STABILITY ANALYSIS AND OPTIMIZATION OF A MULTIBED QUENCH REACTOR FOR AMMONIA SYNTHESIS

A THESIS

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By

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "STABILITY ANALYSIS AND OPTIMIZATION OF A MULTIBED QUENCH REACTOR FOR AMMONIA SYNTHESIS" in fulfilment of the requirement for the award of the Degree of Doctor of Philosophy submitted in the Department of Chemical Engineering of the University is an authentic record of my own work carried out during a period from August, 1984 to July, 1988 under the supervision of Dr.S.K.Saraf.

The matter embodied in this thesis has not been submitted by me for the award of any other Degree.

Dated: July 7, 1988 (SUDHINDRA NATH SINHA)

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ABSTRACT

The stability analysis and optimization of an axial flow three bed quench type ammonia synthesis reactor was carried out to optimize its performance. The reactor operation at optimal cold shot fractions for a given set of the operating and design parameter values will result in the maximization of the rate of production of ammonia and stable operation. This will result in low bed temperatures and reduced total pressure drop. The low bed temperatures will result in increase in catalyst life whereas reduced pressure drop will reduce the operating cost.

Modern large capacity reactors are used for production of ammonia used as a feedstock in the production of urea. Urea is essential to boost agricultural production in India. A realistic and accurate mathematical model of a large capacity multibed autothermic quench-type ammonia synthesis reactor was formulated and solved by modified Milne-Predictor-Corrector numerical integration technique using an appropriate convergence strategy. The optimization of the cold shot distribution was achieved by taking maximization of the rate of ammonia production as an objective function. The Box complex direct search optimization technique was used for sixteen set of conditions over a wide range of values of six operating and design parameters. These parameters were feed gas flow rate, H_2/N_2 ratio in feed, inerts concentration in feed, catalyst activity factor, total volume of catalyst and operating pressure of the reactor.

In order to estimate the model parameters for an industrial reactor for simulation study, data from plant were extracted for the period of steady-state operation over several months. The data had a serious limitation that no measured value of cold shot fractions were available except for the first bed inlet where its value was always kept at zero. Validation of simulation model from the plant data was carried out by obtaining best values of model parameters and cold shot fractions. The estimated model parameters are: frequency factor and activation energy in the reverse reaction rate constant correlation for the catalyst used; correction for fugacity coefficient term; and heat exchange capacity of external heat exchanger. Their best values are found to be $4.11482 * 10^{16}$ mol $NH_3/s/m^3$; 97622.4 kJ/kmol; 1.379; and 316000 W/K at feed flow rate of $0.74*10^6$ Nm^3/h, (where N indicates N.T.P. conditions), respectively. The simulated cold shot values as fractions of total feed gas for the average plant conditions (base case) are found to be 0.245 and 0.100 for the second and the third bed inlet, respectively. Cold shot to the first bed was taken to be zero as per plant practice.

The optimization computations for one set of conditions required generally 5 to 8 minutes of CPU time on DEC 20 computer system. The optimization results indicate that the conversion and the bed temperatures are quite sensitive to the values of the operating and design parameters. Cold shot fractions at optimal conditions are strongly dependent on these parameters. An indiscriminate use of cold shot fractions resulted in either quenching of the reactor or a non optimal performance resulting in significant loss of production, higher bed temperatures and increased pressure drops. The use of optimal cold shot fractions increased the rate of production of ammonia by 20 to 110 t/d (where 1 t = 1000 kg and 1 d = 86.4 ks) compared to actual plant production of 1286.9 t/d, even if the operating and design parameters changed in adverse direction by about 10 to 30 percent from the base value. The rate of ammonia production shows an increase with an increase in flow rate , catalyst activity, operating pressure or total catalyst volume; or and a decrease in inerts concentration. It was found that the region near optimal is not sharp with constraints on upper values of cold shot fractions resulting in the extinction of the reactor. It is further observed that optimal cold shot fractions do show a trend, to an extent linear with repect to change in parameters, namely, feed gas flow rate, catalyst activity factor, total catalyst volume and the reactor operating pressure.

An increase in the rate of ammonia production of 10.3 percent (132 t/d) is observed if the operation is carried out at optimal cold shot fractions to first, second and third bed of 0.110,0.233 and 0.232, respectively, for the base case. It is observed that the effect of change in H_2/N_2 ratio in the feed gas from 3.0 is not significant on reactor performance and rate of ammonia production. It is observed that the reactor stability near its optimal operation is quite sensitive to increase in cold shot fractions and an increase beyond a critical value may result in its extinction or blow-out. The use of simulation model is, therefore, highly desirable to operate the reactor near optimal values of cold shot fractions for any set of parameter values in order to achieve maximum ammonia production rate. Simulation model can also be used for developing a suitable control strategy for cold shot distribution for ensuring optimal reactor operation.

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S.N.SINHA

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NOMENCLATURE

b_o, b_1, b_2, b_3, b_4, b_5 and b_6	coefficients of effectiveness factor correlation that are dependent on gas pressure
C_1, C_2 and C_3	various terms in the reaction rate equation that are independent of gas temperature
C_p	heat capacity of gas, kJ/kmol/K
C_{pj}	heat capacity of component j, kJ/kmol/K
f	catalyst activity factor, dimensionless
F_2	molal flow rate of hydrogen in feed to reactor, mol/s
F_{DH}	fraction of total feed entering through preheating section, dimensionless
F_{Di}	cold shot to bed 'i' as a fraction of total feed to reactor, dimensionless
F_j	molal flow rate of component j in feed to reactor, mol/s
$(-\Delta H_{R2})$	heat of reaction, kJ/kmol of hydrogen converted
k_r	reverse reaction velocity constant, $mol/s/m^3$ of catalyst
K	equilibrium constant of the reaction $3/2\ H_2 + 1/2\ N_2 = NH_3$, dimensionless
K_{C1}, K_{C2} and K_{C3}	coefficients at a given temperature and pressure, dimensional
K_γ	fugacity coefficient term, dimensionless

N	gas flow rate at any point in the reactor, mol/s
N_{iT}	total molal flow rate in a bed, mol/s
N_j	molal flow rate of component j, mol/s
N_{Oj1}	molal flow rate of component j leaving external and internal preheating sections (hypothetical bed 0 exit), mol/s
p	partial pressure of gas constituent, atm (where 1 atm = 101.325 kPa)
P	gas pressure at any point in the reactor, atm
Para1, Para2	parameters for correction of frequency factor and activation energy in the reverse reaction rate constant correlation, respectively; dimensionless
Para3	parameter to account for inadequacy of K_p correlation
$(-r_2)$	rate of reaction without mass transfer limitation in catalyst given as moles of hydrogen converted per unit time per unit catalyst volume, $mol/s/cm^3$
T	gas temperature in catalyst bed, K
T_H	gas temperature on tube side of external heat exchanger, K
T_S	gas temperature in internal preheating section, K
T_{SH}	gas temperature on shell side of external heat exchanger, K
T_{SHE}	gas temperature at the exit of internal preheating section, K

(UA)	heat exchange capacity of bed, $W/K/cm^3$
$(UA)_H$	heat exchange capacity of external heat exchanger, $W/K/cm^3$
v_i	volume of the reactor in bed 'i', cm^3
v_H	volume of the external heat exchanger on tube side, cm^3
x_{i2}	fractional conversion of hydrogen in bed 'i' based on total hydrogen in feed to reactor, dimensionless
y	mole fraction of gas constituents

Greek Symbols

α_j	coefficient proportional to stoichiometric coefficient for component j (α_1 = -1/3, α_2 = -1, α_3 = -2/3, α_4 = α_5 = 0), dimensionless
γ	activity coefficient of gas constituents, dimensionless
ξ	effectiveness factor to account for mass transfer resistance in the catalyst pellet, dimensionless
η	conversion of nitrogen, dimensionless
ω_N	coefficient for pressure drop based on unit bed volume, atm/cm^3
ω_{HN}	coefficient for pressure drop based on unit tube side volume of external heat exchanger, atm/cm^3
ϕ	fugacity of gas constituent, atm

Subscript

eq	corresponds to equilibrium
F	corresponds to feed
H	corresponds to external heat exchanger on tube side
i	designates the catalyst bed number
j	designates components (1-nitrogen, 2-hydrogen, 3-ammonia, 4-methane, and 5-argon)
m	corresponds to maximum reaction rate
N	corresponds to base conditions
S	corresponds to internal preheating section shell side
SH	corresponds to external heat exchanger shell side
T	corresponds to total

CHAPTER I

1. INTRODUCTION

Simulation, optimization and stability analysis of the modern large capacity multibed quench-type (cold-feed cooling) ammonia synthesis reactors is essential for their proper and accurate control and optimal performance.

Ammonia is an essential feedstock for the manufacture of urea which is required in large tonnage for boosting agricultural production. Agriculture contributes to about fifty percent of the national income (Pachaiyapan,1984) and provides livelihoods for about seventy-five percent of Indian population. Nitrogenous fertiliser production is estimated at about six million tons in 1987-88 and is expected to rise further. In order to meet the anticipated requirements, many new plants are coming up mainly based on natural gas as a feedstock requiring huge investments of the order of six billion rupees (1983 price).

The ammonia technology and engineering for its manufacture has rapidly advanced in the last decade and the plants of 1350 t/d (where 1 t = 1000 kg and 1 d = 86.4 ks) capacity and over are common now-a-days. The latest policy of the Indian Government is to standardise the ammonia technology and build new plants on either of the two technologies, namely, Haldor-Topsoe and Kellogg of axial or radial flow designs. In view of the large ammonia production and high capital investment requirements, even a few percent improvement in production from existing plants is worth hundreds of million rupees every year.

Ammonia is produced by catalytic exothermic reversible reaction of hydrogen and nitrogen in the mol ratio of approximately 3:1 at elevated pressures (100 to 1000 atm, where 1 atm = 101.325 kPa) and temperatures (675 to 925 K) using doubly promoted iron catalyst. The current trend is towards low pressure (150 to 200 atm) and low temperature (650 to 770 K) operation using highly active catalyst. It is essential to carry out the reaction in an autothermic reactor with axial or radial flow and quench cooling in between catalyst beds and /or internal heat exchange and external heat exchange. Quench type reactors are more common for ammonia systhesis because of high pressure oparation. In these reactors intermediate cooling of reaction mixture is achieved by the addition of cold-feed to the reaction mixture at the inlet of a catalyst bed. The description of reactors of various designs are given by Walas (1959), Vancini (1971), Zardi (1982) and others. Due to the opposing requirements of temperature for high reaction rate and high equilibrium conversions, the intermediate cooling between catalyst beds of an ammonia synthesis reactor is essential. Autothermal reactor operation involving feed-back of reaction heat to the incoming cold reactor feed are generally found to possess multiplicity of steady-state operating points. This behaviour of autothermal reactor was first explained by van Heerden (1953). The reactor steady-state point corresponding to highest conversion is the desirable operating point. Beside this, in general, there are two other operating points, the intermediate one is unstable and the one corresponding to the lowest conversion is a trivial operating point. The stability limit is observed when both the unstable and stable points (of high conversion) coincide with each other due to relative shifting of heat generation and heat removal curves because of changes in plant operating parameters. Reactor blow-out or extinction is a well known problem experienced in autothermal operation with certain changes in plant operating parameters (Froment and Bischoff, 1979a).

Since van Heerden, several other workers (Shah, 1967; Shipman and Hickman, 1968; Vek, 1977; Gaines, 1977; Rase, 1977; Ramkumar, 1978; Lutschutenkow et al., 1978; Reddy and Husain, 1978; Singh and Saraf, 1979; Sinha et al., 1981; Khayan and Pironti, 1982; Mansson and Andresen, 1986) have presented their work on simulation of ammonia synthesis reactor that have contributed significantly to a better understanding of the behaviour of ammonia synthesis reactor performance. However, the extensive literature survey as presented in Chapter-II shows that no published work is available regarding optimization of an existing industrial reactor for ammonia synthesis of multibed quench-type with internal and/or external heat exchanger taking cold shot distribution as decision variables. Also there is lack of information regarding steady-state stability analysis of such reactors operating at optimum conditions.

Therefore, the objectives of the present study can be summarized as follows:

1. Development of a realistic and accurate simulation model for a three-bed autothermic quench reactor for ammonia synthesis for carrying out simulated performance studies under different design

and operating conditions.

2. Development of reliable and efficient optimization strategies for the maximization of ammonia production rate using cold shot distribution as decision variables.

3. Validation of simulation model and the determination of the kinetic and external heat exchange rate parameters using plant data.

4. Determination of optimal cold shot distribution and corresponding temperature-conversion profile and ammonia production rate for different design and operating conditions.

5. Study of the steady-state reactor stability at optimal operation for different design and operating conditions.

CHAPTER II

2. LITERATURE REVIEW

2.1 Literature review on ammonia synthesis reactor modelling and simulation.

Modelling and analysis of autothermic processes, in particular ammonia synthesis reactor, have attracted considerable attention of research workers after the first reported study of van Heerden (1953). Van Heerden formulated a simplified one dimensional mathematical model for his packed bed catalytic reactor having a large number of tubes placed axially in the bed. The cold feed passes through the tubes countercurrent to the flow of gases in the catalyst bed and gets heated to desired temperature before entering the catalyst bed where exothermic reversible ammonia synthesis reaction occurs.

Van Heerden solved the three coupled differential equations, namely, material and energy balance equations for the reacting gases in the catalyst bed, and energy balance equation for the feed preheating inside the tubes for his simplified mathematical model of the reactor by using a stepwise numerical integration procedure. The solutions so obtained were in quantitative agreement with the actual data obtained for a commercial reactor of the same type.

Van Heerden observed from his analysis that due to reversible and exothermic nature of ammonia formation reaction a plot of heat generation rate due to reaction as a function of catalyst bed inlet temperature has a sigmoid shape but at very high bed inlet temperatures the heat generation rate falls rapidly due to equilibrium limitations at high temperatures. He observed that the catalyst bed temperature first rises, passes through a maximum value and then decreases towards reactor exit. He also observed that a definite range of operating parameters exists for stable operation of an autothermic ammonia synthesis reactor at high conversion conditions in the vicinity of the quenching or blow-out point.

Van Heerden further observed from his theoretical analysis that as catalyst activity or the heat transfer capacity decreases the stability of the reactor decreases, whereas if the feed rate decreases the stability of reactor increases.

Annable (1952) derived a one-dimensional single-bed model of Haber-Bosch type ammonia synthesis reactor using a Temkin-Pyzhev (1940) rate equation. He found that the simulation model results were in close agreement with plant observations. But he did not investigate the effect of change in operating and design variables on the performance of the reactor and its stability using his simulation model.

Kjaer (1958) formulated his mathematical model for a single bed by considering the two-dimensional variation in temperature, axial and radial, and solved the resulting model equations consisting of three partial differential equations using double-step numerical integration technique by hand computation. His results of production rate and average bed temperature were in very good agreement with the plant data. However, the model developed by Kjaer could not explain the radial temperature gradients reported by Slack et al. (1953). The results of Kjaer indicated that the radial temperature gradients may not be significant.

Baddour et al. (1965) studied the behaviour of a TVA ammonia synthesis reactor (Tennesse Valley Authority reactor) using a simplified one-dimensional model to account for axial variation of bed temperature and conversion. They used Temkin and Pyzhev reaction rate equation. The results of the simulation model were found to be within 15 to 20 percent of the plant data for the production rate and bed temperature profile. Their study indicated an improvement in ammonia production rate at higher space velocity of feed gas when reactor is operated at high first bed inlet temperature. However, an increase in space velocity is found to lower the reactor stability. Use of higher ammonia or inerts content in the feed was found to be detrimental, both, to reactor production rate and its stability, even though average bed temperature was not affected significantly. Any decrease in catalyst activity resulted in a decline in both, the reactor stability and its production rate and necessitated an increase in the first bed inlet temperature. The effect of increase in the heat transfer capacity was to increase the reactor stability with increased local overheating of catalyst. However, no significant effect on reactor production rate and average bed temperature was observed. They also observed that bed temperature profile at the optimum conditions was not sensitive to changes in operating conditions.

Shah (1967) developed a one-dimensional model to analyse the behaviour of a two-bed ammonia synthesis reactor with cold shot cooling. Shah made certain assumptions to simplify his model equations while accounting for the non-ideal behaviour of the gases in the reaction rate equation, heat of reaction and specific heat values. He found that these nonidealities have a significant effect on the reactor performance. Realising the inadequacy of the Temkin and Pyzhev rate equation, Shah used the modified Temkin and Pyzhev reaction rate equation in his simulation model. Shah also assumed a linear decrease in pressure with distance in the direction of flow of gas. His results of simulation agreed well with the plant data.

Shah solved his mathematical model consisting of coupled non-linear differential equations using a numerical integration technique known as the Milne Predictor-Corrector (Milne, 1953) and observed that the method of solution was stable and converged rapidly.

Shah observed from his simulation model studies that increase in cold shot fraction decreased the reactor stability; increase in inerts decreased the stability without significantly affecting the production rate; and increase in ammonia content of feed decreased both production rate and stability. He also observed that the increase in the first bed inlet temperature resulted in an increase in production rate till equilibrium inhibition was obtained. Shah further observed that the increase in pressure resulted in higher production rate but any change in H_2/N_2 ratio did not affect the production rate significantly. The effect of change in space velocity and catalyst activity on production was found to be the same as that reported by Baddour et al. (1965).

Shipman and Hickman (1968) carried out simulation and optimization of a five-bed ammonia reactor with external heat exchanger and cold shot quenching. They carried out optimization using independent variables consisting of operating variables of cold shot distributions and design variables of cold shot location, catalyst bed length and heat exchanger length. Search for optimization was carried out for minimising the converter cost using a modified gradient search method.

Shipman and Hickman observed that increase in the number of catalyst beds beyond three is not of much consequence for minimizing reactor cost. Further, cold shot distributions have a significant effect and there exists an optimal distribution. However, near the optimum the small variations in cold shot do not affect the optimal solution significantly.

Gaines (1977) simulated and optimized a four-bed ammonia converter with cold shot cooling and preheating. He used a modified Temkin and Pyzhev reaction rate equation and used the findings of Nielsen (1968) and Dyson and Simon (1968) for making it more realistic. He also considered the effect of catalyst pellet mass transfer resistance by incorporating in the rate equation the effectiveness factor as given by Dyson and Simon (1968). He optimized the bed temperature profile to maximise conversion at the reactor exit and recommended a declining outlet temperature profile from the first to the fourth bed. He found that the last bed outlet temperature is most critical for improving reactor conversion. He concluded that there is an optimal ratio of actual ammonia mol percent to equilibrium ammonia mol percent at the catalyst bed outlet for achieving maximum conversion. The effect of important parameters, such as space velocity, feed temperature, pressure, inerts and ammonia concentration, H_2/N_2 ratio and catalyst activity were found to be similar as reported by earlier workers. His results were in good agreement with plant data.

Vek (1977) considered two types of radial flow four- bed ammonia coverters for modelling and optimization. The first type consisted of two heat exchangers -one internal heat exchanger placed between the first and the second bed and another external heat exchanger at the end of the last bed. The second type consisted of an external heat exchanger only, but with gas recirculation in the first bed. He accounted for variation of overall heat transfer coefficient in reactor. He found his simulation results in agreement with the plant data. From his analysis he observed that first type had better operational stability and a higher ammonia production rate. Typical outputs were between 100 to 130 $t/d/m^3$ of catalyst as compared to 35 to 50 $t/d/m^3$ of catalyst volume obtained normally.

Rase (1977) also presented a case study of multibed ammonia synthesis reactor with cold shot cooling. His range of operating variables include pressure at three values of 150, 225, and 300 atm and inerts in feed at 12 percent. For safe operation of the catalyst the allowable bed temperature was limited to 803

K. Rase observed that operation at lower pressure of 150 atm was more desirable for saving energy costs, and increasing the life and activity of catalyst.

Sinha (1977, 1981) modelled and analysed the behaviour of one-dimensional three-bed ammonia synthesis reactor with cold shot cooling and internal and external heat exchange. The results suggested that ammonia production rate is quite sensitive to operating parameters, such as, first bed inlet temperature, cold shot temperature and its distributions, ammonia and inerts content in the feed, feed pressure and design parameters such as cold shot location. It was observed that ammonia production rate increases with a decrease in ammonia and inerts contents in the feed, increase in space velocity, and increase in the first bed inlet temperature with proper cold shot distributions and location. However, the indiscriminate use of cold shot at a low first bed inlet temperature was found to be disastrous for ammonia production.

Reddy and Husain (1978) modelled a single-bed ammonia synthesis reactor of Casale type with cold shot quenching at the bed inlet using a one-dimensional model. They considered the actual flow route of gases in the reactor and the axial variation of heat transfer capacity. Model parameters were validated using plant data. Reddy and Husain studied the effect of operating parameters on the performance of the reactor. They found that the increase in feed flow rate reduces the ammonia conversion markedly at higher flow rate; H_2/N_2 ratio has an optimum value around 2.5 for maximum conversion; and a decrease in inerts and/or ammonia concentration increases ammonia conversion.

Ramkumar (1978) studied the behaviour of a one-dimensional three-bed ammonia synthesis reactor with cold shot cooling, internal and external heat exchange. He also accounted for the mass transfer resistance in the catalyst pellet by incorporating the effectiveness factor correlation of Dyson and Simon (1968) in the reaction rate equation. He observed that for increasing production rate, the space velocity and first bed inlet temperature should be higher, inerts content in the feed should be lower, and the cold shot distribution and location must be optimal.

Lutschutenkow et al. (1978) also presented the behaviour of a one-dimensional four-bed model of an ammonia synthesis reactor with external heat exchange. They observed maximum ammonia productivity near the autothermal limit. They also observed the bed outlet temperature to be independent of the cold shot at the bed inlet, and the ammonia productivity to depend on the H_2/N_2 ratio in the feed and bed outlet temperature but not the reactor inlet temperature.

Singh and Saraf (1979) modelled and analysed the behaviour of one-dimensional ammonia synthesis reactors of two types. The first type was a three-bed reactor with external heat exchange and inter-bed heat exchanger for cooling without any cold shot. The second type was a single-bed reactor with external heat exchanger and cold shot cooling at the bed inlet. The effect of mass transfer resistances in the catalyst pellet was considered by incorporating effectiveness factor in the reaction rate equation by partially solving the intrapellet diffusion equation at each axial location. They used different rate equations for two types of catalysts. Their simulation results were found to be in good agreement with plant data.

Khayan and Pironti (1982) studied the behaviour of an ammonia converter with heat exchanger using a two-dimensional model to account for axial as well as radial gradients of temperature and concentration. They solved the resulting non-linear coupled partial differential equations using the Crank-Nicolson numerical technique. Their results matched the plant data within 2 percent. They observed that radial gradients are insignificant.

Mansson et al. (1986) carried out optimization study of an ammonia synthesis reactor to maximize exit ammonia mole percent. Performance of the reactor was found by optimizing the bed temperature profile for a given mass flow rate and inlet conditions. Performance was compared with conventional operation. They observed that considerable improvement in performance may be achieved.

The literature review presented above clearly indicates that these simulation and optimization studies have significantly contributed to the understanding of the effect of operational and design parameters on the performance of ammonia synthesis reactors. However no published information is available regarding optimization of an existing industrial multibed quench reactor with internal and/or external heat exchanger for ammonia synthesis taking cold shot distribution as a decision variable for wide range of variation of all important design and operating parameters. Very little published information exists on the steady-state stability analysis of such optimally operating reactors.

It may also be noted that no attempt has been made to review the simulation and optimization literature not specifically related to ammonia synthesis reactor.

2.2. Literature Review on Kinetic, Thermodynamic and Physical Properties:

Shah (1967) reported the kinetic, thermodynamic and thermochemical properties correlations using the data reported by Annable, Hougen and others. Shah gave correlations for reverse reaction rate constant, k_r, taking the Arrhenius form of dependance on temperature and also used a multiplying factor to correct for pressure deviations from 300 atm. His equilibrium constant correlation is a six-constant equation, an exponential function of temperature terms only. K_γ, fugacity coefficient term, is correlated as a five-constant polynomial in temperature and pressure. His heat of reaction correlation is a ten-constant polynomial and heat capacity of ammonia correlation is a seven-constant equation, both equation involving pressure and temperature terms only. For nitrogen hydrogen and methane heat capacity correlations, Shah used four-constant polynomials in temperature with the coefficients of polynomial found for the mean pressure. For argon, the heat capacity was taken at a fixed value as it was independent of temperature and pressure. Shah observed that the more elaborate correlations used by him resulted in predictions by simulation model close to the plant performance.

Dyson and Simon (1968) gave k_r correlation by fitting the data of Nielsen in an Arrhenius form. However unlike shah's approach, there is no pressure correction term in their correlation. They used an equilibrium constant correlation proposed by Gillespie and Beattie, a five-constant equation involving functions of temperature in an exponential form. Dyson et al. also used published correlations for the activity coefficients of H_2, N_2 and NH_3 as four- or five-constant equations involving complex functions of temperature and pressure in an exponential form. They concluded that their correlations are quite precise to give fugacity values comparable to those obtained by more elaborate calculation of fugacity from an equation of state using both Beattie-Bridgman and Redlich-Kwong equations.

Gaines (1977) reported an Arrhenius form of correlation for k_r based on the data of Nielsen, similar to that of Dyson and Simon. The activity coefficients of H_2, N_2 and NH_3 were correlated using equations involving three independent constants and showing temperature pressure and composition dependence. Gaines used a six-constant polynomial for heat of reaction involving pressure and temperature terms with correction for heat of mixing. He used an eight-constant BWR equation of state to compute directly the gas mixture heat capacities by first computing the constants for the mixture by appropriate relations.

Reddy and Husain (1978) have used the same correlations as reported by Shah (1967) for K, K_γ, heat of reaction and heat capacities of individual component.

Singh and Saraf (1979) took the usual Arrhenius form of correlation for k_r with appropriate values of the order of reaction parameter, frequency factor and activation energy for two types of catalysts based on data reported by Guacci et al. Correlations for K and heat capacities used by them are similar to those reported by Dyson and Simon (1968).

Mansson and Andresen (1986) used the usual Arrhenius form of correlation for the rate constants in his reaction rate equation using three empirically determined sets of interdependent values of activation energy and frequency factor. The equilibrium constant correlation was obtained from Gillespie and Beattie as cited by Mansson et al. The activity coefficient correlations for H_2, N_2 and NH_3 is taken based on Beattie and Bridgman, and Beattie work, as cited by Mansson et al., as a complex function of temperature, pressure and mole fractions in a way similar to that of Gaines but incorporating additional terms dependent on mole fractions to make it more accurate.

The heat of reaction correlation was that given by Nielsen, a seven-constant equation in temperature and pressure. Heat capacity correlations were those reported by Gillespie and Beattie as cited by Mansson et al. and heat of mixing was neglected in computing the mixture heat capacity as per the justification given by Nielsen and Strelzoff as cited by Mansson et al.

Hay and Honti (1976a) have presented correlations for thermodynamic properties. Of particular interest is that reported for the equilibrium constant, an exponential function of temperature giving a minimum percentage deviation from the theoretical values of Harrison and Kobe and comparing well with the experimental values reported by Haber, Larson and Dodge, Stephenson and McMahon as cited by Hay and Honti.

Perry's Chemical Engineers HandBook (1950) reports correlations for heat capacities of H_2, N_2 and NH_3, as three-constant polynomials in temperature. A correlation for heat of reaction is also given as a polynomial in temperature. Various other correlations for thermochemical properties are reported in the International Critical Tables (1928), Kirk and Othmer (1978) and by many other authors which vary in their degree of complexity, accuracy and range of application.

CHAPTER III

3. REACTOR MODELLING AND DESIGN RELATIONSHIPS

3.1. Reactor modelling and design relations.

Mathematical modelling of the multibed reactor consists in writing mass, energy and momentum balance equations for each of the reactor sections along with equations defining the boundary conditions imposed by cold shot addition at the bed inlet. The rigorous model precisely defining the heterogeneous ammonia synthesis reaction may be written in the form of partial differential equations for momentum, mass and energy balances in three- dimensional space and time. However such a system of highly non-linear and coupled partial differential equations will be very difficult to solve. This will require excessive computation time and very large memory on the large new generation computers. Convergence problems enhance these difficulties further that are inherent in the solution of autothermal reactor with external and/or internal heat exchange between the reaction mixture and the feed gas. Therefore, a rigorous approach is impractical and recourse must be made to more approximate engineering approach for simulation purpose that simplifies the modelling of converter significantly without sacrificing the accuracy to predict reactor performance and stability of operation keeping in view the extent of uncertainty inherent in the basic data used in the simulation model.

For this study, only the steady-state behaviour is taken into consideration and the change in operating parameters is assumed to be slow enough that reactor operation is regarded as a succession of pseudo-steady states. It is further assumed that there are no gross perturbations that deliberately push the steady operation to another steady state. The validity of the steady-state assumption is discussed by Shah (1967). Yet another argument for considering the operation to be at steady-state is given by Reddy and Husain (1978) by pointing out that since the gas mixture velocity is always high, its residence time is likely to be very small, probably, of the order of a few seconds. Therefore, for the design and performance predictions of commercial reactor, the additional information obtained by considering the unsteady state simulation model is not commensurate with the phenomenal increase in modelling effort and computer time required for its solution.

A simplified flow diagram of a typical three-bed quench type high capacity ammonia synthesis axial flow reactor with internal and external heat exchange capacities is shown in Fig.3.1. The feed gas is divided into four parts; the largest fraction goes to bottom heat exchanger and the remaining gas is distributed into three cold shots for mixing with the gases entering different catalyst beds. The fraction of feed entering the bottom heat exchanger on its shell side gets preheated as a result of heat exchange from the reaction product leaving the third bed and flowing countercurrently on the tube side. This preheated fraction of feed is heated further by exchanging heat from the hot reaction mixture flowing countercurrently in the catalyst bed depending on the amount of heat transfer area available for the

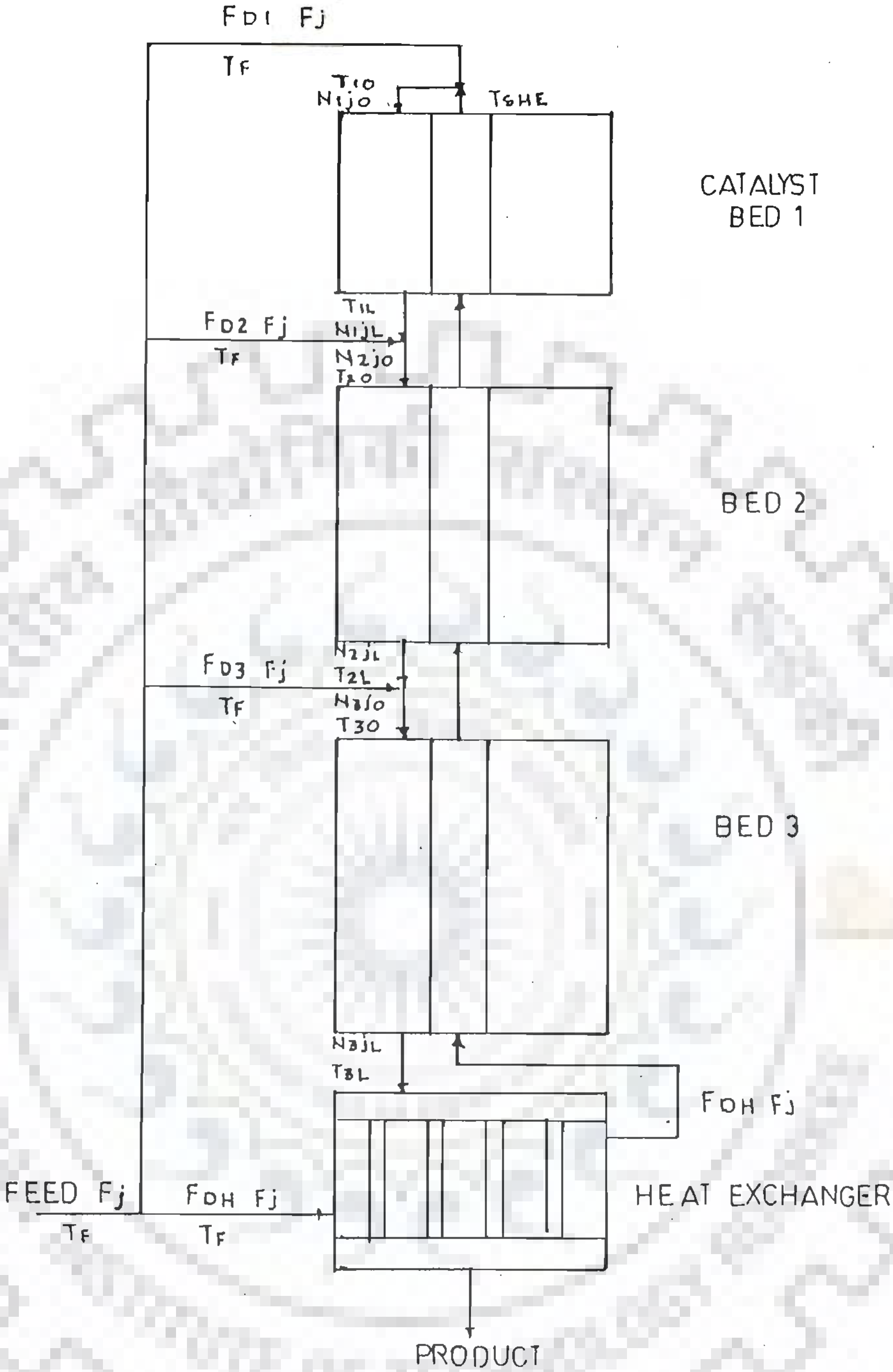

FIG. 3.1. SIMPLIFIED FLOW DIAGRAM OF THREE BED QUENCH TYPE AMMONIA SYNTHESIS REACTOR WITH INTERNAL AND EXTERNAL HEAT EXCHANGE CAPACITY

internal heat exchange. This heated fraction of feed enters the first catalyst bed inlet after mixing with cold shot fraction to the first bed.

Assumptions.

For obtaining mass, energy and momentum balance equations in manageable form, following simplifying assumptions are made:

1. Reactor operation is at steady state.
2. Radial velocity, temperature, pressure and concentration gradients are absent. There is complete mixing in the radial direction in the bed.
3. There is no back mixing in axial direction.
4. Pressure drop variation is linear in the direction of flow. The effect of cold shot is accounted for by assuming that the coefficient of pressure drop varies with 1.8 power of the superficial mass velocity, G, at the inlet of a catalyst bed (Froment and Bischoff, 1979b). This dependence is based on Leva equation for packed beds indicating that the pressure drop is proportional to (fG^2) where f is the friction factor. Hicks has observed that this f is proportional to $(G)^{-0.2}$. Therefore, pressure drop is proportional to $(G)^{1.8}$.
5. Cold shot enters the reactor at the temperature of feed gas and at a pressure equal to the pressure in the reactor at the point of its entry.
6. Heat exchange capacity, that is the product of heat transfer coefficient and heat transfer area per unit catalyst bed volume remains constant throughout the reactor. Similarly, heat exchange

capacity per unit tube side volume in the external heat exchanger is also constant.

7. For gas-solid reaction, the interphase heat and mass transfer and the intraparticle heat transfer resistances are neglected.

8. Intraparticle mass transfer resistance in catalyst pellet is significant and is accounted for by considering the effectiveness factor. A polynomial relationship for the effectiveness factor with gas temperature and composition using pressure as a parameter is used to simplify the simulation model.

Validity of assumptions.

Except during start up and shut down of the reactor, the operation of a continuous process remains at a steady-state. Unsteady-state analysis becomes essential only for predicting the reactor behaviour during the start up and shut down periods.

The radial gradients of velocity, temperature, pressure and concentration across the cross-section of the catalyst bed are insignificant as compared to the axial gradients. This is supported by the findings of Kjaer (1958) and Khayan et al. (1982). These investigators considered the two-dimensional reactor model and found that the radial gradients are negligible.

Axial diffusion of enthalpy is ignored in view of the findings of Eymery (1964) as reported by Reddy and Husain (1982).

The pressure drop across the length of the bed is very small as compared to the pressure of gas at any point in the bed. In industrial converters the total pressure drop is found to be well within five percent of the gas pressure. Therefore, the assumption of linear variation of pressure along the reactor bed is justified. However, a correction has been made in pressure drop correlation from one bed to another to account for the substantial increase in the gas flow rate in a particular bed because of the cold shot additions. The effect of increase in flow rate is taken into account by assuming that the coefficient of pressure drop varies with 1.8 power of superficial mass velocity, G. For a catalyst bed of uniform cross sectional area, it is quite evident that at the inlet of a bed G is proportional to the total feed fraction entering the bed.

In an ammonia synthesis reactor, the overall heat transfer coefficient varies along the bed length because of the changes in flow rate and the variation in physical properties of the gas mixture along the bed length. However, this variation in heat transfer coefficient is small and for all practical purposes, it may be assumed to be constant throughout the bed length. In any case, if considered essential, this variation can be accounted for as the calculations in numerical integration proceed from point to point at which all conditions are known, computing the value of heat transfer coefficient at any point using appropriate correlations.

The mass, momentum and heat balance equations can be written, keeping in view the foregoing assumptions and their justifications, for the ammonia synthesis reaction

$$3/2\ H_2 + 1/2\ N_2 = NH_3 \qquad (3.1.1)$$

over a differential reactor section of catalyst volume dv_i (in bed i).

Mass balance.

The mass balance for hydrogen (subscript 2) is given by,

$$F_2\, dx_{i2} = (-r_2 \xi)\, dv_i \qquad (3.1.2)$$

where,

F_2 = molal flow rate of hydrogen in feed to the reactor, mol/s,

x_{i2} = fractional conversion of hydrogen in bed 'i' based on total hydrogen in feed to reactor, dimensionless;

$(-r_2)$ = rate of reaction without mass transfer limitations in catalyst given as moles of hydrogen converted per unit time per unit of catalyst volume, mol/s/cm^3

ξ = catalyst effectiveness factor to account for mass transfer resistance in the pellet, dimensionless.

Energy balance.

The energy balance equation is obtained by equating the heat of reaction to the summation of the sensible heat gain of the reaction gas mixture and the amount of heat transferred to the synthesis gas (cold feed) in the internal preheating section. This will give,

$$(-\Delta H_{R2})(-r_2 \xi)dv_i = (\sum_{j=1}^{5} N_{ij} C_{pj})_i dT_i + (UA)_i (T_i - T_{si}) dv_i \qquad (3.1.3)$$

where,

$(-\Delta H_{R2})$ = heat of reaction, kJ/kmol of hydrogen converted

N_j = molal flow rate of component j, mol/s

C_{pj} = heat capacity of component j, kJ/kmol/K

T = gas temperature in the catalyst bed, K

(UA) = heat exchange capacity of bed per unit catalyst bed volume, $W/K/cm^3$

T_s = gas temperature in the internal preheating section, K.

For (UA), area of heat transfer, A, is defined per unit volume of catalyst bed. For a given reactor of certain design and configuration, area of heat transfer per unit volume of catalyst bed is likely to be constant throughout the bed length so that (UA) remains constant throughout the bed length as U is assumed constant.

Subscript j designates components (1- nitrogen, 2-hydrogen, 3- ammonia, 4-methane, and 5-argon) and subscript i denotes the catalyst bed number.

The energy balance equation for the feed gas in internal preheating section is:

$$F_{DH} \left(\sum_{j=1}^{5} F_j \; Cp_j \right) dT_{Si} = -(UA)_i \; (T_i - T_{Si}) dv_i \qquad (3.1.4)$$

Where F_{DH} is the fraction of total feed entering through preheating section and negative sign on right hand side takes into account the fact that in internal preheating section the direction of flow of feed gases is opposite to the direction of increase of catalyst bed volume.

For all the three beds the above set of equations (3.1.2), (3.1.3) and (3.1.4) are applicable and subscript i will be replaced by subscripts 1, 2 and 3 as computations are carried out for bed 1, 2 and 3, respectively.

It may be noted that the energy balances assume that heat of mixing for reaction mixture is negligible. Only Gaines (1977) appears to have considered heat of mixing terms in the energy balance, but it is believed that at the reactor operating conditions (temperature 600 to 900 K, pressure 170 to 200 atm, and ammonia mole percent 1.5 to 16.0) the heat of mixing due to the non-ideality of reaction gas mixture may really be insignificant. Further more, appropriate correlations are used to account for variations in specific heat values with temperature and for ammonia with pressure also.

