A(LL)*COSX2+A(MM)*SINX2-X
      X=A(LL)*SINX2+A(MM)*COSX2+X
      A(LM)=(A(LL)-A(MM))*SINCS+A(LM)*(COSX2-SINX2)
      A(LL)=Y
      A(MM)=X
C
C        TESTS FOR COMPLETION
C
C        TEST FOR M = LAST COLUMN
C
  130 IF(M-N) 135,140,135
  135 M=M+1
      GO TO 60
C
C        TEST FOR L = SECOND FROM LAST COLUMN
C
  140 IF(L-(N-1)) 145,150,145
  145 L=L+1
      GO TO 55
  150 IF(IND-1) 160,155,160
  155 IND=0
      GO TO 50
C
C        COMPARE THRESHOLD WITH FINAL NORM
C
  160 IF(THR-ANRMX) 165,165,45
C
```

```
C
C          SORT EIGENVALUES AND EIGENVECTORS
C
  165 IQ=-N
      DO 185 I=1,N
      IQ=IQ+N
      LL=I+(I*I-I)/2
      JQ=N*(I-2)
      DO 185 J=I,N
      JQ=JQ+N
      MM=J+(J*J-J)/2
      IF(A(LL)-A(MM)) 170,185,185
  170 X=A(LL)
      A(LL)=A(MM)
      A(MM)=X
      IF(MV-1) 175,185,175
  175 DO 180 K=1,N
      ILR=IQ+K
      IMR=JQ+K
      X=R(ILR)
      R(ILR)=R(IMR)
  180 R(IMR)=X
  185 CONTINUE
      RETURN
      E N D
```

```
--

         DSQRT.

 LABELS--

.10              10B              .15            35B           .20     D        47B           .25           55
.30              66B              .35     D     117B           .40             130B           .45          160
.50             171B              .55           173B           .60             175B           .62          205
.65             221B              .68           252B           .70             316B           .75          321
.78             357B              .80           417B           .85             423B           .90          430
.95             433B              .100          437B           .105            444B           .110         447
.115            534B              .120          537B           .125    D       642B           .130        1037
.135           1042B              .140         1046B           .145           1052B           .150        1056
.155           1060B              .160         1064B           .165           1073B           .170        1137
.175           1164B              .180   ID      0B            .185    D      1223B


MAP--

      D A        0B            1                  ANORM      D        1302B
      D       1274B                               COSX       D        1312B
      D       1325B                               DABS       D                INTRINSIC
N     -       1233B  ENTRY                        DSQRT.     D                B.E.F.
      R              INTRINSIC                    I          I   U    1276B
      I       1332B                               IJ         I        1331B
      I       1340B                               ILQ        I        1300B
      I       1341B                               IM         I        1337B
      I       1305B                               IMR        I        1342B
```

```
      SUBROUTINE MERSON(X,DELX,DX,DXMIN,TOLKM,N)
      IMPLICIT  DOUBLE  PRECISION (A-H,O-Z)
C     INTEGRATES FROM X TO (X+DELX)
C     DX IS ESTIMATE FOR INTEGRATION STEP NECESSARY
C     DXMIN IS MINIMUM STEP LENGTH TO BE PERMITTED
C     TOLKM IS REQUIRED ACCURACY
C     N IS NUMBER OF DEPENDENT VARIABLES
C     CONTROL TRANSFERRED TO FIRST LABEL IF INTEGRATION FALLS,X AND Y(I)
C     THEN CONTAIN NEW VALUES
C     CONTROL TRANSFERRED TO SECOND LABEL IF INTEGRATION FAILS, X AND
C     Y(I) THEN CONTAIN MOST RECENT CORRECT VALUES
C     IN EITHER CASE, DX CONTAINS CURRENT STEP LENGTH
      COMMON/DEF/Y
      COMMON/GRAD/DY
      COMMON/DER/FGAS
      COMMON/MER/T,DELP,W,PT,GRADP
      COMMON/ERROR/ERR
      COMMON/REPAR/TBASE
      DIMENSION Y(10),YOLD(10),FK(5,10),DY(10)
C
      ISW=0
      XMAX=W
      TOLA=5.*TOLKM
      FINTS=DELX/DX+0.5
      TOLB=TOLA/32.
      INTS=FINTS
      IF(INTS.LT.1)INTS=1
      DX=DELX/INTS
      FMULT=DX/3.
      GO TO 4
C     ERROR CHECK
    1 IF(ERR.GT.TOLA) GO TO 20
      IF(ERR.LT.TOLB) GO TO 21
C     INTEGRATION SATISFACTORY, CALCULATE NEW POINTS
    3 DO 2 I=1,N
    2 Y(I)=YOLD(I)+0.5*FK(1,I)+2.0*FK(4,I)+0.5*FK(5,I)
C  OXYGEN BALANCE--OXYGEN TO CO2 AND H2O
      Y(6)=YOLD(6)-(Y(2)-YOLD(2))-(Y(3)-YOLD(3))*2.-(Y(4)-YOLD(4))*3.-(Y
     1(5)-YOLD(5))*10.5/8.
C    WATER PRODUCED FROM ALL REACTIONS
      Y(8)=YOLD(8)+(Y(2)-YOLD(2))+(Y(3)-YOLD(3))*2.+(Y(4)-YOLD(4))*3.+(Y
     1(5)-YOLD(5))*5./8.
C
C CORRECT CONCENTRATIONS FOR INCREASED FLOW AND DECREASED PRESSURE
      PTN=PT -GRADP*DX
      YOLD(7)=Y(7)
      VOLPLUS=0.
      DO  200  KK=1,8
200   VOLPLUS=VOLPLUS+FGAS*(Y(KK)-YOLD(KK))
      VMOLE=22.400*760.*T/(273.2*PTN)
      VOLPLUS=VOLPLUS*VMOLE
      FGASN=(FGAS*PT/PTN)+VOLPLUS
      RATIO=FGAS/FGASN
      DO  210   KK=1,8
  210 Y(KK)=Y(KK)*RATIO
      FGAS=FGASN
      PT=PTN
```

```
      IF(ISW.LT.1) GO TO 101
      RETURN
  101 IF(XMAX.GT.X+DX) GO TO 160
      DX = XMAX-X
      ISW=1
  160 CONTINUE
      IF(INTS.EQ.1) RETURN
    6 INTS=INTS-1
C     PRESERVE CURRENT VALUES
    4 XOLD=X
C   IN THE NORMAL RUNGE KUTTA MERSON THE 8 WOULD BE REPLACED BY N
      DO 5 I=1,8
    5 YOLD(I)=Y(I)
C    SKIP STEP ADJUSTMENT IF DX IS LAST STEP
      IF (ISW.EQ.1) GO TO 510
      IHALF=0
      GO TO 9
C     ERROR EXCESSIVE, HALVE STEP
   20 DX=0.5*DX
      IF(DX.LT.DXMIN) GO TO 19
      INTS=INTS+INTS
      IHALF=1
      GO TO 8
C     STEP LENGTH TOO SMALL, INTEGRATION FAILS
   19 X=XOLD
      DO 23 I=1,8
   23 Y(I)=YOLD(I)
      RETURN
C     ERROR SMALL, STEP LENGTH MAY BE INCREASED IF POSSIBLE
C     CHECK IF STEP PREVIOUSLY HALVED (PREVENTS CYCLING)
   21 IF(IHALF.EQ.1) GO TO 3
C     CHECK IF INTS EVEN
      IDOUBLE=INTS/2
      IF((IDOUBLE*2).EQ.INTS) GO TO 22
C     NOT POSSIBLE, INTS ODD
      GO TO 3
C     DOUBLE STEP LENGTH
   22 INTS=IDOUBLE
      DX=2.*DX
C     GO BACK TO LAST POINT, AND INTEGRATE WITH NEW DX
    8 FMULT=DX/3.
      DO 7 I=1,8
    7 Y(I)=YOLD(I)
      X=XOLD
  510 CONTINUE
C     MAIN INTEGRATION PROCESS STARTS HERE ****
C     ADVANCE X BY DX
    9 CALL DERIVS(X,N)
      DO 18 IS=1,5
      GO TO (31,30,32,33,30),IS
   31 X=X+FMULT
      GO TO 30
   32 X=X+0.5*FMULT
      GO TO 30
   33 X=XOLD+DX
C     UPDATE Y(I)
   30 DO 10 I=1,N
```