It is worthwhile to mention here that the fractional conversion of hydrogen, x_2, is based on total moles of hydrogen fed to reactor inclusive of all cold shots. Such a choice of X_2 ensures that it increases monotonically as reaction mixture reacts while passing through the catalyst beds.

Additional mass and energy balance equations are needed to obtain the boundary conditions for the solution of reactor balance equations for each catalyst bed. The boundary conditions at each catalyst bed inlet are introduced due to the discontinuities resulting from the addition of cold shots at each bed inlet.

Mass balance equations for catalyst bed i.

At the inlet (Subscript 0).

$$N_{ij0} = F_j \left(F_{DH} + \sum_{i=1}^{i} F_{Di}\right) + \alpha_j F_2 x_{2i0} \qquad (3.1.5)$$

Where,

$i = 1, 2, 3$; and $j = 1, 2, 3, 4, 5$

F_j = molal flow rate of component j in feed to reactor, mol/s

F_{Di} = cold shot to bed i as a fraction of total feed to reactor, dimensionless

At the exit (subseript 1).

$$N_{ij1} = F_j \left(F_{DH} + \sum_{i=1}^{i} F_{Di}\right) + \alpha_j F_2 X_{2i1} \qquad (3.1.6)$$

where,

$i = 1,\ 2,\ 3$ and $j = 1,\ 2,\ 3,\ 4,\ 5$

During cold shot addition at the inlet of any bed it may be noted that since reaction is not occurring, therefore, the value of x_2 at the exit of the previous bed (i-1) is the same as at the inlet of the next bed i

$$X_{2,i-1,1} = X_{2,i,1}$$

Energy balance equations.

At the entry of bed i (after mixing of coldshot).

$$\left(\sum_{j=1}^{5} N_{ij0} C_{pj}\right) T_{i0} = \left(\sum_{j=1}^{5} N_{(i-1)j1} C_{pj}\right) T_{(i-1)1} + F_{Di} \left(\sum_{j=1}^{5} F_j C_{pj}\right) T_F \qquad (3.1.7)$$

where,

$i = 1,\ 2,\ 3$

$N_{0j1} = F_{DH} F_j$

$T_{01} = T_{SHE}$

N_{0j1} is the molal flow rate of component j leaving external and internal preheating sections (hypothetical bed 0 exit), mol/s

T_{SHE} = temperature of the preheated feed gases after passing through the external and internal preheating sections, K

Subscript 0 and 1 designate inlet and exit of the bed, respectively

Coefficient α_j is proportional to stoichiometric coefficient for component j and have values $\alpha_1 = -1/3$, $\alpha_2 = -1$, $\alpha_3 = 2/3$ and $\alpha_4 = \alpha_5 = 0$

Here again equations (3.1.5), (3.1.6), and (3.1.7) are applicable to each bed by putting proper values of i as 1, 2 and 3.

External heat exchanger balances.

In the external heat exchanger (subscript H) no chemical reaction occurs and it is simply a countercurrent heat exchanger to preheat only F_{DH} fraction of the total cold feed gases flowing through the external heat exchanger by all the product gases leaving the last reactor bed.

The energy balance for the feed gas gives, on shell side of heat exchanger

$$F_{DH}\left(\sum_{j=1}^{5} F_j C_{pj}\right)dT_{SH} = -(UA)_H(T_{SH}-T_H)dv_H$$

Where,

T_{SH} = feed gas temperature on shell side of external heat exchanger, K

$(UA)_H$ = heat exchange capacity of external heat exchanger per unit tube side volume, W/K/cm^3

T_H = gas temperature on tube side, K

V_H = tube side volume of external heat exchanger, cm^3.

The negative sign on right hand side again accounts for the fact that the direction of flow of feed gases is opposite to the direction of increase of external heat exchanger volume. Similarly for product gases, on tube side of heat exchanger:

$$\left(\sum_{j=1}^{5} N_{3jl} C_{pj}\right)dT_H = -(UA)_H(T_H-T_{SH})dV_H \qquad (3.1.9)$$

For $(UA)_H$, the same argument also holds as in the case of the heat exchange capacity in catalyst bed side. N_{3jl} is the flow rate, moles of component j leaving third catalyst bed and entering the external heat exchanger on tube side.

The flow rate of moles of component j at any point in bed i, N_{ij} is obtained from the following equation,

$$N_{ij} = F_j \left(F_{DH} + \sum_{i=1}^{i} F_{Di}\right) + \alpha_j F_2 X_{2i} \qquad (3.1.10)$$

The above equation is valid for any of the three catalyst beds, only bed number 1, 2 or 3 will be written in place of subscript i.

The total molal flow rate in a bed, N_{iT} is given by,

$$N_{iT} = \sum_{j=1}^{5} N_{ij} \qquad (3.1.11)$$

which is valid for any of the three beds, only i needs to be replaced by appropriate bed number 1, 2 or 3.

Due to the pressure drop inside the heat exchanger and in the catalyst beds, the pressure of synthesis gas decreases from point to point in the direction of its flow. A suitable expression to estimate the pressure drop and, therefore, the pressure within the reactor is essential. Correlations are available in literature to find the pressure drop of flow of gases through the heat exchanger and the packed beds. For precise calculations these may be used. However, since the pressure drop through the convertor rarely exceeds 3 percent of the convertor pressure and also because changes in molal flow rates due to conversion in any bed is also small, no purpose will be served by using more complicated pressure drop correlations as the accuracy so achieved may be insignificant as compared to the extra complexity added in the simulation model and resultant increase in computer time. In view of this fact, the simulation model assumes that pressure, p, in atm varies linearly along the flow path in any bed i. To account for the changes in the flow rate at any bed inlet due to cold shot addition, the pressure drop, dP_i is corrected for increase in flow of gases at the inlet of bed i, using 1.8 power of molal flow rates.

$$-dP_i = \omega_N \left\{ \sum_{j=1}^{5} N_{ij0} \Big/ \sum_{j=1}^{5} F_{jN} \right\}^{1.8} dv_i \qquad (3.1.12)$$

Where is a coefficient, that is, pressure drop based on unit bed volume, atm/cm^3 ; and subscript N corresponds to a reference or normal value of feed gas flow rate for which ω_N is preassigned, an estimated value obtained from the normally observed pressure drops in the reactor. The above equation can be applied to any bed by assigning i = 1, 2 or 3.

Similarily, pressure drop expression is written for tube side, that is, product gases side of external heat exchanger as below

$$-dp_H = \omega_{HN} \left\{ \sum_{j=1}^{5} N_{3j1} \Big/ \sum_{j=1}^{5} F_{jN} \right\}^{1.8} dv_H \qquad (3.1.13)$$

ω_{HN} is coefficient for pressure drop based on unit tube side volume of external heat exchanger, atm/cm^3 .

A reasonable value for the total pressure drop based on commercial plant data is assumed and the total pressure drop is distributed in a realistic manner for external and internal preheating sections, catalyst beds and product gas side in heat exchanger. For catalyst beds linear pressure drop is assumed in each bed to account for the effect of pressure change on reaction rate, heat of reaction and activity coefficient as indicated earlier in equation 3.1.12. A linear pressure variation is assumed for product gases on tube side of heat exchanger also. However, for preheating sections, an average pressure value, average of inlet and outlet pressures is used because the pressure drop in this section is generally quite small. The foregoing equations require the relationships for reaction rate, heat of reaction and heat capacities as a function of temperature, pressure and composition of gas.

Reaction rate.

The modified Temkin and Pyzhev rate expression as given by Shah (1967) is used in the simulation model. The rate equation used is as follows :

$$-r_2 = 29.4204\, f\, k_r \{(K/K_\gamma)^2 [P^{1.5} N_1 N_2^{1.5} / (N_3 N_T^{1.5})] - (N_3 N_T^{0.5} / (p^{0.5} N_2^{1.5}))\} \quad (3.1.14)$$

Where,

$(-r_2)$ = reaction rate, mol of H_2 reacted/s/m^3 of catalyst

f = catalyst activity factor, dimensionless

Catalyst activity factor, f, may depend on many factors: For a given catalyst, the values of f may change with catalyst life. The fresh catalyst may be assumed to have a limiting value of f as unity and the same may decrease with catalyst age slowly. The catalyst is normally discarded after few years when the f value decreases to about 0.6 to 0.8 depending on the plant practice. In the simulation model f value is given a preassigned value as input data and the same can be made to vary if considered necessary.

k_r = reverse reaction velocity constant, mol/s/m^3 of catalyst

K = equilibrium constant of the reaction 3/2 H_2 +1/2N_2 = NH_3

K_γ = fugacity coefficient term

N = gaseous constituent flow rate at any point in the reactor bed, mol/s

Subscripts indicate the gas component (1, 2, 3 and T refers to N2, H2, NH3 and total components, respectively).

The correlation used for reverse reaction velocity constant is similar to that given by Shah (1967). The parameters specific to the catalyst used are frequency factor or preexponential factor and the activation energy. Adjustment was made in their values given in Shah's correlation through the use of multiplying factors Para1 and Para2 for the modification to the values used by Shah. The best values of Para1 and Para2 and, therefore, the frequency factor and activation energy suited for the catalyst used in the plant were found by validation of the simulation model using plant data as discussed subsequently in chapter-VI. The modified form of the equation used for k_r is as follows.

$$k_r = (300/p)^{0.63} \exp[(33.5566)\,(Para1) - (24092.2)\,(Para2)/T] \qquad (3.1.15)$$

The correlation used for equilibrium constant, K, is that reported by Hay and Honti (1976) that gives an average deviation of 0.00055 in logK and a maximum deviation of 0.0016 in logK over the temperature range of interest.

The equation is as follows:

$$\log_{10} K = (2250.322/T) - 0.8534 - 0.656 * \ln T - 2.58987 * 10^{-4} * T + 1.48961 * 10^{-7} * T^2 \qquad (3.1.16)$$

The fugacity coefficient term , K_γ, is also similar to Shah (1967). However, it was found necessary to adjust the value of K_γ

through the use of another multiplying factor, Para3, to the values given by Shah correlation. Values of K_γ calculated from the correlation used by Shah were found to be lower than the values computed from correlations reported by many other workers. Further, only through this adjustment the model validation using plant data could be achieved more satisfactorily. This aspect is discussed in greater details in chapter VII. The equation used for K_γ is as follows :

$$K_\gamma = (\text{Para3}) * (1.7343 - 8.143 * 10^{-4} * P + 5.714 * 10^{-7} * P * T - 2.6714 * 10^{-3} * T + 2 * 10^{-6} * T^2) \quad (3.1.17)$$

The correlation used for heat of reaction is that given by Gillespie and Beattie as cited by Hay and Honti (1976).

Since the correlation reported by Shah (1967) for heat of reaction was found to be unsatisfactory. The equation used in simulation model is as follows :

$$-\Delta H_{R2} = (2/3) * (0.54526 * P + (840.609 * P/T) + (459.734 * 10^6 * P/T^3) + 5.34685 * T + 0.2525 * 10^{-3} * T^2 - 1.69167 * 10^{-6} * T^3 + 9157.09) * 4.1868 \quad (3.1.18)$$

The correlations used for heat capacities, kJ/kmol/K, of N_2, H_2 and NH_3 are those reported by Perry (1950) and the heat capacity correlation for CH_4 is that given in International Critical Tables (1928). Heat capacity of argon is taken at 20.798 as reported by Shah (1967). The equations used in the model are as follows :

$$C_{p1} = (6.822 + 1.631 * 10^{-3} * t - 0.345 * 10^{-6} * t^2) * 4.1868 \quad (3.1.19)$$

$$C_{p2} = (6.919 + 0.218 * 10^{-3} * t + 0.279 * 10^{-6} * t^{2}) * 4.1868 \quad (3.1.20)$$

$$C_{p3} = (8.497 + 8.001 * 10^{-3} * t - 1.764 * 10^{-6} * t^{2}) * 4.1868 \quad (3.1.21)$$

$$C_{p4} = (3.00 + 0.0228 * T - 4.8 * 10^{-6} * T^{2}) * 4.1868 \quad (3.1.22)$$

$$C_{p5} = 20.798 \quad (3.1.23)$$

where,

$t = T - 273$

T = absolute temperature, K

Subscripts 1, 2, 3, 4 and 5 designate nitrogen, hydrogen, ammonia, methane and argon, respectively, as indicated earlier.

3.2. Effectiveness factor relation.

The effectiveness factor, ξ, correlation as a function of temperature, pressure and gas composition given by Dyson and Simon (1968) is used in the simulation model to account for the mass transfer limitations in rate equation for ammonia synthesis heterogeneous catalytic reaction. The equation used is given below :

$$\xi = b_0 + b_1 * T + b_2 * \eta + b_3 * T^2 + b_4 * \eta^2 + b_5 * T^3 + b_6 * \eta^3 \quad (3.2.1)$$

Where,

η = dimensionless conversion of nitrogen and given by,

$\eta = y_3/(y_3 + 2 * y_1)$

or $\eta = [(1 + ((2 * y_{2F})/(3 * y_{3F})) * x_2)/(1 + 2 * (y_{1F}/y_{3F}))]$

(3.2.2)

Where y_1, y_2, y_3 are mole fractions of nitrogen, hydrogen and ammonia, respectively, at any point in the bed and subscript F indicates mole fractions in the inlet feed. Therefore at a point in the reactor η is known for a known feed gas composition and actual hydrogen fractional conversion, X_2.

In equation (3.2.1) b_0, b_1, b_2, b_3, b_4, b_5 and b_6 are constants with pressure as parameter as given in Table 3.2.1

Table 3.2.1

Constants for equation (3.2.1)

	Pressure, atm		
	150	225	300
b_0	-17.539096	-8.2125534	-4.6757259
b_1	0.07697849	0.03774149	0.02354872
b_2	6.900548	6.190112	4.687353
b_3	$-1.082790 * 10^{-4}$	$-5.354571 * 10^{-5}$	$-3.463308 * 10^{-5}$
b_4	-26.42469	-20.86963	-11.28031
b_5	$4.927648 * 10^{-8}$	$2.379142 * 10^{-8}$	$1.540881 * 10^{-8}$
b_6	38.93727	27.88403	10.46627

The correlation was developed for the case of H_2/N_2 ratio of 3 and inerts concentration of 12.7 mol percent. However, in the present study the same correlation as given above is also used in view of only slight variations in the conditions used for simulation study. Dyson and Simon (1968) observed that the calculated values of effectiveness factors for the conditions other than those specified above had shown variations from those computed by using equation (3.2.1), but the overall effect on the design and performance of industrial ammonia synthesis reactors was negligible. Furthermore, if transport equations

(Dyson and Simon, 1968; Singh and Saraf, 1979) inside the catalyst are used for finding effectiveness factor additional complexities will be added without increasing accuracy significantly.

3.3. Equilibrium conversion relation.

The details of equilibrium conversion relation are given by Ramkumar (1978) for H_2/N_2 ratio of 3 and summarised below along with relation for H_2/N_2 ratio other than 3.

Equilibrium constant for reaction (3.1.1) is given by ,

$$K = \phi_3/(\phi_1^{1/2} * \phi_2^{3/2}) = p_3 * \nu_3/(p_1^{1/2} * p_2^{3/2} * \nu_1^{1/2} * \nu_2^{3/2})$$

$$\text{or } K = K_p * K_\gamma \qquad (3.3.1)$$

where ϕ, p and ν represent fugacity, partial pressure and fugacity coefficient, respectively.

K_p is given as,

$$K_p = P * y_{3eq}/((P * y_{1eq})^{1/2} (P * y_{2eq})^{3/2})$$

$$\text{or } K_p = (1/p) * (y_{3eq}/(y_{1eq}^{1/2} * y_{2eq}^{3/2})) \qquad (3.3.2)$$

Where P is the total gas pressure, and subscript eq refers to mole fractions at equilibrium.

The equilibrium mole fraction of H_2, N_2 and NH_3 may be represented as,

$$y_{1eq} = (y_{1F} - y_{2F} * x_{2eq}/3)/(1-2 * y_{2F} * x_{2eq}/3) \qquad (3.3.3)$$

$$y_{2eq} = (y_{2F} - y_{2F}\ x_{2eq})/(1-2y_{2F}\ x_{2eq}/3) \qquad (3.3.4)$$

$$y_{3eq} = (y_{3F} + 2\ y_{2F}\ x_{2eq}/3)/(1-2\ y_{2F}\ x_{2eq}/3) \qquad (3.3.5)$$

After substituting values of K_p and y_{1eq}, y_{2eq}, y_{3eq} from equations (3.3.2) to (3.3.5) in equation (3.3.1), we get after manipulation

$$K * P/K_\gamma = \{(y_{3F} + 2 * y_{2F} * x_{2eq}/3) * (1-(2/3) * y_{2F} * x_{2eq})\}/\{(y_{1F} - y_{2F} * x_{2eq}/3)^{1/2} * (y_{2F} - y_{2F} * x_{2eq})^{3/2}\} \quad (3.3.6)$$

Where K and K_γ are given by equations (3.1.16) and (3.1.17), respectively, and are functions of pressure and temperature of gas at any position in reactor bed. So for known temperature and pressure at any point and known feed composition, the equilibrium conversion in terms of fraction of hydrogen in feed, x_{2eq}, can be calculated using equation (3.3.6). This requires trial and error procedure or a single variable search method can be used for achieving quick solution within a desired tolerance. Generally, the H_2/N_2 ratio is kept at 3. So for this case equation (3.3.6) can be simplified further to result in a quadratic equation as given below :

$$(1+K_{c1}) * x_{2eq}^2 - [2 * K_{c1} + 3 * (1-y_{3F})/2 * y_{2F}] * x_{2eq} + [K_{c1} - 9 * y_{3F}/4 * y_{2F}^2] = 0 \quad (3.3.7)$$

where $K_{C1} = 3 \quad * K * P/(4 * K_\gamma)$

$= 1.29904 * K * P/K_\gamma$

Therefore, with values of K, K_γ found at any axial position in the bed and with feed gas composition known, the above quadratic equation can be solved without any trial and error to determine the x_{2eq} values, which lies between 0 and 1.

3.4. Conversion corresponding to maximum rate.

From equation (3.1.14) the reaction rate equation can be written as

$$-r_2 = C_1 * k_r * [(K/K_\gamma)^2 * C_2 - C_3] \quad (3.4.1)$$

where $C_1 = 29.4204 * f$ (3.4.2)

$$C_2 = P^{1.5} * y_1 * y_2^{1.5} / y_3 \quad (3.4.3)$$

and $C_3 = y_3 / (P^{0.5} * y_2^{1.5})$ (3.4.4)

C_1, C_2 and C_3 are independent of gas temperature, dimensional.

The maximum of reaction rate as a function of temperature at otherwise constant conditions can be obtained by:

$$[\partial(-r_2)/ \partial T] = 0$$

It may be noted that the reaction rate shows a maxima with respect to temperature of gas in the bed only for an exothermic reversible reaction corresponding to any gas composition, that is, for any specified value of x_2. For a known value of catalyst activity factor, f all C_1, C_2 and C_3 are independent of temperature, and only k_r, K and K_γ depend on temperature. Since k_r, K and K_γ have complex temperature dependence, the normal procedure is to choose a temperature and find the value of x_2 at which the above equation is satisfied. The value of x_2 so obtained is designated as x_{2m}, where subscript m refers to maximum rate conditions.

It is important to note that at any specified temperature, pressure and composition in the bed, the effectiveness factor is uniquely determined and actual reaction rate is reduced by that factor. Thus, for conditions corresponding to maximum reaction rate, the effectiveness factor can again be uniquely determined and the actual rate will again be reduced by that factor and the same will still remain the maximum possible rate for those conditions. Therefore, on differentiating equation (3.4.1) at constant C_1, C_2 and C_3 and equating it to zero, we get after simplification:

$$C_3/C_2 = (K/K_\gamma)^2 + 2 * k_r * K * [(\partial K/\partial T) - (K/K_\gamma)(\partial K_\gamma/\partial T)]/(K_\gamma(\partial k_r/\partial T)) \quad (3.4.5)$$

$$\text{or } C_3/C_2 = K_{c2} \quad (3.4.6)$$

where K_{c2} is equal to right hand side of equation (3.4.5) and is only a function of temperature at a given pressure and can be calculated for known temperature and pressure at any position in the reactor bed. $(\partial K/\partial T)$, $(\partial K_\gamma/\partial T)$ and $(\partial k_r/\partial T)$ are all known from equations (3.1.15) to (3.1.17) by partially differentiating with respect to temperature and substituting the values of temperature and pressure. But the defining equations (3.4.3) and (3.4.4) show that,

$$C_3/C_2 \equiv y_{3m}^2/(P^2 * y_{1m} * y_{2m}^3) = K_{C2} \quad (3.4.7)$$

where subscript m refers to mole fractions at maximum rate condition. Using the procedure as presented in section 3.3, we get

$$K_{C2} = (y_{3F} + 2 * y_{2F} * x_{2m}/3)^2 * (1 - 2 * y_{2F} * x_{2m}/3)^2/\{(P^2 * (y_{1F} - y_{2F} * x_{2m}/3)) * (y_{2F} - y_{2F} * x_{2m})^3\} \quad (3.4.8)$$

Therefore, x_{2m} can be uniquely determined at any position of reactor bed from the above equation for the known temperature, pressure and feed gas compositipon. Equation (3.4.8) can also be solved either by trial and error technique or univariate search technique for finding the value of x_{2m}. For the case when H_2/N_2 ratio is 3 equation (3.4.8) can be further simplified to result in a quadratic equation in x_{2m} as given below,

CHAPTER IV

TECHNIQUE FOR OPTIMIZATION OF AMMONIA SYNTHESIS REACTOR

In the design and operation of ammonia synthesis reactor a number of decision variables exist that are free to be adjusted for achieving optimization. In an existing plant with fixed design parameters and for a given feed flow rate, composition, temperature and pressure, cold shots to various beds can be allocated in such a manner as to give maximum ammonia production rates. At the design stage, catalyst distibution in different beds can also be adjusted in addition to the cold shot distribution to maximize ammonia production rates.

In this study the production rate of ammonia is taken as the objective function to be optimized subject to the implicit constraints given by design relations presented earlier and several explicit constraints for example, sum of cold shot fraction should be between 0 and 1, conversion should be lower than its equilibrium value, etc. In an existing reactor, the objective function, that is, ammonia production rate, is a function of many independent operating variables; for example, feed gas flow rate, feed pressure, bed inlet temperatures, H_2/N_2 mole ratio in feed, ammonia and inerts mole fractions in feed, and cold shot distributions to various catalyst bed inlets. The objective function is also a function of many design parameters; for example, total volume of catalyst, catalyst distribution in different beds, heat exchange capacity in the catalyst bed and external heat exchanger.

The objective function for this study is highly nonlinear and coupled, implicit, constrained, multivariable and discontinuous in nature. It also involves internal loop optimization with severe convergence problem of a multimodal function that is also highly nonlinear, constrained, implicit and coupled in nature.

With the help of high speed digital computers with large memory, sophisticated optimization techniques could be used to solve such problems. Therefore, now it is realistic to attempt to establish an optimization procedure for obtaining the optimum results.

In general the gradient or indirect search methods (Beveridge and Schechter, 1970; Gangiah, 1980) have faster convergence in comparison to direct search methods. The gradient methods are based on evaluation of derivatives whereas the direct search methods are based on evaluation of objective functions without calculating the derivatives. However in practice, as in the present study, it is either extremely difficult or impossible to provide analytical functions for calculating derivatives needed in gradient methods. The function may not be differentiable or the derivatives may be difficult to compute numerically, as in this case where it may lead to magnification of errors and large computation time.

Among direct search methods the complex search method as given by Adelman and stevens (1972), based on the method of Box (1965), Nelder and Mead (1965) and a similar constrained polyhedron search method presented by Gangiah (1980) is selected for use as an optimization technique.

Other methods of direct search are also available based on "evolutionary operation" and "Monte Carlo techniques" (Luus and Jaakola, 1973; Campbell and Gaddy, 1976; Heuckroth et al., 1976). However, as observed by Gangiah (1978, 1980), they are found less efficient in several cases.

4.1. Description of the complex search method (Adelman and Stevens, 1972; Gangiah, 1980; Nelder and Mead, 1965).

This method consists of finding an original feasible "Complex (constrained simplex)" of solutions, eliminating the "worst" of these by reflection through the centroid of the remaining points, and repeating until an optimum has been reached. Worst point is defined as the point at which the objective function is found to have a minimum value. So the direction of search is from the worst through the centroid and step length is obtained by reflection through the centroid on the opposite of worst point. The acceleration in step size is provided by reflection coefficient, α_r, say 1.3 (Adelman and Stevens, 1972; Box, 1965), for mapping the entire feasible region by enlargement of complex so that the convergence at global optima in the constrained feasible region is obtained.

The problem statement in general, can be written as

maximize $Y(X) = f(x_1, x_2, ----, x_n)$

Subject to the implicit constraints

$g_i(x) < 0,\ i = 1, 2, -------, r$

$h_j(x) > 0,\ j = 1, 2, -------, s$

$e_k(x) = 0,\ k = 1, 2, -------, m$

here $m < n$

and the bounds or explicit constraints

$x_{min} < x_i < x_{max}$

$i = 1, 2, --------, (n-m)$

Let x_{ij}, $j = 1, 2, --------, (n-m+1)$ is the jth vertex point and i is the coordinate or number of decision variable.

The centroid of all x_{ij} excluding the worst point x_{ij} (worst),

$$\bar{x}_i = \{1/(2(n - m))\} \sum_{\substack{j = 1 \\ j \neq w}}^{(2(n - m)+1)} x_{ij} \qquad (4.1)$$

here $i = 1, 2, -------, (n-m)$

Algorithm

1. Select the {2 (n-m) + 1} vertices.

2. Test for explicit constraints at a vertex, if constraints are violated the decision variables are set to the bounds.

3. Solve implicit equality constraints numerically. Test for implicit inequality constraints. If any inequality constraint is violated, the corresponding variable is set to the constraint value. If all implicit inequalities are satisfied go to next step

or else proceed to step 5 by assigning the vertex as worst-valued.

4. Evaluate the objective function. If only the worst vertex has been replaced, go to step 8 or else proceed to next step.

5. Repeat steps 2 to 4 for all vertices if it is a newly formed complex or else go to step 6.

6. Compute the centroid of the complex as given in equation (4.1) by finding the worst valued vertex.

7. Find the new vertex to replace the worst valued vertex. This is done by formula

$$x_{ij}(\text{new}) = \bar{x}_i + \alpha_r [\bar{x}_i - x_{ij}(\text{worst})] \quad (4.2)$$

where $\bar{x}_i$ is the ith coordinate of centroid, x_{ij} (new) is the ith coordinate of the new jth point to form a new complex and x_{ij} (worst) is the ith coordinate of the worst jth point in the complex.

8. Repeat steps 2 to 4. If this new trial point replacing the worst is again worst, the point is moved half-way towards the centroid of the remaining points. If this trial also results in the worst valued point, the point is further moved half-way towards the remaining distance from centroid. If this also fails to improve due to special nature of an objective function, the reflection is seen to get new trial vertex.

The procedure terminates when the complex collapses within a certain preassigned tolerance of objective function values or up to a certain number of iterations, whichever is reached first. Otherwise, go to step 6.

In the present case, it is observed that for certain cold shot distributions (several vertices) that are not true optima, the ammonia production rates are nearly the same, and therefore, it is impractical to assign any tolerance other than zero. The search was then terminated by preassigning the number of iterations so that the true constrained optima could be obtained.

The Box complex search has the following advantages over the other optimization techniques (Adelman and Stevens, 1972; Gangiah, 1980).

1. The method is stable, versatile, and the solution is very fast due to fast convergence.

2. Programming is easy.

3. It yields other valuable information about the system apart from the optimum solution. The response of the system is well mapped over a wide range of values of the independent variables. The sensitivity of the optimum, that is response to small changes in independent variables is obtained as the method converges to the optimum and evaluates the response to small perturbations in the variables. This additional information is of great value in both design, operation and optimum control of chemical plants.

4. It is superior to other sequential direct search methods (pattern search, parallel tangents, etc.) and can find the true optimum rather than local optima nearest to the starting point because of the fact that the points in the initial complex are scattered throughout the feasible region, with a good chance that at least one will lie in the vicinity of the true constrained optima.

5. The use of reflection factor greater than 1.0 causes an initial enlargement of the complex due to acceleration in step length, thus assuring a good initial scan of the entire feasible region.

CHAPTER V

5. COMPUTATION TECHNIQUE

5.1 Computation technique for optimization.

The material and energy balance equations written for a differential section of a bed of ammonia synthesis reactor are presented in chapter -III. For such a system of highly non-linear and coupled equations, numerical integration is essential because analytical integration is not possible. A suitable numerical integration technique based on modified Milne-Predictor-Corrector method is used by choosing small step size. Computation accuracy will depend upon the magnitude of step size chosen. Tolerance limits at each step for conversion and temperature are checked against the preassigned limits, chosen in this study as $5x10^{-5}$ for fractional conversion of hydrogen and $5x10^{-3}$ K for temperature. The tolerance limits can be externally changed, if required, as input data. The stepwise procedure is given below:

Step 1. Read data set for reactor conditions and parameters

Step 2. Test the range of search based on the lower and upper limits on T_{SHE}, the temperature of the feed gas at the exit of the internal preheating section. If the program works, go to the next step or alter the bounds until the program works and set the region of search for T_{SHE}.

Step 3. In the region of search assume T_{SHE} with an interval, say 20 K, in T_{SHE} values. The computation starts from the lower limit of the search region and proceeds with 20 K (say) increments until the upper limit of T_{SHE} is reached. Go to the next step if cold shot is added; otherwise, go to step 5.

Step 4. Determine the temperature of resultant stream by the regula falsi interpolation technique since the heat capacity of the mixture is not known. Molal flow rate is calculated by material balance.

Step 5. Carry out the numerical integration, step by step in the forward direction, up to the end of the first bed to establish the exit conditions.

If a cold shot is added to second bed, go to next step or else go to step 7.

Step 6. Determine the temperature and molal flow rate of resultant stream as given in step 4.

Step 7. Carry out the numerical integration, step by step in forward direction, up to the end of the second bed to establish the exit conditions.

If a cold shot is added, go to next step; otherwise, go to step 9.

Step 8. Determine the molar flow rate and temperature of the resultant stream.

Step 9. Carry out numerical integration, step by step in forward direction, up to the end of the third bed to establish exit conditions.

Step 10. Carry out numerical integration for external heat exchanger up to its exit.

Step 11. At the end of last step 10, value of T_{SHI}, the computed temperature of feed entering the external heat exchanger on shell side, is obtaned. T_{SHI} is compared with T_F, the actual feed temperature and if difference, DELT = $[(T_{SHI} - T_F)]$ lies outside the tolerance limit of $\pm 2K$ (fed externally as an input data and may be varied, if desired) then convergence is not achieved. The next T_{SHE} is chosen for carrying out a pattern search. If DELT value for the next T_{SHE} value is of the same sign as that for the preceding T_{SHE} value, repeat step 4 onward for the case of cold shot addition at the first bed inlet or steps 5 onward without cold shot addition.

Step 12. In case convergence is not achieved but the DELT calculated is of the opposite sign to that of the DELT obtained for the preceding T_{SHE} value, then the value of T_{SHE} that results in converged DELT is searched in the interval of the present T_{SHE} and preceding T_{SHE} values according to the convergence criteria of the regula falsi interpolation technique.

Step 13. In case convergence is achieved and T_{SHE} is less than the upper bound of the region of search for T_{SHE}, then steps 3 onwards are repeated with an increment of 20 K (say) in T_{SHE}.

Step 14. The highest converged value of T_{SHE} is taken as the stable and desirable operating point and corresponding ammonia conversion and production rate are taken as the value of objective function for the given data set and the chosen values of decision variables (cold shot and/or catalyst distribution) for which the calculations were carried out.

Step 15. Steps 2 onwards are repeated for optimization over the decision variables (cold shot and/or catalyst distribution) using the Box complex optimization technique discussed earlier in chapter IV.

Step 16. Repeat steps 1 to 15 for the new input data set until the computations for all the input data sets are completed.

5.2. Convergence policy.

During the course of computation as given in section 5.1 convergence is desired in the value of DELT within a prespecified tolerance for getting the value of T_{SHE} that is a solution to the system of equation of ammonia synthesis reactor. In majority of cases it is found that some where in the region of search for T_{SHE} the DELT value will change sign, if any solution, other than trivial solution corresponding to negligible conversion and T_{SHE} value close to T_F value, exists at all. When such a region is isolated or detected then the convergence in DELT is achieved by applying regula falsi technique in the selected region. Another approach is to use golden section search or fibonacci search by taking absolute value of DELT i.e. **I DELT I** as an objective function. However, in this study the Regula falsi technique has been applied with great success to achieve very fast convergence in almost all cases. In the Regula falsi technique the next trial for T_{SHE} is made in the interval of sign changes of DELT by using the following relationship:

For (n + 2)th iteration,

$$T_{SHE,(n+2)} = T_{SHE,(n+1)} + \frac{(T_{SHE,n} - T_{SHE,(n+1)}) * ABS(DELT(N+1))}{ABS(DELT(n+1)) + ABS(DELT(n))} \qquad (5.1)$$

Where n can take any integer value 1, 2, 3 -------------.

For this new point $T_{SHE,(n+2)}$ DELT is calculeted based on the steps discussed in section 5.1 and if convergence is not achieved, for further search the point that has the same sign as DELT among $T_{SHE,n}$ and $T_{SHE,(n+1)}$ is discarded and the next interpolation is made according to equation 5.1.

5.3. Numerical integration procedure.

Modified Milne-Predictor-Corrector method (Milne, 1953; Shah, 1967) is used for numerical integration of nonlinear and coupled differential equations. This method is found to be stable with a fast speed of convergence at each step of numerical integration. The error in computation is less as compared to fourth- order Runge-Kutta method (Lambert, 1974).

This method requires generating first four points by following predictor and corrector steps (Ivo Babuska, 1966):

First point:

This point is the inlet to first bed where on the assumption of temperature T_{SHE}, all the information becomes available. Using relations presented in chapter-III the differential equations in the design relations take the following functional form:

$$\frac{dx}{dv} = f_1 (X, T, P)$$

$$\frac{dT}{dV} = f_2 (X, T, P)$$

$$\frac{dTs}{dv} = f_3 (T, Ts)$$

Second point:

With the first point known, the derivatives at the first point are calculated. The derivatives are used to predict the first guess of the second point, the predictor step. The derivatives are then calculated at this first guess of the second point and using the corrector step the second point estimate is refined till the last guess and its preceding guess value match within a preassigned tolerance limit. This method is stable and in a few iterations convergence is achieved. In symbolic form:

Predictor step.

$$y_2 = y_1 + y_1' \ \Delta h, \quad y_1' = \frac{dy_1}{dh}$$

Corrector step.

$$y_2 = y_1 + (y_2' + y_1') \frac{\Delta h}{2}, \quad y_2' = \frac{dy_2}{dh}$$

where y is a dependent variable such as x, T and T_s; h is an independent variable such as v; Δh is small but finite increment in h; superscript prime refers to first derivative and subscript 1, 2, 3 etc. refer to variable values at first point, second point, third point etc.

Third Point:

Predictor and Corrector steps for the third point are given below. The third point estimates are refined using the corrector step till convergence is achieved.

Predictor step.

$$y_3 = y_2 + (3y_2' - y_1') \frac{\Delta h}{2}$$

Corrector step.

$$y_3 = y_2 + (5y'_3 + 8y'_2 - y'_1)\frac{\Delta h}{12}, \quad y'_3 = \frac{dy_3}{dh}$$

Fourth point:

The fourth-point predictor and corrector steps are given below. The fourth-point estimates are refined till convergence is obtained.

Predictor step.

$$y_4 = y_3 + \frac{\Delta h}{12}(23\, y'_3 - 16y'_2 + 5y'_1)$$

Corrector step.

$$y_4 = y_3 + \frac{\Delta h}{24}(9y'_4 + 19\, y'_3 - 5y'_2 + y'_1),$$

After the first four points have been generated, the Milne-Predictor- Corrector step is applied to generate remaining points. As Milne-Predictor-Corrector technique is more stable and very fast in convergence, only single application of corrector step may, in general, give accurate values for the new point within the tolerance limit.

Fifth point:

Predictor step.

$$y_5 = y_1 + \frac{4\Delta h}{3}(2y'_2 - y'_3 + 2y'_4)$$

Corrector step.

$$y_5 = y_3 + \frac{\Delta h}{3}(y'_3 + 4y'_4 + y'_5)$$

For the sixth point onwards a modifier step in between predictor and corrector steps is also used that further accelerates convergence by making use of the magnitude of error at previous point between values from predictor and corrector. This error is added in the value obtained from predictor step to guess in advance values that are used for finding the derivative in the corrector step.

Modifier step at ith point:

$$\Delta_{(i-1)} = y_{(i-1)} - y_{(i-1)}$$

(converged corrector step value) (predictor step value)

Sixth point onward for ith point:

Predictor step.

$$y_i = y_{i-4} + \frac{4\Delta h}{3}\left(2y'_{(i-3)} - y'_{(i-2)} + 2y'_{(i-1)}\right)$$

Corrector step.

Using a y_i (modified), that is, $y_i + \Delta_{(i-1)}$, the y'_i for corrector step is found.

$$y_i = y_{(i-2)} + \frac{\Delta h}{3}\left(y'_{(i-2)} + 4y'_{(i-1)} + y'_i\right)$$

(corrector step)

where i = 6, 7, ------.

5.4. Computer program features.

A computer program to simulate and optimize ammmonia synthesis reactor performance has been written in FORTRAN - 77 and executed on DEC 2025 system of Roorkee University Regional Computer Centre. It consists of a main program and 24 subroutines having over 2500 statements. The program is efficient and requires minimum possible computation time and memory requirements. It takes about 25 seconds CPU time to compile, about 4 seconds of CPU time for loading and linking the program, and about 6 to 8 seconds of CPU time to run a single data set of operating and design conditions after carrying out the search over the entire feasible operating region of T_{SHE}. Complete solution of the system of equations is obtained for both high conversion and thermally unstable and stable operating points, if such points exist, while ignoring the trivial low conversion and low temperature point. It could be located in 10 to 15 iterations. Further, it took about 5 to 8 minutes of CPU time for optimization of cold shot distribution to maximize ammonia production depending on the initial points of complex search (fed as a part of the input data), the degree of difficulty experienced by the system equations in arriving at the optimum and the precision to which the maximization of objective function (ammonia production rate) is desired.

The main program is arranged in three sections, namely, **READ DATA**, policy of convergence and optimization section, and **PRINT RESULTS**. Numerous comment statements have been used in the main program and the subroutines to make them more understandable. The computer program listing is given in Appendix-B. The program has following additional features:

1. The optimization could be done with an option of feeding a single data set and the self-generation of the remaining vertices of complex or feeding all the data sets of the vertices. It can further start the optimization search with known values of data sets and their corresponding objective function values without recalculating the objective function again. This would be advantageous when one wants to further test an optimum result based on the earlier searches by using the best possible Box complex for which objective function values are already available. This can help in establishing the optimum beyond any shadow of doubt.

2. The program has an option to carry out optimization or just to carry out a single search for a single data set or multiple data sets.

3. The program has an option to consider the particle effectiveness factor either as unity corresponding to the absence of mass transfer limitation or to compute the effectiveness factor at each point using the Dyson and Simon (1968) relationship.

4. The program has an option to print detailed results at each point in the bed or at some interval or to print only the summary of results at the inlet and outlet of each bed.

5. The program has an option to make searches at new vertices either by taking the actual values generated or at values rounded to a certain preassigned decimal point or only to search at

certain preassigned levels of the variables by shifting the actual value of the variable to its nearest preassigned level. This feature is important in order to search the cold shot distributions only at values that can be readily adjusted in plant.

CHAPTER-VI

6. ESTIMATION OF SIMULATION MODEL PARAMETERS FROM PLANT DATA

6.1 Purpose of estimation of Parameters and parameters description.

For any mathematical model that is developed on theoretical consideration of mass and energy balances it is always necessary to adjust and tune certain parameters that are dependent on the specific process conditions so as to make the simulation model predictions closer to plant performance. In the case of ammonia synthesis reactor simulation, the parameters that are specific to the catalyst used are the preexponential or frequency factor and the activation energy in the reverse reaction rate constant. Adjustment was made through the use of Para1 and Para2, respectively, as the multiplying factors to the base values for the frequency factor and activation energy values reported by Shah (1967), see equation 3.1.15. It was also found necessary to adjust the value of the fugacity coefficient, K_γ, through the use of Para3, multiplying factor to the correlation for K_γ reported by Shah (1967), see equation 3.1.17.

The heat exchange capacity of the external heat exchanger, which depends on the heat exchanger design, was also estimated after making corrections for changes in the flow rates by the parameter estimation technique.

6.2. Parameter estimation technique.

The objective function for estimation of optimal value of the parameter is taken as the minimization of the sum of squares, that is found to be multimodal, constrained, multivariable and nonlinear in nature. Therefore the complex search technique (discussed in chapter-V) is used along with external adjustment of the direction and step size in between searches to reach the minimum of sum of squares. Actual plant data for an axial flow multibed quench type ammonia synthesis reactor of a modern Indian plant has been chosen to simulate its performance using the simulation package developed during this investigation. In the plant only temperatures at the end of each bed, ammonia concentration at the end of last bed, first bed inlet temperature and the tube side external heat exchanger exit temperature are monitored. Inlet feed composition, temperature, pressure and pressure drop across the reactor are also measured. Table 6.2.1 gives selected data for different conditions as obtained from the plant log sheets for several months. The data was selected for a period during which plant operation was found to be steady.

It was found that the cold shot distribution, the most important variable for reactor operation, is not measured at the plant. It was necessary to consider cold shot distribution also as a variable while estimating model parameters. For more accurate prediction of the model parameters, it is desirable to know the bed temperatures at the inlet and also at several intermediate points in the catalyst bed as well as the ammonia concentration at least at the end and the beginning of each

Table 6.2.1

Selected Plant Data Extracted from a Typical Ammonia Plant Log Sheets:

Catalyst: Volume = 67.6 m^3, Distribution Bed1: Bed2: Bed3 = 1:1.4:2.0

Data Set	Feed Pressure (atm)	Feed Flow Rate Nm^3/h	Feed Temp. K	Feed Composition: H_2/N_2 Ratio	NH_3 mol %	CH_4 mol %	A_r mol %	Total Press Drop, atm	Reactor Temperature: 1st Inlet	Bed Exit	2nd Bed Exit	3rd Bed Exit	Exit NH_3 mol % 3rd Bed
1.	190.0	0.740*10^6	414.0	3.00	1.61	8.80	4.04	2.7	652	783	752	749	13.42
2.	192.0	0.800*10^6	415.0	3.11	1.89	9.30	3.97	2.6	654	778	759	759	13.40
3.	173.0	0.740*10^6	414.0	2.82	1.70	7.00	4.25	2.8	655	784	765	756	13.12
4.	185.0	0.785*10^6	413.0	3.04	1.84	8.52	3.84	2.7	653	781	761	757	13.60
5.	184.0	0.775*10^6	417.0	2.96	1.71	8.59	4.65	2.8	651	775	763	757	13.47
6.	186.0	0.760*10^6	414.0	3.28	1.70	6.88	4.27	2.8	656	792	765	758	13.14
7.	183.0	0.770*10^6	417.0	3.08	1.70	7.74	4.06	2.7	655	782	768	761	13.45
8.	183.0	0.780*10^6	417.0	3.03	1.72	8.25	3.80	2.8	652	778	763	758	13.20

Note: Units of feed flow rate are given as Nm^3/hr. The prefix N before m^3 merely indicates m^3 at the N.T.P. conditions.

bed. In view of the limitations of data as discussed above, the model parameter values estimated from the plant data have some inherent accuracy limitations.

The objective function for minimization is chosen as the sum of the squares of the difference in the computed and observed values of bed exit temperature for each of the three beds and the ammonia mole percent at the exit of last bed. Since the difference in the values of ammonia mole percent at the exit of last bed is an order of magnitude smaller than the difference in the values for each of the bed exit temperature, a suitable weighting function was used. This is used as a multiplier to the square of the difference in the computed and observed values of ammonia mole percent in order to make the objective function more sensitive to small mismatch in the ammonia concentration. The value of weighting function chosen for the present study is 200.

6.3. Selection of physical properties, thermodynamic and kinetic correlations.

Several correlations (Perry, 1950; Shah, 1967; Dyson and Simon, 1968; Hay and Honti, 1976; Gaines, 1977; Reddy and Husain, 1978; Singh and Saraf, 1979; Mansson and Andresen, 1986) are reported in literature that vary in their degree of complexity, accuracy and range of application for the physical, thermodynamic and kinetic properties required for ammonia synthesis reactor simulation. The physical and thermodynamic properties required are the specific heat, heat of reaction, equilibrium constant and activity coefficient for the pressure, temperature and composition of the reaction mixture at the different axial positions in the reactor. Computation of specific heats of the reaction mixture requires the specific heat correlation for individual constituents of the reaction mixture, namely, nitrogen, hydrogen, ammonia, methane and argon. Specific heat of the mixture is evaluated by summing up the individual molal contributions by neglecting heat of mixing. This assumption is quite realistic because all constituents, except ammonia, behave close to ideally at the temperature and pressure condition existing in the bed. The effect of non-ideality of ammonia is not likely to be important because of high temperature and relatively low concentration, two to fifteen mole percent in the reaction mixture.

The kinetic parameters needed in simulation model are the reverse reaction rate constant for the ammonia synthesis reaction catalyst and the order of reaction parameter, α. It may be noted here that in the present study the order of reaction parameter is assumed to have a constant value of 0.5. The validity of this assumption has been discussed by many workers (Shah, 1967; Dyson and Simon, 1968; Gaines, 1977; Reddy and Husain, 1978). However, Singh and Saraf (1979) have preferred to use values of 0.55 and 0.69 for the two catalysts considered in their study. The usual Arrhenius form of expression is used for the temperature dependence of the reverse reaction rate constant with the proviso to determine the most appropriate value of the frequency factor and activation energy using plant data as pointed out in section 3.1.

The correlations selected for this study are presented in chapter-V, see equations 3.1.15 to 3.1.22. These correlations are simple, widely used and predicts reasonably accurate values of the thermochemical properties at the reactor conditions. More accurate and elaborate correlations could have been used but that may not be of much use in view of the small improvements in computed results and large increase in computation time. The conclusions of Mansson and Andresen (1986) with reference to the effect of non-ideal behaviour of reaction mixture support the above observation. It may also be noted that the plant data may never be quite accurate and elaborate due to the inherent limitations in the measurement of parameters by the instruments that are used. So searching for a very accurate correlation may not be worthwhile. However, more accurate correlations can always be substituted in the simulation model, if considered necessary.

The main aim of present investigation is not to find the best correlation for the properties but only to use reasonably accurate correlations for developing a reliable and efficient simulation model, validated from the plant data, and to use this simulation model for establishing the optimal operating and design conditions for maximizing ammonia production rate.

6.4. Description of procedure for kinetic and thermodynamic parameter estimation.

The most optimal values of kinetic and thermodynamic parameters namely, Para1, Para2 and Para3 are determined from the plant data using the simulation program developed for an axial flow multibed quench type ammonia synthesis reactor. This is done by first delinking the external heat exchanger from the reactor as the heat exchanger performance will not effect the computations of temperature and concentration profile in the bed since the first bed inlet temperature is known from the plant data. The computation will then only depend on kinetics of the catalyst and the conditions in the bed. For model validation computations the simulation program had to be modified to some extent to take care of the special computation algorithm requirements for the model validation. For the model validation, computations start with the known value of the first bed inlet temperature for the plant and computes the bed exit temperature up to the third bed with first set of guessed values of the five variables, namely, Para1, Para2, Para3 and cold shots fractions at the inlet of second and third beds. It is to be noted that no cold shot fraction is added at the inlet to first bed as per the present plant practice and the plant supplier's recommendations.

From the actual (plant) and computed bed exit temperatures for all three beds and the exit ammonia concentration from the last bed, the objective function, that is, the sum of squares of the errors is then computed as discussed in the section 6.2. The objective function so generated is found to be highly nonlinear, constrained and multimodal. Therefore, a direct search technique, the Box complex search, is used to find the most optimal values of the five variables. The parameter estimation by this optimization procedure also required external intervention for changing the direction and step size of the search for the above referred five parameters in order to jump one region of local minima to another region of local minima. In this way the true minima of objective function was established. Without external intervention, the search terminated sometimes at a local minima. Similar computations were carried out for three sets of plant operating conditions.

6.5. Procedure for the estimation of external heat exchanger heat exchange capacity:

For a given plant operating condition data set, after establishing the optimal values of Para1, Para2 and Para3 and second and third bed inlet cold shot fractions the heat exchange capacity $(UA)_H$ of the external heat exchanger was found by computing the heat exchanger tube and shell side temperature profile. It was carried out by making a guessed value of heat exchange capacity, preferably taken on higher side than that calculated approximately by estimating the total ammounts of heat transfer and average temperature difference for heat exchange. The heat exchange capacity is based on per unit heat exchanger tube side volume. From the computed temperature profile, it was then possible to locate a position at which the temperature on the shell side matched closely with the actual feed temperature. From this, the guess for the $(UA)_H$ value was improved to obtain an accurate value of heat exchange capacity $(UA)_H$ within 2 to 3 iterations. In this way, the heat exchange capacity values were found for the three data sets of plant operating conditions. It was observed that heat exchange capacity at high flow rate was significantly higher showing its dependence on the flow rate. Therefore a 0.8 power dependence of heat transfer coefficient on flow rate was assumed based on the well known Dittus-Boelter heat transfer coefficient correlation (McAdams, 1954) for heating and cooling inside tubes. It may be noted that Kramer and Westerterp (1963b) have also reported that the overall heat transfer coefficient U is approximately proportional to $(\text{flow rate})^{3/4}$. On this basis the best average value of heat exchange capacity was obtained for the base condition flow rate of $0.74 * 10^6$ Nm^3/h from the three heat exchange capacity values. It may be noted that the units of feed flow rate are given as Nm^3/h in this study. The letter N before m^3 merely indicates m^3 of the feed gas at the N.T.P. conditions. Eventhough such use of N in S.I. units is not permissible, but for ease of comparison of gas flow rates with varying temperature and pressure, the use of N to refer N.T.P. conditions is frequently found in engineering practice.

6.6. Reliability and accuracy of the validated simulation model:

After determining the best values of parameters Para1, Para2, Para3, $(UA)_H$ and the cold shot fractions at the inlet of second and third bed by the optimization and averaging procedure as discussed above, it was considered desirable to find the sum of squares for the selected data sets using the best parameter values. This was carried out to see how best the model validation had been achieved and to establish the reliability and accuracy of simulation model for using it for reactor performance analysis and optimization. Two strategies for testing the accuracy were tried. The first was to consider the first bed inlet temperature as obtained from the plant data as the starting point and test the model validation. This resulted in some mismatch in calculated and actual feed temperatures. The second strategy was to make iterations to obtain calculated and actual feed temperatures within a certain tolerance. The latter strategy resulted in some mismatch in the calculated and actual temperatures at the first bed inlet. It may be noted here that the observed values of feed temperatures in the plant are likely to be much more accurate than the observed values of first bed inlet temperature. This may be attributed to some variations in the actual axial location of the temperature sensing probe at the inlet of a catalyst bed. Exact location of the temperature sensing probe will significantly influence the recorded value of the first bed inlet temperature. A difference of 5 to 10 K between measured and computed first bed inlet temperatures due to above mentioned reason may not be unusual. It may, however, be noted that slight variations in the physical location of the feed temperature-sensing probe will not affect the temperature measurement at all.

CHAPTER-VII

7. RESULTS AND DISCUSSION

7.1. Parameter estimation for reactor simulation model.

Adopting the procedure for parameter estimation as discussed in section 6.1, the simulation package is made quite accurate for a modern ammonia synthesis reactor selected for the present optimization study. An accurate model is essential for applying the results of the simulation and optimization in the plant with confidence and also for developing a reliable and accurate on-line control.

7.1.1. Plant performance data for an axial flow multibed quench-type ammonia synthesis reactor.

The plant data is shown in detail in Table 6.2.1 and discussed in section 6.2. In all, eight data sets were extracted from the log sheets of the plant for the period during which the plant conditions were steady that also coincided with the time at which feed and product gas samples were drawn for composition analysis. The time of data ensured compatibility of composition analysis and the operating parameters. The bed temperatures shown are the average of two temperature observations from probes located opposite each other at any axial position. The two temperatures were found to be within 3K, indicating negligible radial dispersion. The base set of operating conditions was selected on the basis of average values of parameters existing in the plant and is reported as data set 1 in Table 6.2.1.

It is observed from Table 6.2.1 that some operating parameters that include operating pressure (173.0 atm in data set 3) and feed gas flow rate ($0.80 * 10^6$ Nm^3/h in data set 2) deviate from the base value by about 10 percent. It was, therefore, considered desirable to use data sets no. 1, 2 and 3 for independent parameter estimation, that is, to find three sets of optimum values of model parameters as discussed in section 6.1. Based on these three set of values, the best estimates of parameter values were made as discussed in sections 7.1.3 and 7.1.4.

7.1.2. Selection of kinetic, thermodynamic and physical property correlations.

The reasons for the selection of the various correlations that are used in mathematical model are discussed in section 6.3.

Reverse reaction rate constant correlation, k_r.

The kinetic parameter, k_r (for an arbitrary condition of 200 atm and 773 K) and the corresponding values of frequency factor and activation energy are presented for the various correlations that are reported by Shah (1967), Gaines (1977), Singh and Saraf (1979) and Dyson and Simon (1968) in Table 7.1.2.1 for comparison. The correlation used in the present investigation is a modification of Shah's correlation as given by Equation 3.1.15. The corresponding values of parameters obtained by parameter estimation technique and used in the present work are also given in Table 7.1.2.1.

All the parameter values have been converted to the same

Table 7.1.2.1

Comparison of Frequency Factor and Activation Energy

Values in the Reverse Reaction Rate Constant, k_r.

Correlation/ Reference	Frequency Factor $mol/s/m^3$	Activation Energy kJ/kmol	k_r, mol $NH_3/s/m^3$ at 200 atm and 773 K	Remark
Shah (1967)	$0.94829*10^{16}$	100869.2	276.2	
Present work	$4.11482*10^{16}$	97622.4	3268.3	*
Gaines (1977)	$0.12968*10^{16}$	94700.8	254.0	
Singh and Saraf (1979)	$0.01434*10^{16}$	82297.0	1297.4	**
	$0.04491*10^{16}$	90379.6	334.4	***
Dyson and Simon (1968)	$0.04916*10^{16}$	85896.0	1462.9	

Note: * Modification of Shah's correlation obtained by data validation.

** Montecatini Edison catalyst

*** Haldor-Topsoe catalyst

units and per mol ammonia formed for ease in comparison. Units for reverse reaction rate constant, frequency factor and activation energy are mol $NH_3/s/m^3$, mol $NH_3/s/m^3$, and kJ/kmol, respectively. It can be observed from the table that k_r values at 200 atm and 773 K range between 254.0 (correlation of Gaines, 1977) to 3268.3 (present work). The value of reaction rate constant obviously depends on the inherent activity of the catalyst and it appears that the catalyst used in the reactor for the plant under consideration is quite active. The current trend in ammonia synthesis is to use relatively low-pressure (150-200 atm) and high-activity catalyst.

It may be pointed out that when Shah's (1967) correlations were used for data validation with the plant values of first bed inlet temperatures the conversion was found to be significantly lower as compared to the plant values due to low reaction rates predicted by the rate equation of Shah. It may be observed from Table 7.1.2.1 that the frequency factor and the activation energy values obtained by validation of model from the plant data and used in the present work are also comparable to values reported by Shah, Gaines, Singh and Saraf, and Dyson and Simon. Data in the Table 7.1.2.1 show that the activation energy values range from 82297.0 to 100869.2 kJ/kmol. The value of the activation energy obtained from model validation in the present study is 97622.4 kJ/kmol which appears to be very reasonable.

K, Equilibrium Constant Correlation.

For the reaction $3/2\ H_2 + 1/2\ N_2 = NH_3$ the values of K are computed at two arbitrary temperatures of 723 and 773 K for the correlations reported by Hay and Honti (1976), Shah (1967), Gaines (1977), and Dyson and Simon (1968). Gaines used the same correlation used by Dyson and Simon.

As observed from the Table 7.1.2.2. the K values at 723 and 773 K range between 0.00662 to 0.00769 and o.00376 to 0.00437, respectively. In the present investigation, the correlation of Hay and Honti has been used and an average deviation from reported experimental data is reported as 0.00055 in log K with a maximum deviation of 0.0016 in log K over the temperature range of interest. It may be observed that the K values obtained from the correlation of Shah are always on the high side while that of Dyson and Simon are slightly on the low side. The K values decrease with increase in temperature which is consistent thermodynamically for an exothermic reversible reaction.

Fugacity Coefficient Term, K_{ν}.

The values of K_{ν} are computed from the correlations of Shah (1967), Dyson and Simon (1968), and Gaines (1977) and obtained from the data reported by Dodge (1944) and Denbigh (1981) for a comparison with those used in the present work, a modification of Shah's correlation (equation 3.1.17).

It may be noted that all correlations depend on gas temperature and pressure except that of Gaines which is also dependent on gas composition. The K_{ν} values have been calculated at conditions of 100 atm and 723 K, 300 atm and 723 K, and 300 atm and 773 K for comparison since the data reported by Dodge and Denbigh are available at these conditions. The Dyson and Simon values are very close to those reported by Denbigh and Dodge

Table 7.1.2.2

Comparison of Equilibrium Constant, K.

(Reaction Equation: $3/2\ H_2 + 1/2\ N_2 = NH_3$)

Correlation/ Reference	K Values at Gas Condition		Remarks
	723K	773K	
Hay and Honti (1976a)	0.00678	0.00384	*
Shah (1967)	0.00769	0.00437	
Gaines (1977)	0.00662	0.00376	**
Dyson and Simon (1968)	0.00662	0.00376	**

Note: * Used in present investigation.

** Gillespie and Beattie Correlation as cited by Dyson and Simon (1968).

Table 7.1.2.3

Comparison of Fugacity Coefficient Term, K .

(for reaction 3/2 H_2 + 1/2 N_2 = NH_3)

Correlation/ Reference	K Values at Gas Condition			Remarks
	100 atm	300 atm	300 atm	
	723 K	723 K	773 K	
Denbigh, K.G. (1981)	0.910	0.747	--	*
Dodge, B.F. (1944)	0.929	0.757	0.773	*
Shah (1967)	0.808	0.728	0.753	
Present Work	1.114	1.004	1.038	**
Dyson and Simon (1968)	0.909	0.746	0.767	
Gaines (1977)	1.526	3.551	3.329	***

Note: * Experimental data.

** Modification of Shah values by a multiplying factor obtained by model validation with the use of plant data.

*** For gas composition (mol %):

H_2 = 53.0, N_2 = 17.7, NH_3 = 14.8, CH_4 = 9.9, Ar = 4.0

while Shah's values are on the low side and those of Gaines are quite high for all conditions.

It may be noted that the values of K_ϕ used in the present investigation appear to be reasonable, slightly higher than those of Denbigh and Dodge but considerably lower than those of Gaines.

Heat of Reaction, $(-\Delta H_{r\,NH_3})$.

The values of heat of reaction were obtained from reported data and computed from the correlations given by Gillespie and Beattie as cited by Hay and Honti (1976), Perry (1950), Shah (1967), Gaines (1977), Nielsen (1968), Kirk and Othmer (1978) and (1929) for comparison. Table 7.1.2.4 shows the values at different conditions.

It may be observed that the heat of reaction increases with increase in the pressure and/or temperature. The Perry and Nielsen correlations are independent of pressure while those of Gillespie and Beattie, Shah and Gaines are also dependent on pressure for accounting the nonideality introduced due to pressure. It may be observed that the values obtained from the correlation of Shah are nearly fifty percent higher and those obtained from the correlation of Gaines are nearly ten percent lower than those obtained from other sources, namely, Gillespie and Beattie, Perry, Nielsen, Kirk and Othmer and the International Critical Tables.

Table 7.1.2.4

Comparison of Values of Heat of Reaction, $(-\Delta H_r)_{NH_3}$.

(for reaction $3/2\ H_2 + 1/2\ N_2 = NH_3$)

Correlation/ Reference	$(-\Delta H_r)_{NH_3}$ at Gas Condition, kJ/kmol NH_3 formed				
	100 atm 723 K	300 atm 723 K	300 atm 773 K	200 atm 833 K	1 atm 291 K
Gillespie and Beattie *	53624.5	56073.8	56304.1	55592.3	44861.6
Perry (1950)	53494.7	53494.7	54206.5	55048.1	46054.8
Shah (1967)	76199.8	76873.8	79867.4	83602.0	61797.2
Gaines (1977) **	47658.3	48462.2	48985.6	49291.2	41270.1
Nielsen (1968)	53348.2	53348.2	53972.0	54625.2	45837.1
Kirk Othmer (1978) ***	--	--	--	--	46276.7
ICT (1930a) ***	--	--	--	--	45853.8

Note: * As cited by Hay and Honti (1976b) and also used in present investigation.

** Correlation from Kazarnovskii data as cited by Gaines (1977).

*** Reported data.

Heat Capacities of Ammonia, Hydrogen, Nitrogen, Methane and Argon.

The values of heat capacities were computed from the correlations given by Shah (1967), Perry (1950) and the International Critical Tables (1930a, 1930b, 1930c, and 1930d) for comparison at four conditions of 100 atm and 723 K; 300 atm and 723 K; 300 atm and 773 K; and 200 atm and 833 K. It is observed from Table 7.1.2.5 that with increase in gas temperature at constant pressure the heat capacity increases except for ammonia heat capacity computed from Shah's correlation. This is thermodynamically consistent. The values of heat capacity of ammonia calculated from Shah's correlation are higher while those obtained from correlations in the International Critical Tables are lower. Therefore, in the present investigations, the correlations given in Perry's Handbook are considered more suitable and are used in the present work. Similarly, the correlations given in Perry's Handbook are considered more satisfactory for hydrogen and nitrogen and are used in the present work. For methane, the correlation given in the International Critical Tables is used. For argon the constant value reported by Shah is used.

7.1.3. Estimation of Kinetic and Thermodynamic Parameters.

The procedure for estimation of kinetic and thermodynamic parameters have been discussed in detail in section 6.4. After selecting the appropriate correlations based on the reasons analyzed in section 7.1.2, the parameter estimation was carried out for the three data sets (set nos. 1, 2 and 3 in Table 6.2.1).

Table 7.1.2.5

Comparison of Heat Capacities of NH_3, H_2, N_2 and CH_4.

Correlation/ Reference	Gas Constituent	Cp, kJ/kmol/K 100 atm 723 K	300 atm 723 K	300 atm 773 K	200 atm 833 K	Remarks
Shah (1967)	NH_3	60.58	61.84	58.15	55.35	
	H_2	29.48	29.48	29.60	29.77	
	N_2	30.90	30.90	31.19	31.53	
	CH_4	58.70	58.70	61.21	64.18	
Perry (1950)	NH_3	49.15	49.15	50.49	52.00	*
	H_2	29.60	29.60	29.73	29.85	*
	N_2	31.36	31.36	31.61	31.95	*
ICT (1929)	NH_3	39.86	39.86	40.28	40.78	
ICT (1930b)	H_2	28.93	28.93	29.10	29.31	
ICT (1930c)	N_2	88.34	88.34	95.04	102.91	
ICT (1930d)	CH_4	71.09	71.09	74.36	78.13	*

Note: * Used in present investigation.

The results of the computations for minimization of sum of squares of errors are summarised in Table 7.1.3.1. It is observed that for the first data set (base condition) the match in actual bed temperature and computed ones has been brought down to within about 2K. The match in ammonia concentration is also very good and the difference is only 0.264 mol %. These resulted in a sum of squares of error value of 9.1. The optimal parameter values are computed to be 1.076634, 0.967812 and 1.450 for Para1, Para2 and Para3, respectively. Using the computed values of Para1 and Para2, the frequency factor and activation energy values are found to be $12.40973 * 10^{16}$ $mol/s/m^{3}$ and 97622.4 kJ/kmol, respectively. In the case of increased flow rate of $0.80 * 10^{6}$ Nm^{3}/h the optimal Para1, Para2 and Para3 values are found to be 1.01867, 0.967812 and 1.357, respectively, to result in a sum of squares of errors of 17.9 with the absolute maximum difference in bed outlet temperature and ammonia concentration of 3.7 K and 0.053 mol percent.

Using the computed values of Para1 and Para2, the frequency factor and the activation energy values are found to be $1.77430 * 10^{16}$ and 97622.4, respectively. Similarly from the table it is observed that at decreased pressure of 173 atm, the optimal Para1, Para2 and Para3 values are obtained to be 1.03757, 0.967812 and 1.330, respectively. The match in temperature and ammonia concentration is again very good with absolute maximum difference in temperature and concentration is found to be 3.2 K and 0.021 mol percent, respectively, and the sum of squares of errors of only 18.7. Using the computed values of Para1 and

Table 7.1.3.1

Summary of Results for Parameter Estimation.

S. NO.	Operating Pressure (atm)	Feed Gas Flow Rate (Nm^3/h)	Feed Temp. (K)	Bed Outlet Temp., K 1st	2nd	3rd	External Heat Exchanger Exit Temp. (K)	Ammonia Conc. at Outlet of 3rd Bed mol %	Sum of Squares of Error	$(UA)_H$ W/K	Para1	Para2	Para3	Remarks
1.	190	0.74 * 10^6	414	783	752	749	588	13.42	--	--	--	--	--	*
				780.7	753.6	750.0		13.684	9.1	294165	1.07664	0.967812	1.450	**
				- 2.3	1.6	1.0		0.264						***
2.	192	0.80 * 10^6	415	778	759	759	588	13.40	--	--	--	--	--	*
			417.4	781.7	760.8	757.9	592.4	13.453	17.9	354600	1.01867	0.967812	1.357	**
			2.4	3.7	1.8	- 1.1	4.4	0.053						***
3.	173	0.74 * 10^6	414	784	765	756	587	13.12	--	--	--	--	--	*
			412.1	786.3	768.2	757.8	590.4	13.141	18.7	320645	1.03757	0.967812	1.330	**
			- 1.9	2.3	3.2	1.8	3.4	0.021						***

Note: * Plant data.
** Computed results.
*** Difference of computed value and corresponding plant data.
Units of feed flow rate are given as Nm^3/h, cubic meter per hour at N.T.P. condition.

Para2, the frequency factor and activation energy are found to be $3.34553 * 10^{16}$ and 97622.4. It may be observed that the three sets of optimal values of Para1, Para2 and Para3 obtained by validation of the model by comparing with the plant data for the same catalyst, differ to some extent from each other. The difference in values may be attributed to not so accurate plant data. Therefore, an average of the three values is used in the simulation model. The average values for the three parameters are:

Para 1 = 1.04429, Frequency factor = $4.11482 * 10^{16}$

Para 2 = 0.967812, Activation energy = 97622.4

Para 3 = 1.379

The average values are reported in Table 7.1.2.1 and are discussed in section 7.1.2. It may be noted here that the corresponding validated optimal values of cold shots obtained during parameter estimation for the three data sets are (0.245, 0.100), (0.254, 0.090) and (0.176, 0.160) at the inlet of the second and third beds, respectively. The cold shot at the inlet of the first bed is taken to be zero as per the present practice in the plant.

7.1.4. Estimation of Heat Exchange Capacity of the External Heat Exchanger, $(UA)_H$.

The procedure for estimation of $(UA)_H$, W/K as given in section 6.5 was used to obtain the best values for the three data sets as shown in Table 7.1.3.1. The three values corresponding to the data sets 1, 2 and 3 are 294165, 354600 and 320645 W/K. As discussed in section 6.5, it is reasonable to account for the effect of flow rate on $(UA)_H$ by assuming a 0.8 power dependence on flow rate of overall heat transfer coefficient, U (McAdams, 1954; Kramer and Westerterp, 1963b). For comparison the $(UA)_H$ value obtained for data set 2 at a flow rate of $0.80 * 10^6$ Nm^3/h when converted to the base value flow rate of $0.74 * 10^6$ Nm^3/h becomes 333165. Again the three values are different although the difference in maximum and minimum values at base value of flow rate of $0.74 * 10^6$ Nm^3/h is about 13%. This may be attributed to a large extent to the temperature measurement errors in the plant data. Therefore, an average value is used and $(UA)_H$ is computed in simulation model by:

$$(UA)_H = 316000\ ((\text{feed gas flow rate, } Nm^3/h)/(0.74 * 10^6))^{0.8}\ W/K$$

7.1.5. Comparison of Reactor Simulation Model Predictions with Actual Plant Performance.

As discussed in section 6.6 the reliability of the model is tested at the average value of Para1, Para2, Para3, $(UA)_H$ and the cold shot values obtained by model validation. The results of computations for sum of squares of errors for all eight data sets (given in Table 6.2.1) are shown in Table 7.1.5.1.

It is observed that by using strategy 1, the sum of squares of errors values range from 20 to 180 and by using iterative strategy 2, the sum of squares of errors values range from 38.9 to 253.0. The value of sum of squares of errors and the computed value of temperature and concentration all along show a very good match. The match in ammonia concentration is also quite good. It,

Table 7.1.5.1

Comparison of Simulation Results With Plant Data At Average Value Of Estimated Parameters.
Para1 = 1.04429, Para2 = 0.967812, Para3 = 1.379

Data Set No.	Operating Pressure, (atm)	Feed Gas Flow Rate, (10^6 Nm^3/h)	Simulated Cold Shot Fraction 2nd Bed	3rd Bed	Feed Temp., (K)	First Bed Inlet Temp., (K)	Bed Outlet Temp. (K) 1st	2nd	3rd	External Heat Exchanger Exit Temp., (K)	Ammonia Prodn., t/d	Mol %	Sum Of Squares Of Error	$(UA)_H$ W/K (computed)	Remark
1.	190	0.740	0.245	0.100	414	652	783	752	749	588	1313	13.42	-	316000	*
					395.2	652.0	784.9	759.5	754.6	586.6		13.68	106.8		**
					414.3	658.3	788.5	761.9	756.2	596.5	1287.2	13.50	253.0		***
2.	192	0.800	0.254	0.090	415	654	778	759	759	588	1393.8	13.40	-	336370	*
					414.8	654.0	781.3	754.0	752.9	596.3	1394.0	13.83	180.0		**
					415.1	654.1	781.4	754.1	752.9	596.5	1393.6	13.83	182.0		***
3.	173	0.740	0.176	0.160	414	655	784	765	756	587		13.12	-	316000	*
					410.1	655.0	784.3	765.2	753.9	590.6	1251.4	13.23	20.1		**
					414.2	656.4	785.0	765.7	754.2	592.8	1247.5	13.19	38.9		***
4.	185	0.785	0.223	0.120	413	653	781	761	757	588	1370.4	13.60	-	331280	*
					409.0	653.0	781.6	759.3	752.7	592.5	1364.1	13.74	45.1		**
					413.1	654.4	782.8	759.9	753.1	594.6	1359.9	13.70	64.8		***
5.	184	0.775	0.215	0.129	417	651	775	763	757	587		13.47	-	327890	*
					401.8	651.0	779.5	759.2	751.7	588.4	1339.3	13.52	65.1		**
					417.2	656.1	783.7	761.2	753.1	596.4	1324.1	13.38	184.0		***
6.	186	0.760	0.215	0.091	414	656	792	765	758	589		13.14	-	322800	*
					418.0	656.0	788.8	767.3	761.3	595.5	1280.1	13.17	69.7		**
					414.1	654.6	787.9	766.8	761.0	593.5	1284.3	13.22	49.9		***
7.	183	0.770	0.206	0.110	417	655	782	768	761	589		13.45	-	326190	*
					419.1	655.0	785.3	765.1	757.9	596.3	1301.0	13.22	93.2		**
					417.1	654.3	784.8	764.9	757.7	595.3	1303.2	13.24	76.5		***
8.	183	0.780	0.215	0.110	417	652	778	763	758	588		13.20	-	329580	*
					411.0	652.0	781.5	761.8	755.3	592.6	1337.3	13.43	53.4		**
					417.1	654.1	783.3	762.6	755.8	595.8	1330.7	13.37	100.0		***

NOTE: * Plant data.

** Strategy 1. First bed inlet temperature is taken as plant data (actual), a noniterative procedure.

*** Strategy 2. First bed inlet temperature is searched to match calculated and actual feed temperatures, an iterative procedure.

therefore, establishes that the values of model parameters found from plant data are indeed good for further analysis and optimization of the plant performance.

7.2. Choice of Variables and Their Ranges for Simulation Studies.

Operation of an ammonia reactor is generally associated with changes in the values of operating variables. Important operating variables for a multibed reactor are: cold shot distribution, feed gas flow rate, concentration of inerts (methane and argon) in the feed gas, hydrogen to nitrogen ratio in the feed gas, catalyst activity, operating pressure, and feed gas temperature. At the design stage, a designer can also vary total catalyst volume and catalyst distribution.

Performance of a multibed ammonia synthesis reactor is greatly affected by cold shot distribution. Low cold shot rates as well as high cold shot rates have a pronounced effect on the reduction of ammonia production. Injudicious increases in the cold shot rates result in the quenching of the reactor. In order to study the effect of changes in the operating and/or design variables on the ammonia production rate, it was considered vital to have the optimal cold shot distributions for each of the condition. Otherwise, non-optimal cold shot distribution will totally mask the true effect of the changes in other variables. Accordingly, cold shot distributions are not treated as operating variables, but instead the cold shot distribution is optimized for each set of operating and or design conditions.

Surprisingly, the data obtained from a modern commercial multibed axial flow ammonia reactor did not have any measured values for cold shot flow rates/distribution because of lack of facilities for such meeasurements. In the present study, the cold shot distribution for the base case was obtained by validating the plant data. This aspect has been discussed in detail in the preceding section (section 7.1). The base value for each of the operating variable was chosen as the most probable value at which the plant is operating. The changes in operating variables were, in general, restricted to ten percent on either side of the base value (as observed from the plant data for few months), except for catalyst activity factor. The base value of catalyst activity factor was chosen as unity and the effect of deterioration in catalyst activity was investigated at the catalyst activity factor of 0.9, 0.8 and 0.7. Changes in the feed gas temperature as well as catalyst distribution in different beds were not investigated because of their irrelevance in the present context. The catalyst volume was changed only to compare the effect of such changes from those obtained from the corresponding changes in the feed gas flow rate. The base values of operating and/or design variables and their ranges of variations are given in Table 7.2.1. The values of some of the operating and/or design variables kept unchanged of their base values are also given in Table 7.2.1. The base values for these variables were also obtained either from the actual plant data or obtained from the validation of the model by use of plant data (section 7.1).

Table 7.2.1

Operating and Design Parameters Average Value and Range Investigated.

S.No.	Description of the Variable	Unit	Selected Values for Simulation Study: Base Condition	Selected Values for Simulation Study: Range of Variations
	Parameter Varied			
1.	Feed Gas Pressure	atm	190	170 to 210
2.	Flow Rate	Nm^3/h	$0.740 * 10^6$	$0.667 * 10^6$ to $0.820 * 10^6$
3.	H_2/N_2 Ratio	--	3.0	2.5 to 3.2
4.	Inerts in Feed:	mol %	12.84	10.68 to 13.95
	CH_4	mol %	8.80	6.88 to 9.30
	Ar	mol %	4.04	3.80 to 4.65
5.	Catalyst Activity Factor	--	1.0	0.7 to 1.0
6.	Catalyst Total Volume	m^3	67.6	61.0 to 75.0
	Parameters Kept Unchanged			
1.	Catalyst Distribution	--	1.0:1.4:2.0	--
2.	External Heat Exchange Capacity	W/K	316000	--
3.	Internal Preheating Section Heat Exchange Capacity (Catalyst Bed Side)	W/K	0.0	--
4.	Feed Gas Temperature	K	414	--
5.	NH_3 in Feed Gas	mol %	1.61	--

Note: Here prefix N before m^3 stands for N.T.P. conditions.

7.3. Simulation Results for Base Conditions.

The simulation program was run on Roorkee University Regional Computer Centre main frame Computer System, DEC 20. Optimization of cold shot fractions for a single set of conditions took nearly 5 to 8 minutes of CPU time. The results of optimization are summarised in Tables 7.3.1.1 and 7.3.1.2. The detailed computed profiles of bed temperature (K) and ammonia concentration (mol percent) are presented in Appendix A, Tables A.1 through A.7, for the sixteen sets of conditions investigated. The detailed results are tabulated at shorter intervals towards the end of each bed to clearly understand the contribution of each additional increment of catalyst volume. It may be noted that for numerical integration each bed was divided into 100 equal increments. Figures 7.1 through 7.15 show the effect of changes in operating and design parameters on the optimal performance and the stability of the reactor. Except for set no. 0, all other sets represent the performance of reactor at the optimal cold shot distributions. Set No. 0 designates the base condition with simulated value of cold shot fractions (since actual cold shot fractions at the first and second bed inlets are not known due to lack of measuring facilities in the plant) obtained by validation of the model by comparison with plant data. Set No. 1 also represents the base conditions except that the cold shot fractions added at the inlet of each of the three beds are at the optimal values obtained from the optimization studies.