```
         FK(IS,I)=FMULT*DY(I)
         GO TO (11,12,13,14,10),IS
C        PREDICTOR AT (X+DX/3.)
      11 Y(I)=YOLD(I)+FK(1,I)
         GO TO 10
C        CORRECTOR FOR (X+DX/3.)
      12 Y(I)=YOLD(I)+0.5*(FK(1,I)+FK(2,I))
         GO TO 10
C        ADVANCE TO (X+DX/2.)
      13 Y(I)=YOLD(I)+0.375*FK(1,I)+1.125*FK(3,I)
         GO TO 10
C        ADVANCE TO (X+DX)
      14 Y(I)=YOLD(I)+1.5*FK(1,I)-4.5*FK(3,I)+6.0*FK(4,I)
      10 CONTINUE
         IF(IS.EQ.5) GO TO 16
C        EVALUATE DERIVATIVES
         CALL DERIVS(X,N)
         GO TO 18
C        ON LAST INTEGRATION, EVALUATE ERROR
      16 ERR=0.0
         DO 17 I=1,N
         EI=DABS(FK(1,I)-4.5*FK(3,I)+4.0*FK(4,I)-0.5*FK(5,I))
         IF(ERR.LT.EI) ERR=EI
      17 CONTINUE
      18 CONTINUE
         GO TO 1
         END
```

```
OCKS--

   24B  /DEP/                          2B  /DER/                        2B  /ERROR/                        24B  /GRAD/
   12B  /MER/                          2B  /REPAR/

--

       DERIVS    GOTOER.

 LABELS--

.1           102B             .2    ID        0B             .3           114B             .4             561
.5    ID       0B             .6            557B             .7    ID       0B             .8             671
.9           721B             .10    D     1217B             .11         1027B             .12           104
.13         1077B             .14          1141B             .16         1235B             .17    ID
.18    D    1332B             .19           630B             .20          605B             .21            64
.22          660B             .23   ID        0B             .30          777B             .31            741
.32          752B             .33           766B             .101         526B             .160           55
.200  ID       0B             .210  ID        0B             .510         720B
```

```
          SUBROUTINE DERIVS(X,N)
          IMPLICIT DOUBLE PRECISION (A-H,O-Z)
           DOUBLE  KAI,KR12I,KR34I,KR5I,KR23I,KA,KR12,KR23,KR34,KR5
          DOUBLE  NN
          COMMON /STOIC/NN
          COMMON/GRAD/DY
          COMMON/CONST/RT
          COMMON/DEP/Y
          COMMON/DER/FGAS
          COMMON/PARA1/KA,KR12,KR23,KR34,KR5,ASITES
          DIMENSION Y(10),DY(10)
          V=ASITES/(FGAS*3600.)
          DEN=KA*Y(6)+(KR12+NN*KR5)*Y(1)+(KR23+(NN-1.)*KR5)*Y(2)+KR34*Y(3)
          DY(1)=-V*(KR12+KR5)*KA*Y(1)*Y(6)/DEN
          DY(2)=V*KA*Y(6)*(KR12*Y(1)-KR23*Y(2)-KR5*Y(2))/DEN
          DY(3)=V*KA*Y(6)*(KR23*Y(2)-KR34*Y(3))/DEN
          DY(4)=V*KA*Y(6)*KR34*Y(3)/DEN
          DY(5)=8.*V*KA*KR5*Y(6)*(Y(1)+Y(2))/DEN
      C
          RETURN
          END

OCKS--

   2B  /CONST/                      24B  /DEP/                        2B  /DER/                           24B  /GRAD/
  14B  /PARA1/                       2B  /STOIC/

MAP--

S     D           12B /PARA1/                     DEN         D         357B
S     -          332B ENTRY                       DY          D           0B /GRAD/       10
      D            0B /DER/                       KA          D           0B /PARA1/
      D   U      361B                             KR12        D           2B /PARA1/
      D   U      347B                             KR23        D           4B /PARA1/
      D   U      351B                             KR34        D           6B /PARA1/
      D   U      353B                             KR5         D          10B /PARA1/
      D   U      355B                             N           I  AU       0B
      D            0B /STOIC/                     RT          D           0B /CONST/
      D          363B                             X           D  AU       0B
      D            0B /DEP/       10

OGRAM-UNIT LENGTH         21 SYMBOLS

 STORAGE USED          .560 SECONDS
AL DATA - ARRAY(I,J)
 = 426
80
0000D-03   0.                    0.                    0.
          .748000000000D-02     .195400000000D-01     0.
          .223600000000D-03     .129200000000D-04     .954300000000D-05
0000D-04  .125600000000D-03     .576600000000D-02     .171100000000D-01
0000D-03  .143200000000D-04     .623200000000D+03     .154000000000D+03
0000D+01  .109900000000D+04     .719400000000D-02     .154000000000D+03
AL DATA - ARRAY(I,J)
```

```
  .100000000000D+01   .977000000000D+03   .617100000000D-02    .950000000000D+02
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 527
NN=    9.95480
  .573400000000D-03  0.                  0.                   0.
 0.                   .305800000000D-02   .177900000000D-01   0.
 0.                   .379800000000D-03   .181100000000D-04    .744300000000D-05
  .128200000000D-03   .184300000000D-03   .256000000000D-02    .165500000000D-01
  .247300000000D-03   .249600000000D-04   .653200000000D+03    .550000000000D+02
  .100000000000D+01   .872000000000D+03   .401500000000D-02    .550000000000D+02
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 529
NN=    9.96160
  .579800000000D-03  0.                  0.                   0.
 0.                   .257600000000D-02   .193000000000D-01   0.
 0.                   .380100000000D-03   .161900000000D-04    .589500000000D-05
  .110700000000D-03   .150200000000D-03   .239000000000D-02    .175300000000D-01
  .223200000000D-03   .202700000000D-04   .628200000000D+03    .650000000000D+02
  .100000000000D+01   .879000000000D+03   .478100000000D-02    .650000000000D+02
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 531
NN=    9.95080
  .705500000000D-03  0.                  0.                   0.
 0.                   .754500000000D-02   .175000000000D-01   0.
 0.                   .408200000000D-03   .186700000000D-04    .695600000000D-05
  .105500000000D-03   .162100000000D-03   .469100000000D-02    .160000000000D-01
  .254600000000D-03   .222000000000D-04   .628200000000D+03    .100000000000D+03
  .100000000000D+01   .992000000000D+03   .534400000000D-02    .100000000000D+03
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 605
NN=    9.93050
  .387100000000D-03  0.                  0.                   0.
 0.                   .523800000000D-02   .188200000000D-01   0.
 0.                   .226300000000D-03   .119100000000D-04    .657300000000D-05
  .938000000000D-04   .140600000000D-03   .422300000000D-02    .170400000000D-01
  .587400000000D-03   .200100000000D-04   .643200000000D+03    .850000000000D+02
  .100000000000D+01   .980000000000D+03   .620000000000D-02    .850000000000D+02
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 610
NN=    8.96880
  .598000000000D-03  0.                  0.                   0.
 0.                   .269000000000D-02   .208000000000D-01   0.
 0.                   .422000000000D-03   .191000000000D-04    .440000000000D-05
  .538000000000D-04   .135000000000D-03   .217000000000D-02    .186000000000D-01
  .152900000000D-03   .506000000000D-04   .656200000000D+03    .100000000000D+03
  .100000000000D+01   .985000000000D+03   .721400000000D-02    .100000000000D+03
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 517
NN=    9.70440
  .308100000000D-03  0.                  0.                   0.
 0.                   .605500000000D-02   .159500000000D-01   0.
 0.                   .132600000000D-03   .625300000000D-05    .528600000000D-05
  .176400000000D-03   .300200000000D-03   .544600000000D-02    .172800000000D-01
  .442400000000D-03   .597700000000D-04   .629200000000D+03    .550000000000D+02
  .100000000000D+01   .875000000000D+03   .387600000000D-02    .550000000000D+02
     ALPH
  .223200000000D+01   .184900000000D+02   .349500000000D+03    .838900000000D+03
  .284800000000D+01  -.206990000000D+05  -.255270000000D+05   -.234080000000D+05
 -.280120000000D+05  -.229600000000D+05   .180124759000D+05   0.
      UM1
  .121398978237D+05  -.941552974318D+04   .244622011287D+04   -.487078706588D+02
```

```
  RUN NUMBER = 428
NN=     9.98030
  .375800000000D-03  0.                     0.                     0.
 0.                  .516400000000D-02      .276200000000D-01     0.
 0.                  .205500000000D-03      .120800000000D-04      .765200000000D-05
  .299500000000D-04  .135900000000D-03      .396000000000D-02      .166700000000D-01
  .384500000000D-03  .178300000000D-04      .643200000000D+03      .112000000000D+03
  .100000000000D+01  .972000000000D+03      .615800000000D-02      .112000000000D+03
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 430
NN=    10.19630
  .520900000000D-03  0.                     0.                     0.
 0.                  .366400000000D-02      .204200000000D-01     0.
 0.                  .327500000000D-03      .155200000000D-04      .120400000000D-04
  .111700000000D-03  .168300000000D-03      .279200000000D-02      .184400000000D-01
  .191700000000D-03  .127700000000D-04      .627200000000D+03      .100000000000D+03
  .100000000000D+01  .962000000000D+03      .578800000000D-02      .100000000000D+03
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 504
NN=     9.98400
  .383700000000D-03  0.                     0.                     0.
 0.                  .513800000000D-02      .187300000000D-01     0.
 0.                  .235000000000D-03      .129200000000D-04      .984900000000D-05
  .840000000000D-04  .113100000000D-03      .409000000000D-02      .168300000000D-01
  .924900000000D-04  .146000000000D-04      .643200000000D+03      .112000000000D+03
  .100000000000D+01  .972000000000D+03      .615100000000D-02      .112000000000D+03
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 512
NN=     9.93260
  .367500000000D-03  0.                     0.                     0.
 0.                  .519100000000D-02      .186500000000D-01     0.
 0.                  .219500000000D-03      .115900000000D-04      .651400000000D-05
  .871100000000D-04  .123100000000D-03      .415000000000D-02      .166900000000D-01
  .498600000000D-03  .174500000000D-04      .643200000000D+03      .970000000000D+02
  .100000000000D+01  .970000000000D+03      .622000000000D-02      .970000000000D+02
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 515
NN=    10.00510
  .648900000000D-03  0.                     0.                     0.
 0.                  .502900000000D-02      .190900000000D-01     0.
 0.                  .440000000000D-03      .233000000000D-04      .134500000000D-04
  .917200000000D-04  .145800000000D-03      .412200000000D-02      .171400000000D-01
  .414800000000D-03  .184300000000D-04      .651200000000D+03      .970000000000D+02
  .100000000000D+01  .100500000000D+04      .654100000000D-02      .970000000000D+02
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 523
NN=     9.83230
  .646000000000D-03  0.                     0.                     0.
 0.                  .508700000000D-02      .159700000000D-01     0.
 0.                  .324500000000D-03      .169800000000D-04      .107100000000D-04
  .235500000000D-03  .341400000000D-03      .330800000000D-02      .156100000000D-01
  .290400000000D-03  .570000000000D-04      .630200000000D+03      .410000000000D+02
  .100000000000D+01  .852000000000D+03      .344200000000D-02      .410000000000D+02
  EXPERIMENTAL DATA - ARRAY(I,J)
  RUN NUMBER = 524
NN=     9.92710
  .350100000000D-03  0.                     0.                     0.
 0.                  .535800000000D-02      .186700000000D-01     0.
 0.                  .203400000000D-03      .109600000000D-04      .575800000000D-05
  .920300000000D-04  .128500000000D-03      .405300000000D-02      .172500000000D-01
  .263100000000D-03  .184000000000D-04      .643200000000D+03      .950000000000D+02
```

PROGRAM NO. 7:

This program was used to evaluate the predicted values of the transformed responses from the model, given the final parameter estimates obtained from program 5. NMAX, the number of the minimization of determinant criterion was set equal to zero. With NMAX specified, this program will estimate the parameters in the model according to the Box and Draper [56] Criterion as given by equation 7.36 on page 91.

```
ATTACH,MACLIB.
FTN(POUND=*/+-,OPT=2,T,P=3)
LDSET(LIB=MACLIB)
LGO(PL=32000)
      PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C         PROGRAM 2
C     THIS PROGRAM CALCULATES KINETIC PARAMETERS BY BOX - DRAPER METHOD
C     THE FOLLOWING SUBROUTINES ARE USED
C**************    SUBROUTINES************
C     SIMPLX
C     OBJECT
C     MERSON
C     DERIVS
C     DETER
C     --------------       ----------    ---I------    ---------     ------
C********                                                              ********
C     *****FIVE INDEPENDENT RESPONSES-OX,DTA,PA,PI,CO2/CO
      COMMON/PARA1/KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5
      COMMON/PARA3/EAS
      COMMON/CONST/NN,R,NEX,NP,NC
      COMMON/STRAY/ARRAY
      COMMON/REFAR/TBASE
      COMMON/EIGEN/Z
      COMMON/ACTIV/ACTY
C
      DIMENSION ARRAY(25,50),XX(11)
      DIMENSION Z(3,5)
      DIMENSION RKO(5)
C     **********  CURRENT ESTIMATES OF PARAMETRRS  ********
      REAL KAI,KR12I,KR23I,KR34I,KR5I,NN
C      ******      CONSTANTS      *********
C     NR ---RESPONSES
      TBASE =370.0
      NR=5
C      TBASE  IS TEMPERATURE USED FOR REPARAMETERIZATION BY HUNTER/ATKINSON
C     METHOD
      R=-1.9872
C     NP NUMBER OF PARAMETERS
      NP=11
      NC=5
C     NMAX MAXIMUM NUMBER OF MINIMIZATIONS OF DETERMINANT CRITERION
      NMAX=0
C
C
C     READ INITIAL PARAMETER ESTIMATES
C      NOTE THAT INITIAL ESTIMATES OF PRE EXPONENTIAL FACTORS ARE ALREADY
C     REPARAMETERIZED BY HUNTER/ATKINSON METHOD
      READ(5,113) KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5,EAS,ACTY
      WRITE(6,*) EA,E12,E23,E34,E5,EAS
C     *************       READ IN EXPERIMENTAL DATA     *************
      READ(5,101)NEX
      DO 10  J=1,NEX
      READ(5,102)KRUN,NN
      READ(5,103)  (ARRAY(I,J),I=1,24)
      WRITE(6,105)KRUN,NN
      WRITE(6,104)
      WRITE(6,103)  (ARRAY(I,J),I=1,24)
   10 CONTINUE
      WRITE(6,994)
```