TABLE.NO. 7.3.1.1

SUMMARY OF COMPUTED RESULTS

et No.	Parameter Varied	Value Of Parameter	Cold Shot Distribution 1st Bed	2nd Bed	3rd Bed	Total	Mol % NH3 At Outlet Of 3rd Bed	Production Rate OF NH3, t/d	Total Pressure Drop, atm
1	2	3	4	5	6	7	8	9	10
0*	-	-	0.000	0.245	0.100	0.345	13.502	1287.2	2.77
1	-	-	0.110	0.233	0.232	0.575	14.880	1419.2	2.26
2(A)	Flow rate, Nm^3/h	0.667*10^6	0.123	0.253	0.234	0.610	15.188	1306.4	1.83
2(B)	Flow rate	0.820*10^6	0.098	0.230	0.219	0.547	14.631	1547.3	2.78
3(A)	H/N ratio	2.5	0.109	0.237	0.236	0.582	14.914	1421.7	2.25
3(B)	-do-	2.8	0.108	0.240	0.234	0.582	14.918	1422.4	2.25
3(C)	-do-	3.2	0.108	0.237	0.226	0.571	14.845	1416.3	2.27
4(A)	Inerts Conc. mol %	10.68	0.145	0.250	0.234	0.629	15.387	1467.0	2.19
4(B)	-do-	13.95	0.089	0.249	0.220	0.558	14.647	1397.1	2.29
5(A)	Catalyst Activity factor	0.7	0.030	0.193	0.192	0.415	13.764	1312.5	2.56
5(B)	-do-	0.8	0.080	0.232	0.203	0.515	14.322	1366.2	2.38
5(C)	-do-	0.9	0.096	0.237	0.220	0.553	14.631	1395.6	2.30
6(A)	Catalyst Volume, m^3	61.0	0.096	0.239	0.214	0.549	14.646	1397.1	2.17
6(B)	-do-	75.0	0.120	0.253	0.235	0.608	15.184	1447.8	2.37
7(A)	Operating pressure, atm	170.0	0.089	0.235	0.199	0.523	14.167	1351.3	2.34
7(B)	-do-	210.0	0.146	0.253	0.231	0.630	15.691	1495.4	2.21

Note: See Table 7.2.1 for base conditions

TABLE NO. 7.3.1.2

TEMPERATURE AND AMMONIA CONCENTRATION VALUES AT BED INLET AND OUTLET FOR DIFFERENT CONDITIONS

Set No.	Internal Preheating Section Outlet Temp., K	Temperature And Conversion In The Bed											
		1st Bed				2nd Bed				3rd Bed			
		Inlet		Outlet		Inlet		Outlet		Inlet		Outlet	
		Temp. (K)	Mol % NH3	Temp. (K)	Mol % NH3	Temp. (K)	Mol % NH3	Temp. (K)	Mol % NH3	Temp. (K)	Mol % NH3	Temp. (K)	Mol % NH3
1	2	3	4	5	6	7	8	9	10	11	12	13	14
0	658.3	658.3	1.61	788.5	10.32	692.9	7.81	761.9	12.74	729.6	11.52	756.2	13.50
1	695.1	640.1	1.61	779.8	10.98	675.4	7.96	751.9	13.47	678.3	10.48	737.8	14.88
2(A)	702.3	636.4	1.60	779.0	11.18	665.4	7.83	746.8	13.68	673.7	10.60	735.4	15.19
2(B)	687.8	641.4	1.61	777.5	10.72	676.8	7.87	750.9	13.18	681.7	10.43	738.6	14.63
3(A)	695.4	640.0	1.61	779.5	10.99	672.8	7.90	750.5	13.50	676.0	10.45	736.2	14.91
3(B)	695.7	640.6	1.61	780.3	10.99	672.3	7.87	750.3	13.49	676.5	10.47	736.6	14.92
3(C)	694.7	640.9	1.61	780.1	10.95	674.6	7.91	751.1	13.40	679.6	10.50	738.3	14.85

1	2	3	4	5	6	7	8	9	10	11	12	13	14
4 (A)	709.6	629.9	1.61	773.3	11.37	665.7	7.98	749.0	13.85	675.1	10.73	739.1	15.39
4 (B)	689.5	645.6	1.61	780.9	10.72	670.7	7.64	747.1	13.13	678.4	10.38	736.0	14.65
5 (A)	668.3	656.5	1.61	779.9	9.83	698.1	7.75	762.8	12.37	700.2	10.13	749.7	13.76
5 (B)	683.5	647.2	1.61	776.3	10.37	678.6	7.67	749.9	12.76	686.0	10.31	740.5	14.32
5 (C)	690.4	643.9	1.61	780.4	10.76	675.6	7.81	750.3	13.16	680.9	10.40	738.2	14.63
6 (A)	690.6	644.3	1.61	780.7	10.75	675.8	7.80	750.4	13.14	682.9	10.46	739.5	14.65
6 (B)	700.1	636.1	1.61	776.8	11.20	665.0	7.83	746.4	13.68	673.1	10.60	734.9	15.18
7 (A)	6[illegible].5	639.7	1.61	769.3	10.29	671.1	7.60	741.4	12.63	680.3	10.25	733.3	14.17
7 (B)	709.6	629.8	1.61	773.9	11.61	665.7	8.11	748.9	14.09	676.3	10.95	740.1	15.69

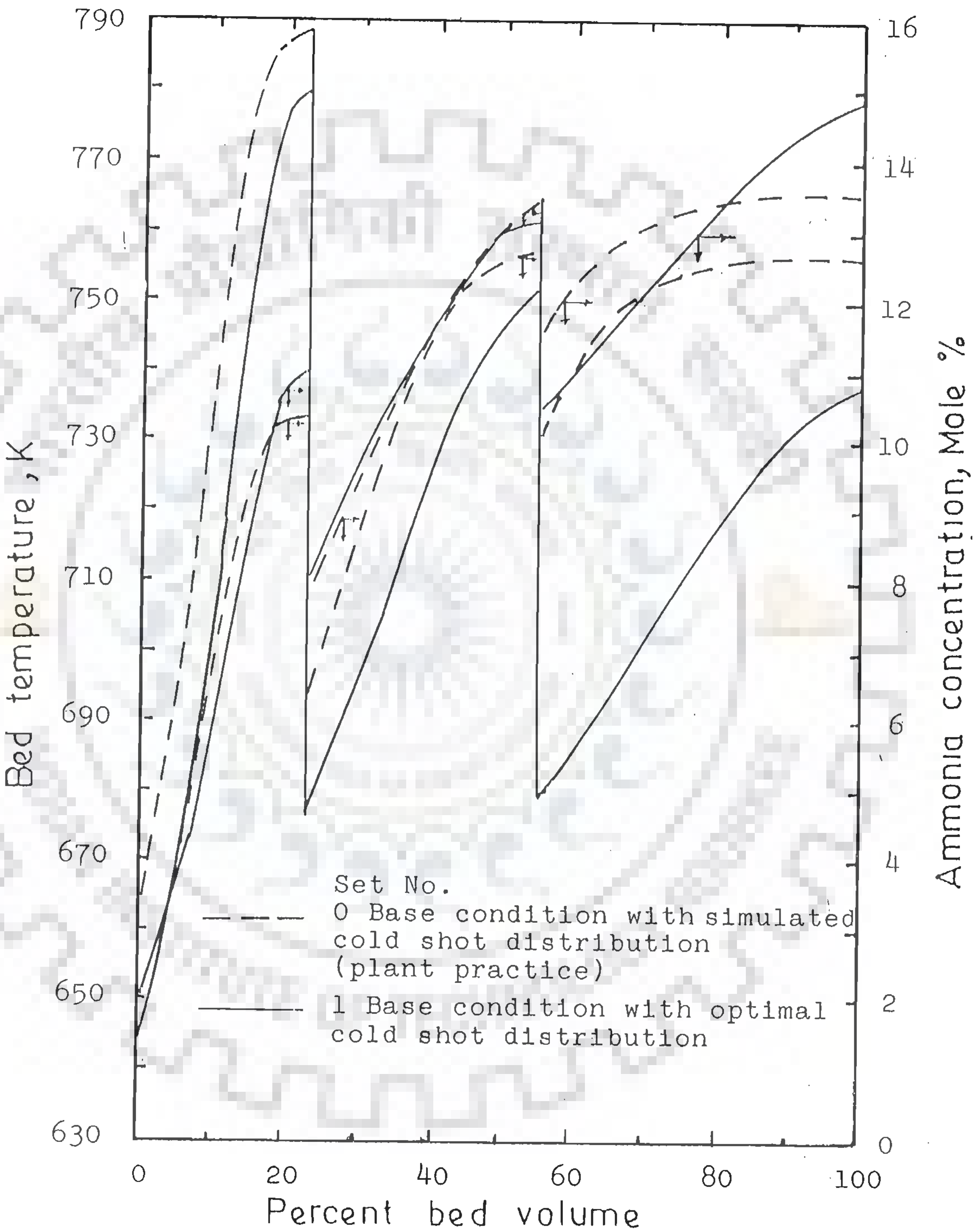

FIG. 7.1 AMMONIA CONCENTRATION AND TEMPERATURE PROFILES IN CATALYST BEDS (See Table 7.2.1 for Base Conditions)

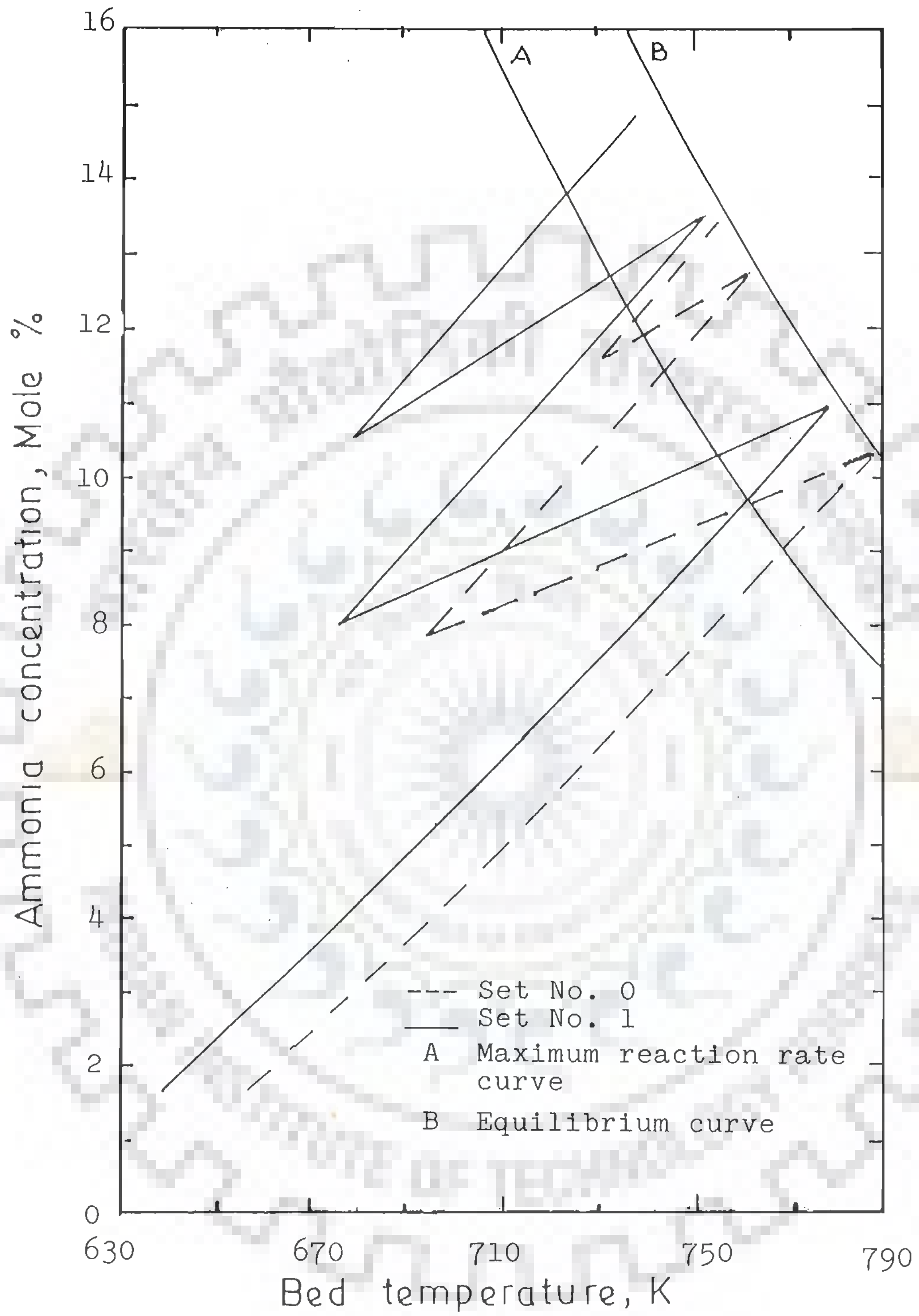

FIG. 7.2 AMMONIA CONCENTRATION VERSUS TEMPERATURE IN CATALYST BEDS (See Table 7.2.1 for Base Conditions)

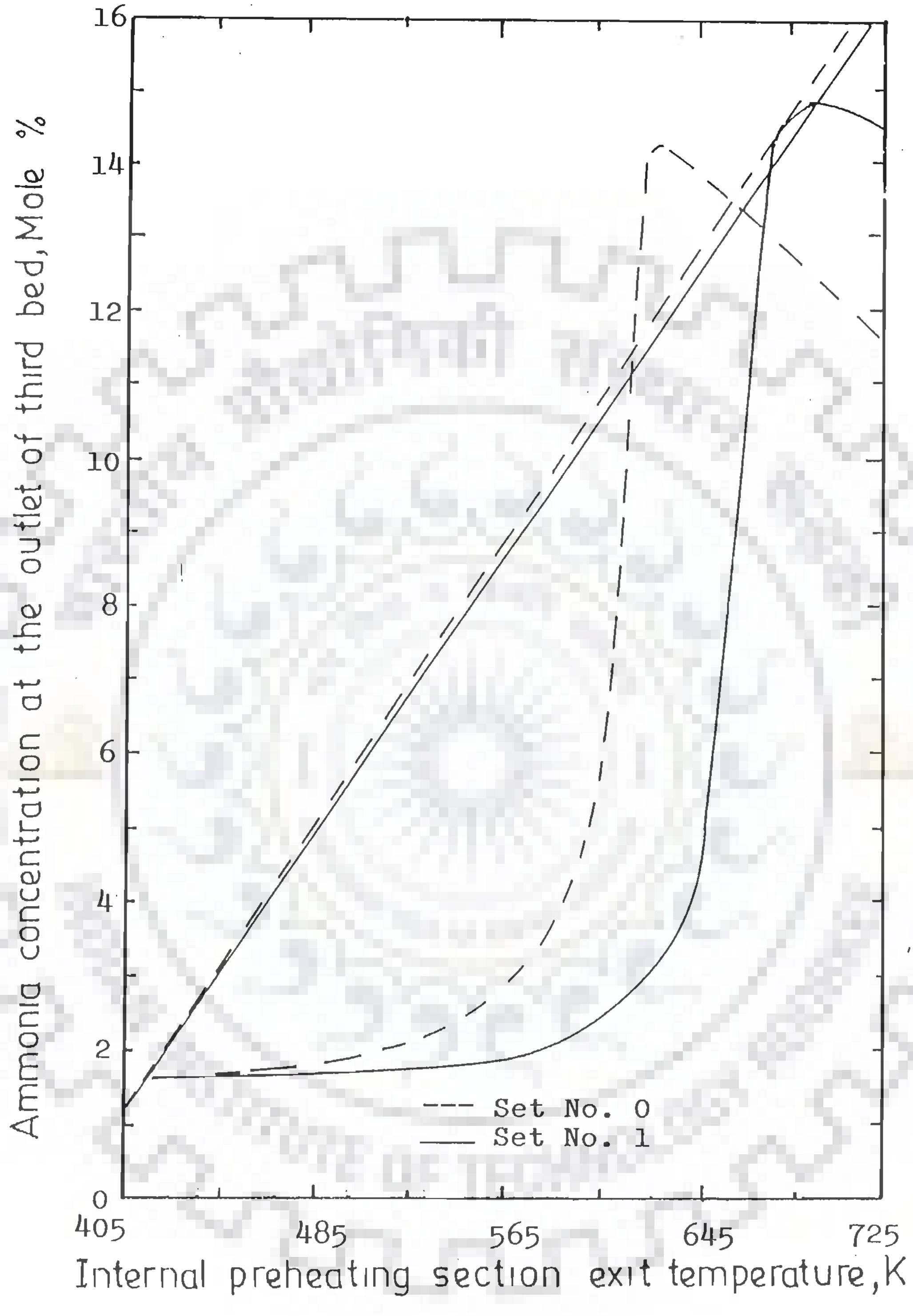

FIG. 7.3 REACTOR OPERATING POINTS AND THEIR STABILITY (See Table 7.2.1 for Base Conditions)

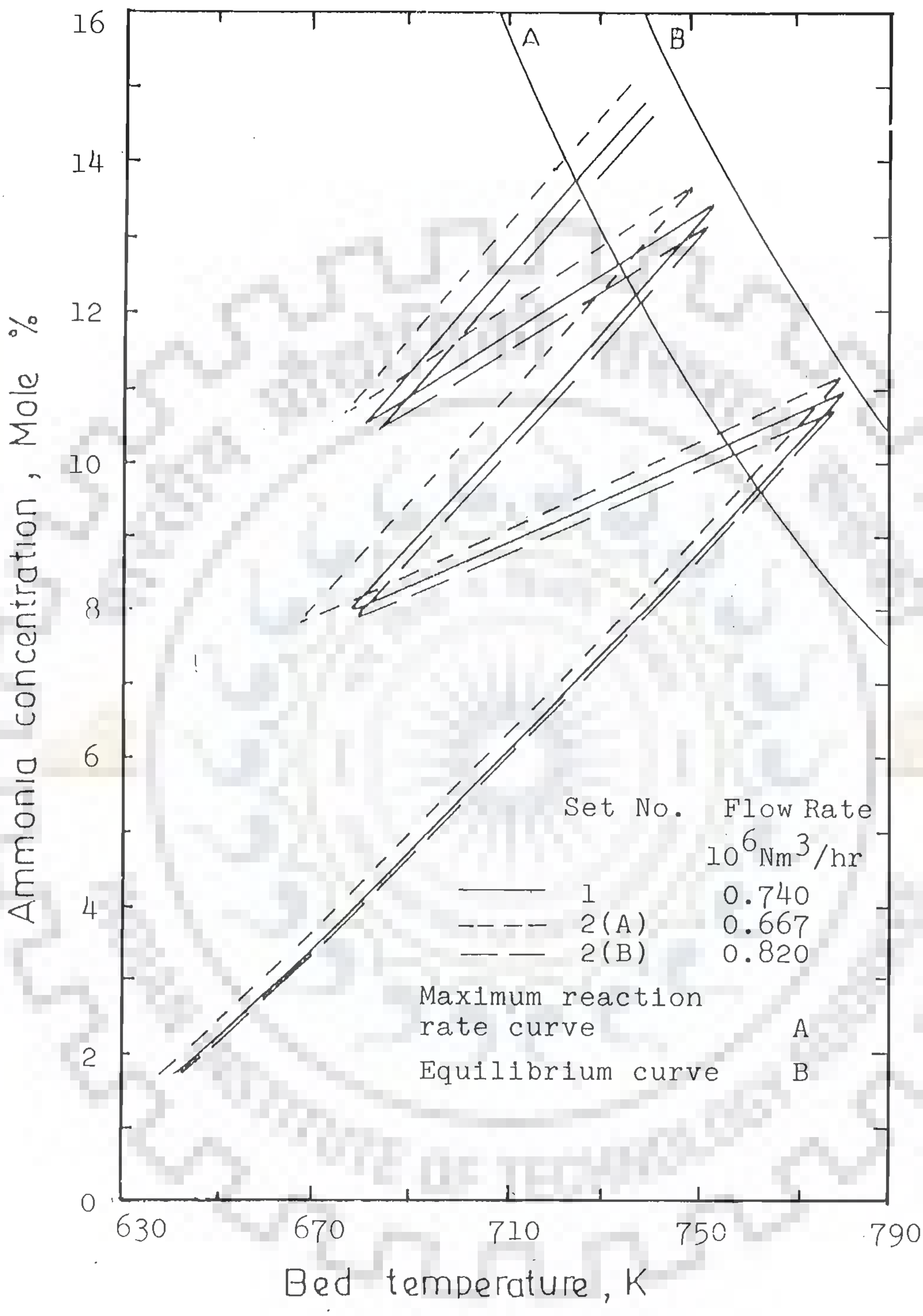

FIG. 7.4 EFFECT OF FEED FLOW RATE ON AMMONIA CONCENTRATION-TEMPERATURE PROFILE IN CATALYST BEDS FOR OPTIMAL COLD SHOT DISTRIBUTION (Base conditions, set No.1, are given in Table 7.2.1)

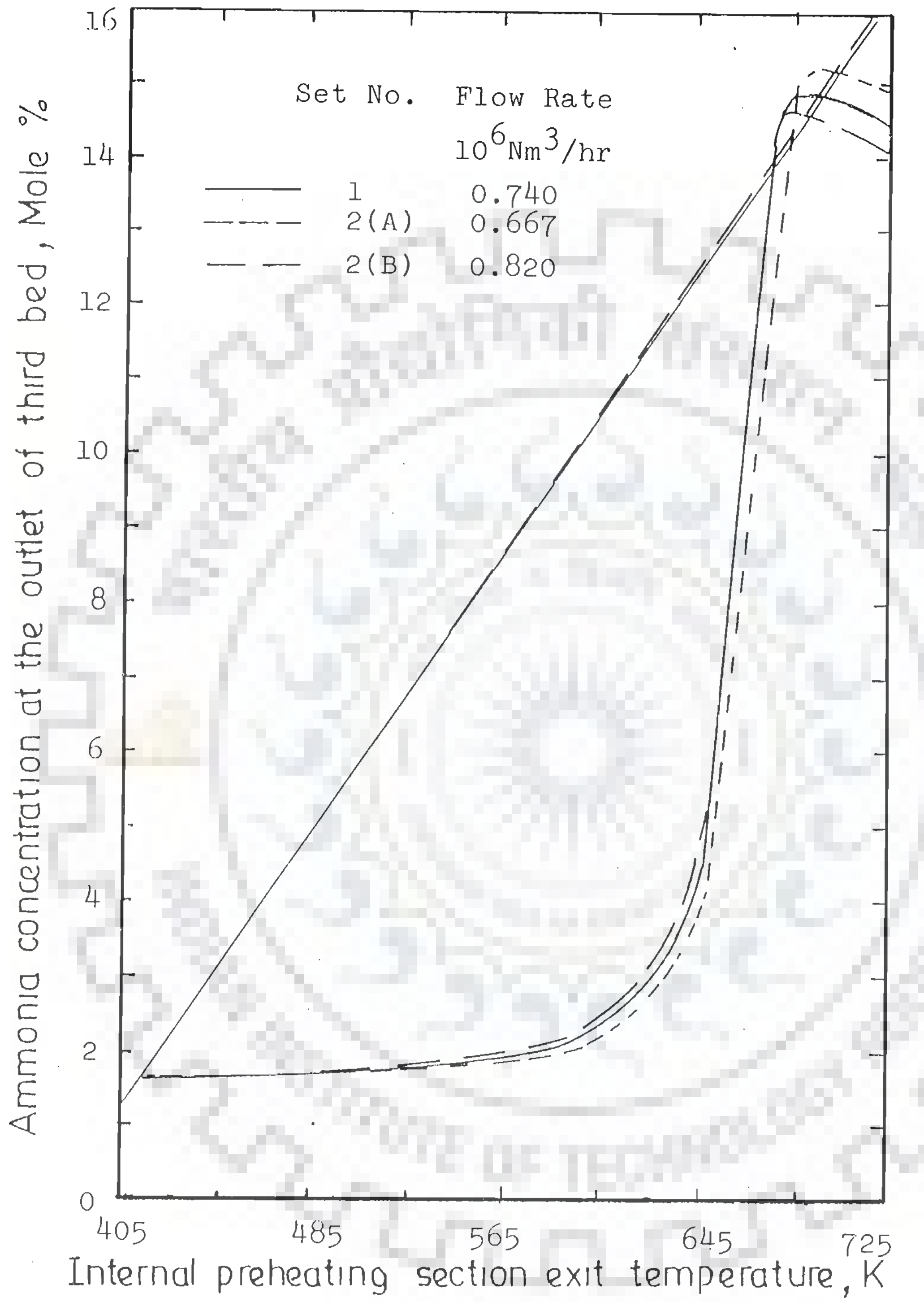

FIG. 7.5 EFFECT OF FEED FLOW RATE ON REACTOR OPERATING POINTS AND THEIR STABILITY (Base conditions, set No.1, are given in Table 7.2.1)

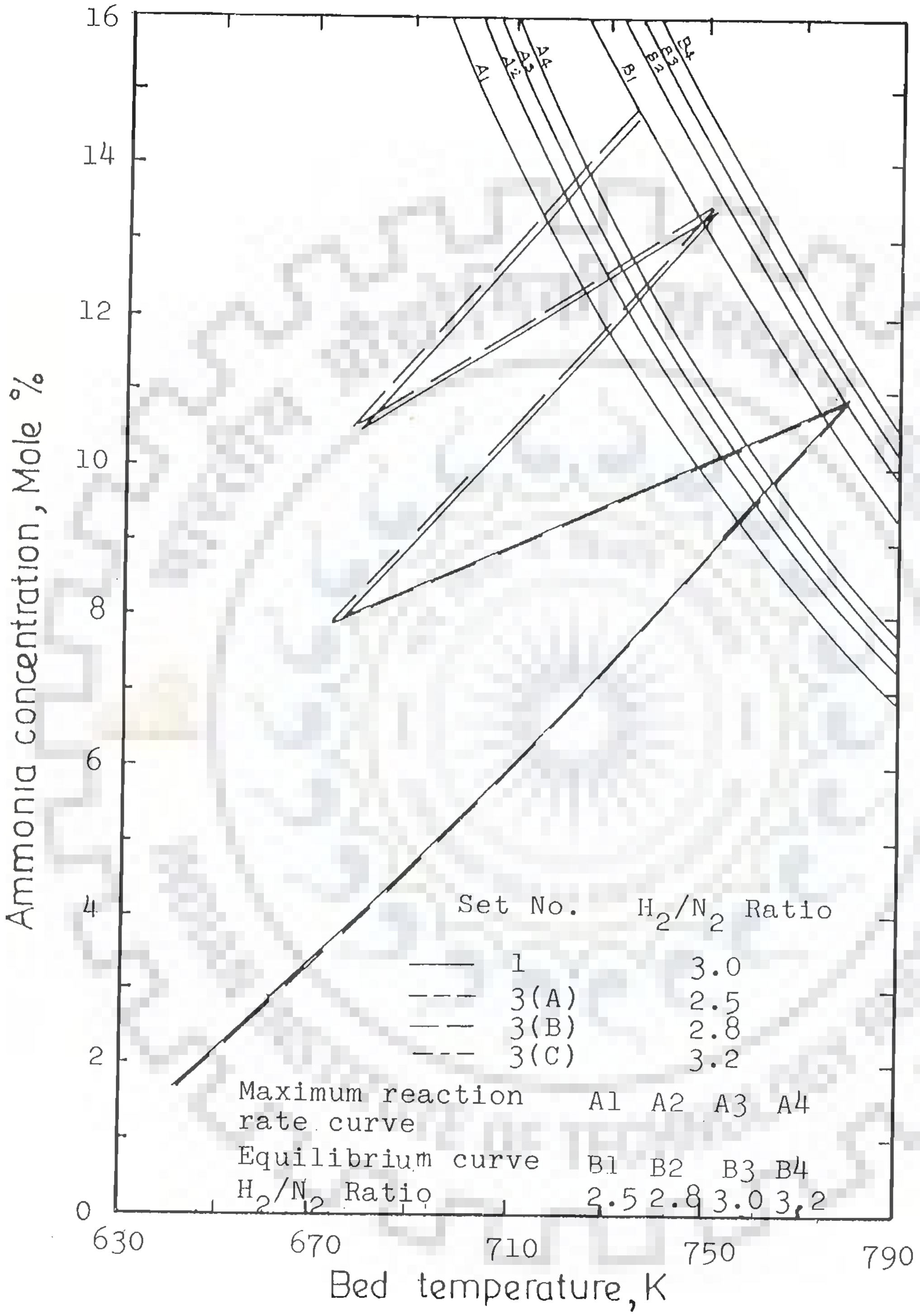

FIG. 7.6 EFFECT OF H_2/N_2 MOLE RATIO ON AMMONIA CONCENTRATION–TEMPERATURE PROFILE IN CATALYST BEDS FOR OPTIMAL COLD SHOT DISTRIBUTION (Base conditions, set No.1, are given in Table 7.2.1)

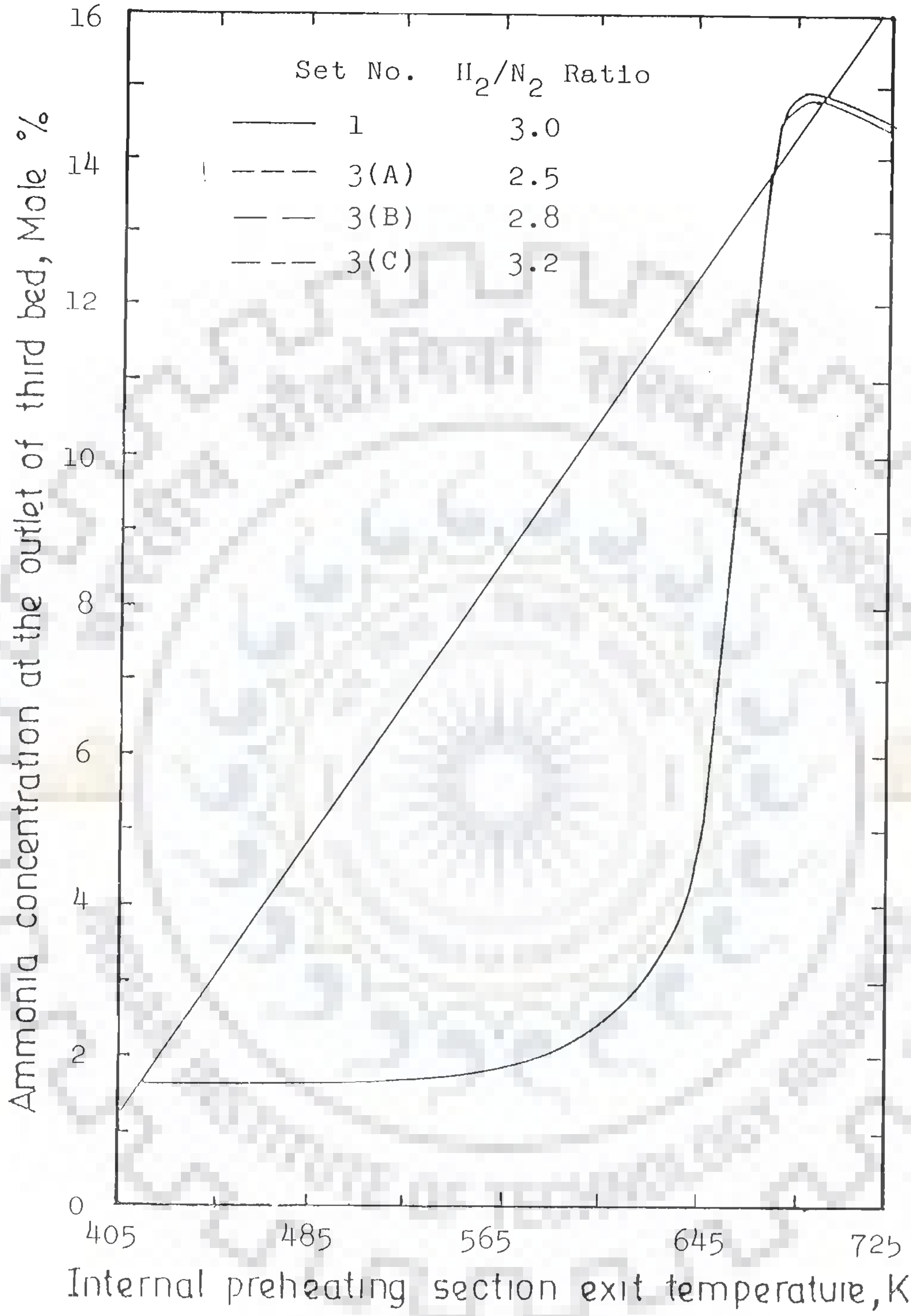

FIG. 7.7 EFFECT OF H_2/N_2 RATIO ON REACTOR OPERATING POINTS AND THEIR STABILITY (Base conditions, set No.1, are given in Table 7.2.1)

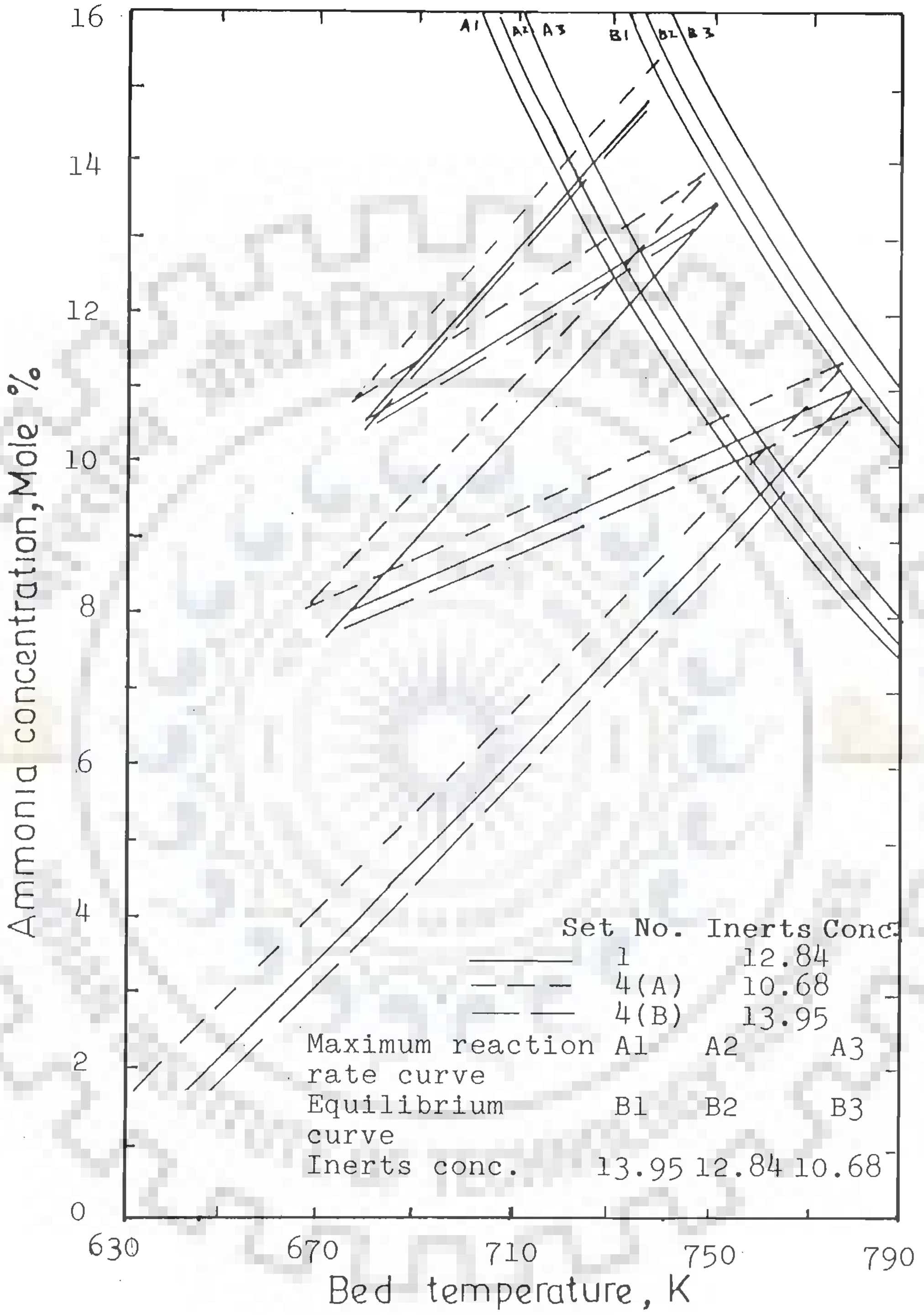

FIG. 7.8 EFFECT OF INERTS CONCENTRATION ON AMMONIA CONCENTRATION-TEMPERATURE PROFILE IN CATALYST BEDS FOR OPTIMAL COLD DISTRIBUTION (Base conditions, set No.1, are given in Table 7.2.1)

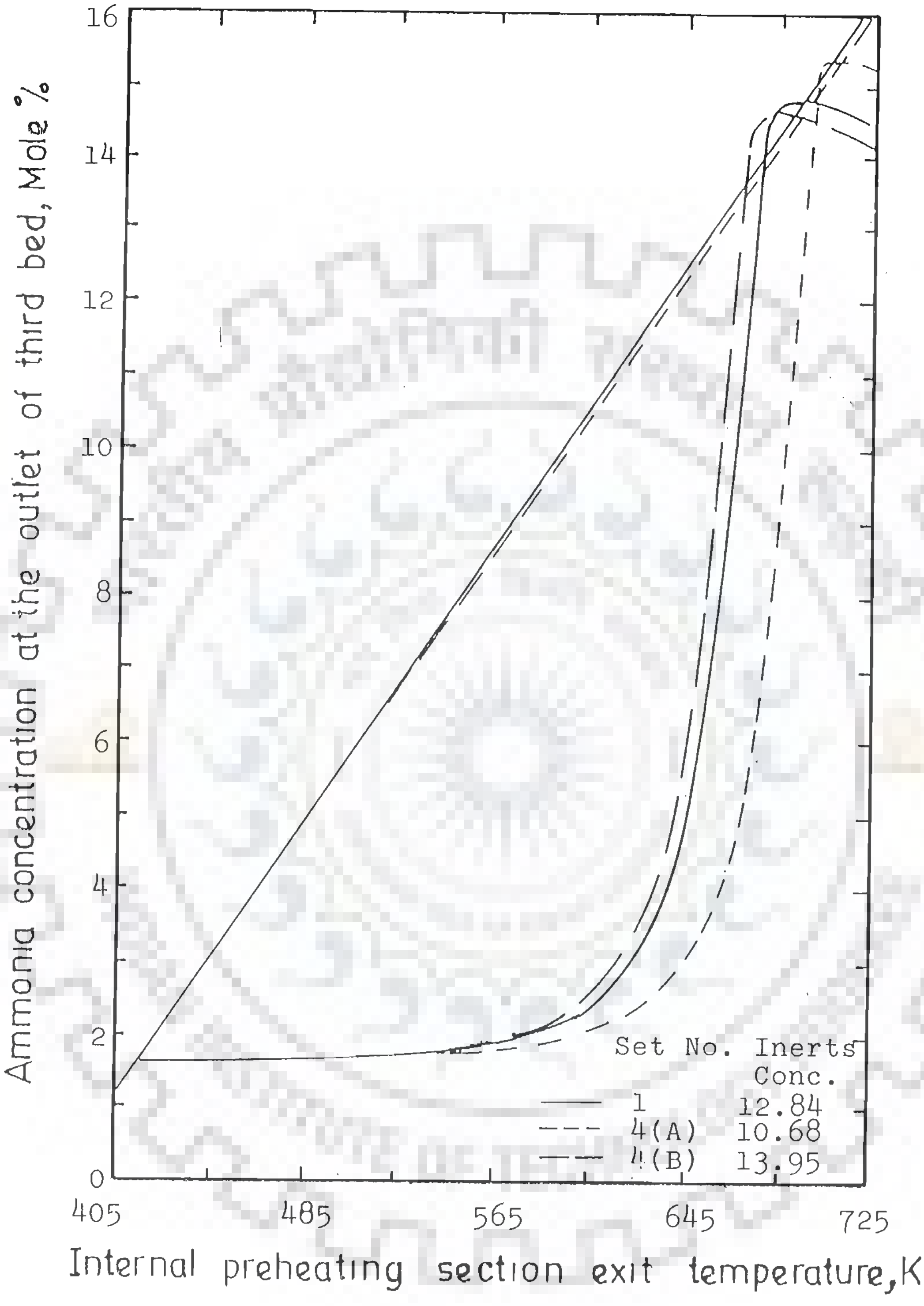

FIG. 7.9 EFFECT OF INERTS CONCENTRATION ON REACTOR OPERATING POINTS AND THEIR STABILITY (Base conditions, set No.1, are given in Table 7.2.1)

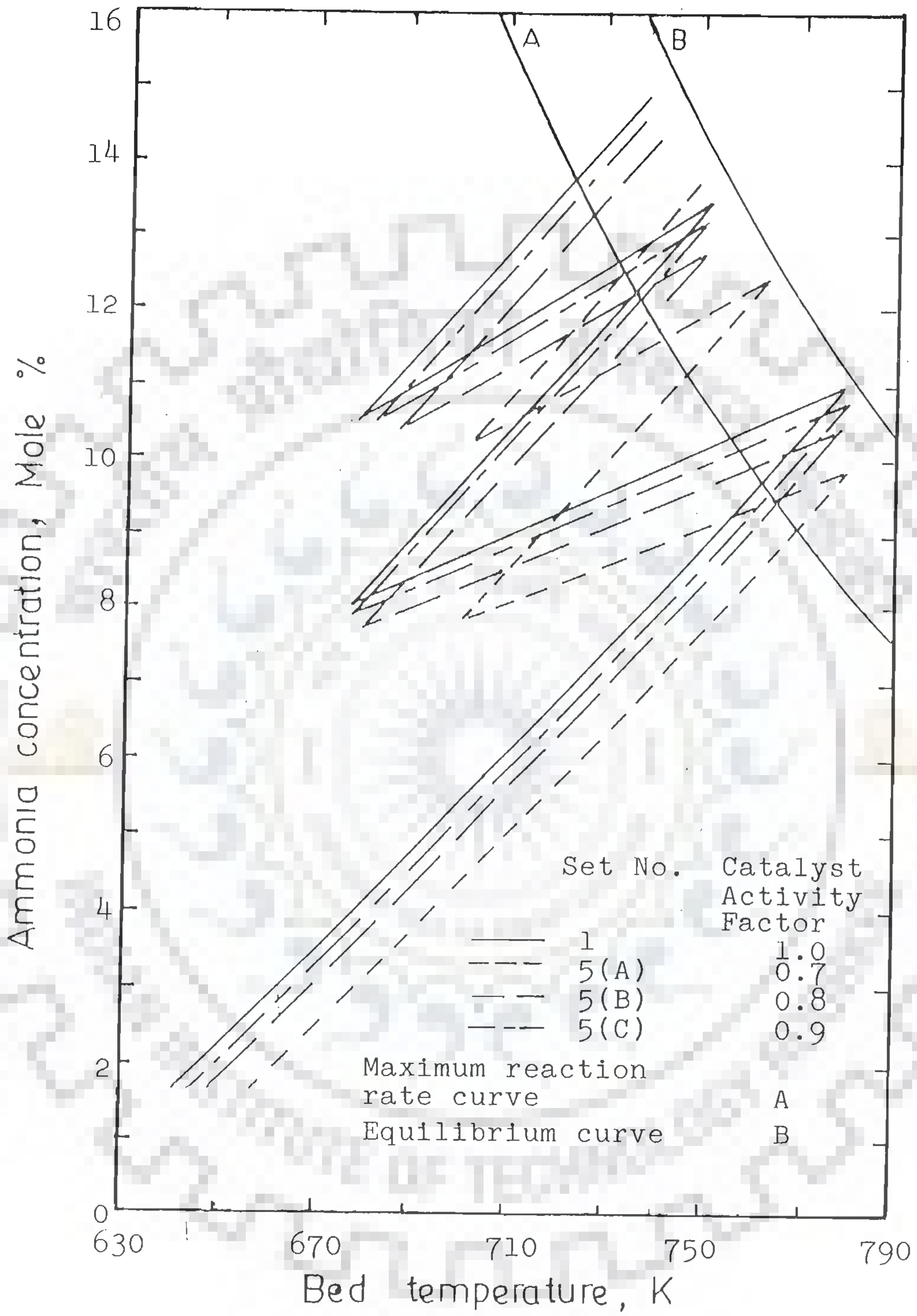

FIG. 7.10 **EFFECT OF CATALYST ACTIVITY FACTOR ON AMMONIA CONCENTRATION-TEMPERATURE PROFILE** IN CATALYST BEDS FOR OPTIMAL COLD SHOT DISTRIBUTION (Base conditions, set No.1, are given in Table 7.2.1)