```
      WRITE(6,993) KAI,EA,KR12I,E12,KR23I,E23,KR34I,E34,KR5I,E5
      WRITE(6,108) EAS
      WRITE(6,906) ACTY
906   FORMAT(1X,*ACTIVITY FACTOR=*,E12.5)
113   FORMAT(4E20.12)
108   FORMAT(6X, * ACTIVE SITE PARAMETER = *, F13.5)
      READ(5,555)   ((Z(I,J),J=1,5),I=1,3)
      PRINT*,  ≠OTHORGONAL EIGENVECTORS≠
      WRITE(6,555)   ((Z(I, J),J=1,5),I=1,3)
555   FORMAT(5E15.5)
C     NORMALISE PARAMETERS  ***********************************
C
C     NORMALIZE INITIAL PARAMETER ESTIMATES
      DO 11 I=1,NP
      XX(I)=1.
   11 CONTINUE
C
      TBASE=TBASE+273.2
C     CONVERT INITIAL ESTIMATES OF REPARAMETERIZED PRE EXPONENTIAL FACTORS FOR
C     PRINTING ACTUAL VALUES
      RKO(1)=KAI*EXP(EA/(TBASE*R))
      RKO(2)=KR12I*EXP(E12/(TBASE*R))
      RKO(3)=KR23I*EXP(E23/(TBASE*R))
      RKO(4)=KR34I*EXP(E34/(TBASE*R))
      RKO(5)=KR5I*EXP(E5/(TBASE*R))
      WRITE(6,1000)(RKO(L),L=1,NR)
      R=1.9872
C     CALL OPTIMISATION ROUTINE
      CALL SIMPLX(NP,NMAX,XX)
C
C        **********     FORMAT STATEMENTS    ******
  101 FCRMAT(I3)
  102 FORMAT(I3,5X,3F8.4)
  103 FORMAT(8E10.4)
  104 FORMAT(2X,* EXPERIMENTAL DATA - ARRAY(I,J) *)
  105 FORMAT(2X, * RUN NUMBER = *,I3,/,1X, *NM= *,F10.5)
  106 FORMAT(8F10.0)
  994 FORMAT(/21X, *FREQUENCY FACTORS* 6X *ACTIVATION ENERGIES */ )
  993 FCRMAT(* ADSORPTION* 10X,E13.4,10X,F12.0 /
     1 * CXYLENE - OTA* 7X,E13.4,10X,F12.0 /
     2 * OTA-PI*14X,E13.4,F22.0/
     4 *PI - PA * E26.4,F22.0 /
     4 * ORGARNICS - CO2*6X,E13.4,F22.0/)
 1000 FORMAT(1X,5E15.4)
      STOP
      END
      SUBROUTINE SIMPLX(NP,NMAX,XX)
C     SIMPLEX METHOD OF OPTIMIZATICN (NELDER AND MEAD MODIFICATION)
C
C     PROGRAM IS BASED ON ALGORITM SHOW IN COMPUTER J.,VOL.7,308 (1965)
C     AND ON EXISTING PROGRAMS
C
      DIMENSION U(12),PHI(11),X(11,12),PHIH(11),PHIS(11),PHIL(11),
     1  PHIO(11),PHIR(11),PHIC(11),PHIE(11)
      DIMENSION XX(11)
C----------------------------
C     X(I,J)  I NO.OF PARAMETERS  J=1  INITIAL CALCULATION POINT
C     EPS   ERROR TOLERANCE
C     NMAX   MAX. NUMBER OF FUNCTION EVALUATIONS
C     K   NUMBER OF INDEPENDENT VARIABLES IN OBJECTIVE FUNCTION
```

```
C     ALPHA BETA GAMMA  REFLECTION CONTRACTION EXPANSION COEFFICIENTS
      ALPHA=1.0
      BETA=0.5
      GAMMA=2.0
      EPS=1.0E-08
      DELTX=0.2
      K=NP
      KK=K+1
      NCOUNT=0
C     VARIABLE INDICATING SIMPLEX METHOD HAS STOPPED
C     CONVER=0. (NOT STOPPED),CONVER=1. (STOPPEC)
      CONVER=0.
      UH=US=UL=0.

C      AS ONLY ONE INITIAL ESTIMATE IS READ FOR EACH PARAMETER THE OTHER
C     POINTS IN THE SIMPLEX ARE SET UP BY INCREMENTING THESE ESTIMATES AS
C     FOLLOWS -----------------------
C     VARIABLES XX(I) ARE NORMALISED WITH RESPECT TO INITIAL VALUES
      DO 100 I=1,K
      X(I,1)=XX(I)
  100 CONTINUE
C---------------------------
      DO 3 J=2,KK
      DO 1 I=1,K
    1 X(I,J)=X(I,1)
    3 X(J-1,J)=X(J-1,1)+DELTX

C       ----------------------
C     EVALUATE FUNCTION INITIALLY AT K+1 FEASIBLE POINTS
    2 DO 6 J=1,KK
      DO 4 I=1,K
      PHI(I)=X(I,J)
    4 CONTINUE
      NCOUNT=NCOUNT+1
      CALL OBJECT(PHI ,SUM,NCOUNT)
      IF(NCOUNT.GT.NMAX) GO TO 48
      IF(CONVER.EQ.1.) GO TO 48
    6 U(J)=SUM
      GO TO 8
    8 CONTINUE
C     FINC RELATIVE ORDER OF FUNCTION VALUES
      UH=U(1)
      JH=1
      DO 10 J=2,KK
      IF(U(J).LT.UH)GO TO 10
      UH=U(J)
      JH=J
   10 CONTINUE
      UL=U(1)
      JL=1
      DO 12 J=2,KK
      IF(U(J).GT.UL) GO TO 12
      UL=U(J)
      JL=J
   12 CONTINUE
      US=UL
      DO 14 J=1,KK
      IF(J.EQ.JH)GO TO 14
      IF(U(J).LE.US)GO TO 14
      US=U(J)
```

```
      JS=J
   14 CONTINUE
C     OBTAIN THE CORRESPONDING INDEPENDENT VARIABLES
      DO 16 I=1,K
      PHIH(I)=X(I,JH)
      PHIS(I)=X(I,JS)
   16 PHIL(I)=X(I,JL)
      WRITE(6,17)NCOUNT,UH,US,UL,(PHIL(I),I=1,K)
   17 FORMAT(1X,*NO*,I4,*FUNCT. H S L*,3E12.4,*LOW VAR*,10F7.4)
      IF(NCOUNT.GE.NMAX)GO TO 48
      IF(CONVER.EQ.1.)GO TO 48
C     CALCULATE THE CENTROID
      DO 20 I=1,K
      SUM=0.
      DO 18 J=1,KK
      IF(J.EQ.JH)GO TO 18
      SUM=SUM+X(I,J)
   18 CONTINUE
   20 PHIC(I)=SUM/(FLOAT(K))
C     REFLECTION
      DO 21 I=1,K
      PHIR(I)=PHIO(I)+ALPHA*(PHIO(I)-PHIH(I))
      IF(PHIR(I).LE.0.05) PHIR(I)=0.05
   21 CONTINUE
      NCOLNT=NCOUNT+1
      CALL OBJECT(PHIR, UR,NCCUNT)
      WRITE(6,19)
   19 FORMAT(1X,*REFLECTION*)
      IF((US.GE.UR).AND.(UR.GE.UL))GO TO 28
      IF(UR.LT.UL)GO TO 32
      IF((UH.GT.UR).AND.(UR.GT.US))GO TO 40
C     CONTRACTION  (I.E. UR.GT.UH)
   23 DO 24 I=1,K
      PHIC(I)=PHIO(I)+BETA*(PHIH(I)-PHIO(I))
      IF(PHIC(I).LE.0.05) PHIC(I)=0.05
   24 CONTINUE
      NCOUNT=NCOUNT+1
      CALL OBJECT(PHIC, UC,NCOUNT)
C     SUCCESSFUL CONTRACTION
      WRITE(6,25)
   25 FORMAT(1X,*CONTRACTION*)
      IF(UC.LT.UH)GO TO 44
C     SHRINKING (I.E. CONTRACTION UNSUCCESSFUL)
      DO 26 J=1,KK
      IF(J.EQ.JL)GO TO 26
      DO 29 I=1,K
      X(I,J)=.5*(X(I,J)+PHIL(I))
   29 CONTINUE
   26 CONTINUE
      WRITE(6,27)
   27 FORMAT(1X,*SHRINKING*)
      GO TO 2
C     REPLACE PHIH BY PHIR AND RESTART
   28 DO 30 I=1,K
   30 X(I,JH)=PHIR(I)
      U(JH)=UR
      GO TO 8
C     EXPANSION  (I.E. UR.LT.UL)
   32 DO 34 I=1,K
      PHIE(I)=PHIO(I)+GAMMA*(PHIR(I)-PHIO(I))
```