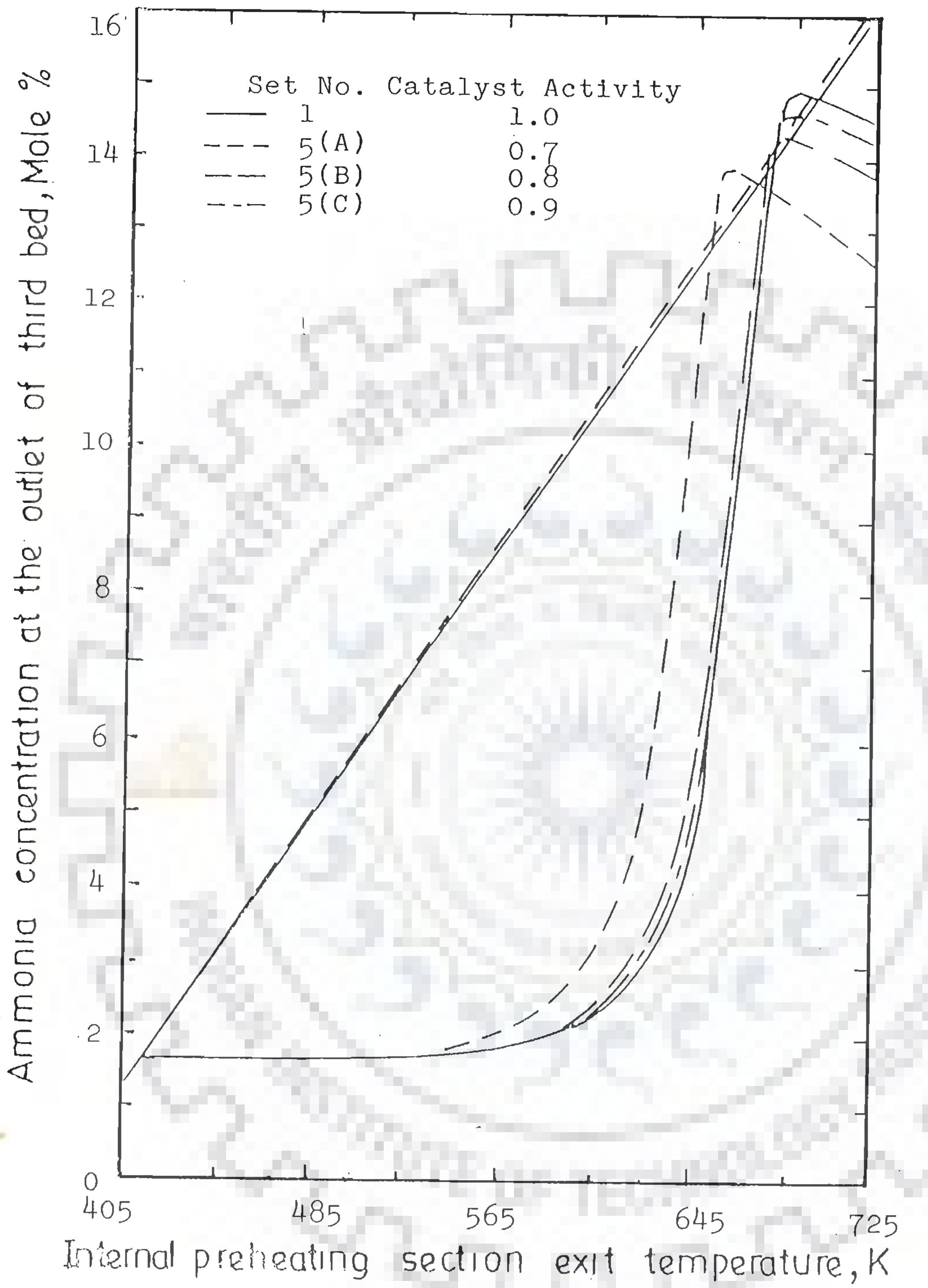

FIG. 7.11 EFFECT OF CATALYST ACTIVITY FACTOR ON REACTOR OPERATING POINTS AND THEIR STABILITY (Base conditions, set No.1, are given in Table 7.2.1)

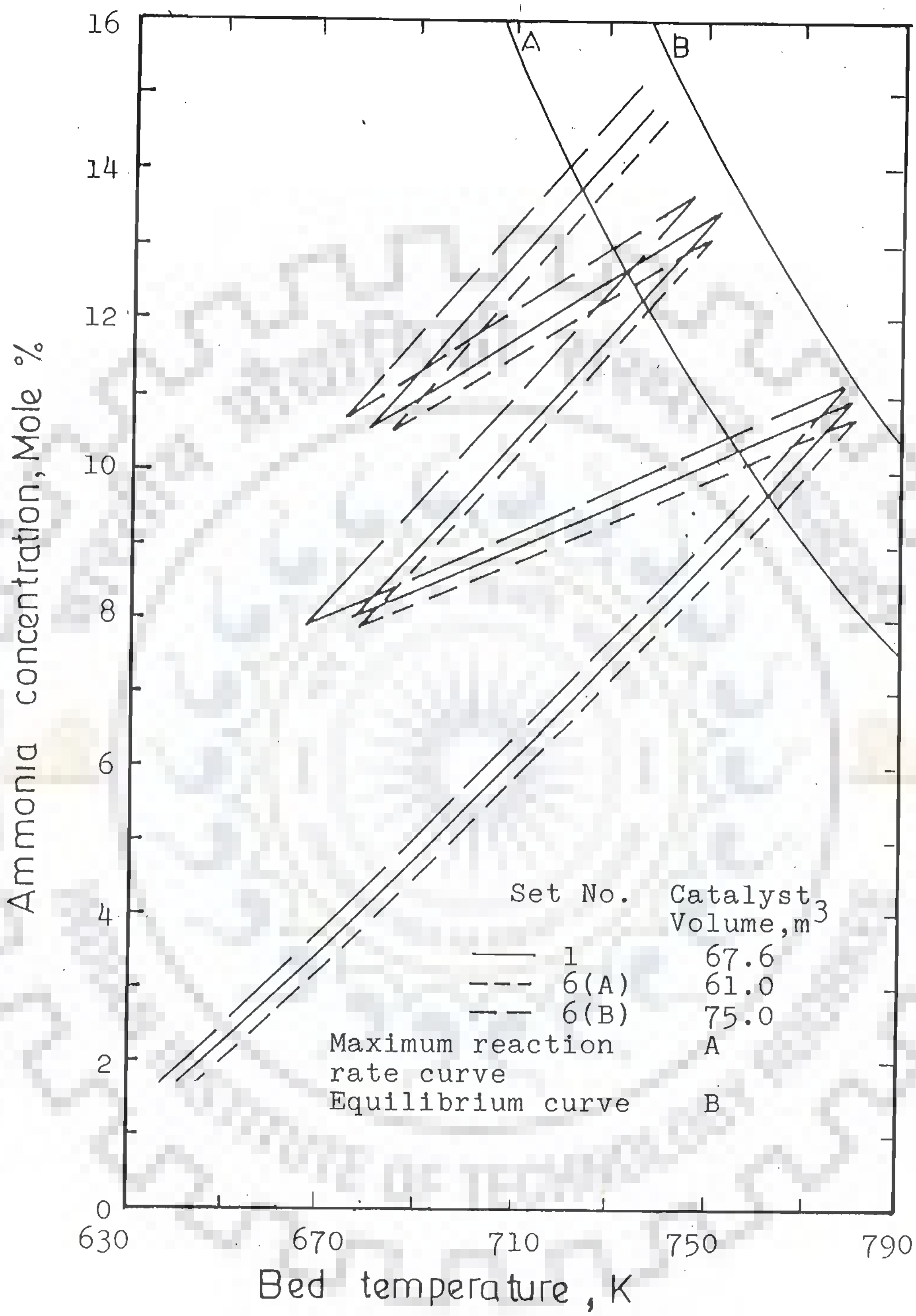

FIG. 7.12 EFFECT OF CATALYST VOLUME ON AMMONIA CONCENTRATION-TEMPERATURE PROFILE IN CATALYST BEDS FOR OPTIMAL COLD SHOT DISTRIBUTION (Base conditions, set No.1, are given in Table 7.2.1)

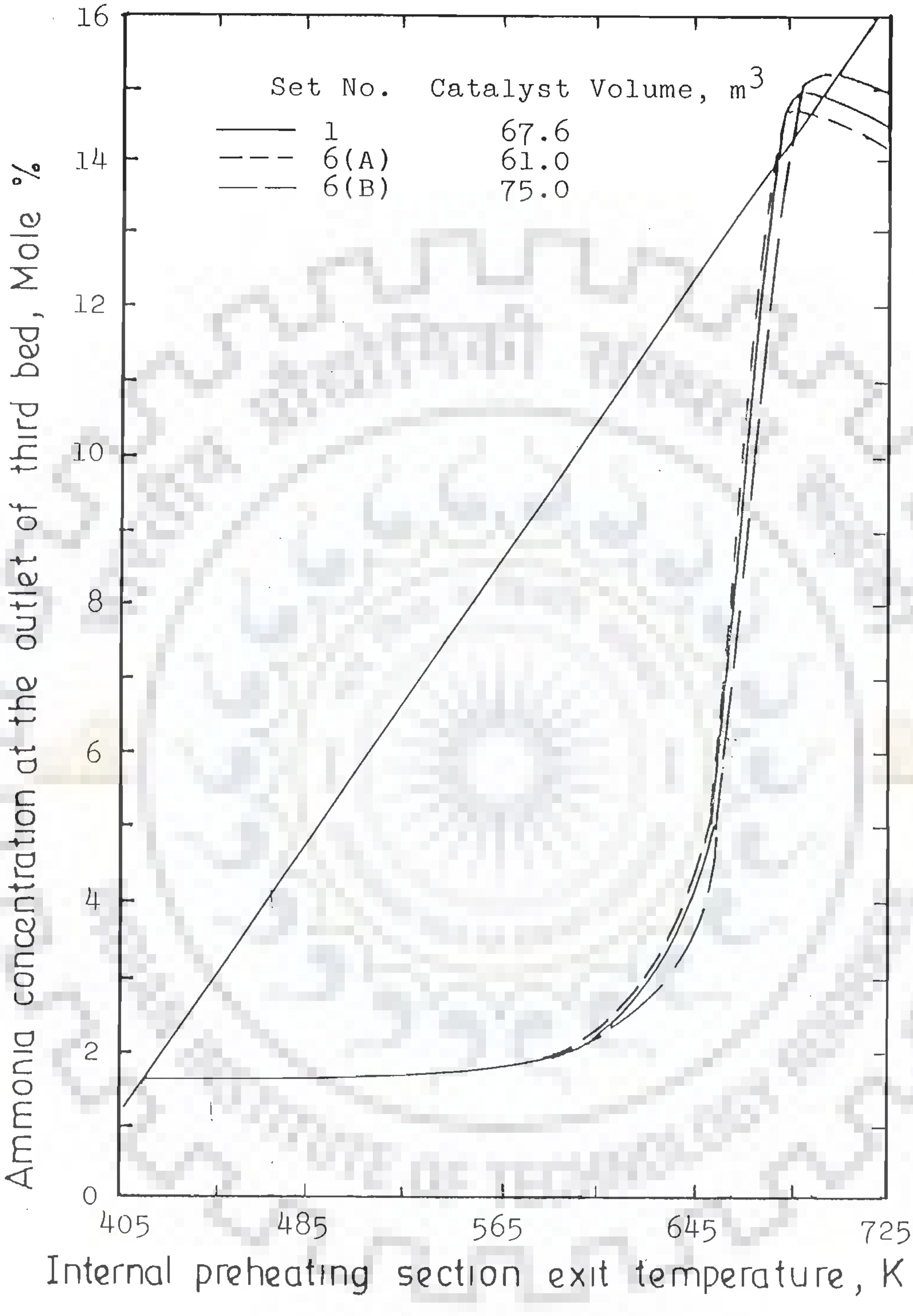

FIG. 7.13 EFFECT OF CATALYST VOLUME ON REACTOR OPERATING POINTS AND THEIR STABILITY (Base conditions, set No.1, are given in Table 7.2.1)

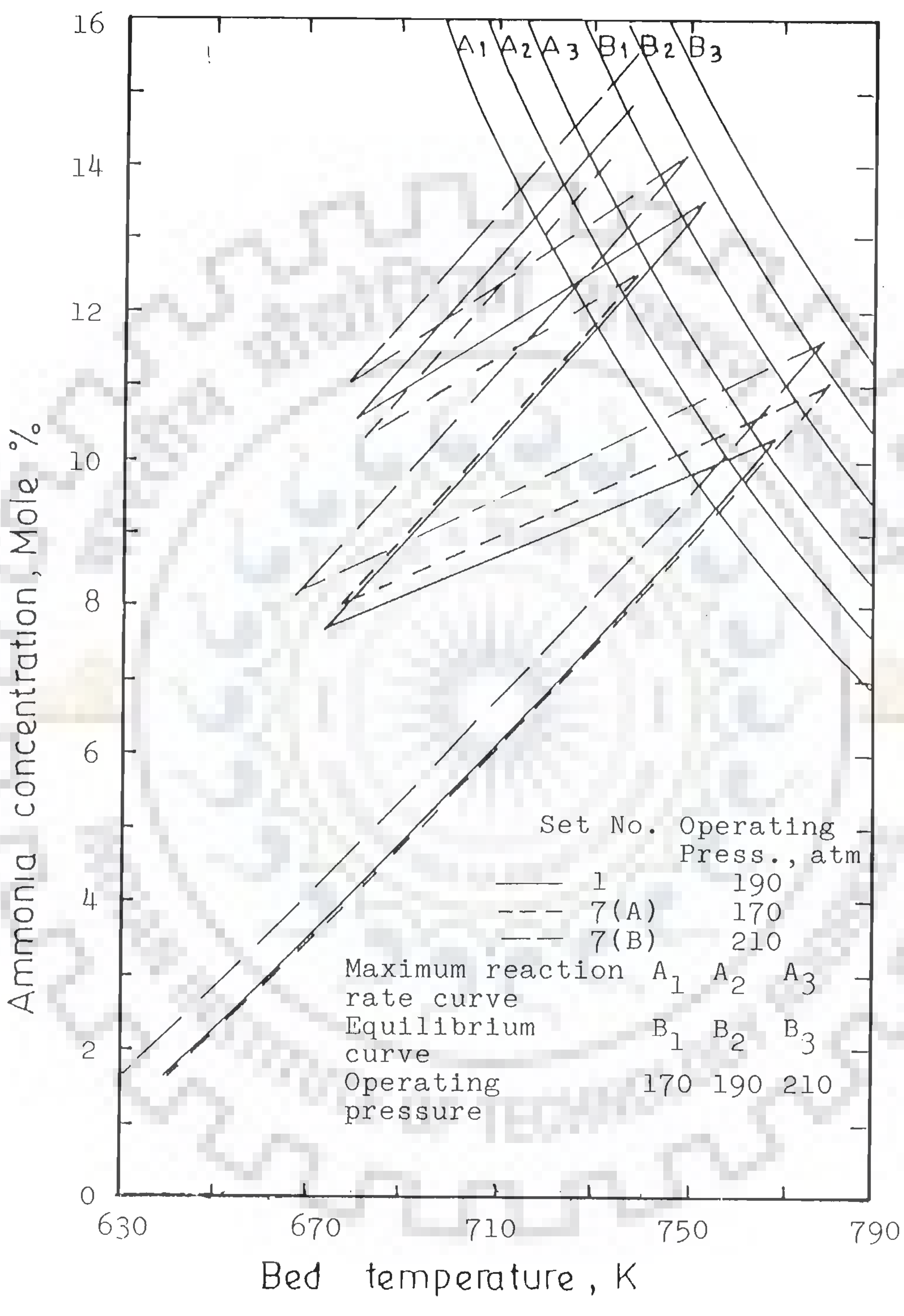

FIG. 7.14 EFFECT OF OPERATING PRESSURE ON AMMONIA CONCENTRATION-TEMPERATURE PROFILE IN CATALYST BEDS FOR OPTIMAL COLD SHOT DISTRIBUTION (Base conditions, set No.1, are given in Table 7.2.1)

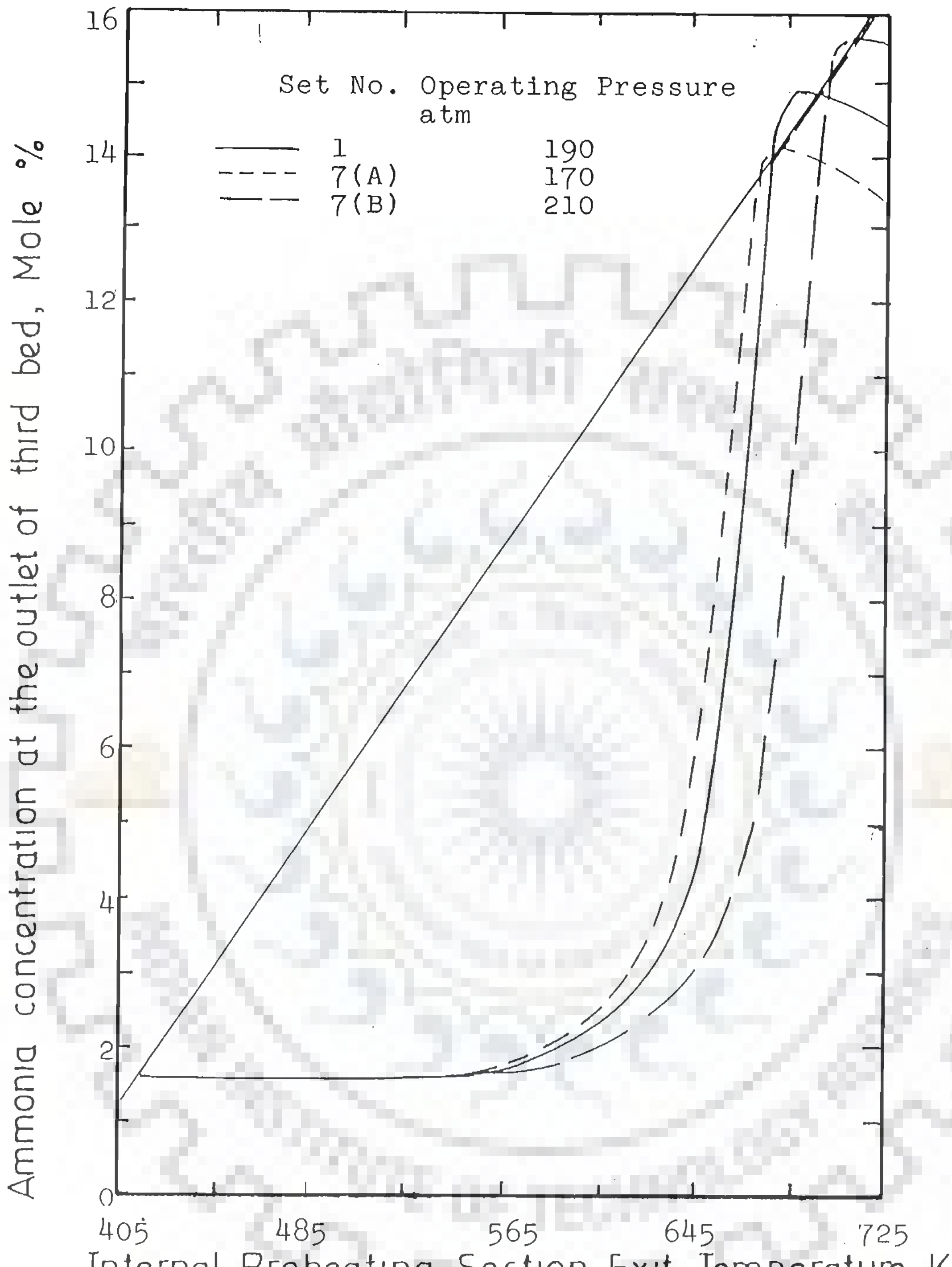

FIG. 7.15 EFFECT OF OPERATING PRESSURE ON REACTOR OPERATING POINTS AND THEIR STABILITY (Base conditions, set No.1, are given in Table 7.2.1)

For set No. 0 and 1 Table A.1 and Figures 7.1 give the detailed temperature and ammonia concentration profiles for each of the three beds in the reactor. Figure 7.2 shows the changes in the ammonia concentration as a function of the temperature in each of the three beds in the reactor along with the changes in ammonia concentration at the equilibrium conditions and also at the maximum reaction rate conditions at different bed temperatures. Further from Fig. 7.2 the variations in the actual temperature and ammonia concentration conditions in the bed can be clearly seen vis-a-vis equilibrium and maximum rate conditions. Figure 7.2 also helps in identifying the directional changes required for the cold shot distributions for maximizing the ammonia production. Figure 7.3 shows the three steady-state operating points (points of intersection) of the reactor for set No. 0 and 1 on typical heat removal and generation curves used commonly to explain the stability behaviour of the reactor operation. More detailed discussions are given in subsequent subsections.

7.3.1. Strategy of Optimization by Cold Shot Distribution.

As already discussed in chapter IV, in an operating plant with fixed design parameters and pre-specified feed conditions, the variables that are free to be adjusted for maxmizing rate of production of ammonia are the cold shot fraction at the inlet to various beds. In particular, for the type of reactor investigated, these are the three cold shot fractions at the inlet of first, second and third bed, respectively. Therefore, in the present study the cold shot fractions were taken as independent variables for the optimization in order to maximize the rate of production of ammonia.

During the course of optimization computations experience was gained to evolve a two-step procedure to locate optimal cold shot fractions quickly. In the first step, computations were made for, say, 12 iterations. The cold shot values so obtained corresponding to the maximum rate of ammonia production for 12 iterations were readjusted to make the total cold shots about 10 to 20 percent higher. The adjustment of cold shot was done based on the approach of actual ammonia concentration at the outlet of a particular bed to its corresponding equilibrium value (shown in Table A.1 under column 6 and 10 for set No.0 and 1 respectively). In case the ratio of actual to equilibrium ammonia concentration at the outlet of a particular bed is found to be between 0.95 to 1.00, the cold shot to that bed inlet was correspondingly increased. This was done considering the presence of equilibrium inhibition due to low cold shot value. On the other hand if the actual to equilibrium concentration ratio is below 0.95, the cold shot fraction is correspondingly decreased. The value of the ratio of actual to equilibrium ammonia concentration at the outlet of a bed around 0.95 for optimal is also supported by the observations of Gaines (1977).

With the new adjusted value of cold shot fractions as starting point it was possible to locate optima within 12 to 17 iterations. This strategy proved to be very efficient and the CPU time required for locating the true optima was cosiderably reduced. The number of iterations obviously depended on the closeness of starting point to the optima. The optimal cold shot fractions at the inlet of the first, second and the third bed are found to be 0.110, 0.233 and 0.232, respectively, for the base conditions as given in Table A.1 set No.1.

7.3.2. Temperature Profile

For the base conditions, set No. 0 and 1, Figure 7.1 shows the profiles for the bed temperature (in K) and ammonia concentration (in mol percent) of the three bed quench-type ammonia synthesis reactor considered for this investigation.

The cold shot fractions to the first, second and the third beds for set 0 are 0.000, 0.245, 0.100, respectively. As can be seen from Fig. 7.1, the bed temperature has initially a high and linear rate of increase. However, later the rate of increase in bed temperature decreases successively from the first bed to the third bed. The observed initial rates of increase in bed temperature (in K per unit total percent bed volume) for the first, second and the third bed are 7.7, 3.0 and 1.6 for set No. 0 and 7.1, 2.9 and 1.5 for set 1, respectively. The initial linear rise in temperature is due to the fact that rate of reaction is not being inhibited by equilibrium, as equilibrium concentration is much higher compared to actual concentration, as is evident from Table A.1 under column 6 and 10. It is well known that the addition of cold shot at the point where reaction is equilibrium inhibited results in increasing the conversion as observed in case of set 0 and set 1 from Figure 7.1 and Table A.1. Addition of cold shot at the first, second and the third bed results in an increase in ammonia conversion. The optimal cold shot distribution for set 1 resulted in somewhat lower rate of temperature rise as a result of lower bed inlet temperatures. The decrease in the rate of temperature rise from the first to the third bed was due to the fact that ammonia concentrations of the gas become higher as one moves from the first to the third bed inlet.

In case of set No. 0, base condition with non-optimal cold shot, it is observed from Figure 7.1 that toward the end of first and second bed the temperature profile flattened out earlier than what was observed with set No. 1. This is because inadequate cold shot additions at the inlet of each bed result in a higher bed temperature for set 0 as compared to set 1. The higher bed temperature in set 0 resulted in an early equilibrium inhibition. This effect is much more pronounced in third bed for set 0 where nearly fifty percent of third bed volume is ineffective due to equilibrium inhibition compared to a total absence of equilibrium inhibition conditions in set No. 1.

Based on the above discussion, it is evident that non-optimal cold shot distribution results in higher bed temperature and quicker equilibrium inhibition whereas optimal cold shot lowers the bed temperature and removes equilibrium inhibition. The lower bed temperatures are also good for catalyst life. The maximum temperature was found to be 788.5 K in case of set 0 compared to set 1 value of 779.8 K.

7.3.3. Conversion profile.

The conversion profile for set Nos. 0 and 1 are shown in

Figure 7.1 and the detailed results are given in Table A.1. Columns 4 and 8 of this Table give actual ammonia concentrations while columns 5 and 9 give concentration at maximum rate for set Nos. 0 and 1, respectively. Whereas columns 6 and 10 give concentrations at equilibrium for set Nos. 0 and 1, respectively. Figure 7.2 shows the concentration as a function of the bed temperature as the reaction progresses along the bed. Figure 7.2 also shows maximum reaction rate and equilibrium curves.

As observed for bed temperature profiles, it is also clear from Figure 7.1 that rate of increase in ammonia concentration is initially high and linear. However for set 1, unlike temperature profile, the ammonia concentration increase is more than that for set 0 which resulted in higher conversions in each bed. The concentration of ammonia, in mol percent, for set 1 increases from 1.61 to 10.98, 7.96 to 13.47 and 10.48 to 14.88 in the first, second and the third bed respectively. Whereas the corresponding increase in ammonia concentration for set 0 are 1.61 to 10.32, 7.81 to 12.74 and 11.52 to 13.50, respectively. The use of non-optimal cold shot distributions for set 0 results in higher bed temperatures which in turn lowers the equilibrium concentration causing equilibrium inhibition at the end of the first and the second bed and from the middle of the third bed in the reactor. This further emphasises the need for optimal cold shot distribution to achieve not only maximum ammonia conversion but also lower bed temperatures. The increase in exit ammonia concentration and corresponding rate of ammonia production at optimal cold shot distribution is quite substantial, about 10.3

percent (132.3 t/d) of the simulated base value.

Further, it may be observed from Figure 7.2 and Table A.1 that the ratio of the actual conversion to the equilibrium conversion at the outlet of first, second and third bed are 0.983, 0.957 and 0.947 respectively for set 1 and corresponding values for set 0 are 0.995, 0.985 and 1.00 respectively. It may be noted that when actual conversion becomes extremely close to equilibrium conversion value (ratios of actual to equilibrium conversion values of o.999 to 1), the tolerance limit chosen for H_2 conversion ($5 * 10^{-5}$) for Milne-Predictor-Corrector method is too large to give precise conversion value for next step. Therefore, if actual H_2 conversion at any bed point is $5 * 10^{-5}$ (approximately 0.002 ammonia mol %) or less than the equilibrium conversion, then it is safe to assume that equilibrium conversion value has been achieved. This situation can be observed for last three bed points in the third bed for set 0 in Table A-1.

The set 0 values obviously indicate the need for readjustment of cold shot to establish the optimal, as obtained in set 1, by adopting the strategy given in section 7.3.1. because only 0.083 increase in ammonia mol percent is observed in the last 50 percent of catalyst volume in the third bed.

7.3.4. Performance Analysis at Optimal Operation and General Considerations.

Based on computations for optimization, it was quite significant to observe that the optimal condition is not sharp but instead the region around it is flat. Many more combination of cold shot fractions were possible at which the rate of ammonia production (or the corresponding exit ammonia concentration) was within 0.3 percent of the optimal value. Some such sets of cold shot fractions at the inlet of the first, second and the third beds are (0.092, 0.275, 0.205), (0.110, 0.233, 0.224), (0.085, 0.275, 0.205), (0.085, 0.275, 0.212), (0.110, 0.225, 0.232), and (0.110, 0.233, 0.216) and the corresponding rates of ammonia production are 1417.4, 1417.8, 1415.9, 1415.9, 1415.4 and 1415.0 t/d, rspectively.

However, the increase in any of the cold shot fractions above optimal resulted in quenching of the reaction. In the base case (set 1) it was observed that an increase in magnitude above optimal in any of the cold shot fractions at the inlet of first, second or third bed by 0.002, 0.003 or 0.003 respectively resulted in quenching of the reactor. The computation results for optimal cold shot distribution further showed that the reaction rate values at the exit of a bed and at the inlet of next bed differ significantly. For the base case, the reaction rate values at the outlet of first, inlet of second, outlet of second and inlet of third bed were 22.6, 13.8, 15.3 and 10.5 mol NH_3/s m^3 respectively. However, Kramer and Westerterp (1963a) report that at the optimal cold shot addition the reaction rate values at outlet of a bed should be equal to the rate value at the inlet of the next bed. This could not be substantiated from the present investigations. As discussed in section 7.3.3, the ratio of actual to equilibrium conversion at the outlet of the three beds vary between 0.947 to 0.983 with an average value of 0.962. This is found to substantiate the observations of Gaines (1977) that at optimal condition this ratio should be near about 0.935.

From the computation results of optimization it may be summarised that at the optimal condition the reactor performance improved substantially resulting in considerable increase in rate of ammonia production, decrease in bed temperature and consequent increase in catalyst life. It is also observed from Table A.1 that the total pressure drop across the reactor also decreased substantially. From a value of 2.77 atm for base case (set 0) to 2.26 atm in case of optimal condition, set 1. This is about 18.4 percent reduction and it will result in considerable saving in electrical energy required by the gas recirculation/ booster system.

7.3.5. Reactor Stability.

Figure 7.3 shows the three possible steady-state operating points of the reactor along with S (sigmoid) shaped heat generation curve and a near straight line heat removal curve. The intersections of heat removal line with heat generation curve give the three possible operating points for the reactor. The S-shaped curve for heat generation was obtained by plotting ammonia exit concentrations, % NH_3, (in mol percent) and corresponding grid values of internal preheating section exit temperature, T_{SHE}. The ammonia concentration, % NH_3, and T_{SHE} values were generated during the grid search. For grid search, the range for T_{SHE} was chosen from 600 to 725 K with an interval of 25 K. The grid search is used for converging on actual feed temperature value for a given set of conditions with one set of trial value of cold shot fractions. The procedure is discussed in section 5.1. It may be noted that for any chosen vlaue of T_{SHE}, a corresponding exit ammonia concentration, % NH_3, is obtained by continuing computation up to step 10 (section 5.1). The computed value of % NH_3 is proportional to the heat generation term. The plot of grid points (T_{SHE}, % NH_3) is S-shaped similar to that reported by several other workers (Gaines, 1977; Kramer and Westerterp, 1963b; Reddy and Husain, 1978; Shah, 1967; van Heerden, 1953). The points for heat generation curve (T_{SHE}, % NH_3) for set 0 are (600.0, 4.81), (625.0, 14.20), (650.0, 13.75), (675.0, 13.02), (700.0, 12.31) and (725.0, 11.61), and the corresponding points for set 1 are (600.0, 2.19), (625.0, 2.96), (650.0, 5.07), (675.0, 13.88), (700.0, 14.83), and (725.0, 14.46) respectively. It may be noted that for any assumed value of T_{SHE}, at the end of computation step 10 (section 5.1), the computed temperature of feed entering the external heat exchanger on shell side, T_{SHI}, is obtained. The value of T_{SHI} shall be equal to (within the limit of convergence) the actual feed temperature, T_F, only if T_{SHE} corresponds to one of the possible operating points of the reactor. For establishing all the possible reactor operating points computations had to be continued up to step 13 (section 5.1). As shown in Figure 7.3, the three possible operating points for base case (set 0) are (414.0, 1.61), (618.9, 11.47) and (658.3, 13.50) whereas the corresponding points for set 1 are (414.0, 1.61), (674.9, 13.84) and (695.1, 14.88). The heat removal curve is obtained by joining the three possible operating points by a straight line (since they were found to lie on a straight line) for each set of conditions. The three operating points will also lie on the S-shaped curve as well as heat removal curve. As discussed in section 2.1 and also reported by van Heerden (1953), Shah (1967), Gaines (1977) and others (Kramer and Westerterp, 1963b; Reddy and Husain, 1978), the highest operating point is the desirable and stable operating point for each set of conditions. In case of set 0 and set 1 these are (658.3, 13.50) and (695.1, 14.88), respectively. The two S-shaped curves and heat removal curves are different obviously because of the different reaction paths followed for the two sets 0 and 1 having two different sets of cold shot fractions.

It is observed from Figure 7.3 that the optimal allocation of cold shot results in higher operating point being located nearer to the blowout point on the optimal S-shaped curve as compared to the corresponding locations for non-optimal set 0. This is very much to be expected as the maxima of the S-shaped curve is always nearer the blowout point. It may be further noted that even a small increase in the optimal cold shot fraction at the inlet of any bed (say, two percent) for set 1 will result in quenching. Whereas even large changes in the cold shot fraction at the inlet of any bed (say, fifty percent) for set 0 may still not result in quenching. This further clarifies the relatively poorer stability at optimal cold shot fractions. In the present investigations for optimal cold shot fractions the maxima of the S-shaped curve could not be achieved because it required a further fine tuning of cold shot fractions to such small fractional values that are not feasible to be implemented in the actual plant operation. Therefore, in the present investigations during the search, the cold shot fraction values were rounded off to the third decimal place. This also provides for better reactor stability by moving somewhat away from the blow out point.

It may be, therefore, summarized that operation near optimal will always be at some sacrifice of reactor stability as observed from Figure 7.3 for the two cases of set 0 and set 1. However, this sacrifice pays richly in the form of quite substantial increase in the rate of ammonia production, decrease in bed temperatures with consequent increase in catalyst life and decrease in electrical energy requirements for the gas booster/recirculation system due to decrease in reactor pressure drop.

7.4. Effect of Variations in Design and Operating Parameters on Reactor Performance.

The values chosen for the operation and design parameters for a three bed quench type reactor for ammonia synthesis are given in Table 7.2.1. For studying the effect of variations in the six operating and design parameters, it was considered desirable to vary only one parameter at a time in the range specified in Table 7.2.1, while keeping all the other parameters corresponding to the base condition values. As discussed earlier, it may be noted here that cold shot fraction to each bed inlet in not taken as a pre-specified parameter but is considered as an independent variable for the optimization for any chosen set of conditions. The two additional values of the varying parameter (except for H_2 / N_2 ratio and activity factor), namely, at the minimum and the maximum of the range, were used for obtaining simulation results. For H_2 / N_2 ratio and activity factor one more value within the range (other than the base value) was chosen in addition to minimum and maximum values of the range. These two (or three) computed results along with those obtained for the base conditions form a set for each parameter variation. Each of the six parameters, that were permitted to vary, were treated as an independently varying parameter in order to study the effect of the same. The results of this sensitivity analysis can be very useful in the evolution of optimal conditions for design and operation of the multibed quench-type reactors for ammonia synthesis. The detailed computed results are given in Appendix-A, Tables A.1 to A.7. The summary of the computed results of simulation are given in Tables 7.3.1.1 and 7.3.1.2.

The general trends for changes in bed temperature and conversion in the reactor were similar to those obtained for the base conditions. Thus, further discussion on the same is not considered essential. The effect of the variations in the design and operating parameters can be discussed properly with the help of tabulated results as given in Tables 7.3.1.1, 7.3.1.2, and Appendix-Tables A.1 to A.7, and Figures 7.4 through 7.15.

7.4.1. Feed Gas Flow Rate.

It is observed from Figure 7.4, Tables 7.3.1.1, 7.3.1.2 and A.2 that the decrease in feed gas flow rate by about 10 percent from the base condition value of $0.74 * 10^{6}$ (in cubic meter per hour at N.T.P. conditions) to $0.667 * 10^{6}$ results in an increase in conversion and decrease in bed temperature. The exit ammonia concentration (mol percent) increases to 15.188 (2.07 percent increase from base value). The behaviour is to be expected due to increase in residence time with decrease in flow rate. But the rate of ammonia production decreased by about 8 percent because increase in conversion was not commensurate with the decrease in flow rate. The total pressure drop is found to be 1.83 atm, a reduction of about 20 percent from set 1. As observed from Figure 7.5, there was no noticeable change in reactor stability and it remained nearly the same (slightly better). The effect of increase in flow rate to $0.82 * 10^6$ Nm^3/h (11 percent increase from base value) results in decrease in the conversion and, in general, increase in bed temperature except in the third bed where bed temperature is slightly higher. The rate of ammonia production increases by 9.0 percent due to the combined effect of increase in flow rate and decrease in conversion (1.67 percent decrease from base value). The pressure drop increases by 23 percent to 2.78 atm due to higher flow rate. It is also observed from Figure 7.5 that the stability is nearly the same (slightly poorer). From Figure 7.4 and Table A.2, it may be observed that the ratios of actual to equilibrium ammonia concentration at the first, second and third bed outlets are 0.994, 0.932 and 0.947, respectively with an average value of 0.958. Similar effect of change in feed gas flow rate on reactor performance is reported by Shah (1967), Gaines (1977), Reddy and Husain (1978) and others. About 35 iterations including some quenched ones (no operating point except the trivial low conversion) were required to locate the optimal cold shot distribution in each case. The total cold shot fraction values ranged between 0.313 to 0.614. It is further observed from Table A.2 that the optimal allocation of cold shot fractions to each of the first, second and the third bed showed a declining trend with increase in flow rate. The values of cold shot fractions to each of the bed inlet and the total cold shot fraction for feed gas flow rates of $0.667 * 10^6$,

$0.740 * 10^6$ and $0.820 * 10^6$ Nm^3/h are (0.123, 0.253, 0.234, 0.610), (0.110, 0.233, 0.232, 0.575) and (0.098, 0.230, 0.219, 0.547) respectively. Therefore, the reactor operation at the cold shot values corresponding to optimum conditions of set 1 will result in non-optimal performance in case of decrease in flow rate whereas it will quench the reactor in case of significant increase in flow rate. This emphasises the need for establishing the new optimal cold shot distribution with the help of simulation model if change in feed gas flow rate becomes essential.