```
      IF(PHIE(I).LE.0.05) PHIE(I)=0.05
   34 CONTINUE
      NCOUNT=NCOUNT+1
      CALL OBJECT(PHIE, UE,NCOUNT)
      WRITE(6,35)
   35 FORMAT(1X,*EXPANSION*)
      IF(UE.LT.UL)GO TO 36
C     UNSUCCESSFUL EXPANSION
      GO TO 28
C     SUCCESSFUL EXPANSION (REPLACE PHIH BY PHIE)
   36 DO 38 I=1,K
   38 X(I,JH)=PHIE(I)
      U(JH)=UE
      GO TO 8
C     REPLACE PHIH BY PHIR AND CONTRACT
   40 DO 42 I=1,K
      X(I,JH)=PHIR(I)
   42 PHIH(I)=PHIR(I)
      U(JH)=UH=UR
      GO TO 23
C     SUCCESSFUL CONTRACTION
   44 DO 46 I=1,K
   46 X(I,JH)=PHIC(I)
      U(JH)=UC
      GO TO 8
   48 CONTINUE
      RETURN
      END
      SUBROUTINE OBJECT (XXX,SUM,NCOUNT)
      COMMON/REPAR/TBASE
      COMMON/DEP/ Y
      COMMON/STRAY/ARRAY
      COMMON /PARA1/KAI,KR12I,KR23I,KR34I,KR5I,EA,E12,E23,E34,E5
      COMMON/PARA2/KA,KR12,KR23,KR34,KR5
      COMMON/PARA4/ASITES
      COMMON/PARA3/EAS
      COMMON/CONST/NN,R,NEX,NF,NC
      COMMON/MER/T,DELP,W,PT,GRADP
      COMMON/DER/FGAS
      COMMON/ERROR/ERR
      COMMON/EIGEN/Z
      COMMON/ACTIV/ACTY
      DIMENSION ARRAY(25,50)
      DIMENSIONA(144)
      DIMENSIONY(10)
      DIMENSION YY(10)
      DIMENSION XXX(11)
      DIMENSION RES(5,50)
      DIMENSION ZED(50)
      DIMENSION YCAL(5,50)
      DIMENSION SSR(10),RSS(10)
      DIMENSION ARRA(25,50)
      DIMENSION  YYY(3,50)
      DIMENSION Z(3,5)
      REALKAI,KR12I,KR23I,KR34I,KR5I,NN
      REAL KA,KR12,KR23,KR34,KR5
      TOT=0.
      DO 25 I=1,50
      DO25J=1,5
      RES(J,I)=0.
```

```
   25 CONTINUE
      DO 8888 LM=1,5
      SSR(LM)=0.0
      RSS(LM)=0.0
 8888 CONTINUE
      NMAX=0
      NP=5
      DO 4 I=1,25
      A(I)=0.
    4 CONTINUE
      DO 3 I=1,NP
      XXX(I)=ABS(XXX(I))
    3 CONTINUE
      RKA=KAI*XXX(1)
      RK12=KR12I*XXX(3)
      RK23=KR23I*XXX(5)
      RK34=KR34I*XXX(7)
      RK5=KR5I*XXX(9)
      EAC=EA*XXX(2)
      E12C=E12*XXX(4)
      E23C=E23*XXX(6)
      E34C=E34*XXX(8)
      E5C=E5*XXX(10)
      EASC=EAS*XXX(11)
      WRITE(6,777)
  777 FORMAT( //,21X, *FREQUENCY FACTORS* 6X *ACTIVATION ENERGIES */)
      WRITE(6,776)RKA,EAC,RK12,E12C,RK23,E23C,RK34,E34C,RK5,E5C
      WRITE(6,220) EASC
  776 FORMAT(* ADSORPTION* 10X,E13.4,10X,F12.0 /
     1 * OXYLENE - OTA*7X,E13.4,10X,F12.0 /
     2 * OTA-PI*14X,E13.4,F22.0/
     3* PI - PA* E26.4,F22.0/
     4 * ORGANICS - CO2*6X,E13.4,F22.0/)
  220 FORMAT(1X,* ACTIVE SITE PARAMETER = *,F10.4)
C
      DO 201 J=1,NEX
      DO 2 I=1,9
      Y(I)=ARRAY(I,J)
    2 CONTINUE
      T=ARRAY(19,J)
      DELP=ARRAY(20,J)
      W=ARRAY(21,J)
      PT=ARRAY(22,J)
      FGAS=ARRAY(23,J)
      GRADP=ARRAY(24,J)
C    ***REPARAMETERIZE BY ATKISON-HUNTER METHOD-K=K0*EXP((E/R*(1/T-1/T0))********
      TSTAR=(TBASE-T)/(TBASE*T)
      RT=TSTAR/R
      KA=RKA*EXP(EAC*RT)
      KR12=RK12*EXP(E12C*RT)
      KR23=RK23*EXP(E23C*RT)
      KR34=RK34*EXP(E34C*RT)
      KR5=RK5*EXP(E5C*RT)
      ASITES=EXP(ACTY)*EXP(EASC*RT)
  221 FORMAT(1X,* FRACTION OF ACTIVE SITES =*,E12.4)
  888 CONTINUE
C-----------------------------------------------------------------------------------------
      X=0.
      DX=.005
      TOLKM=1.0E-08
```

```
      DXMIN=0.0001
      N=5
      DELX=W
      CALL MERSCN(X,DELX,DX,DXMIN,TOLKM,N)
C     TRANSFORM OBSERVED RESPCNSES (BOX,HUNTER,MACGREGOR,ERJAVEC -PAPER)
C     FORM 3 INDEPENDENT LINEAR COMBINATIONS OF THE EIGENVECTORS AND THE FIVE
C     OBSERVED   RESPONSES.
      ARRA(10,J)=ARRAY(10,J)*Z(1,1)+ARRAY(11,J)*Z(1,2)+ARRAY(12,J)*Z(1,3
     1)+ARRAY(13,J)*Z(1,4)+ARRAY(14,J)*Z(1,5)
      ARRA(11,J)=ARRAY(10,J)*Z(2,1)+ARRAY(11,J)*Z(2,2)+ARRAY(12,J)*Z(2,3
     1)+ARRAY(13,J)*Z(2,4)+ARRAY(14,J)*Z(2,5)
      ARRA(12,J)=ARRAY(10,J)*Z(3,1)+ARRAY(11,J)*Z(3,2)+ARRAY(12,J)*Z(3,3
     1)+ARRAY(13,J)*Z(3,4)+ARRAY(14,J)*Z(3,5)
      TOT=TOT+1.
      ZED(J)=TOT
C     TRANSFORM  THE  PREDICTED  RESPONSES.
      YYY(1,J)=Y(1)*Z(1,1)+Y(2)*Z(1,2)+Y(3)*Z(1,3)+Y(4)*Z(1,4)+Y(5)*Z(1,
     15)
      YYY(2,J)=Y(1)*Z(2,1)+Y(2)*Z(2,2)+Y(3)*Z(2,3)+Y(4)*Z(2,4)+Y(5)*Z(2,
     15)
      YYY(3,J)=Y(1)*Z(3,1)+Y(2)*Z(3,2)+Y(3)*Z(3,3)+Y(4)*Z(3,4)+Y(5)*Z(3,
     15)
      KK=0
      DO  201  JJ=1,3
      II=JJ+9
      RES(JJ,J)=ARRA(II,J)-YYY(JJ,J)
C     CALCULATE THE RESIDUAL SUM OF SQUARE FOR EACH RESPONSE
      SSR(JJ)=SSR(JJ) +PES(JJ,J)*RES(JJ,J)
      DO  201  K=1,3
      III=K+9
      KK=KK+1
      B=(ARRA(II,J)-YYY(JJ,J))*(ARRA(III,J)-YYY(K,J))
      B=B*100000000000.
      A(KK)=B+A(KK)
  201 CONTINUE
      IF(NCOUNT.LT.NMAX)GO TO 20
      NCOUNT=0
C     CALCULATE  RESIDUAL SUM OF SQUARES
      SSR(4)=SSR(1)+SSR(2)+SSR(3)
      WRITE(6,9995)
9995  FORMAT(10X,*THE RESIDUAL SUMS OF SQUARES *)
      WRITE(6,9997)  SSP(1),SSR(2),SSR(3),SSR(4)
9997  FORMAT(1X,*R1=*,E13.5,*R2=*,E13.5,*R3=*,E13.5,*TOTAL= *,E13.5,//)
      WRITE(6,6698)
6698  FCRMAT(20X, *RESP1 *,20X,*RESP2*,20X,*RESP3* )
      WRITE(6,6697)
6697  FORMAT(8X,3(1X,*OBS*,10X,*CAL*,5X))
      DO 6601 J=1,NEX
      DO  6600  JJ=1,3
      II=JJ+9
      YY(JJ)=ARRA(II,J)
 6600 CONTINUE
      WRITE(6,6699)  (YY(I),YYY(I,J),I=1,3)
6699  FORMAT(1X,3(2E10.3,5X))
 6601 CONTINUE
   20 CONTINUE
      N=3
      CALL DETER(A,D,N)
      WRITE(6,301)D,NCOUNT
      SUM=0
```

```
  401 FORMAT(1X,5E15.4)
  301 FORMAT(///,1X,*DETERMINANT*,E20.6,10X,*N=*,I3)
  981 FORMAT(///,*CONCENTRATION FROM MERSON (GM.MOLES/CC.)*//
     1 * DISTANCE* 57X *CARBON*      )
  982 FORMAT(13X *O-XYLENE* 8X *OTA* 7X *PHTHALIDE* 3X *PHTH.ANHYD.* 4X
     1 *DIOXIDE* 7X *OXYGEN* 5X *NITROGEN* 7X *WATER* 4X *PRESSURE* 4X
     3 *ERROR*/)
  960 FORMAT(F6.3,3X,8E13.3,F9.1,E13.3)
      RETURN
      END
      SUBROUTINE MERSON(X,DELX,DX,DXMIN,TOLKM,N)
C     INTEGRATES FROM X TO (X+DELX)
C     DX IS ESTIMATE FOR INTEGRATION STEP NECESSARY
C     DXMIN IS MINIMUM STEP LENGTH TO BE PERMITTED
C     TOLKM IS REQUIRED ACCURACY
C     N IS NUMBER OF DEPENDENT VARIABLES
C     CONTROL TRANSFERRED TO FIRST LABEL IF INTEGRATION FALLS,X AND Y(I)
C     THEN CONTAIN NEW VALUES
C     CONTROL TRANSFERRED TO SECOND LABEL IF INTEGRATION FAILS, X AND
C     Y(I) THEN CONTAIN MOST RECENT CORRECT VALUES
C     IN EITHER CASE, DX CONTAINS CURRENT STEP LENGTH
      COMMON/PARA4/ASITES
      COMMON/PARA2/KA,KR12,KR23,KR34,KR5
      COMMON/DEP/Y
      COMMON/GRAD/DY
      COMMON/CONST/NN,R,NEX,NP,NC
      COMMON/DER/FGAS
      COMMON/MER/T,DELP,W,PT,GRADP
      COMMON/ERROR/ERR
      COMMON/REPAR/TBASE
      DIMENSION Y(10),YOLD(10),FK(5,10),DY(10)
      REAL KA,KR12,KR23,KR34,KR5
C
      ISW=0
      XMAX=W
      TOLA=5.*TOLKM
      FINTS=DELX/DX+0.5
      TOLB=TOLA/32.
      INTS=FINTS
      IF(INTS.LT.1)INTS=1
      DX=DELX/INTS
      FMULT=DX/3.
      GO TO 4
C     ERROR CHECK
    1 IF(ERR.GT.TOLA) GO TO 20
      IF(ERR.LT.TOLB) GO TO 21
C     INTEGRATION SATISFACTORY, CALCULATE NEW POINTS
    3 DO 2 I=1,N
      IF(Y(1) .LE. 0.0) Y(1)=0.0
      IF(Y(2) .LE. 0.0) Y(2)=0.0
    2 Y(I)=YOLD(I)+0.5*FK(1,I)+2.0*FK(4,I)+0.5*FK(5,I)
C   OXYGEN BALANCE--OXYGEN TO CO2 AND H2O
      Y(6)=YOLD(6)-(Y(2)-YOLD(2))-(Y(3)-YOLD(3))*2.-(Y(4)-YOLD(4))*3.-(Y
     1(5)-YOLD(5))*10.5/8.
C    WATER PRODUCED FROM ALL REACTIONS
      Y(8)=YOLD(8)+(Y(2)-YOLD(2))+(Y(3)-YOLD(3))*2.+(Y(4)-YOLD(4))*3.+(Y
     1(5)-YOLD(5))*5./8.
C
C CORRECT CONCENTRATIONS FOR INCREASED FLOW AND DECREASED PRESSURE
      PTN=PT -GRADP*DX
```

```
      YOLD(7)=Y(7)
      VOLPLUS=0.
      DO 200 KK=1,8
  200 VOLPLUS=VOLPLUS +FGAS*(Y(KK)-YOLD(KK))
      VMOLE=22.400*760.*T/(273.2*PTN)
      VOLPLUS=VOLPLUS*VMOLE
      FGASN=(FGAS*PT/PTN)+VOLPLUS
      RATIO=FGAS/FGASN
      DO 210 KK=1,8
  210 Y(KK)=Y(KK)*RATIO
      FGAS=FGASN
      PT=PTN
      IF(ISW.LT.1) GO TO 101
      RETURN
  101 IF(XMAX.GT.X+DX) GO TO 160
      DX = XMAX-X
      ISW=1
  160 CONTINUE
      IF(INTS.EQ.1) RETURN
    6 INTS=INTS-1
C     PRESERVE CURRENT VALUES
    4 XOLD=X
C   IN THE NORMAL RUNGE KUTTA MERSON THE 8 WOULD BE REPLACED BY N
      DO 5 I=1,8
      IF(Y(1) .LE. 0.) YOLD(1)=0.0
      IF(Y(2) .LE. 0.) YOLD(2)=0.0
    5 YOLD(I)=Y(I)
C    SKIP STEP ADJUSTMENT IF DX IS LAST STEP
      IF (ISW.EQ.1) GO TO 510
      IHALF=0
      GO TO 9
C     ERROR EXCESSIVE, HALVE STEP
   20 DX=0.5*DX
      IF(DX.LT.DXMIN) GO TO 19
      INTS=INTS+INTS
      IHALF=1
      GO TO 8
C     STEP LENGTH TOO SMALL, INTEGRATION FAILS
   19 X=XOLD
      DO 23 I=1,8
   23 Y(I)=YOLD(I)
      RETURN
C     ERROR SMALL, STEP LENGTH MAY BE INCREASED IF POSSIBLE
C     CHECK IF STEP PREVIOUSLY HALVED (PREVENTS CYCLING)
   21 IF(IHALF.EQ.1) GO TO 3
C     CHECK IF INTS EVEN
      IDOUBLE=INTS/2
      IF((IDOUBLE*2).EQ.INTS) GO TO 22
C     NOT POSSIBLE, INTS ODD
      GO TO 3
C     DOUBLE STEP LENGTH
   22 INTS=IDOUBLE
      DX=2.*DX
C     GO BACK TO LAST POINT, AND INTEGRATE WITH NEW DX
    8 FMULT=DX/3.
      DO 7 I=1,8
    7 Y(I)=YOLD(I)
      X=XOLD
  510 CONTINUE
C     MAIN INTEGRATION PROCESS STARTS HERE ****
```