7.4.2. H_2/N_2 Ratio in Feed Gas.

It is observed from Figure 7.6, Table 7.3.1.1, 7.3.1.2 and A.3 that the decrease in H_2/N_2 ratio from the base value of 3.0 results in a slight improvement in the third bed outlet ammonia concentration as well as the rate of ammonia production. For H_2/N_2 ratio of 2.5, 2.8, 3.0 (base value) and 3.2 the rate of ammonia production in t/d are 1421.7 (+0.2 percent increase), 1422.4 (+0.23), 1419.2 (0.00) and 1416.2 (-0.20), respectively. The reactor stability as observed from Figure 7.7 also remains essentially the same as the plots nearly overlap each other. The best condition is at a value of H_2/N_2 ratio of 2.8. Similar observations are also reported by other authors including Shah (1967), Gaines (1977) and Reddy and Husain (1978). However, Reddy and Husain found the best value at H_2/N_2 ratio of 2.5 for a single bed reactor with high internal heat exchange capacity that may be due to non-optimal cold shot conditions at the bed inlet.

The optimal cold shot fractions for four H_2/N_2 ratios are also nearly the same. The first, second, third bed and the total cold shot fractions for the H_2/N_2 ratio of 2.5, 2.8, 3.0 and 3.2 are: (0.109, 0.237, 0.236, 0.582); (0.108, 0.240, 0.234, 0.582); (0.110, 0.233, 0.232, 0.575) and (0.108, 0.237, 0.226, 0.571), respectively. Only slight decrease in total cold shots requirement is observed as the H_2/N_2 is increased from 2.8 to 3.2. There is no definite trend in the individual cold shot fraction values because of the reasons already discussed earlier that the region near optimal is flat and there could be other combination of individual cold shot fractions that will be nearly optimal, Therefore it may be summarized that optimal performance is not quite sensitive to changes in H_2/N_2 ratio in the vicinity of 3.0 and plant operation at a value of 3.0 would be desirable from operational point of view. This will then not require continuous adjustments of make up feed gas H_2/N_2 ratio.

7.4.3. Inerts Concentration in Feed Gas.

It is observed from Figure 7.8 and Tables 7.3.1.1, 7.3.1.2 and A.4 that the effect of increase in concentration of mol percent inerts (consisting of methane and argon) from 10.68 to 13.95 with the base value of 12.84 was to decrease the conversion and increase the first bed temperature. However, the second and the third bed temperatures are lower compared to base case. The rate of production were found to be 1467.0, 1419.2 and 1397.1 t/d, respectively, for the three values of the inerts concentration, that is, 10.68, 12.84, and 13.95 mole percent. The increase in inerts lowers the partial pressures of hydrogen and nitrogen and decreases the rate of reaction unless equilibrium inhibition is observed due to high temperature. In such a case, the inerts acting as heat carriers will shift the equilibrium favorably. Similar observations about the effect of change in inerts content on the reactor performance is also reported by Shah (1967), Gaines (1977), Reddy and Husain (1978) and Mansson and Andresen (1986).

The first, second, and the third bed and total cold shot fractions for the inerts concentration of 10.68, 12.84 and 13.95 mol percent are (0.145, 0.250, 0.234, 0.629), (0.110, 0.233, 0.232, 0.575) and (0.089, 0.249, 0.220, 0.558) respectively. Except in the case of second bed cold shot fractions other cold shot fractions do show a trend and the values decrease with increase in inerts. It is observed from Figure 7.9 that the reactor stability somewhat deteriorates with decrease in inerts concentration. However, the increase in pressure drop with the increase in inerts concentration is only marginal.

7.4.4. Catalyst Activity Factor.

It is observed from Figure 7.10 and Tables 7.3.1.1, 7.3.1.2 and A.5 that at the catalyst activity factor values of 0.7, 0.8, 0.9, and 1.0 the rate of ammonia production in t/d was found to be 1312.5, 1366.2, 1395.6 and 1419.2, respectively. The corresponding optimal values of the first, second, third and total cold shot fractions are (0.030, 0.193, 0.192, 0.415); (0.080, 0.232, 0.203, 0.515); (0.096, 0.237, 0.220, 0.553) and (0.110, 0.233, 0.232, 0.575) for the activity factors of 0.7, 0.8, 0.9 and 1.0, respectively. The above also indicates a trend in the variation of the individual and total cold shot fractions. As the activity factor declines the cold shot fraction values also decline, but the decline in total cold shot fractions is not proportional to the decline in activity. This emphasises the fact that with a decline in the catalyst activity a new set of optimal cold shot fraction has to be found and used for getting the maximum advantage (production); otherwise, the reaction will quench or operation may be non-optimal. It is further observed that the total pressure drop increases at optimal cold shot fractions with the decrease in catalyst activity. This increase ranges from 2.0 to 14.0 percent of the base value of 2.26 atm.

The highest bed temperatures are found to be nearly the same with operation at changed activity factors. The stability of the reactor is found to deteriorate with decline in catalyst activity as observed from Figure 7.11.

It may, therefore, be summarised that the reactor may be operated with some loss of production even with used catalyst having lower activity factor. However, the cold shot distributions have to be readjusted to an appropriate lower value found by optimization. It was observed from computations for catalyst activity factor of 0.6 and lower that except for trivial operating point of low conversion no other operating point exists for activity factor of 0.6 and less. It is worthwhile to observe that the readjustment of cold shot distribution at lower optimal values helps in maintaining ammonia production rate close to fresh catalyst conditions even when the decline in catalyst activity factor may be quite significant (for 30 percent decline in catalyst activity factor, the decline in ammonia production rate is only 7.5 percent of the base condition). It may be further observed that after a certain decline in activity factor, say, below 0.7, the catalyst may have to be replaced as economical operation will not be possible. Similar observations about the effect of decline in catalyst activity factor have also been reported by Gaines (1977) and van Heerden (1953).

7.4.5. Total Volume of Catalyst.

It was observed from Figure 7.12 and Tables 7.3.1.1, 7.3.1.2 and A.6 that at the total catalyst volumes of 61.0, 67.6 and 75.0 m^3, the exit ammonia concentration in mol percent were 14.646, 14.880 and 15.184, respectively. This increase in ammonia mole percent is obvious because increase in catalyst volume at constant feed gas flow rate at base value increases the residence time and is analogous to the effect of decrease in feed gas flow rate at constant catalyst volume. The effect of the decrease in feed gas flow rate for a constant total catalyst volume at base value is already discussed in section 7.4.1. The optimal values of the first, second, third bed and the total cold shot fractions are (0.096, 0.239, 0.214, 0.549); (0.110, 0.233, 0.232, 0.575) and (0.120, 0.253, 0.235, 0.608) for the total catalyst volumes of 61.0, 67.6 and 75.0 m^3, respectively. Except for the second bed, the cold shot fractions show an increasing trend with the increase in catalyst volume at constant flow rate. The highest bed temperatures are virtually unchanged. Similar observations have been reported by Mansson and Andresen (1986) about the effect of change in catalyst volume on reactor performance. Figure 7.13 indicates that the stability of the reactor increases slightly with the increase in total catalyst volume.

7.4.6. Feed Gas Pressure (Operating Pressure).

It may be observed from Figure 7.14 and Tables 7.3.1.1, 7.3.1.2 and A.7 that at feed gas pressures (operating pressures) of 170.0, 190.0 and 210.0 atm the respective rates of production of ammonia are 1351.3, 1419.2 and 1495.4 tpd. The highest bed temperature at 170.0 atm is found to be about 20 K lower than that observed at the base value of pressure (190atm), set 1.

The optimal values of the first, second, third and the total cold shot fractions at operating pressures of 170.0, 190.0 and 210.0 atm are (0.089, 0.235, 0.199, 0.523); (0.110, 0.233, 0.232, 0.575) and (0.146, 0.253, 0.231, 0.630), respectively. The first bed and the total cold shot fraction values show an increasing trend with an increase in the operating pressure. It may be emphasised here that the increase in pressure greatly favours ammonia formation, but readjustment of cold shot fraction to a new set of optimal values is essential to keep the reaction away from quenching and also to maximize ammonia production rate. Stability of the reactor is found to improve significantly with increase in operating pressure. Similar observations are reported by Shah (1967), Gaines (1977), and Mansson and Andresen (1986) about the effect of change in operating pressure on reactor performance.

7.4.7. Sensitivity Analysis.

It was observed from the discussions in previous sections that the reactor performance, in particular, conversion to ammonia, is quite sensitive to changes in the parameters of feed gas flow rate, inerts content of feed gas, catalyst activity factor, total volume of the catalyst and operating pressure. The increase in the flow rate or inerts concentration, decrease in the catalyst activity factor, catalyst volume or operating pressure result in significant decrease in exit conversion. The excessive increase in flow rate or inerts will result in quenching effect and the rate of reaction will become so small that the reactor will quench. Similarly a decrease in catalyst activity, catalyst volume or operating pressure will result in quenching of the reactor. The effect of changes in H_2/N_2 ratio studied in the present investigation is found to be quite small and insignificant in nature. A slightly better performance is obtained at the H_2/N_2 ratio of 2.8. However this will require continuous readjustment of make up feed gas H_2/N_2 ratio. This may, therefore, be undesirable from the point of view of plant operation.

For a complex multidimensional problem, sensitivity analysis is a powerful tool to identify the dominant variables. Table 7.4.7 summarizes the effects of various design and operation parameters on ammonia production rate following the procedure discussed by Rudd and Watson (1968).

Table 7.4.7.

Comparison of Parameter Sensitivity.

Parameter	Unit	Base Value	Range of Variation	Sensitivity* Absolute	Sensitivity* Relative
Flow Rate	Nm^3/h	0.740 * 106	$0.667 * 10^6$ to 0.820 * 106	0.170	1.00
H_2/N_2 Ratio	--	3.0	2.5 to 3.2	0.006	0.04
Inerts Concentration	mol %	12.84	10.68 to 13.95	0.048	0.28
Catalyst Activity	--	1.0	0.7 to 1.0	0.060	0.35
Catalyst Volume	m^3	67.6	61.0 to 75.0	0.036	0.21
Operating Pressure	atm	190	170 to 210	0.102	0.60

* Absolute Sensitivity = (fractional change in maximum ammonia production rate at optimal cold shot distribution)/(change in parameter as a fraction of expected range of variation)

Relative Sensitivity = (Absolute sensitivity of parameter)/(Maximum of absolute sensitivities)

It may be observed from the relative sensitivity values given in the last column of the Table 7.4.7 that the maximum ammonia production rate at optimal cold shot distribution is highly sensitive to flow rate and operating pressure with relative sensitivity values as 1.00 and 0.60, respectively. Whereas ammonia production rate is moderately sensitive to catalyst activity factor, inerts concentration and catalyst volume with relative sensitivity values as 0.35, 0.28 and 0.21, respectively. However, ammonia production rate is almost insensitive to H_2/N_2 ratio in the feed and shows a relative sensitivity value of 0.04 only.

7.4.8. General Considerations.

It was observed from the computation results of optimization investigations that the value of individual cold shot fractions was very sensitive to the variations in operating parameters value and there existed, for each bed, an absolute maximum value beyond which the reactor quenched irrespective of the decrease in the cold shot to other beds. This limit for the first bed cold shot fraction is found to vary between 0.03 to 0.16 depending on the parameter varied and its value. For the second and the third bed cold shot fractions this limit was in the range from 0.19 to 0.35.

It was further observed that in general it is best to operate ammonia synthesis reactor near its blowout point to maximize conversion to ammoniaso as to obtian low bed temperatures and reduced pressure drop. However, this means sacrificing in terms of reactor stability. Some compromise, therefore, may be desirable to operate the reactor at cold shot fraction values somewhat lower than the optimal in order to achieve good stability for small unintended perturbations in parameter values. It must be noted here that this compromise is at the cost of reduced rate of ammonia production. Therefore, the cold shot values can not be set much below the optimal to take care of even higher magnitude of disturbances in the parameters taking place in the plant. Rather, it will be more desirable to find the new set of optimal cold shot values for the new parameter values which may now exist as a consequence of higher disturbances, and operate the plant at some what lower cold shot values than the new set of optimal values. As discussed earlier, the region near optimal values of the cold shot fraction is rather flat, therefore a slight lowering of the values of the cold shot fraction from optimal, in order to achieve better reactor stability will result in only a slight decrease in the rate of the ammonia production.

7.5. Conditions for Optimal Design and Operation.

Based on the results of optimization and the discussions presented in the foregoing sections it is observed that the operation of reactor should be maintained at near optimal cold shot distribution corresponding to a given set of values of the parameters. The concentration of inerts should be maintained as low as possible for high ammonia production rate. H_2/N_2 ratio should be kept at 3.0 as reduction to 2.8 gives only a marginal advantage in production rate compared to inconvenience in operation. The feed gas pressure (operating pressure) should be kept as high as permissible by reactor design (mechanical strength) considerations. The catalyst should be discarded after a period of time (about a few years depending upon the catalyst used and its condition) when the activity factor declines by about 20 to 30 percent. The reactor operation at the above conditions will certainly result in significant improvements in ammonia productivity.

CHAPTER-VIII

8. CONCLUSIONS AND RECOMMENDATIONS

8.1. Conclusions.

8.1.1. A realistic, accurate and stable simulation model for a modern multibed quench reactor for ammonia synthesis was developed. The simulation model was tested over a wide range of variations in the design and the operating variables and the model seems to give reliable information on reactor performance. The model is capable of simulating the external and internal heat exchange as well as the addition of cold shot at the inlet of each bed.

8.1.2. A reliable and efficient optimization algorithm was developed for the maximization of ammonia production rate using cold shot distribution as an optimization variable.

8.1.3. The simulation model was validated using plant data of a large capacity three-bed quench reactor. The kinetic and heat exchange rate parameters of the reactor were established. These are:

(i) Frequency factor for the reverse reaction rate constant

$= 4.11482 * 10^{16}$ mol NH_3/s/m^3 catalyst

(ii) Activation energy for the reverse reaction rate constant

= 97622.4 kJ/kmol

(iii) Correction for fugacity coefficient term in the rate equation

= 1.379

(iv) External heat exchange capacity, $(UA)_H$, at feed gas flow rate of $0.74 * 10^6$ Nm^3/h

= 316000 W/K

8.1.4. The cold shot distribution as practiced at the time of plant data collection was found to be nonoptimal resulting in an ammonia production rate of 1286.9 t/d. Merely by using an optimal cold shot distribution without any other change gave an ammonia production rate of 1419.2 t/d - an increase of 10.28 percent over the prevalent ammonia production rate of the plant.

8.1.5. For an existing ammonia plant, the adjustment of cold shot distribution to an optimal value appears to be the most practical and powerful choice for the maximization of ammonia production rate. The simulation model developed in the course of this investigation can play a vital role for achieving the above objective.

8.1.6. The effect of variation of six design or operating parameters, namely, feed gas pressure, feed gas flow rate, H_2/N_2 ratio in feed gas, inerts concentration in feed gas, catalyst activity factor and catalyst volume, was studied. The simulated results showing the effect of these parameters on optimal cold shot distribution and ammonia production rate are summarized in Table 7.3.1.1. Variations in H_2/N_2 ratio appears to have insignificant effect on reactor performance and, therefore, use of H_2/N_2 ratio of 3 is recommended.

8.1.7. The simulated results in Table 7.3.1.1. clearly indicate that the undesirable effect of adverse variation in parameter values can be greatly minimized by the adjustment of cold shot distribution to a new optimal value for any change in parameter values. It is significant to note that loss in ammonia production rate is restricted to about 7.52, 1.56 and 4.78 percent for a decrease in catalyst activity, catalyst volume and operating pressure by 30, 9.76 and 10.52 percent of the base values, respectively.

8.1.8. Conditions of steady-state stability were established for the first time for a three-bed quench-type ammonia synthesis reactor at optimal cold shot distribution corresponding to maximum ammonia production rate for wide variation in parameter values. In all the cases, it was found that the highest ammonia production rate could be achieved at conditions close to blowout point.

8.1.9. For optimal operation close to blowout point even pressure drop and catalyst bed temperatures were found to be lower with consequent decrease in energy requirement for gas booster/ recirculation system and increase in catalyst life.

8.1.10. Stability consideration dictate that the reactor be operated slightly away from the blowout point in order to ensure good stability even when some unintended small perturbations in parameter values occur. Reduction in ammonia production rate for such an operation is likely to be insignificant (probably less than 0.5 percent) because the optimal conditions are not very sharp and region around them appears to be flat in nature.

8.2. Recommendations.

8.2.1. It is recommended that the results of this study must be implemented on the plant for which the simulation model was developed.

8.2.2. Similar studies must be carried out for other industrial reactors including radial flow reactors for ammonia synthesis.

8.2.3. All ammonia synthesis reactors should have facilities for precise measurement and control of cold shot fraction at the inlet of each bed in addition to the facilities for the precise temperature and possibly ammonia concentration measurements at the inlet and the outlet of each bed.

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APPENDIX-A

TABLE NO.A.1.

COMPUTED PROFILES OF AMMONIA MOLE PERCENT AND TEMPERATURE IN THE BED FOR DIFFERENT COLD SHOT DISTRIBUTIONS

		Set No. 0, Base condition				Set No.1, Base condition with optimal cold shots			
Bed Pt. No.	% Of Total Cata-lyst Volume	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equil-ibrium	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equil-ibrium
1	2	3	4	5	6	7	8	9	10
1	0.0	658.3	1.613	23.765	28.519	640.1	1.613	27.320	32.121
11	2.3	673.2	2.543	21.096	25.750	652.4	2.377	24.903	29.683
21	4.5	689.0	3.542	18.510	23.002	665.5	3.200	22.482	27.197
31	6.8	706.3	4.666	15.942	20.201	679.9	4.126	19.989	24.576
41	9.1	725.6	5.941	13.434	17.398	696.3	5.193	17.409	21.810
51	11.4	746.1	7.333	11.147	14.755	714.8	6.428	14.805	18.943
56	12.5	756.1	8.024	10.162	13.592	724.9	7.107	13.543	17.514
61	13.6	765.3	8.662	9.336	12.606	735.1	7.814	12.335	16.141
66	14.8	772.9	9.203	8.695	11.827	745.4	8.523	11.240	14.860
71	15.9	778.7	9.619	8.235	11.261	754.9	9.195	10.290	13.744
76	17.0	782.8	9.908	7.930	10.887	763.2	9.782	9.532	12.842
81	18.2	785.3	10.092	7.739	10.655	769.6	10.246	8.980	12.170
86	19.3	786.9	10.203	7.632	10.516	774.2	10.574	8.606	11.717
91	20.5	787.7	10.266	7.568	10.439	777.1	10.785	8.378	11.439
95	21.4	788.1	10.296	7.539	10.403	778.5	10.891	8.265	11.298
98	22.0	788.4	10.311	7.525	10.382	779.3	10.945	8.205	11.225
101	22.7	788.5	10.321	7.515	10.372	779.8	10.983	8.166	11.178
1	22.7	692.9	7.806	17.887	22.324	675.4	7.963	20.739	25.371
11	25.9	702.6	8.474	16.454	20.764	683.4	8.519	19.398	23.952
21	29.1	712.9	9.190	15.033	19.194	692.2	9.125	18.022	22.476
31	32.3	723.4	9.937	13.684	17.677	701.5	9.781	16.631	20.960
41	35.5	733.7	10.675	12.468	16.283	711.3	10.477	15.267	19.458
51	38.6	743.0	11.348	11.454	15.111	721.1	11.189	13.984	18.022
56	40.2	747.0	11.640	11.038	14.627	725.9	11.538	13.396	17.351
61	41.8	750.4	11.895	10.691	14.220	730.5	11.873	12.852	16.728
66	43.4	753.3	12.110	10.408	13.880	734.8	12.187	12.361	16.169
71	45.0	755.7	12.285	10.183	13.613	738.6	12.474	11.932	15.671
76	46.6	757.6	12.422	10.009	13.407	742.0	12.727	11.570	15.245
81	48.2	759.0	12.530	9.872	13.245	744.9	12.943	11.266	14.894
86	49.8	760.1	12.610	9.775	13.126	747.3	13.122	11.017	14.605
91	51.4	760.9	12.669	9.699	13.040	749.2	13.267	10.825	14.379
95	52.6	761.3	12.705	9.659	12.986	750.5	13.359	10.701	14.231
98	53.6	761.6	12.726	9.634	12.960	751.2	13.417	10.629	14.143
101	54.5	761.9	12.744	9.608	12.933	751.9	13.466	10.562	14.066
1	54.5	729.6	11.522	12.917	16.809	678.3	10.476	20.214	24.818
11	59.1	739.2	12.226	11.837	15.559	685.0	10.954	19.110	23.649
21	63.6	746.4	12.764	11.074	14.666	692.1	11.463	18.004	22.450
31	68.2	751.1	13.115	10.603	14.110	699.4	11.996	16.901	21.257
41	72.7	753.8	13.314	10.341	13.804	706.8	12.544	15.835	20.086
51	77.3	755.1	13.416	10.208	13.646	714.1	13.086	14.844	18.985
56	79.5	755.5	13.445	10.173	13.602	717.6	13.347	14.390	18.469
61	81.8	755.8	13.466	10.147	13.570	721.0	13.596	13.962	17.992
66	84.1	755.9	13.478	10.127	13.548	724.1	13.831	13.581	17.554
71	86.4	756.1	13.488	10.111	13.532	726.9	14.047	13.234	17.166
76	88.6	756.1	13.493	10.106	13.521	729.5	14.241	12.927	16.814
81	90.9	756.2	13.498	10.096	13.510	731.7	14.414	12.665	16.511
86	93.2	756.2	13.499	10.096	13.510	733.7	14.562	12.441	16.254
91	95.5	756.2	13.501	10.091	13.505	735.3	14.689	12.250	16.038
95	97.3	756.2	13.502*	10.086	13.499	736.4	14.775	12.128	15.891
98	98.6	756.2	13.500*	10.086	13.499	737.2	14.830	12.043	15.801
101	100.0	756.2	13.502*	10.086	13.499	737.8	14.880	11.975	15.716

	Set No. 0	Set No. 1
Total Pressure Drop, atm	2.77	2.26
Cold Shot Distribution:		
First Bed	0.000	0.110
Second Bed	0.245	0.233
Third Bed	0.100	0.232
Total	0.345	0.575

* These values should be read as 13.499, that is equal to equilibrium value.

TABLE NO.A.2

COMPUTED PROFILES OF AMMONIA MOLE PERCENT AND TEMPERATURE IN THE BED FOR DIFFERENT FEED FLOW RATES

Set No. 2(A), Flow rate = 0.667 — Set No. 2(B), Flow rate=0.820

Bed Pt. No.	% Of Total Catalyst Volume	Bed Temp. (K)	NH3 Mole % Actual	NH3 Mole % At Max. Rate	NH3 Mole % At Equilibrium	Bed Temp. (K)	NH3 Mole % Actual	NH3 Mole % At Max. Rate	NH3 Mole % At Equilibrium
1	2	3	4	5	6	7	8	9	10
1	0.0	636.4	1.604	28.075	32.875	641.4	1.607	27.055	31.850
11	2.3	649.6	2.419	25.458	30.245	652.5	2.296	24.877	29.655
21	4.5	663.7	3.309	22.811	27.539	664.2	3.028	22.710	27.429
31	6.8	679.5	4.329	20.056	24.648	676.8	3.835	20.500	25.121
41	9.1	697.9	5.530	17.177	21.561	690.9	4.747	18.221	22.691
51	11.4	719.0	6.944	14.280	18.351	706.6	5.785	15.908	20.165
56	12.5	730.3	7.721	12.895	16.780	715.1	6.355	14.760	18.890
61	13.6	741.7	8.513	11.622	15.312	724.0	6.957	13.635	17.618
66	14.8	752.5	9.273	10.526	14.022	733.2	7.582	12.553	16.391
71	15.9	761.8	9.933	9.659	12.992	742.3	8.214	11.549	15.228
76	17.0	768.8	10.440	9.050	12.255	751.1	8.830	10.650	14.170
81	18.2	773.5	10.780	8.661	11.785	759.1	9.396	9.892	13.267
86	19.3	776.3	10.983	8.437	11.512	765.9	9.880	9.286	12.542
91	20.5	777.8	11.095	8.319	11.366	771.2	10.261	8.840	12.001
95	21.4	778.5	11.145	8.265	11.303	774.4	10.489	8.586	11.690
98	22.0	778.8	11.168	8.240	11.272	776.2	10.619	8.442	11.517
101	22.7	779.0	11.184	8.225	11.251	777.5	10.721	8.334	11.381
1	22.7	665.4	7.826	22.501	27.211	676.8	7.871	20.482	25.101
11	25.9	672.8	8.338	21.182	25.836	684.3	8.382	19.254	23.797
21	29.1	680.9	8.900	19.813	24.393	692.2	8.935	17.998	22.450
31	32.3	689.8	9.517	18.398	22.881	700.7	9.529	16.734	21.071
41	35.5	699.2	10.187	16.964	21.325	709.6	10.158	15.486	19.699
51	38.6	709.2	10.898	15.559	19.783	718.6	10.807	14.291	18.363
56	40.2	714.2	11.262	14.882	19.027	723.1	11.130	13.727	17.729
61	41.8	719.2	11.624	14.236	18.304	727.5	11.447	13.202	17.125
66	43.4	724.0	11.979	13.635	17.624	731.6	11.751	12.713	16.568
71	45.0	728.6	12.318	13.078	16.993	735.5	12.038	12.266	16.055
76	46.6	732.9	12.634	12.585	16.425	739.1	12.302	11.874	15.604
81	48.2	736.7	12.918	12.154	15.931	742.3	12.539	11.533	15.206
86	49.8	740.0	13.166	11.790	15.508	745.1	12.745	11.240	14.866
91	51.4	742.8	13.376	11.496	15.161	747.4	12.920	11.001	14.583
95	52.6	744.6	13.515	11.303	14.938	749.0	13.039	10.841	14.396
98	53.6	745.8	13.603	11.183	14.794	750.0	13.117	10.737	14.269
101	54.5	746.8	13.681	11.074	14.672	750.9	13.184	10.650	14.165
1	54.5	673.7	10.604	21.016	25.663	681.7	10.428	19.638	24.205
11	59.1	680.4	11.085	19.880	24.465	688.2	10.888	18.599	23.098
21	63.6	687.5	11.599	18.724	23.232	694.9	11.373	17.554	21.973
31	68.2	695.0	12.144	17.566	21.985	701.8	11.878	16.528	20.850
41	72.7	702.7	12.709	16.437	20.751	708.8	12.393	15.542	19.759
51	77.3	710.3	13.275	15.373	19.572	715.7	12.900	14.622	18.735
56	79.5	713.9	13.551	14.882	19.027	719.0	13.145	14.198	18.257
61	81.8	717.5	13.815	14.423	18.510	722.1	13.380	13.804	17.811
66	84.1	720.8	14.066	14.000	18.033	725.0	13.601	13.440	17.398
71	86.4	723.8	14.297	13.624	17.607	727.8	13.806	13.110	17.027
76	88.6	726.6	14.506	13.288	17.230	730.2	13.993	12.820	16.688
81	90.9	729.0	14.691	12.997	16.901	732.4	14.160	12.563	16.397
86	93.2	731.1	14.851	12.756	16.620	734.4	14.307	12.340	16.141
91	95.5	732.8	14.986	12.553	16.385	736.0	14.434	12.154	15.925
95	97.3	734.0	15.077	12.414	16.226	737.2	14.521	12.027	15.778
98	98.6	734.8	15.136	12.329	16.129	737.9	14.580	11.943	15.677
101	100.0	735.4	15.188	12.250	16.038	738.6	14.631	11.869	15.592

	Set No. 2(A)	Set No. 2(B)
Total Pressure Drop, atm	1.83	2.78
Cold Shot Distribution:		
First Bed	0.123	0.098
Second Bed	0.253	0.230
Third Bed	0.234	0.219
Total	0.610	0.547

APPENDIX_A

TABLE NO.A.3

COMPUTED PROFILES OF AMMONIA MOLE PERCENT AND TEMPERATURE IN THE BED FOR DIFFERENT H_2/N_2 RATIOS

		Set No.3 (A), H2/N2 ratio =2.5				Set No.3 (B), H2/N2 ratio=2.8				Set No.3 (C), H2/N2 ratio=3.2			
Bed Pt. No.	% Of Total Catalyst Volume	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equilibrium	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equilibrium	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equilibrium
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	0.0	640.0	1.614	25.056	29.477	640.6	1.614	26.363	31.019	640.9	1.613	27.953	32.883
11	2.3	652.5	2.395	22.784	27.180	653.4	2.405	23.946	28.580	653.3	2.384	25.454	30.357
21	4.5	665.8	3.234	20.518	24.850	666.9	3.258	21.523	26.086	666.5	3.214	22.948	27.795
31	6.8	680.6	4.131	18.188	22.399	681.9	4.224	19.034	23.465	681.1	4.150	20.372	25.079
41	9.1	697.3	5.277	15.774	19.806	699.0	5.343	16.460	20.692	697.6	5.226	17.718	22.228
51	11.4	716.4	6.553	13.343	17.111	718.5	6.643	13.876	17.827	716.3	6.468	15.054	19.285
56	12.5	726.8	7.256	12.161	15.779	728.9	7.355	12.629	16.415	726.3	7.147	13.766	17.831
61	13.6	737.3	7.985	11.047	14.498	739.6	8.089	11.466	15.074	736.5	7.851	12.545	16.434
66	14.8	747.7	8.709	10.043	13.328	749.9	8.810	10.428	13.860	746.6	8.552	11.440	15.150
71	15.9	757.2	9.381	9.200	12.322	759.2	9.470	9.567	12.840	756.0	9.212	10.492	14.027
76	17.0	765.1	9.947	8.544	11.539	766.9	10.017	8.911	12.050	764.1	9.785	9.740	13.128
81	18.2	771.0	10.373	8.088	10.988	772.5	10.421	8.461	11.502	770.3	10.233	9.192	12.464
86	19.3	775.0	10.658	7.798	10.629	776.1	10.688	8.175	11.154	774.7	10.550	8.821	12.017
91	20.5	777.4	10.833	7.621	10.418	778.4	10.849	8.006	10.945	777.5	10.753	8.594	11.738
95	21.4	778.5	10.917	7.542	10.320	779.4	10.926	7.928	10.848	778.9	10.856	8.483	11.600
98	22.0	779.1	10.958	7.501	10.271	779.9	10.965	7.885	10.802	779.6	10.908	8.423	11.531
101	22.7	779.5	10.937	7.473	10.232	780.3	10.990	7.861	10.772	780.1	10.945	8.387	11.483
1	22.7	672.8	7.899	19.387	23.667	672.3	7.872	20.602	25.120	674.6	7.910	21.485	26.254
11	25.9	680.8	8.419	18.149	22.363	680.1	8.408	19.322	23.769	682.4	8.447	20.143	24.832
21	29.1	689.4	9.052	16.870	20.992	668.5	8.995	17.994	22.353	690.9	9.033	18.758	23.357
31	32.3	698.7	9.708	15.570	19.582	697.6	9.633	16.651	20.897	699.9	9.665	17.363	21.846
41	35.5	708.6	10.409	14.289	18.171	707.2	10.316	15.315	19.434	709.3	10.337	15.989	20.329
51	38.6	718.6	11.132	13.071	16.810	717.1	11.025	14.032	18.006	719.0	11.030	14.681	18.867
56	40.2	723.5	11.490	12.505	16.168	721.9	11.379	13.438	17.330	723.7	11.373	14.071	18.182
61	41.8	728.2	11.835	11.985	15.576	726.7	11.724	12.877	16.696	728.3	11.707	13.507	17.534
66	43.4	732.7	12.161	11.514	15.037	731.1	12.053	12.362	16.113	732.6	12.025	12.986	16.941
71	45.0	736.7	12.459	11.097	14.556	735.3	12.359	11.910	15.586	736.6	12.319	12.523	16.405
76	46.6	740.2	12.723	10.741	14.142	739.0	12.635	11.513	15.123	740.2	12.584	12.119	15.938
81	48.2	743.2	12.949	10.447	13.798	742.2	12.876	11.174	14.735	743.3	12.815	11.781	15.542
86	49.8	745.7	13.137	10.208	13.519	744.9	13.080	10.899	14.410	745.9	13.012	11.499	15.212
91	51.4	747.7	13.288	10.023	13.302	747.2	13.247	10.675	14.150	748.0	13.173	11.276	14.952
95	52.6	749.0	13.384	9.902	13.163	748.6	13.357	10.534	13.983	749.4	13.279	11.128	14.777
98	53.6	749.8	13.445	9.830	13.076	749.5	13.426	10.443	13.876	750.3	13.346	11.038	14.670
101	54.5	750.5	13.496	9.772	13.004	750.3	13.485	10.367	13.790	751.1	13.403	10.959	14.580
1	54.5	676.0	10.448	18.858	23.112	676.5	10.465	19.878	24.361	679.6	10.505	20.583	25.307
11	59.1	682.6	10.925	17.836	22.028	683.0	10.936	18.818	23.233	686.3	10.984	19.462	24.109
21	63.6	689.7	11.433	16.804	20.921	690.0	11.437	17.736	22.075	693.4	11.491	18.331	22.890
31	68.2	697.0	11.969	15.774	19.800	697.2	11.965	16.668	20.915	700.6	12.022	17.210	21.675
41	72.7	704.5	12.521	14.772	18.705	704.7	12.509	15.624	19.771	708.0	12.565	16.134	20.490
51	77.3	711.9	13.070	13.835	17.664	712.0	13.053	14.643	18.689	715.2	13.100	15.139	19.377
56	79.5	715.5	13.336	13.405	17.183	715.5	13.317	14.193	18.179	718.7	13.356	14.681	18.867
61	81.8	718.9	13.591	13.004	16.728	718.9	13.571	13.769	17.707	721.9	13.601	14.255	18.385
66	84.1	722.0	13.831	12.632	16.314	722.1	13.811	13.379	17.267	725.0	13.830	13.871	17.949
71	86.4	725.0	14.052	12.302	15.941	725.0	14.034	13.024	16.865	727.7	14.041	13.523	17.558
76	88.6	727.6	14.253	12.015	15.608	727.7	14.237	12.713	16.510	730.2	14.230	13.221	17.210
81	90.9	729.9	14.430	11.759	15.319	730.1	14.418	12.441	16.197	732.4	14.396	12.958	16.906
86	93.2	731.9	14.585	11.544	15.069	732.1	14.576	12.206	15.929	734.3	14.540	12.740	16.655
91	95.5	733.6	14.715	11.365	14.862	733.9	14.711	12.014	15.707	735.9	14.662	12.556	16.440
95	97.3	734.8*	14.804*	11.245	14.725*	735.1	14.804	11.879	15.552	737.0	14.744	12.431	16.295
98	98.6	735.6*	14.863*	11.166	14.630*	735.9	14.865	11.791	15.453	737.7	14.798	12.350	16.203
101	100.0	736.2*	14.914*	11.097	14.551*	736.6	14.918	11.719	15.365	738.3	14.845	12.280	16.122
Total Pressure Drop, atm					2.25		2.25				2.27		
Cold Shot Distribution:													
First Bed					0.109		0.108				0.108		
Second Bed					0.237		0.240				0.237		
Third Bed					0.236		0.234				0.226		
Total					0.582		0.582				0.571		

* Values should correspond to equilibrium values.

APPENDIX_A

TABLE NO.A.4

COMPUTED PROFILES OF AMMONIA MOLE PERCENT AND TEMPERATURE IN THE BED FOR DIFFERENT INERTS CONCENTRATIONS

Set No.4(A), Inerts concentration=10.68 Set No.4(B), Inerts Conc. =13.95

Bed Pt. No.	% Of Total Cata-lyst Volume	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equil-ibrium	Bed Temp. (K)	NH3 Mole % Actual	At. Max. Rate	At Equil-ibrium
1	2	3	4	5	6	7	8	9	10
1	0.0	629.9	1.613	30.779	35.775	645.6	1.613	25.620	30.306
11	2.3	640.7	2.268	28.466	33.483	659.2	2.463	23.076	27.720
21	4.5	652.2	2.974	26.109	31.104	673.6	3.380	20.548	25.097
31	6.8	664.9	3.767	23.640	28.565	689.7	4.420	17.978	22.356
41	9.1	679.4	4.683	21.018	25.822	707.9	5.619	15.365	19.507
51	11.4	696.2	5.760	18.257	22.859	728.1	6.986	12.828	16.662
56	12.5	705.5	6.370	16.838	21.309	738.7	7.710	11.661	15.315
61	13.6	715.5	7.029	15.423	19.742	748.9	8.425	10.614	14.096
66	14.8	726.0	7.734	14.037	18.179	758.3	9.086	9.736	13.051
71	15.9	736.9	8.470	12.728	16.673	766.1	9.644	9.055	12.234
76	17.0	747.6	9.204	11.539	15.291	771.9	10.066	8.573	11.651
81	18.2	757.5	9.889	10.534	14.105	775.9	10.352	8.265	11.274
86	19.3	765.7	10.467	9.764	13.179	778.3	10.530	8.076	11.043
91	20.5	771.8	10.902	9.221	12.520	779.7	10.633	7.969	10.915
95	21.4	775.2	11.143	8.933	12.171	780.4	10.682	7.921	10.853
98	22.0	777.0	11.272	8.785	11.992	780.7	10.706	7.896	10.823
101	22.7	778.3	11.365	8.678	11.863	780.9	10.722	7.882	10.802
1	22.7	665.7	7.983	23.488	28.409	670.7	7.642	21.033	25.600
11	25.9	673.0	8.471	22.147	27.015	678.0	8.139	19.822	24.328
21	29.1	680.9	9.009	20.747	25.535	685.8	8.681	18.570	22.994
31	32.3	689.5	9.600	19.298	23.990	694.1	9.266	17.293	21.627
41	35.5	698.8	10.245	17.824	22.392	703.0	9.893	16.021	20.235
51	38.6	708.7	10.937	16.357	20.778	712.1	10.549	14.787	18.863
56	40.2	713.8	11.295	15.642	19.984	716.7	10.881	14.193	18.204
61	41.8	718.8	11.655	14.954	19.212	721.3	11.210	13.633	17.568
66	43.4	723.8	12.013	14.302	18.475	725.7	11.532	13.104	16.968
71	45.0	728.7	12.361	13.690	17.782	729.8	11.839	12.617	16.414
76	46.6	733.2	12.691	13.141	17.145	733.7	12.127	12.176	15.909
81	48.2	737.4	12.994	12.651	16.585	737.3	12.390	11.791	15.464
86	49.8	741.1	13.265	12.226	16.094	740.4	12.622	11.459	15.078
91	51.4	744.3	13.499	11.879	15.683	743.1	12.823	11.181	14.754
95	52.6	746.4	13.658	11.642	15.412	744.9	12.960	10.997	14.536
98	53.6	747.8	13.761	11.497	15.240	746.1	13.050	10.874	14.394
101	54.5	749.0	13.851	11.368	15.085	747.1	13.129	10.772	14.275
1	54.5	675.1	10.730	21.743	26.585	678.4	10.377	19.715	24.213
11	59.1	681.9	11.206	20.552	25.325	684.9	10.841	18.676	23.107
21	63.6	689.1	11.717	19.341	24.030	691.7	11.331	17.632	21.984
31	68.2	696.7	12.261	18.118	22.710	698.7	11.844	16.594	20.857
41	72.7	704.6	12.829	16.920	21.398	705.8	12.368	15.592	19.756
51	77.3	712.5	13.403	15.787	20.139	712.8	12.887	14.656	18.723
56	79.5	716.3	13.684	15.257	19.550	716.2	13.137	14.226	18.238
61	81.8	720.0	13.956	14.760	18.992	719.4	13.377	13.826	17.787
66	84.1	723.5	14.214	14.307	18.481	722.3	13.604	13.456	17.373
71	86.4	726.7	14.454	13.897	18.010	725.1	13.813	13.125	16.997
76	88.6	729.6	14.672	13.534	17.597	727.6	14.004	12.828	16.657
81	90.9	732.2	14.865	13.218	17.234	729.8	14.174	12.570	16.363
86	93.2	734.4	15.033	12.948	16.932	731.8	14.323	12.349	16.105
91	95.5	736.3	15.174	12.728	16.673	733.5	14.450	12.161	15.893
95	97.3	737.6	15.270	12.580	16.503	734.6	14.537	12.035	15.748
98	98.6	738.4	15.333	12.482	16.392	735.3	14.596	11.952	15.648
101	100.0	739.1	15.387	12.400	16.292	736.0	14.647	11.879	15.564

	Set 4(A)	Set 4(B)
Total Pressure Drop, atm	2.19	2.29
Cold Shot Distribution:		
First Bed	0.145	0.089
Second Bed	0.250	0.249
Third Bed	0.234	0.220
Total	0.629	0.558

APPENDIX-A

TABLE NO.A.5

COMPUTED PROFILES OF AMMONIA MOLE PERCENT AND TEMPERATURE IN THE BED

FOR DIFFERENT CATALYST ACTIVITIES

	Set NO. 5(A), Catalyst Activity = 0.7					Set No.5(B), Catalyst Activity=0.8				Set No.5(C), Catalyst Activity=0.9			
	% Of Total Catalyst Volume	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equilibrium	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equilibrium	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equilibrium
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	0.0	656.5	1.613	24.107	28.867	647.2	1.613	25.910	30.704	643.9	1.613	26.567	31.369
[illegible]	2.3	667.2	2.278	22.155	26.851	658.1	2.290	23.829	28.588	655.7	2.351	24.270	29.042
21	4.5	678.2	2.970	20.256	24.864	669.4	3.003	21.779	26.459	668.2	3.137	21.991	26.689
31	6.8	689.9	3.713	18.374	22.856	681.6	3.781	19.705	24.283	681.9	4.011	19.662	24.237
41	9.1	702.4	4.528	16.494	20.813	695.0	4.648	17.601	22.016	697.1	5.003	17.282	21.673
51	11.1	716.1	5.424	14.633	18.747	709.8	5.621	15.480	19.693	714.2	6.137	14.888	19.033
56	12.5	723.3	5.903	13.722	17.723	717.7	6.150	14.434	18.522	723.4	6.757	13.717	17.718
61	13.6	730.7	6.401	12.836	16.711	725.9	6.704	13.407	17.369	732.9	7.403	12.590	16.431
66	14.8	738.2	6.911	11.985	15.733	734.3	7.277	12.425	16.243	742.4	8.060	11.543	15.222
71	15.9	745.7	7.427	11.188	14.805	742.8	7.859	11.507	15.172	751.6	8.701	10.609	14.126
76	17.0	753.1	7.936	10.454	13.940	751.0	8.430	10.665	14.192	760.0	9.292	9.821	13.186
81	18.2	760.1	8.422	9.801	13.159	758.6	8.968	9.938	13.326	767.0	9.795	9.195	12.436
86	19.3	766.4	8.868	9.240	12.454	765.4	9.416	9.336	12.601	772.5	10.186	8.740	11.885
91	20.5	771.9	9.256	8.780	11.927	771.0	9.844	8.865	12.033	776.3	10.465	8.433	11.507
95	21.4	775.6	9.519	8.482	11.564	774.5	10.097	8.576	11.680	778.4	10.617	8.269	11.303
[illegible]	22.0	777.9	9.636	8.299	11.340	776.6	10.249	8.408	11.475	779.5	10.699	8.181	11.199
01	22.7	779.9	9.828	8.146	11.152	778.3	10.373	8.274	11.313	780.4	10.761	8.117	11.121
1	22.7	698.1	7.748	17.120	21.499	678.6	7.671	20.195	24.798	675.6	7.812	20.690	25.325
11	25.9	706.3	8.316	15.937	20.195	685.4	8.140	19.075	23.610	683.0	8.314	19.476	24.036
21	29.1	714.9	8.917	14.766	18.896	692.7	8.643	17.934	22.381	690.8	8.857	18.227	22.697
31	32.3	723.8	9.538	13.646	17.636	700.4	9.181	16.780	21.127	699.2	9.443	16.964	21.331
41	35.5	732.5	10.159	12.612	16.454	708.5	9.750	15.637	19.868	707.9	10.065	15.716	19.952
51	38.6	740.7	10.749	11.701	15.401	716.7	10.339	14.534	18.641	716.9	10.709	14.511	18.611
56	40.2	744.5	11.021	11.308	14.944	720.9	10.637	14.006	18.045	721.4	11.033	13.946	17.975
61	41.8	747.9	11.273	10.955	14.528	725.0	10.932	13.499	17.473	725.8	11.351	13.402	17.363
66	43.4	751.0	11.499	10.645	14.165	729.0	11.221	13.024	16.929	730.0	11.660	12.901	16.786
71	45.0	753.7	11.699	10.377	13.847	732.8	11.500	12.579	16.419	734.0	11.953	12.441	16.260
76	46.6	756.0	11.870	10.157	13.586	736.4	11.766	12.170	15.948	737.7	12.225	12.033	15.784
81	48.2	758.0	12.015	9.974	13.364	739.8	12.013	11.801	15.519	741.1	12.472	11.669	15.362
86	49.8	759.6	12.134	9.826	13.191	742.8	12.238	11.475	15.139	744.0	12.690	11.360	15.005
91	51.4	760.9	12.231	9.704	13.046	745.5	12.439	11.194	14.810	746.5	12.876	11.100	14.699
95	52.6	761.9	12.294	9.628	12.954	747.5	12.582	10.996	14.578	748.2	13.004	10.929	14.500
[illegible]	53.6	762.3	12.334	9.583	12.895	748.7	12.677	10.867	14.429	749.3	13.087	10.815	14.368
1	54.5	762.6	12.369	9.538	12.847	749.9	12.765	10.753	14.291	750.3	13.160	10.722	14.253
1	54.5	700.2	10.130	16.780	21.121	686.0	10.307	18.949	23.469	680.9	10.400	19.783	24.361
1	59.1	707.2	10.627	15.790	20.031	692.3	10.752	17.969	22.419	687.2	10.854	18.753	23.264
21	63.6	714.2	11.135	14.832	18.967	698.7	11.218	16.993	21.356	693.9	11.333	17.718	22.148
31	68.2	721.2	11.632	13.935	17.963	705.4	11.700	16.038	20.311	700.8	11.834	16.694	21.034
41	72.7	727.8	12.128	13.126	17.039	712.0	12.188	15.122	19.290	707.8	12.345	15.705	19.940
51	77.3	733.8	12.571	12.425	16.243	718.5	12.666	14.275	18.339	714.6	12.853	14.777	18.908
56	79.5	736.5	12.770	12.128	15.891	721.6	12.896	13.880	17.899	717.9	13.099	14.346	18.428
61	81.8	738.9	12.952	11.859	15.581	724.6	13.116	13.516	17.485	721.1	13.336	13.946	17.975
66	84.1	741.1	13.115	11.622	15.306	727.3	13.325	13.180	17.102	724.1	13.560	13.575	17.554
71	86.4	743.0	13.259	11.418	15.072	729.9	13.519	12.874	16.751	726.9	13.770	13.234	17.166
76	88.6	744.6	13.383	11.246	14.866	732.3	13.697	12.595	16.437	729.4	13.962	12.933	16.820
81	90.9	746.1	13.489	11.095	14.694	734.4	13.858	12.356	16.158	731.7	14.136	12.665	16.517
86	93.2	747.2	13.579	10.975	14.550	736.3	14.000	12.144	15.914	733.7	14.289	12.436	16.249
91	95.5	748.2	13.653	10.872	14.434	737.9	14.124	11.959	15.699	735.4	14.422	12.239	16.021
95	97.3	748.9	13.703	10.805	14.352	739.1	14.211	11.832	15.553	736.6	14.514	12.101	15.863
[illegible]	98.6	749.3	13.735	10.763	14.302	739.8	14.270	11.748	15.458	737.4	14.576	12.011	15.761
01	100.0	749.7	13.764	10.722	14.258	740.5	14.322	11.674	15.368	738.2	14.631	11.932	15.671
otal Pressure Drop, atm					2.56		2.38				2.30		
H3 Shot Distribution:													
rst Bed					0.030		0.080				0.096		
ond Bed					0.193		0.232				0.237		
ird Bed					0.192		0.203				0.220		
otal					0.415		0.515				0.553		

APPENDIX-A

TABLE NO. A.6

COMPUTED PROFILES OF AMMONIA MOLE PERCENT AND TEMPERATURE IN THE BED FOR DIFFERENT CATALYST VOLUMES

Set No. 6(A), Catalyst volume = 61.0 | Set No. 6(B), Catalyst volume=75.0

Bed Pt. No.	% of Total Cata-lyst Volume	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equil-ibrium	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equil-ibrium
1	2	3	4	5	6	7	8	9	10
1	0.0	644.3	1.613	26.473	31.274	636.1	1.613	28.130	32.934
11	2.3	656.3	2.355	24.166	28.930	649.1	2.422	25.537	30.324
21	4.5	668.8	3.146	21.879	26.567	663.1	3.304	22.907	27.635
31	6.8	682.6	4.026	19.548	24.114	678.9	4.316	20.159	24.759
41	9.1	697.9	5.025	17.160	21.542	697.1	5.506	17.293	21.685
51	11.4	715.1	6.166	14.766	18.902	718.0	6.908	14.401	18.487
56	12.5	724.3	6.788	13.602	17.583	729.3	7.680	13.013	16.912
61	13.6	733.8	7.436	12.484	16.305	740.7	8.471	11.732	15.435
66	14.8	743.4	8.094	11.444	15.105	751.5	9.233	10.619	14.132
71	15.9	752.5	8.733	10.521	14.017	760.9	9.903	9.735	13.083
76	17.0	760.8	9.317	9.745	13.094	768.1	10.422	9.105	12.324
81	18.2	767.7	9.812	9.135	12.361	773.0	10.774	8.700	11.832
86	19.3	773.0	10.193	8.695	11.827	775.9	10.988	8.467	11.549
91	20.5	776.8	10.464	8.398	11.465	777.5	11.105	8.339	11.392
95	21.4	778.8	10.611	8.240	11.266	778.3	11.158	8.284	11.324
98	22.0	779.9	10.690	8.156	11.168	778.6	11.183	8.255	11.293
101	22.7	780.7	10.749	8.092	11.090	778.8	11.199	8.240	11.272
1	22.7	675.8	7.802	20.672	25.299	665.0	7.835	22.552	27.266
11	25.9	683.1	8.303	19.452	24.010	672.5	8.343	21.238	25.896
21	29.1	690.9	8.846	18.210	22.678	680.5	8.902	19.874	24.458
31	32.3	699.3	9.431	16.953	21.312	689.3	9.515	18.463	22.951
41	35.5	708.0	10.052	15.705	19.940	698.7	10.180	17.033	21.405
51	38.6	717.0	10.695	14.500	18.599	708.6	10.887	15.632	19.862
56	40.2	721.5	11.018	13.935	17.963	713.6	11.249	14.955	19.110
61	41.8	725.9	11.336	13.396	17.351	718.5	11.611	14.308	18.380
66	43.4	730.1	11.644	12.895	16.780	723.4	11.965	13.700	17.700
71	45.0	734.1	11.937	12.436	16.254	728.0	12.305	13.142	17.062
76	46.6	737.8	12.209	12.022	15.778	732.3	12.622	12.644	16.494
81	48.2	741.1	12.456	11.664	15.357	736.1	12.909	12.207	15.987
86	49.8	744.1	12.673	11.355	14.999	739.5	13.160	11.837	15.564
91	51.4	746.6	12.861	11.095	14.694	742.3	13.373	11.538	15.211
95	52.6	748.3	12.988	10.924	14.489	744.2	13.515	11.340	14.977
98	53.6	749.4	13.071	10.810	14.357	745.4	13.606	11.214	14.832
101	54.5	750.4	13.145	10.712	14.242	746.4	13.684	11.105	14.705
1	54.5	682.9	10.463	19.464	24.017	673.1	10.597	21.108	25.756
11	59.1	689.4	10.931	18.416	22.900	679.7	11.072	19.983	24.569
21	63.6	696.3	11.424	17.369	21.766	686.7	11.580	18.830	23.347
31	68.2	703.3	11.937	16.334	20.641	694.1	12.119	17.683	22.104
41	72.7	710.4	12.457	15.351	19.548	701.7	12.679	16.551	20.874
51	77.3	717.3	12.967	14.440	18.528	709.3	13.242	15.486	19.699
56	79.5	720.5	13.211	14.022	18.063	713.0	13.517	14.988	19.146
61	81.8	723.6	13.443	13.635	17.624	716.5	13.782	14.522	18.623
66	84.1	726.5	13.661	13.283	17.224	719.8	14.034	14.099	18.145
71	86.4	729.2	13.861	12.970	16.860	722.9	14.268	13.711	17.706
76	88.6	731.6	14.042	12.686	16.539	725.7	14.480	13.369	17.316
81	90.9	733.7	14.203	12.446	16.260	728.2	14.669	13.072	16.981
86	93.2	735.5	14.343	12.239	16.021	730.3	14.833	12.820	16.688
91	95.5	737.1	14.462	12.064	15.818	732.1	14.973	12.606	16.448
95	97.3	738.1	14.544	11.943	15.682	733.4	15.068	12.462	16.283
98	98.6	738.9	14.599	11.864	15.592	734.2	15.129	12.372	16.180
101	100.0	739.5	14.646	11.795	15.514	734.9	15.184	12.292	16.084

	Set 6(A)	Set 6(B)
Total Pressure Drop, atm	2.17	2.37
Cold Shot Distribution:		
First Bed	0.096	0.120
Second Bed	0.239	0.253
Third Bed	0.214	0.235
Total	0.549	0.608

APPENDIX-A

TABLE NO.A.7

COMPUTED PROFILES OF AMMONIA MOLE PERCENT AND TEMPERATURE IN THE BED FOR DIFFERENT OPERATING PRESSURES

Set No. 7(A), Operating pressure = 170.0 Set No. 7(B), Pressure = 210.0

Bed Pt. No.	% Of Total Catalyst Volume	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equilibrium	Bed Temp. (K)	NH3 Mole % Actual	At Max. Rate	At Equilibrium
1	2	3	4	5	6	7	8	9	10
1	0.0	639.7	1.613	25.810	30.574	629.8	1.613	30.934	35.722
11	2.3	650.2	2.268	23.771	28.491	640.6	2.280	28.693	33.517
21	4.5	661.1	2.960	21.754	26.399	652.1	2.996	26.412	31.238
31	6.8	673.0	3.720	19.699	24.237	664.7	3.799	24.004	28.797
41	9.1	686.1	4.570	17.601	21.985	679.1	4.723	21.455	26.157
51	11.4	700.6	5.531	15.480	19.656	695.6	5.806	18.747	23.296
56	12.5	708.5	6.056	14.423	18.475	704.8	6.418	17.357	21.791
61	13.6	716.7	6.608	13.385	17.305	714.7	7.080	15.965	20.262
66	14.8	725.1	7.183	12.388	16.158	725.1	7.788	14.589	18.735
71	15.9	733.6	7.769	11.449	15.072	735.8	8.528	13.272	17.247
76	17.0	741.9	8.347	10.593	14.066	746.5	9.275	12.064	15.863
81	18.2	749.7	8.892	9.846	13.180	756.4	9.983	11.027	14.650
86	19.3	756.5	9.376	9.235	12.446	765.0	10.596	10.203	13.678
91	20.5	762.0	9.775	8.760	11.869	771.5	11.072	9.608	12.965
95	21.4	765.5	10.026	8.477	11.522	775.3	11.347	9.286	12.574
98	22.0	767.6	10.176	8.309	11.319	777.4	11.497	9.110	12.366
101	22.7	769.3	10.295	8.181	11.162	778.9	11.607	8.985	12.213
1	22.7	671.1	7.598	20.013	24.569	665.7	8.109	23.823	28.609
11	25.9	677.7	8.055	18.908	23.392	672.9	8.600	22.533	27.279
21	29.1	684.8	8.548	17.782	22.180	680.7	9.139	21.176	25.863
31	32.3	692.4	9.076	16.637	20.936	689.1	9.731	19.771	24.380
41	35.5	700.3	9.635	15.502	19.681	698.3	10.375	18.333	22.843
51	38.6	708.5	10.218	14.401	18.451	707.9	11.067	16.895	21.288
56	40.2	712.6	10.513	13.875	17.859	712.9	11.426	16.186	20.512
61	41.8	716.7	10.806	13.369	17.282	717.9	11.789	15.502	19.759
66	43.4	720.6	11.094	12.890	16.734	722.9	12.152	14.849	19.027
71	45.0	724.4	11.372	12.446	16.226	727.7	12.506	14.236	18.339
76	46.6	728.0	11.637	12.033	15.750	732.3	12.846	13.673	17.700
81	48.2	731.4	11.883	11.664	15.323	736.6	13.164	13.164	17.125
86	49.8	734.4	12.107	11.340	14.944	740.4	13.451	12.718	16.614
91	51.4	737.1	12.307	11.058	14.611	743.7	13.703	12.345	16.180
95	52.6	739.0	12.448	10.861	14.385	746.1	13.878	12.091	15.891
98	53.6	740.3	12.542	10.732	14.231	747.6	13.992	11.927	15.699
101	54.5	741.4	12.628	10.619	14.093	748.9	14.093	11.785	15.536
1	54.5	680.3	10.250	18.469	22.919	676.3	10.946	21.904	26.621
11	59.1	686.6	10.698	17.485	21.854	683.1	11.434	20.733	25.398
21	63.6	693.1	11.168	16.511	20.788	690.4	11.958	19.542	24.140
31	68.2	699.7	11.652	15.553	19.735	698.0	12.514	18.339	22.856
41	72.7	706.4	12.140	14.650	18.724	705.9	13.093	17.166	21.579
51	77.3	712.8	12.615	13.815	17.788	713.7	13.677	16.050	20.354
56	79.5	715.8	12.840	13.434	17.357	717.5	13.963	15.525	19.777
61	81.8	718.6	13.054	13.083	16.958	721.2	14.239	15.038	19.236
66	84.1	721.3	13.255	12.767	16.591	724.6	14.500	14.594	18.735
71	86.4	723.8	13.439	12.478	16.260	727.8	14.743	14.187	18.280
76	88.6	726.0	13.606	12.223	15.970	730.7	14.964	13.831	17.875
81	90.9	727.9	13.754	12.001	15.711	733.2	15.160	13.516	17.525
86	93.2	729.6	13.883	11.811	15.491	735.4	15.330	13.256	17.224
91	95.5	731.1	13.994	11.648	15.301	737.3	15.474	13.035	16.976
95	97.3	732.1	14.071	11.538	15.172	738.6	15.572	12.884	16.803
98	98.6	732.7	14.121	11.465	15.088	739.4	15.635	12.793	16.694
101	100.0	733.3	14.167	11.402	15.016	740.1	15.691	12.708	16.602

	Set 7(A)	Set 7(B)
Total Pressure Drop, atm	2.34	2.21
Cold Shot Distribution:		
First Bed	0.089	0.146
Second Bed	0.235	0.253
Third Bed	0.199	0.231
Total	0.523	0.630

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C  OM START    PART 1 OF THE MAIN PROGRAM FOR SUMULATION OF AMMONIA SYNT
C     MULTIBED QUENCH TYPE HIGH CAPACITY REACTOR
C     INPUT STATEMENT PROGRAM
      DIMENSION PF(50),TF(50),F11(50),F22(50),F33(50),F44(50),
     1F55(50),FD22(50),FD33(50),FD44(50),Z11(50),Z22(50),Z33(50),
     2AZ(210,4),AP(210,4),AX(210,4),AT(210,4),AXRMNL(210,4),APATDL(100),
     2AZPL(210,4),APL(210,4),ATL(210,4),ANXL(210,4),ATHL(210,4),
     2AXENL(210,4),AXEL(210,4),ACXL(210,4),ACTL(210,4),ACTHL(210,4),
     3ATH(210,4),ACX(210,4),ACT(210,4),ACTH(210,4),ATH12(800)
     4,ATEM(100),ADEL(100),ATEP(100),ATEMP(100),ADET(100),FAIPL(17,20)
     5,ANX(210,4),AZP(210,4),M12(20),XLH(8),YLH(8),ADELT(800),APATD(100)
     6,VFT(50),FC1(50),FC2(50),FC3(50),FC4(50),FC5(50),FC5N(50),
     7VCAT(50),DBED2(50),DBED3(50),HLL(50),UAR(50),UAH(50),FF1(50),
     8PFN(20),TFN(20),VFTN(20),FC1N(20),FC2N(20),FC3N(20),FC4N(20),
        8AXMAX(8),ATMAX(8),ATHMAX(8),ALPS8(8),SINTL(210,4),XLPX(20,20),
        8QR1AV(210,4),WRXN(210,4),WRXNS(210,4),RINTL(210,4),OBLPF(20),
     9FD22N(20),DBED3N(20),HLLN(20),UARN(20),UAHN(20),RATION(50),
     AFF1N(20),RATIO(50),AGXLP(2,50),LPAQX(50),
     CFD33N(20),FD44N(20),VCATN(20),DBED2N(20),EFZIB(210,4)
        1,QR1B(210,4),EFZIA(8),ALZP(210,4),
     DAXEN(210,4),AXRMN(210,4),XEN(80,20),XRMN(80,20),AXE(210,4),
     EAXRM(210,4),PDROP(8),
     FOBJLPN(50),OBJF(50),AQX(50,20),AQX1(20,20),NLEV(20)
        1,TA(15,4,5),AMMD(12),OBLPN(12),NBPTS(4,5),NLPD(15,4,5),
        1ATPL2(20,50),OBJF2(50),ANH3L(50),NOBJLP(20),
        1OBJF82(50),OBJF8(50),OBJF92(50),OBJF9(50),
        1AQX8(50,20),AQX9(50,20),
        1AZ7PL(8,50),AZ8PL(3,50),AZ9PL(7,50)
        1,STLP(11,50),SALP(11,50),STLP2(3,50),SALP2(3,50),
        1AZ11PL(30,50),AZ12PL(30,50),AZ14PL(17,50),AZ15PL(7,50),
        1AZ2PL(11,50),AZ3PL(11,50),AZ4PL(8,50),AZ5PL(8,50),
        1AZ6PL(8,50),FD55N(20),FD55(50),
        1OBJF3(50),OBJF4(50),OBJF5(50),
        1XLPX1(20,20),XLPX2(20,20),OBLPF1(20),OBLPF2(20),
        1N1DLPT(12),LPOBJN(12),APDRPL(12),APDRLP(50)
C       8AXE2(4,310,4),AXRM2(4,310,4),
      COMMON/CB1/F1,F2,F3,F4,F5,LQQ,ITYPE,PARA1,PARA2,PARA3
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     1,PARA4,IOP26,IOP29,FF
     1/CB2/AZ,AP,AX,AT,ATH,AXMAX
     1,ATMAX,ATHMAX,ALPS8,W11L2,QR1AV,AXE2,AXRM2
     1,WRXN,WRXNS,RINTL,SINTL,EFZI8,QR1B,EFZIA,PDROP,IOL1/CB3/
   1AFD1,AFD2,AFD3,AFD4,Z1,Z2,Z3,HL,XW,UV,C4,RUA,HUA,C5,C61,C62,M15,K7
   2,FI11,FI12,FI13,FI21,FI22,FI23,FI31,FI32,FI33,FI41,FI42,FI43,M01,
   3FI51,FI52,FI53,PH1,PH2,PB11,S2,S11,S12,FTF1,S112,S122,AR1,AR2,
   4AR3,AR4,AR5,Q11,Q21,Q31,Q41,Q51,Q12,Q22,Q32,Q42,Q52,
     4IEL2P,UARLP,K5,KL51,IOPT3,AFD0,
   5Q13,Q23,Q33,Q43,Q53,HA11,HA21,HA31,HA41,HA51,HA61,HA71,HA12,M16,
   6HA22,HA32,HA42,HA52,HA62,HA72,HA13,HA23,HA33,HA43,HA53,HA63,K8,
   7HA73,HA14,HA24,HA34,HA44,HA54,HA64,HA74,NZ1,NZ2,NZ3,NZ4,MZ1,MZ2,
   8MZ3,MZ4,HAA21,HAA22,HAA23,HAA24,AHA21,AHA22,AHA23,AHA24,BHA21,
   9BHA22,BHA23,BHA24,HAB21,HAB22,HAB23,HAB24,AHA31,AHA32,AHA33,AHA34
   A/CB4/ANX,ZTI,PAM,AZP/CB20/ACX,ACT,ACTH
   B/CB7/ICSIZE,IOPT1,EFFAH,EFFAL
     1/CB9/FFL,RHNL,XINCL,XINCL2,TOL81,PHYL,PNIL,PAML,DELE,DELM
     1,IOL8,M88,IOP11,IOL81
     1/CB6/AXE,AXRM,AXEN,AXRMN,M12/CB71/NVARI,FAIPL,ND7PL,IOL8P
     1/CB74/AQXLP,G1,G2,G3,G4,G5,G6,G7,G8,G9,G10,G11,G12,G13,G14,
     1G15,G16,G17,G18,G19,G20,G21,G22,G23,G24,G25,G26,G27,
     1G28,G29,G30,G31,G32,G33,G34,G35,G36,G37,FDLIM
    OPEN(UNIT=3,DEVICE='DSK',FILE='DAA8.OUT')
    OPEN(UNIT=1,DEVICE='DSK',FILE='DAA2.DAT')
    OPEN(UNIT=2,DEVICE='DSK',FILE='DA17.DAT')
    OPEN(UNIT=4,DEVICE='DSK',FILE='ADAA8.OUT')
    OPEN(UNIT=8,DEVICE='DSK',FILE='D17.DAT')
      OPEN(UNIT=11,DEVICE='DSK',FILE='LP3.DAT')
      OPEN(UNIT=12,DEVICE='DSK',FILE='LPMANS.OUT')
    READ (1,*)UARLP,IEL2P,IOL8P,ITYP11,NOBLP1,ITYPE,ITYPE8,WTFN,
     1W11,W11LI,W11LP,W11HL,PARA1,PARA2
     1,PARA3,PARA4,IOP26,IOP29,IOP201,
     1CSP11,CSP12,CSP1F,CSP22,IOPL8,
     1XINCL,XINCL2,TOL81,IOL8,IOL81,IOLP8,M88,
     1IOL1,IOL2,CSP33,C3,C2,C4,C51,C611,C621,EFFAH,EFFAL,
     1VW,IHH1,IHH2,IHH3,IHH4,C71,C72,C73,C74,KJ81,
   2M5,M81,M82,IJ1,IJ2,IJ3,IJ4,J5,
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     2K5L,M15,M16,M161,M162,K7,K8,FLPF,IOP11,
    3IOP12,ICSIZE,IOPT1,IOPT2,NDPTS,ND2PL,ND3PL,ND4PL,NDLPS,
     3NLPCSD,FACT,IOPT3,NVARI
     3,AC2,AIP5,TOL8,IOPT4,FDLIM,
     4IOPT5,IOPT8,XV,TV,THV,NXAXIS,NYAXIS,SPY1,SPX1,SPX2,HGT,ANGL,NUM
    5,(PFN(I),TFN(I),VFTN(I),RATION(I),FC3N(I),FC4N(I),FC5N(I),FD22N(I)
    6,FD33N(I),FD44N(I),FD55N(I),VCATN(I),DBED2N(I),DBED3N(I),HLLN(I)
     7,UARN(I),UAHN(I),FF1N(I),OBJLPN(I),NOBJLP(I)
     7,N1DLPT(I),LPOBJN(I),OBLPN(I),I=1,M5),
     8(XLH(I),I=1,NXAXIS),(YLH(I),I=1,NYAXIS),(NLEV(J),J=1,17)
     8,((FAIPL(I,J),J=1,NVARI),I=1,12),((AQXLP(I,J),I=1,2),J=1,NVARI)
    READ(2,*)((AQX1(I,J),I=1,NLEV(J)),J=1,17)
     KL511=K5L-1;KL51=KL511;K5=K5L
     READ(11,*)((NBPTS(K1,J),(TA(I,K1,J),NLPD(I,K1,J),I=1,NBPTS(K1,J)
     1,K1=1,K5),AMMD(J),APDRPL(J),J=1,M5)
     PRINT 8902
     IF(ITYPE.NE.2)GO TO 8903
     TYPE 8902
8902 FORMAT(2X,'((NBPTS(K1,J),(TA(I,K1,J),NLPD(I,K1,J),I=1,NBPTS(K1,J
     1,K1=1,K5),AMMD(J),APDRPL(J),J=1,M5)')
8903 PRINT *,((NBPTS(K1,J),(TA(I,K1,J),NLPD(I,K1,J),I=1,NBPTS(K1,J))
     1,K1=1,K5),AMMD(J),APDRPL(J),J=1,M5)
     IF(ITYPE.NE.2)GO TO 8900
     TYPE *,((NBPTS(K1,J),(TA(I,K1,J),NLPD(I,K1,J),I=1,NBPTS(K1,J))
     1,K1=1,K5),AMMD(J),APDRPL(J),J=1,M5)
8900 CONTINUE
     PRINT 791
     IF(ITYPE.NE.2)GO TO 650
     TYPE 791
791   FORMAT(2X,'DATA REQUIRED:'//2X,'UARLP,IEL2P,IOL8P,ITYP11,
     1NOBLP1,ITYPE,ITYPE8,
     1WTFN,W11,W11LI,W11LP,W11HL
     1,PARA1,PARA2,PARA3,PARA4,IOP26,IOP29,IOP201,
     1CSP11,CSP12,CSP1F,CSP22,IOPL8,
     1XINCL,XINCL2,TOL81,IOL8,IOL81,IOLP8,M88,
     1IOL1,IOL2,CSP33,C3,C2,C4,C51,C611,C621,EFFAH,EFFAL,
     1VW,IHH1,IHH2,IHH3,IHH4,C71,C72,C73,C74,KJ81,
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     2M5,M81,M82,IJ1,IJ2,IJ3,IJ4,J5,
        2K5L,M15,M16,M161,M162,K7,K8,FLPF,IOP11,
     3IOP12,ICSIZE,IOPT1,IOPT2,NDPTS,ND2PL,ND3PL,ND4PL,NDLPS,
        3NLPCSD,FACT,IOPT3,NVARI
        3,AC2,AIP5,TOL8,IOPT4,FDLIM,
        4IOPT5,IOPT8,XV,TV,THV,NXAXIS,NYAXIS,SPY1,
        1SPX1,SPX2,HGT,ANGL,NUMBP
     5,(PFN(I),TFN(I),VFTN(I),RATION(I),FC3N(I),FC4N(I),FC5N(I),FD22N(I)
     6,FD33N(I),FD44N(I),FD55N(I),VCATN(I),DBED2N(I),DBED3N(I),HLLN(I)
        7,UARN(I),UAHN(I),FF1N(I),OBJLPN(I),NOBJLP(I)
        1,N1DLPT(I),LPOBJN(I),OBLPN(I),I=1,M5),
        8(XLH(I),I=1,NXAXIS),(YLH(I),I=1,NYAXIS),(NLEV(J),J=1,17)
        8,((FAIPL(I,J),J=1,NVARI),I=1,12),((AQXLP(I,J),I=1,2),J=1,NVARI)
     8,((AQX1(I,J),I=1,NLEV(J)),J=1,17)
        8,PARA1,PARA2,PARA3,PARA4,IOP26,IOP29,IOP201
     8,IHH1,IHH2,IHH3,IHH4,W11,W11L,W11H,J5,M81,M15,M16,M161,
        8K7,K8,C71,C72,C73,C74,FF,
     2UV,C2,IOPT2,ICSIZE,IOPT3,IOPT8,IOPT1,IOPT4,NUMBP'//
        22X,'DATA SUPPLIED:'/)
650       PRINT *,UARLP,IEL2P,IOL8P,ITYP11,NOBLP1,ITYPE,ITYPE8,
        1WTFN,W11,W11LI,
        1W11LP,W11HL,PARA1,PARA2,PARA3,PARA4,IOP26,IOP29,IOP201
        1,CSP11,CSP12,CSP1F,CSP22,IOPL8,
        1XINCL,XINCL2,TOL81,IOL8,IOL81,IOLP8,M88,
        1IOL1,IOL2,CSP33,C3,C2,C4,C51,C611,C621,EFFAH,EFFAL,
        1VW,IHH1,IHH2,IHH3,IHH4,C71,C72,C73,C74,KJ81,
     2M5,M81,M82,IJ1,IJ2,IJ3,IJ4,J5,
        2K5L,M15,M16,M161,M162,K7,K8,FLPF,IOP11,
     3IOP12,ICSIZE,IOPT1,IOPT2,NDPTS,ND2PL,ND3PL,ND4PL,NDLPS,
        3NLPCSD,FACT,IOPT3,NVARI
        3,AC2,AIP5,TOL8,IOPT4,FDLIM,
        4IOPT5,IOPT8,XV,TV,THV,NXAXIS,NYAXIS,SPY1,SPX1,SPX2,HGT,ANGL,NUM
     5,(PFN(I),TFN(I),VFTN(I),RATION(I),FC3N(I),FC4N(I),FC5N(I),FD22N(I)
     6,FD33N(I),FD44N(I),FD55N(I),VCATN(I),DBED2N(I),DBED3N(I),HLLN(I)
        7,UARN(I),UAHN(I),FF1N(I),OBJLPN(I),NOBJLP(I)
        7,N1DLPT(I),LPOBJN(I),OBLPN(I),I=1,M5),
        8(XLH(I),I=1,NXAXIS),(YLH(I),I=1,NYAXIS),(NLEV(J),J=1,17)
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```
   8,((FAIPL(I,J),J=1,NVARI),I=1,12),((AQXLP(I,J),I=1,2),J=1,NVARI)
 8,((AQX1(I,J),I=1,NLEV(J)),J=1,17)
   IF(ITYPE.NE.2)GO TC 656
  TYPE *,UARLP,IEL2P,ICL8P,ITYP11,NOBLP1,ITYPE,ITYPE8,WTFN,W11,
   1W11LI,W11LP,W11HL,PARA1,PARA2,PARA3,PARA4,IOP26,IOP29,IOP201
   1,CSP11,CSP12,CSP1F,CSP22,IOPL8,
   1XINCL,XINCL2,TOL81,IOL8,IOL81,IOLP8,M88,
   1IOL1,IOL2,CSP33,C3,C2,C4,C51,C611,C621,EFFAH,EFFAL,
   1VW,IHH1,IHH2,IHH3,IHH4,C71,C72,C73,C74,KJ81,
 2M5,M81,M82,IJ1,IJ2,IJ3,IJ4,J5,
   2K5L,M15,M16,M161,M162,K7,K8,FLPF,IOP11,
 3IOP12,ICSIZE,IOPT1,IOPT2,NDPTS,ND2PL,ND3PL,ND4PL,NDLPS,
   3NLPCSD,FACT,IOPT3,NVARI
   3,AC2,AIP5,TOL8,IOPT4,FDLIM,
   4IOPT5,IOPT8,XV,TV,THV,NXAXIS,NYAXIS,SPY1,SPX1,SPX2,HGT,ANGL,NUMI
 5,(PFN(I),TFN(I),VFTN(I),RATION(I),FC3N(I),FC4N(I),FC5N(I),FD22N(I)
 6,FD33N(I),FD44N(I),FD55N(I),VCATN(I),DBED2N(I),DBED3N(I),HLLN(I)
   7,UARN(I),UAHN(I),FF1N(I),OBJLPN(I),NOBJLP(I)
   7,N1DLPT(I),LPOBJN(I),OBLPN(I),I=1,M5),
   8(XLH(I),I=1,NXAXIS),(YLH(I),I=1,NYAXIS),(NLEV(J),J=1,17)
   8,((FAIPL(I,J),J=1,NVARI),I=1,12),((AQXLP(I,J),I=1,2),J=1,NVARI)
 8,((AQX1(I,J),I=1,NLEV(J)),J=1,17)
656   CONTINUE
C  SEE READ STATEMENT FOR DATA BEFORE OUTPUT STATEMENTS PROGRAM AFTER
C  STATEMENT NO.701 IN THE MAIN PROGRAM
C  PART 2 OF THE MAIN PROGRAM FOR SIMULATION OF AMMONIA SYNTHESIS REA(
C  : INTERNAL PREHEATER OUTLET STREAM TEMPERATURES PREDICTION USING TI
C  AND ERROR TECHNIQUE BY MATCHING CALCULATED FEED TEMPERATURES WITH I
C  FEED TEMPERATURE
  GO TO 404
405 MJK1=1;LPS=1;XVI=1.0/XV;TVI=1.0/TV;THVI=1.0/THV
   ISIGPL=1;ISIPL1=1;ISIPL2=1;ND7PL=1
   ILPS2=1;MLPK1=0;M1LP=1;M8LP=1;NOBLP=0;NV1LP=0;NV2LP=0
  ISM=1 ;  MM1=1 ; IM=1 ; IOPT5=1;M=1;LQQ=1;NVLPI=0;KL51=K5-1
   G2=VFTN(1);G4=RATION(1);G6=FC3N(1);G8=FC4N(1);G10=FC5N(1)
   G12=FD22N(1);G14=FD33N(1);G16=FD44N(1);G18=PFN(1);G20=TFN(1)
   G22=VCATN(1);G24=DBED2N(1);G26=DBED3N(1);G28=HLLN(1);G30=UARN(1)
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      G32=UAHN(1);G34=FD55N(1);G35=PARA1;G36=PARA2;G37=PARA3
      SSE=0.0;SSE1=0.0;SSE2=0.0;SSE3=0.0;SSE4=0.0;SSE5=0.0
      SSE6=0.0;SSE7=0.0;SSE8=0.0;NDPTS=NLPCSD;ABCD2=-100.0
      IF(IOL2.EQ.1)NDPTS=N1DLPT(MJK1)
      DO 872 J=1,4
      DO 872 I=1,310
      AZ(I,J)=0.0;AP(I,J)=0.0;AX(I,J)=0.0;ANX(I,J)=0.0
      AT(I,J)=0.0;ATH(I,J)=0.0;AZP(I,J)=0.0
872   CONTINUE
      IF(IOL2.NE.1)GO TO 205
      IOPT2=1;ITYP11=1
      GO TO 7224
  205 CONTINUE
      IF(IOL2.EQ.1)GO TO 7224
      IF(NOBJLP(MJK1)-1)7210,7224,7227
7227  ITYPE8=2;IOPT2=2
      IF(M1LP.EQ.1)GO TO 7224
      IF(NOBJLP(MJK1).EQ.11)GO TO 7212
      M1LP=M1LP-1
      GO TO 7211
7210  CONTINUE
      GO TO 7224
7211  NDPT1S=N1DLPT(MJK1)
      IF(M1LP.GE.ND3PL)GO TO 8712
      CALL PNEXT(NV1LP,NOBJLP(MJK1),M1LP,AQX8,ISIPL1)
      IF(NV1LP.GT.NVARI)GO TO 8755
      M3LP=2
      CALL PCONV(M1LP,M3LP,AQX8)
      IF(M1LP.LE.NDPT1S)GO TO 147
      CALL ACOMP(LPIK,AQX8,M1LP,NVARI)
      IF(LPIK.EQ.0)GO TO 147
      OBJF82(M1LP)=OBJF82(LPIK);OBJF5(M1LP)=OBJF5(LPIK)
      OBJF8(M1LP)=OBJF8(LPIK);LPIK=0
C     CALL FUNOBJ(OBJF8,M1LP,LPOBJN(MJK1),PATD,SSE,SSE1,SSE2,SSE3,
C     1SSE4,SSE5,SSE6,SSE7,SSE8)
8755 CALL OPTIMA(OBJF8,M1LP,AQX8,AQX1,IOPT8,NVARI,AC2,NLEV,
      1NOPTM1,TOL8,NMAX11,NDPT1S,XLPX1,
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```
      1OBLPF1,NLN81,ALPC11,YLPN1,IOL8P)
      IF(NOPTM1.EQ.0)GO TO 8621
      GO TO 8714
8712  NMAX11=M
8711  CONTINUE
      NOPTM1=NMAX11;M1LP=1;ISIPL1=1;ND7PL=1
8714  CONTINUE
      IF(NOBLP.NE.11)GO TO 701
C     DO 8712 L=1,NVARI
C     AQX9(M8LP,L)=AQX8(NOPTM1,L)
C8712 CONTINUE
      OBJF9(M8LP)=OBJF5(NOPTM1);NV1LP=0
      IF(OBJF33.EQ.0.0)GO TO 694
      OBJF92(M8LP)=OBJF5(NOPTM1)*OBJF33
      GO TO 7226
694   OBJF92(M8LP)=OBJF5(NOPTM1)
      GO TO 7226
8621  NPT1S2=NDPT1S*NDLPS
      IF(M1LP.GE.ND3PL)GO TO 8711
      M3LP=2
      CALL PCONV(M1LP,M3LP,AQX8)
      CALL ACOMP(LPIK,AQX8,M1LP,NVARI)
      IF(LPIK.EQ.0)GO TO 147
      OBJF82(M1LP)=OBJF82(LPIK);OBJF5(M1LP)=OBJF5(LPIK)
      OBJF8(M1LP)=OBJF8(LPIK);LPIK=0
      GO TO 8755
7212  CONTINUE
      NOBLP=NOBJLP(MJK1);M1LP=M1LP-1;NOBJLP(MJK1)=10
      GO TO 7211
7226  NDP1S=3
      IF(IOL8P.EQ.1)NDP1S=2
      IF(M8LP.GE.ND4PL)GO TO 701
      CALL PNEXT(NV2LP,NOBLP,M8LP,AQX9,ISIPL2)
      DO 8422 L=1,NVARI
      AQX8(1,L)=AQX9(M8LP,L)
8422  CONTINUE
      IF(NV2LP.GT.NVARI)GO TO 8255
```