```
C     ADVANCE X BY DX
    9 CALL DERIVS(X,N)
      DO 18 IS=1,5
      GO TO (31,30,32,33,30),IS
   31 X=X+FMULT
      GO TO 30
   32 X=X+0.5*FMULT
      GO TO 30
   33 X=XOLD+DX
C     UPDATE Y(I)
   30 DO 10 I=1,N
      FK(IS,I)=FMULT*DY(I)
      GO TO (11,12,13,14,10),IS
C     PREDICTOR AT (X+DX/3.)
   11 Y(I)=YOLD(I)+FK(1,I)
      GO TO 10
C     CORRECTOR FOR (X+DX/3.)
   12 Y(I)=YOLD(I)+0.5*(FK(1,I)+FK(2,I))
      GO TO 10
C     ADVANCE TO (X+DX/2.)
   13 Y(I)=YOLD(I)+0.375*FK(1,I)+1.125*FK(3,I)
      GO TO 10
C     ADVANCE TO (X+DX)
   14 Y(I)=YOLD(I)+1.5*FK(1,I)-4.5*FK(3,I)+6.0*FK(4,I)
   10 CONTINUE
      IF(IS.EQ.5) GO TO 16
C     EVALUATE DERIVATIVES
      CALL DERIVS(X,N)
      GO TO 18
C     ON LAST INTEGRATION, EVALUATE ERROR
   16 ERR=0.0
      DO 17 I=1,N
      EI=ABS(FK(1,I)-4.5*FK(3,I)+4.0*FK(4,I)-0.5*FK(5,I))
      IF(ERR.LT.EI) ERR=EI
   17 CONTINUE
   18 CONTINUE
      GO TO 1
      END
      SUBROUTINE DERIVS(X,N)
      COMMON/GRAD/DY
      COMMON/DEP/Y
      COMMON/DER/FGAS
      COMMON/CONST/NN,R,NEX,NP,NC
      COMMON/PARA2/KA,KR12,KR23,KR34,KR5
      COMMON/PARA4/ASITES
      DIMENSION Y(10),DY(10)
      REAL KA,KR12,KR23,KR34,KR5
      REALKAI,KR12I,KR23I,KR34I,KR5I,NN
      V=ASITES/(FGAS*3600.)
      DEN=KA*Y(6)+(KR12+NN*KR5)*Y(1)+(KR23+(NN-1.)*KR5)*Y(2)+KR34*Y(3)
      DY(1)=-V*(KR12+KR5)*KA*Y(1)*Y(6)/DEN
      DY(2)=V*KA*Y(6)*(KR12*Y(1)-KR23*Y(2)-KR5*Y(2))/DEN
      DY(3)=V*KA*Y(6)*(KR23*Y(2)-KR34*Y(3))/DEN
      DY(4)=V*KA*Y(6)*KR34*Y(3)/DEN
      DY(5)=8.*V*KA*KR5*Y(6)*(Y(1)+Y(2))/DEN
C
      RETURN
      END
      SUBROUTINE DETER(A,D,N)
      DIMENSION A(144),L(12),M(12)
```

```
C     DETERMINANT PART OF MCMASTER PROGRAM  MINV
C
C        DESCRIPTION OF PARAMETERS
C           A - INPUT MATRIX, DESTROYED IN COMPUTATION AND REPLACED BY
C               RESULTANT INVERSE.
C           N - ORDER OF MATRIX A
C           D - RESULTANT DETERMINANT
C           M - WORK VECTOR OF LENGTH N
C           L - WORK VECTOR OF LENGTH N
C        METHOD
C           THE STANDARD GAUSS-JORDAN METHOD IS USED. THE DETERMINANT
C           IS ALSO CALCULATED. A DETERMINANT OF ZERO INDICATES THAT
C           THE MATRIX IS.SINGULAR
C
C           SEARCH FOR LARGEST ELEMENT
C
      D=1.0
      NK=-N
      DO 80 K=1,N
      NK=NK+N
      L(K)=K
      M(K)=K
      KK=NK+K
      BIGA=A(KK)
      DO 20 J=K,N
      IZ=N*(J-1)
      DO 20 I=K,N
      IJ=IZ+I
   10 IF( ABS(BIGA)- ABS(A(IJ))) 15,20,20
   15 BIGA=A(IJ)
      L(K)=I
      M(K)=J
   20 CONTINUE
C
C        INTERCHANGE ROWS
C
      J=L(K)
      IF(J-K) 35,35,25
   25 KI=K-N
      DO 30 I=1,N
      KI=KI+N
      HOLD=-A(KI)
      JI=KI-K+J
      A(KI)=A(JI)
   30 A(JI) =HOLD
C        INTERCHANGE COLUMNS
C
   35 I=M(K)
      IF(I-K) 45,45,38
   38 JP=N*(I-1)
      DO 40 J=1,N
      JK=NK+J
      JI=JP+J
      HOLD=-A(JK)
      A(JK)=A(JI)
   40 A(JI) =HOLD
C
C        DIVIDE COLUMN BY MINUS PIVOT (VALUE OF PIVOT ELEMENT IS
C        CONTAINED IN BIGA)
C
```

```
   45 IF(BIGA) 48,46,48
   46 D=0.0
      RETURN
   48 DO 55 I=1,N
      IF(I-K) 50,55,50
   50 IK=NK+I
      A(IK)=A(IK)/(-BIGA)
   55 CONTINUE
C
C        REDUCE MATRIX
C
      DO 65 I=1,N
      IK=NK+I
      IJ=I-N
      DO 65 J=1,N
      IJ=IJ+N
      IF(I-K) 60,65,60
   60 IF(J-K) 62,65,62
   62 KJ=IJ-I+K
      A(IJ)=A(IK)*A(KJ)+A(IJ)
   65 CONTINUE
C     -------------------------------------------------------------
C     DIVIDE ROW BY PIVOT
      KJ=K-N
      DO 75 J=1,N
      KJ=KJ+N
      IF(J-K) 70,75,70
   70 A(KJ)=A(KJ)/BIGA
   75 CONTINUE
C        PRODUCT OF PIVOTS
C
      D=D*BIGA
C
C        REPLACE PIVOT BY RECIPROCAL
C
      A(KK)=1.0/BIGA
   80 CONTINUE
      RETURN
      END
   .237733297544E+01   .185248389895E+02   .348589563858E+03   .821941610451E+03
   .241296152204E+01  -.156369136569E+05  -.279826444459E+05  -.201865710734E+05
  -.338462012401E+05  -.196835985995E+05   .236719891269E+05   .350300402337E+00
 14
426      10.0438
0.3945E-030.        0.        0.        0.        0.7480E-020.1954E-010.
0.        0.2236E-030.1292E-040.9543E-050.8059E-040.1256E-030.5766E-020.1711E-01
0.2445E-030.1432E-040.6232E+030.1540E+030.1000E+010.1099E+040.7194E-020.1540E+03
428      9.9803
0.3758E-030.        0.        0.        0.        0.5164E-020.2762E-010.
0.        0.2055E-030.1208E-040.7652E-050.8995E-040.1359E-030.3960E-020.1667E-01
0.3845E-030.1783E-040.6432E+030.1120E+030.1000E+010.9720E+030.6158E-020.1120E+03
430      10.1963
0.5209E-030.        0.        0.        0.        0.3664E-020.2042E-010.
0.        0.3275E-030.1552E-040.1204E-040.1117E-030.1683E-030.2792E-020.1844E-01
0.1917E-030.1277E-040.6272E+030.1000E+030.1000E+010.9620E+030.5788E-020.1000E+03
504      9.9840
0.3837E-030.        0.        0.        0.        0.5138E-020.1873E-010.
0.        0.2350E-030.1292E-040.9849E-050.8400E-040.1131E-030.4090E-020.1683E-01
0.9249E-040.1460E-040.6432E+030.1120E+030.1000E+010.9720E+030.6151E-020.1120E+03
512      9.9326
```

```
0.3675E-030.        0.        0.        0.        0.5191E-020.1865E-010.
0.        0.2195E-030.1159E-040.6514E-050.8711E-040.1231E-030.4150E-020.1669E-01
0.4986E-030.1745E-040.6432E+030.9700E+020.1000E+010.9700E+030.6220E-020.9700E+02
515      10.0051
0.6489E-030.        0.        0.        0.        0.5029E-020.1909E-010.
0.        0.4400E-030.2330E-040.1345E-040.9172E-040.1458E-030.4122E-020.1714E-01
0.4148E-030.1843E-040.6512E+030.9700E+020.1000E+010.1005E+040.6541E-020.9700E+02
523       9.8323
0.6460E-030.        0.        0.        0.        0.5087E-020.1597E-010.
0.        0.3245E-030.1698E-040.1071E-040.2355E-030.3414E-030.3808E-020.1561E-01
0.2904E-030.5700E-040.6302E+030.4100E+020.1000E+010.8520E+030.3442E-020.4100E+02
524       9.9271
0.3501E-030.        0.        0.        0.        0.5358E-020.1867E-010.
0.        0.2034E-030.1096E-040.5758E-050.9203E-040.1285E-030.4053E-020.1725E-01
0.2631E-030.1840E-040.6432E+030.9500E+020.1000E+010.9770E+030.6171E-020.9500E+02
527       9.9548
0.5734E-030.        0.        0.        0.        0.3058E-020.1779E-010.
0.        0.3798E-030.1811E-040.7443E-050.1282E-030.1843E-030.2560E-020.1655E-01
0.2473E-030.2496E-040.6532E+030.5500E+020.1000E+010.8720E+030.4015E-020.5500E+02
529       9.9616
0.5798E-030.        0.        0.         0.       0.2576E-020.1930E-010.
0.        0.3801E-030.1619E-040.5895E-050.1107E-030.1502E-030.2390E-020.1753E-01
0.2232E-030.2027E-040.6282E+030.6500E+020.1000E+010.8790E+030.4781E-020.6500E+02
531       9.9508
0.7055E-030.        0.        0.        0.        0.7545E-020.1750E-010.
0.        0.4082E-030.1867E-040.6956E-050.1055E-030.1621E-030.4691E-020.1600E-01
0.2546E-030.2220E-040.6282E+030.1000E+030.1000E+010.9920E+030.5344E-020.1000E+03
605       9.9305
0.3871E-030.        0.        0.        0.        0.5238E-020.1882E-010.
0.        0.2263E-030.1191E-040.6573E-050.9380E-040.1406E-030.4223E-020.1704E-01
0.5874E-030.2001E-040.6432E+030.8500E+020.1000E+010.9800E+030.6200E-020.8500E+02
610       8.9688
0.5980E-030.        0.        0.        0.        0.2690E-020.2080E-010.
0.        0.4220E-030.1910E-040.4400E-050.5380E-040.1350E-030.2170E-020.1860E-01
0.1529E-030.5060E-040.6562E+030.1000E+030.1000E+010.9850E+030.7214E-020.1000E+03
517       9.7044
0.3081E-030.        0.        0.        0.        0.6055E-020.1595E-010.
0.        0.1326E-030.6253E-050.5286E-050.1764E-030.3002E-030.5446E-020.1728E-01
0.4424E-030.5977E-040.6292E+030.5500E+020.1000E+010.8750E+030.3876E-020.5500E+02
    0.99778E+00    0.44419E-01   -0.49063E-01    0.20406E-02    0.67130E-02
    0.26868E-02   -0.53756E-01   -0.34789E-02    0.93406E+00   -0.35301E+00
    0.79268E-02    0.81633E+00    0.57555E+00    0.38364E-01   -0.28530E-01
      ENDLISTING
≠       6400 END OF RECORD
≠       6400 END OF RECORD
≠       6400 ENC OF RECORD

                                        CDTOT    766
```

APPENDIX C

EXPERIMENTAL CONDITIONS AND RESULTS

The following table (C.1) lists the experimental conditions used and the product composition measured for the packed bed experimentation.

To simplify the presentation the following column headings have been adopted. The coding system is as follows.

1. Run number
2. Temperature of reaction (°C)
3. Total gas flow at inlet conditions (cc/min at N.T.P.)
4. Inlet o-xylene concentration (gm moles/liter) x 10^4
5. Inlet oxygen concentration (gm moles/liter) x 10^4
6. Total absolute pressure in reactor (m m Hg)
7. Pressure drop across reactor (m m Hg)
8. Carbon balance ratio
9. Hydrogen balance ratio
10. Exit o-xylene concentration (gm moles/liter) x 10^6
11. Exit o-tolualdehyde concentration (gm moles/liter) x 10^6
12. Exit phthalide concentration (gm moles/liter) x 10^6
13. Exit phthalic anhydride concentration (gm moles/liter) x 10^6
14. Exit carbon dioxide concentration (gm moles/liter) x 10^6
15. Exit carbon monoxide concentration (gm moles/liter) x 10^6

Table C.1

Table of Experimental Conditions and Results

INLET CONDITIONS

1	2	3	4	5	6	7	8	9
426	350	267.	3.945	74.80	1099.	154.	1.00	1.00
428	370	200.	3.758	51.64	972.	112.	0.99	1.01
430	354	181.	5.209	36.64	962.	100.	1.04	0.94
504	370	200.	3.837	51.38	972.	112.	1.05	0.90
512	370	200.	3.675	51.91	970.	97.	1.04	1.16
515	378	212.	6.489	50.29	1005.	97.	1.01	1.10
517	356	117.	3.081	60.55	850.	41.	1.08	0.98
523	357	99.	6.460	50.87	977.	95.	1.02	0.82
524	370	200.	3.501	53.58	872.	55.	1.04	1.01
527	380	114.	5.734	30.58	879.	65.	1.02	0.94
529	355	140.	5.798	25.76	992.	100.	0.98	0.93
531	355	177.	7.055	75.45	980.	85.	0.92	0.88
605	370	200.	3.871	52.38	985.	100.	1.02	1.07
610	383	226.	5.980	26.90	875.	55.	0.94	0.92

PRODUCT COMPOSITIONS

1	10	11	12	13	14	15	16
426	223.6	12.92	9.543	80.57	111.22	14.30	10.0438
428	205.5	12.08	7.652	89.95	118.07	17.83	9.9803
430	327.5	15.52	12.04	111.7	155.53	12.77	10.1963
504	235.0	12.92	9.849	84.00	98.50	14.60	9.984
512	219.5	11.59	6.514	87.11	105.76	17.45	9.9326
515	440.0	23.20	13.45	91.72	127.37	18.43	10.0051
517	132.6	6.253	5.286	176.4	240.43	59.77	9.8323
523	324.5	16.98	10.71	235.5	284.4	57.00	9.9271
524	203.4	10.96	5.758	92.03	110.10	18.40	9.9548
527	379.8	18.11	7.443	128.7	159.34	24.95	9.9616
529	380.1	16.19	5.895	110.7	129.93	20.27	9.9508
531	408.2	18.67	6.956	105.5	139.9	22.20	9.9305
605	226.3	11.91	6.573	93.80	120.59	20.01	8.9688
610	422.0	19.12	4.35	45.60	85.4	50.70	9.7044