```
      M3LP=2
      CALL PCONV(M8LP,M3LP,AQX9)
      CALL ACOMP(LPIK,AQX9,M8LP,NVARI)
      IF(LPIK.EQ.0)GO TO 147
      OBJF92(M8LP)=OBJF92(LPIK)
      OBJF9(M8LP)=OBJF9(LPIK);LPIK=0
C     CALL FUNOBJ(OBJF9,M8LP,LPOBJN(MJK1),PATD,SSE,SSE1,SSE2,SSE3,
C     1SSE4,SSE5,SSE6,SSE7,SSE8)
8255 CALL OPTIMA(OBJF9,M8LP,AQX9,AQX1,IOPT8,NVARI,AC2,NLEV,
      1NOPTM2,TOL8,NMAX12,NDP1S,XLPX2,
      1OBLPF2,NLN82,ALPC12,YLPN2,IOL8P)
      IF(NOPTM2.NE.0)GO TO 701
      NPT1S2=NDP1S*NDLPS
      IF(M8LP.GE.ND4PL)GO TO 701
      DO 8423 L=1,NVARI
      AQX8(1,L)=AQX9(M8LP,L)
8423  CONTINUE
      M3LP=2
      CALL PCONV(M8LP,M3LP,AQX9)
      CALL ACOMP(LPIK,AQX9,M8LP,NVARI)
      IF(LPIK.EQ.0)GO TO 147
      OBJF92(M8LP)=OBJF92(LPIK)
      OBJF9(M8LP)=OBJF9(LPIK);LPIK=0
      GO TO 8255
7224  CONTINUE
      IF(OBJLPN(M).EQ.0.0)GO TO 575
      PATD=OBJLPN(M);APATD(MJK1)=PATD;PATD1=PATD;IM8=1
      MLPK1=MLPK1+1;OBJF(M)=PATD
      FC12=100.0-(FC3N(MJK1)+FC4N(MJK1)+FC5N(MJK1))
      LFC1N=100*FC12*RATION(MJK1)/(1+RATION(MJK1))+0.5
      FC1N(MJK1)=LFC1N*0.01;FC2N(MJK1)=FC12-FC1N(MJK1)
      GO TO 719
575   CONTINUE
      IF(ITYPE8.NE.1)GO TO 890
      IF(ICSIZE.EQ.2)GO TO 170
      PRINT 173
      IF(ITYPE.NE.2)GO TO 196
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```
      TYPE 173
173   FORMAT(2X,'ACTUAL VALUE OF EFFECTIVENESS FACTOR CALCULATED AND I
     1LUDED IN REACTION  RATE CALCULATION '/)
      GO TO 196
170   PRINT 182
      IF(ITYPE.NE.2)GO TO 196
      TYPE 182
182   FORMAT(2X,'FOR THIS DATA SET CALCULATION IS BASED ON EFFECTIVENE
     1 FACTOR OF UNITY'/)
196   IF(IOPT3.NE.1)GO TO 197
      PRINT 80
      IF(ITYPE.NE.2)GO TO 83
      TYPE 80
80    FORMAT(2X,'RUNGE-KUTTA FOURTH ORDER NUMERICAL INTEGRATION TECHNI
     1 IS BEING USED'/)
      GO TO 83
197   PRINT 84
      IF(ITYPE.NE.2)GO TO 83
      TYPE 84
84    FORMAT(2X,'MILNE PREDICTOR-CORRECTOR NUMERICAL INTEGRATION TECHN
     1UE IS BEING USED'/)
83    IF(IOPT2.EQ.1)GO TO 890
      IF(IOPT8-2)893,894,767
893   PRINT 768
      IF(ITYPE.NE.2)GO TO 890
      TYPE 768
768   FORMAT(2X,'FOR OPTIMISATION SEARCH IS AT ACTUAL VALUES OF VARIAB
     1S THAT ARE SLIGHTLY ROUNDED OFF'/)
      GO TO 890
894   PRINT 773
      IF(ITYPE.NE.2)GO TO 890
      TYPE 773
773   FORMAT(2X,'FOR OPTIMISATION SEARCH IS AT ROUNDED OFF VALUE OF THE
     1VARIABLES'/)
      GO TO 890
767   PRINT 776
      IF(ITYPE.NE.2)GO TO 890
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```
          TYPE 776
776       FORMAT(2X,'FOR OPTIMISATION SEARCH IS AT CERTAIN SPECIFIED VALUE
         1OF THE VARIABLES'/)
890        CONTINUE
          IF(IOL2.EQ.1)GO TO 143
          IF(M1LP.NE.1)GO TO 147
          IF(M8LP.NE.1)GO TO 147
          IF(M.EQ.1) GO TO 143
        IF(IOPT2.EQ.2) GO TO 147
        IF(M.GT.NDPTS) GO TO 147
  143 F=FF1N(MJK1);PARA1=G35;PARA2=G36;PARA3=G37;FF=VFTN(MJK1)/FLPF
          FC12=100.0-(FC3N(MJK1)+FC4N(MJK1)+FC5N(MJK1))
          LFC1N=100*FC12*RATION(MJK1)/(1+RATION(MJK1))+0.5
          FC1N(MJK1)=LFC1N*0.01;FC2N(MJK1)=FC12-FC1N(MJK1)
        CALL FLOWR(F11(MJK1),F22(MJK1),F33(MJK1),F44(MJK1),F55(MJK1),
       1VFTN(MJK1),FC1N(MJK1),FC2N(MJK1),FC3N(MJK1),FC4N(MJK1),IOPT5)
          PHY=FC1N(MJK1);PNI=FC2N(MJK1);PAM=FC3N(MJK1)
          PME=FC4N(MJK1);PAR=FC5N(MJK1);RHN=RATION(MJK1)
        VCAT1=VCATN(MJK1)*1.0E6
        Z11(MJK1)=VCAT1/(1+DBED2N(MJK1)+DBED3N(MJK1))
        Z22(MJK1)=Z11(MJK1)*DBED2N(MJK1)
        Z33(MJK1)=VCAT1-(Z11(MJK1)+Z22(MJK1))
          H1=Z11(MJK1)/IHH1;H2=Z22(MJK1)/IHH2;H3=Z33(MJK1)/IHH3
          H4=HLLN(MJK1)*1.0E6/IHH4
          GO TO 146
147        VFT(M)=G1;RATIO(M)=G3;FC3(M)=G5;FC4(M)=G7;FC5(M)=G9
          FD22(M)=G11;FD33(M)=G13;FD44(M)=G15;PF(M)=G17
          TF(M)=G19;VCAT(M)=G21;DBED2(M)=G23;DBED3(M)=G25;HLL(M)=G27
          UAR(M)=G29;UAH(M)=G31;FD55(M)=G33;PARA1=G35;PARA2=G36
          PARA3=G37;FF1(M)=FF1N(MJK1)
          FC12=100.0-(FC3(M)+FC4(M)+FC5(M))
          LFC1=100*FC12*RATIO(M)/(1+RATIO(M))
          FC1(M)=LFC1*0.01;FC2(M)=FC12-FC1(M)
        CALL FLOWR(F11(M),F22(M),F33(M),F44(M),F55(M),VFT(M),FC1(M),
       1FC2(M),FC3(M),FC4(M),IOPT5)
          PHY=FC1(M);PNI=FC2(M);PAM=FC3(M);PME=FC4(M)
          PAR=FC5(M);RHN=RATIO(M)
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```
      VCAT1=VCAT(M)*1.0E6
      Z11(M)=VCAT1/(1+DBED2(M)+DBED3(M))
      Z22(M)=Z11(M)*DBED2(M)
      Z33(M)=VCAT1-(Z11(M)+Z22(M))
        H1=Z11(M)/IHH1;H2=Z22(M)/IHH2;H3=Z33(M)/IHH3
        H4=HLL(M)*1.0E6/IHH4
146      IF(IOPT3.EQ.1) GO TO 215
      HA11=0.5*H1 ; HA21=0.083333*H1 ; HA31=0.5*HA21 ; HA41=4.0*H1
      HA51=2.666667*H1 ; HA61=2.0*H1 ;HA71=0.333333*H1 ; HA12=0.5*H2
      HA13=0.5*H3 ; HA14=0.5*H4 ; HA22=0.0833333*H2
      HA23=0.0833333*H3 ; HA24=0.0833333*H4 ; HA32=0.5*HA22
      HA33=0.5*HA23;HA34=0.5*HA24 ;HA42=4.0*H2 ;HA43=4.0*H3
      HA44=4.0*H4;HA52=2.666667*H2;HA53=2.666667*H3;HA54=2.666667*H4
      HA62=2.0*H2;HA63=2.0*H3;HA64=2.0*H4;HA72=0.333333*H2
      HA73=0.333333*H3;HA74=0.333333*H4;HAA21=5.0*HA21
      HAA22=5.0*HA22;HAA23=5.0*HA23;HAA24=5.0*HA24
      AHA21=23.0*HA21;AHA22=23.0*HA22;AHA23=23.0*HA23
      BHA24=16.0*HA24;HAB21=8.0*HA21;HAB22=8.0*HA22;HAB23=8.0*HA23
      AHA24=23.0*HA24;BHA21=16.0*HA21;BHA22=16.0*HA22;BHA23=16.0*HA23
      HAB24=8.0*HA24;AHA31=9.0*HA31;AHA32=9.0*HA32;AHA33=9.0*HA33
      AHA34=9.0*HA34;BHA31=19.0*HA31;BHA32=19.0*HA32
      BHA33=19.0*HA33;BHA34=19.0*HA34;CHA31=5.0*HA31
      CHA32=5.0*HA32;CHA33=5.0*HA33;CHA34=5.0*HA34
215     CONTINUE
        IF(IOL2.EQ.1)GO TO 2780
        IF(M1LP.NE.1)GO TO 584
        IF(M8LP.NE.1)GO TO 584
        IF(M.EQ.1)GO TO 2780
        IF(IOPT2.EQ.2)GO TO 584
        IF(M.LE.NDPTS)GO TO 2780
584     CONTINUE
      UV=TF(M);T=TF(M);Z1=Z11(M);Z2=Z22(M);XW=PF(M);F5=F55(M)
      Z3=Z33(M);HL=HLL(M)*1.0E6;F1=F11(M);F2=F22(M);F3=F33(M);F4=F44(M)
      RUA=UAR(M)*1.0E-6;HUA=UAH(M)*1.0E-6
      AFD2=FD22(M);AFD3=FD33(M);AFD4=FD44(M);AFD0=FD55(M)
        GO TO 2483
2780    UV=TFN(MJK1);T=TFN(MJK1);Z1=Z11(MJK1)
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      Z2=Z22(MJK1);XW=PFN(MJK1)
      Z3=Z33(MJK1);HL=HLLN(MJK1)*1.0E6
      F1=F11(MJK1);F2=F22(MJK1);F3=F33(MJK1)
      F4=F44(MJK1);F5=F55(MJK1);RUA=UARN(MJK1)*1.0E-6
      HUA=UAHN(MJK1)*1.0E-6;AFD2=FD22N(MJK1);AFD3=FD33N(MJK1)
      AFD4=FD44N(MJK1);AFD0=FD55N(MJK1)
 2483 FT=F1+F2+F3+F4+F5;FTV=FT*80.64;J=1
      FTT1=100./FT
      FFQ1=FF**1.8;ZTI=100./(Z1+Z2+Z3+HL)
      C5=C51*FFQ1;C61=C611*FFQ1;C62=C621*FFQ1
      ZC1=Z1*0.000001
      ZC3=Z3*0.000001;ZC2=Z2*0.000001;HCL=HL*0.000001
      RUAI=RUA*1.0E+06;HUAI=HUA*1.0E+06;CTVO=ZC1+ZC2+ZC3+HCL
      AFD1=1.0-AFD2-AFD3-AFD4;AFD01=AFD1-AFD0;CTVLP=CTVO/(ZC1+ZC2+ZC3)
      W1=W11;C21=C2;XWC5=C5*XW*AFD1**1.8
      PH1=XW-0.75*XWC5;PB11=XW-XWC5;S2=AFD1+AFD4;S11=S2+AFD2
      S12=S11+AFD3;PH2=XW-0.25*XWC5
      FTF1=2.0*F1/(3.0*FT*S2);S112=S11/S2;S122=S12/S2
      FI11=F1*S2;FI21=F2*S2;FI31=F3*S2;FI41=F4*S2;FI51=F5*S2
      FI12=F1*S11 ;FI22=F2*S11;FI32=F3*S11;FI42=F4*S11;FI52=F5*S11
      FI13=F1*S12;FI23=F2*S12;FI33=F3*S12;FI43=F4*S12;FI53=F5*S12
      ZH1=IHH1;ZH2=IHH2;ZH3=IHH3;ZH4=IHH4;NZ1=IHH1-3
        IC71=C71;IC72=C72;IC73=C73;IC74=C74
      MZ1=IHH1/IC71;NZ2=IHH2-3;NZ3=IHH3-3
      NZ4=IHH4-3;MZ2=IHH2/IC72;MZ3=IHH3/IC73;MZ4=IHH4/IC74;AR1=F1*AFD1
      AR2=F2*AFD1;AR3=F3*AFD1;AR4=F4*AFD1;AR5=F5*AFD1;Q11=FI11-AR1
      Q21=FI21-AR2;Q31=FI31-AR3 ; Q41=FI41-AR4 ; Q51=FI51-AR5
      Q12=F1*AFD2 ; Q22=F2*AFD2 ; Q32=F3*AFD2 ; Q42=F4*AFD2
      Q52=F5*AFD2 ; Q13=F1*AFD3 ; Q23=F2*AFD3 ; Q33=F3*AFD3
        Q43=F4*AFD3;Q53=F5*AFD3
      RFTI=0.01*FTT1 ; AY3=F3*RFTI
       FFL=F;RHNL=RHN;PHYL=PHY;PNIL=PNI;PAML=PAM
      UV20=UV+CSP11;LP8=1
        IF(W11L.LT.UV20)W11L=UV20
        W11L20=W11L+CSP11;W11L2=UV+W11LI;M106=0;M107=0
C     MODIFICATION TO MAIN PROGRAM
       ICONV=0 ; MMN=0;F1CCN=F1*0.9792;M7=0;IM17=1;IM8=1;IM80=2;IM83=2
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      GO TO 407
287   CSP1=CSP11;CSP2=CSP22;CSP3=CSP33*2
      IF(IOL2.EQ.1)GO TO 1192
      IF(J5.EQ.0)GO TO 1192
      IF(M81.EQ.1)GO TO 1192
      ISIG=1;W11H=W11HL;W1=W11H
353   TH12=W1;ATH12(J)=W1
      IF(J.EQ.1)GO TO 371
      CALL COMPA(ADELT,ATH12,J,MMN)
      IF(MMN.NE.0)GO TO 368
 371  K5=K5L;KL51=K5-1
      CALL FEEDT(TF1,W1,F,H1,H2,H3,H4,VW,C71,C72,C73,C74,BHA31,BHA32,
     1BHA33,BHA34,CHA31,CHA32,CHA33,CHA34,J1,K11)
      M7=M7+1
      IF(LQQ.EQ.2)GO TO 362
      IF(AT(MQ1,K11)-W11L2)362,362,386
386   DELT1=TF1-T;ADELT(J)=DELT1
      TPRD=XW-AP(M12(K5),K5)
      M106=M106+1;STLP(M106,M)=ATH(1,1)
      SALP(M106,M)=ANX(M12(KL51),KL51)
      IF(ITYPE8.NE.1)GO TO 291
      PRINT 423,M7,W1,DELT1,(K1,ANX(1,K1)
      1,AXEN(1,K1),AXRMN(1,K1),AX(1,K1),AT(1,K1),ATH(1,K1)
      1,EFZI8(1,K1)
      1,QR1B(1,K1),ALPS8(K1),AXMAX(K1),ATMAX(K1),ATHMAX(K1)
      1,ANX(M12(K1),K1),AXEN(M12(K1),K1),AXRMN(M12(K1),K1)
      1,AX(M12(K1),K1),AT(M12(K1),K1)
      1,ATH(M12(K1),K1),EFZI8(M12(K1),K1)
      1,QR1B(M12(K1),K1),EFZIA(K1),PDROP(K1)
      1,AP(M12(K1),K1),K1=1,KL51)
      IF(HL.EQ.0.0)GO TO 8425
      PRINT 707,AT(1,K5),ATH(1,K5),AT(M12(K5),K5),
      1ATH(M12(K5),K5),PDROP(K5),AP(M12(K5),K5),TPRD
8425  CONTINUE
      IF(ITYPE.NE.2)GO TO 291
      TYPE 423,M7,W1,DELT1,(K1,ANX(1,K1)
      1,AXEN(1,K1),AXRMN(1,K1),AX(1,K1),AT(1,K1),ATH(1,K1)
```

```
     1,EFZI8(1,K1)
     1,QR1B(1,K1),ALPS8(K1),AXMAX(K1),ATMAX(K1),ATHMAX(K1)
     1,ANX(M12(K1),K1),AXEN(M12(K1),K1),AXRMN(M12(K1),K1)
     1,AX(M12(K1),K1),AT(M12(K1),K1)
     1,ATH(M12(K1),K1),EFZI8(M12(K1),K1)
     1,QR1B(M12(K1),K1),EFZIA(K1),PDROP(K1)
     1,AP(M12(K1),K1),K1=1,KL51)
     IF(HL.EQ.0.0)GO TO 291
     TYPE 707,AT(1,K5),ATH(1,K5),AT(M12(K5),K5),
     1ATH(M12(K5),K5),PDROP(K5),AP(M12(K5),K5),TPRD
291  IF(ABS(DELT1).GT.C4)GO TO 281
     IF(ITYPE8.NE.1)GO TO 281
     IF(IOP11.EQ.1)GO TO 281
     PRINT 406,((AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),
     1ATH(M1,K1),ACX(M1,K1),ACT(M1,K1),ACTH(M1,K1),M1=M15,M12(K11)
     1,M16),K1=K7,K5,K8)
     IF(ITYPE.NE.2)GO TO 281
     TYPE 406,((AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),
     1ATH(M1,K1),ACX(M1,K1),ACT(M1,K1),ACTH(M1,K1),M1=M15,M12(K11)
     1,M16),K1=K7,K5,K8)
281  CONTINUE
     IF(IOPL8.EQ.2)GO TO 516
     IF(W1.EQ.W11H)GO TO 398
     IF(W1.EQ.W11L)GO TO 398
516  IF(J.EQ.1)GO TO 395
     IF(M7.GT.M8)GO TO 398
317  IF(ABS(W2-W1).GT.CSP11)GO TO 395
398  W11H8=ATH12(J);M7=0
     IF(ISIG.NE.1)GO TO 377
     ISIG=-1;W11H=W11H8;W11L=W11LP;W1=W11L;CSP3=CSP33*2;LP8=1;J=J+1
     GO TO 353
395  IF(LP8.EQ.2)GO TO 290
     CSP3=CSP33*0.5;W1=W1+CSP3*ISIG
     GO TO 296
290  CSP3=CSP3*0.5
     W1=W1+CSP3*ISIG
296  J=J+1
```

```
           IF(W1.LT.W11L)W1=W11L
           GO TO 353
 362       CSP3=CSP3*0.5;W2=W1;W1=W1-CSP3*ISIG;LQG=1;LP8=2
           GO TO 353
 368       DELT1=ADELT(MMN);ADELT(J)=DELT1
           GO TO 317
 377       W11L=W11H8;IW11H=W11H*0.2;W11H=IW11H*5
           IW11L=W11L*0.2+0.50;W11L=IW11L*5
           IF(ITYPE8.NE.1)GO TO 120
           PRINT 278,W11H,W11L
           IF(ITYPE.NE.2)GO TC 120
           TYPE 278,W11H,W11L
 278       FORMAT(/2X,'FOR THIS DATA SET THE FEASIBLE REGION OF SEARCH FOR
           1D TEMPERATURE(K):',F7.1,2X,'TO',2X,F7.1/)
 120       DW11HL=W11H-W11L;W1=W11L;M7=0;CSP3=CSP33
           ICSP1=DW11HL*CSP1F;CSP1=ICSP1
           IF(CSP1.GT.CSP11)CSP1=CSP11
           IF(CSP1.LT.CSP12)CSP1=CSP12
           M8=DW11HL/CSP1+M82;W1=W11L;J=J+1
           IF(M8.LT.M81)M8=M81
           CSP2=CSP1*0.5+1.0
           IF(CSP2.GT.CSP22)CSP2=CSP22
           W11L20=W11L
           GO TO 305
 1192      CONTINUE
 305       TH12=W1;ATH12(J)=W1
           IF(M81.EQ.1)GO TO 53
           IF(J5.EQ.0)M8=M81
           IF(M7.GE.M8)GO TO 1503
        IF(J.EQ.1) GO TO 53
        CALL COMPA(ADELT,ATH12,J,MMN)
        IF(MMN.NE.0)GO TO 272
    53 K5=K5L;KL51=K5-1
          CALL FEEDT(TF1,W1,F,H1,H2,H3,H4,VW,C71,C72,C73,C74,BHA31,BHA32,
      1BHA33,BHA34,CHA31,CHA32,CHA33,CHA34,J1,K11)
          IF(M81.EQ.1)GO TO 62
          M7=M7+1
```

```
            IF(LQQ.EQ.2)GO TO 67
            IF(AT(MQ1,K11)-W11L2)71,71,62
 62         DELT1=TF1-T;ADELT(J)=DELT1
            W26=W1;DELT26=DELT1
            M106=M106+1;STLP(M106,M)=ATH(1,1)
            SALP(M106,M)=ANX(M12(KL51),KL51)
            GO TO 421
 67         CONTINUE
            IF(J5.EQ.0)GO TO 299
 2753       W1=W1+CSP1;LQQ=1
            GO TO 1192
   272 DELT1=ADELT(MMN)
 260        CONTINUE
            IF(M81.EQ.1)GO TO 401
            IF(J5.EQ.0)GO TO 321
        IF(ABS(DELT1)-C4)1170,1170,191
 191        CONTINUE
 152        IM=IM+1;W2=W1+CSP1;J=J+1
            IF(ICONV.EQ.0)GO TO 1152
 341        IF(W2.LT.W11H)GO TO 1152
            W2=W11H;IM8=2
 1152       CONTINUE
 308        TH12=W2;ATH12(J)=W2
            IF(M7.GE.M8)GO TO 1503
        IF(J.EQ.2)GO TO 1155
        CALL COMPA(ADELT,ATH12,J,MMN)
        IF(MMN.NE.0)GO TO 1272
  1155 K5=K5L;KL51=K5-1
            CALL FEEDT(TF2,W2,F,H1,H2,H3,H4,VW,C71,C72,C73,C74,BHA31,BHA32,
       1BHA33,BHA34,CHA31,CHA32,CHA33,CHA34,J1,K11)
            M7=M7+1
            IF(LQQ.EQ.2)GO TO 68
            IF(AT(MQ1,K11)-W11L2)72,72,64
 64         DELT2=TF2-T;ADELT(J)=DELT2
            IF(W2.GE.W11H)IM8=2
            W26=W2;DELT26=DELT2
            M106=M106+1;STLP(M106,M)=ATH(1,1)
```

```
         SALP(M106,M)=ANX(M12(KL51),KL51)
         GO TO 424
68       W2=W2+CSP1;LQQ=1
         IF(IM8.EQ.2)GO TO 503
         IF(W2.LT.W11H)GO TC 308
         IM8=2;W2=W11H
      GO TO 1152
 1272 DELT2=ADELT(MMN)
         IF(W2.GE.W11H)IM8=2
 1260 IF(ABS(DELT2)-C4)1170,1170,153
  153 DW12=(W1-W2)*1.5
      IF(DELT1)1,503,5
    1 IF(DELT2)2,2,7
    5 IF(DELT2)7,7,2
2        IM=1;W1=W2;DELT1=DELT2;W2=W1+CSP1;J=J+1
         IF(IM8.EQ.2)GO TO 503
         IF(W2.GT.W11H)W2=W11H
         GO TO 308
    7 J=J+1
      IF(M7.GE.M8)GO TO 1503
116       W3=W2+(W1-W2)*ABS(DELT2)/(ABS(DELT2)+ABS(DELT1))
         IW3=W3
      TH12=W3;ATH12(J)=W3
      CALL COMPA(ADELT,ATH12,J,MMN)
      IF(MMN.NE.0) GO TO 1188
         K5=K5L;KL51=K5-1
      CALL FEEDT(TF3,W3,F,H1,H2,H3,H4,VW,C71,C72,C73,C74,BHA31,BHA32,
     1BHA33,BHA34,CHA31,CHA32,CHA33,CHA34,J1,K11)
         M7=M7+1
         IF(LQQ.EQ.2)GO TO 69
         IF(AT(MQ1,K11)-W11L2)73,73,66
66       DELT3=TF3-T;ADELT(J)=DELT3
         GO TO 427
69       W2=W3;LQQ=1
      GO TO 116
 1188 DELT3=ADELT(MMN)
 1520 IF(ABS(DELT3)-C4)1170,1170,188
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```
 188 IF(DELT3)11,1170,35
  11 IF(DELT2)17,17,26
  35 IF(DELT2)26,26,17
  17 W2=W3;DELT2=DELT3
     GO TO 7
  26 W1=W3;DELT1=DELT3
     GO TO 7
1170   IF(MMN.NE.0)GO TO 953
       M107=M107+1;STLP2(M107,M)=ATH(1,1)
       SALP2(M107,M)=ANX(M12(KL51),KL51)
       MM2=M106;M106=M106+1
       STLP(M106,M)=STLP(MM2,M);SALP(M106,M)=SALP(MM2,M)
       STLP(MM2,M)=ATH(1,1);SALP(MM2,M)=ANX(M12(KL51),KL51)
       GO TO 401
 321  ICONV=ICONV+1;M7=0
       PATD=AX(M12(K11),K5)*F1CON;APATD(MJK1)=PATD
       OBJF2(M)=PATD
       IF(ITYPE8.NE.1)GO TO 125
       PRINT 1718,PATD
       IF(ITYPE.NE.2)GO TO 125
       TYPE 1718,PATD
1718   FORMAT(2X,'PRODUCTION RATE OF AMMONIA(TONS PER DAY)=',F7.1/)
125    CONTINUE
       IF(IOL2.EQ.1)GO TO 1871
       IF(M81.EQ.1)GO TO 209
1871   CONTINUE
       APATDL(ICONV)=PATD
       IF(ICONV.LE.1)GO TO 2717
       IF(APATDL(ICONV).LT.APATDL(ICONV-1))GO TO 2735
2717   DO 2726 K1=K7,K5,K8
       DO 2726 M1=M15,M12(K11),M16
       AZPL(M1,K1)=AZP(M1,K1)
       APL(M1,K1)=AP(M1,K1)
       ANXL(M1,K1)=ANX(M1,K1)
       ATL(M1,K1)=AT(M1,K1)
       ATHL(M1,K1)=ATH(M1,K1)
       AXENL(M1,K1)=AXEN(M1,K1)
```

```
           AXRMNL(M1,K1)=AXRMN(M1,K1)
           AXEL(M1,K1)=AXE(M1,K1);ACXL(M1,K1)=ACX(M1,K1)
           ACTL(M1,K1)=ACT(M1,K1);ACTHL(M1,K1)=ACTH(M1,K1)
     2726  CONTINUE
           PATD1=APATDL(ICONV)
     2735  W1=W11L20;IM80=1
           IF(ICONV.GE.J5)GO TO 503
           IF(IM8.EQ.2)GO TO 503
           GO TO 953
     953   IM=1;W1=W26;DELT1=DELT26;W2=W1+CSP1;J=J+1
           IF(W2.GT.W11H)W2=W11H
           GO TO 308
     1503  PRINT 1505,M8
     1505 FORMAT(2X,'NO CONVERGENCE ACHIEVED IN',I5,2X,'ITERATIONS.THEREFORE
         1SWITCHING TO NEXT DATA SET.'/)
     503   IF(ICONV.EQ.0)GO TO 299
          PATD=PATD1;IM8=1
          APATD(MJK1)=PATD
           DO 2744 K1=K7,K5,K8
           DO 2744 M1=M15,M12(K11),M16
           AZP(M1,K1)=AZPL(M1,K1);AP(M1,K1)=APL(M1,K1)
           ANX(M1,K1)=ANXL(M1,K1);AT(M1,K1)=ATL(M1,K1)
           ATH(M1,K1)=ATHL(M1,K1);AXEN(M1,K1)=AXENL(M1,K1)
           AXRMN(M1,K1)=AXRMNL(M1,K1);AXE(M1,K1)=AXEL(M1,K1)
           ACX(M1,K1)=ACXL(M1,K1);ACT(M1,K1)=ACTL(M1,K1)
           ACTH(M1,K1)=ACTHL(M1,K1);ALZP(M1,K1)=CTVLP*AZP(M1,K1)
     2744  CONTINUE
           MSLP3=0;MSLP4=0;MSLP5=0;I=0;J=0;M101=M12(K11)-1
           DO 673 K1=K7,KL51,K8
           J=J+1;MSLP5=MSLP5+1
           AZ8PL(J,M)=EFZIA(K1);AZ9PL(J,M)=PDROP(K1)
           DO 673 M1=M15,M12(K11),M101
           I=I+1;MSLP3=MSLP3+1;MSLP4=MSLP4+1
           AZ2PL(I,M)=AT(M1,K1);AZ3PL(I,M)=ATH(M1,K1)
           AZ4PL(I,M)=ANX(M1,K1);AZ5PL(I,M)=AXEN(M1,K1)
           AZ6PL(I,M)=AXRMN(M1,K1);AZ7PL(I,M)=QR1B(M1,K1)
     673   CONTINUE
```

```
      DO 674 M1=M15,M12(K11),M101
      I=I+1;MSLP3=MSLP3+1
      AZ2PL(I,M)=AT(M1,K5)
      AZ3PL(I,M)=ATH(M1,K5)
674   CONTINUE
      MSLP6=MSLP5+2;AZ9PL((J+1),M)=PDROP(K5)
      AZ9PL((J+2),M)=TPRD
      I=0;MSLP=0
      IF(IOP201.NE.1)GO TO 677
      DO 675 K1=K7,KL51,K8
      DO 675 M1=5,M101,M16
      I=I+1;MSLP=MSLP+1
      AZ11PL(I,M)=AT(M1,K1);AZ12PL(I,M)=ANX(M1,K1)
675   CONTINUE
      M167=2*M16;I=0;MSLP1=0
      DO 676 K1=K7,K5,K8
      DO 676 M1=7,M101,M167
      I=I+1;MSLP1=MSLP1+1
      AZ14PL(I,M)=ATH(M1,K1)
676   CONTINUE
      I=0;MSLP2=0
      DO 677 M1=7,M101,M167
      I=I+1;MSLP2=MSLP2+1
      AZ15PL(I,M)=AT(M1,K5)
677   CONTINUE
      J1=M;J11=1
      IF(IOP201.EQ.1)GO TO 7048
      WRITE(12,7049),(I,TPRD,PFN(I),TFN(I),VFTN(I),RATION(I)
      1,FC3N(I),FC4N(I),FC5N(I),FD44N(I),FD22N(I),FD33N(I)
      2,VCATN(I),OBJF2(I),
      2DBED2N(I),DBED3N(I),HLLN(I),UARN(I),UAHN(I)
      2,FF1N(I),I=MJK1,MJK1)
C     PRINT 7049,(I,TPRD,PFN(I),TFN(I),VFTN(I),RATION(I)
C     1,FC3N(I),FC4N(I),FC5N(I),FD44N(I),FD22N(I),FD33N(I)
C     2,VCATN(I),OBJF2(I),
C     2DBED2N(I),DBED3N(I),HLLN(I),UARN(I),UAHN(I)
C     2,FF1N(I),I=MJK1,MJK1)
```

```
      WRITE(3,7058),M106,M107,((STLP2(J,I),SALP2(J,I),J=1,M107),
     8(STLP(J,I),SALP(J,I),J=1,M106),I=M,M)
C     PRINT 7058,M106,M107,((STLP2(J,I),SALP2(J,I),J=1,M107),
C    8(STLP(J,I),SALP(J,I),J=1,M106),I=M,M)
 7058 FORMAT(2I3,(6(F6.1,F7.3)/))
      WRITE(12,7050),((M1,ALZP(M1,K1),AT(M1,K1),ANX(M1,K1),
     2AXRMN(M1,K1),AXEN(M1,K1),M1=1,M12(K11)),K1=1,KL51)
 7050 FORMAT(2(I4,2F6.1,3F7.3)/)
C     PRINT 7050,((M1,AZP(M1,K1),AT(M1,K1),ANX(M1,K1),
C    2AXRMN(M1,K1),AXEN(M1,K1),M1=1,M12(K11)),K1=1,KL51)
      IF(IOP201.NE.1)GO TO 7037
 7048 CONTINUE
      IF(IOPT2.NE.1)GO TO 7037
      WRITE(3,7049),(I,TPRD,PFN(I),TFN(I),VFTN(I),RATION(I)
     1,FC3N(I),FC4N(I),FC5N(I),FD44N(I),FD22N(I),FD33N(I)
     2,VCATN(I),OBJF2(I),
     2DBED2N(I),DBED3N(I),HLLN(I),UARN(I),UAHN(I)
     2,FF1N(I),I=M,M)
C     PRINT 7014,((STLP(J,I),SALP(J,I),J=1,M106),
C    1(STLP2(J,I),SALP2(J,I),J=1,M107),I=M,M)
 7014 FORMAT(1X,10(F6.1,F7.3))
 7051 FORMAT(6(F6.1,F7.3)/)
      WRITE(3,7051),((STLP(J,I),SALP(J,I),J=1,M106),
     1(STLP2(J,I),SALP2(J,I),J=1,M107),I=M,M)
      IF(ITYPE.NE.2)GO TO 7030
      TYPE 7014,((STLP(J,I),SALP(J,I),J=1,M106),
     1(STLP2(J,I),SALP2(J,I),J=1,M107),I=M,M)
 7030 CONTINUE
C     PRINT 7016,((AZ11PL(J,I),J=1,MSLP),(AZ14PL(J,I),J=1,MSLP1)
C    1,(AZ15PL(J,I),J=1,MSLP2),I=M,M)
 7016 FORMAT(1X,21(F6.1))
 7052 FORMAT(2X,12(F6.1))
      WRITE(3,7052),((AZ11PL(J,I),J=1,MSLP),(AZ14PL(J,I),J=1,MSLP1)
     1,(AZ15PL(J,I),J=1,MSLP2),I=M,M)
      IF(ITYPE.NE.2)GO TO 7031
      TYPE 7016,((AZ11PL(J,I),J=1,MSLP),(AZ14PL(J,I),J=1,MSLP1)
     1,(AZ15PL(J,I),J=1,MSLP2),I=M,M)
```

```
 7031     CONTINUE
 C        PRINT 7018,((AZ12PL(J,I),J=1,MSLP),I=M,M)
 7018     FORMAT(2X,18(F7.3))
 7053     FORMAT(2X,11(F7.3))
          WRITE(3,7053),((AZ12PL(J,I),J=1,MSLP),I=M,M)
          IF(ITYPE.NE.2)GO TO 7032
          TYPE 7018,((AZ12PL(J,I),J=1,MSLP),I=M,M)
 7032     CONTINUE
 C        PRINT 7020,((AZ2PL(J,I),AZ3PL(J,I),J=1,MSLP3),I=M,M)
 7020     FORMAT(2X,21(F6.1))
 7054     FORMAT(2X,12(F6.1))
          WRITE(3,7054),((AZ2PL(J,I),AZ3PL(J,I),J=1,MSLP3),I=M,M)
          IF(ITYPE.NE.2)GO TO 7033
          TYPE 7020,((AZ2PL(J,I),AZ3PL(J,I),J=1,MSLP3),I=M,M)
 7033     CONTINUE
 C        PRINT 7022,((AZ4PL(J,I),AZ5PL(J,I),AZ6PL(J,I),AZ7PL(J,I),
 C        1J=1,MSLP4),I=M,M)
 7022     FORMAT(2X,4(3F7.3,E11.3))
 7055     FORMAT(2X,2(3F7.3,E11.3))
          WRITE(3,7055),((AZ4PL(J,I),AZ5PL(J,I),AZ6PL(J,I),AZ7PL(J,I),
          1J=1,MSLP4),I=M,M)
          IF(ITYPE.NE.2)GO TO 7034
          TYPE 7022,((AZ4PL(J,I),AZ5PL(J,I),AZ6PL(J,I),AZ7PL(J,I),
          1J=1,MSLP4),I=M,M)
 7034     CONTINUE
 C        PRINT 7024,((AZ8PL(J,I),J=1,MSLP5),I=M,M)
 7024     FORMAT(1X,18(F7.3))
 7056     FORMAT(2X,11(F7.3))
          WRITE(3,7056),((AZ8PL(J,I),J=1,MSLP5),I=M,M)
          IF(ITYPE.NE.2)GO TO 7035
          TYPE 7024,((AZ8PL(J,I),J=1,MSLP5),I=M,M)
 7035     CONTINUE
 C        PRINT 7026,((AZ9PL(J,I),J=1,MSLP6),I=M,M)
          WRITE(3,7057),((AZ9PL(J,I),J=1,MSLP6),I=M,M)
          IF(ITYPE.NE.2)GO TO 7037
          TYPE 7026,((AZ9PL(J,I),J=1,MSLP6),I=M,M)
 7037     CONTINUE
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APPENDIX-B

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RS
7026   FORMAT(1X,18(F7.2))
       IF(IOL2.NE.1)GO TO 8256
7057   FORMAT(2X,11(F7.2))
       J1=MJK1;J11=MJK1
8256   CONTINUE
       ANH3L(J1)=ANX(M12(K11),K5);I1=0
       APDRLP(J1)=AP(M12(K11),K5)
       DO 8744 K1=K7,K5,KJ81
       DO 8744 I=1,NBPTS(K1,J11)
       I1=I1+I
       IF(NBPTS(K1,J11).EQ.1)GO TO 8745
       MN81=M15+NLPD(I,K1,J11)
       GO TO 8746
8745   CONTINUE
       MN81=M12(K11)
8746   ATPL2(I1,J1)=AT(MN81,K1)
       ERRT=TA(I,K1,J11)-ATPL2(I1,J1);SET=ERRT*ERRT;SSE1=SSE1+SET
       ERRT1=ATPL2(I1,J1)-ATPL2(I1,1);SET1=ERRT1*ERRT1;SSE2=SSE2+SET1
8744   CONTINUE
       ERAM=AMMD(J11)-ANH3L(J1);ERAM1=ANH3L(J1)-ANH3L(1)
       APDL=APDRPL(J11)-APDRLP(J1);SEPD=APDL*APDL
       APDL1=APDRLP(J1)-APDRLP(1);SEPD1=APDL1*APDL1
       SSE3=SSE3+SEPD;SSE4=SSE4+SEPD1
       SEA=ERAM*ERAM*WTFN;SSE5=SSE5+SEA;SSE1=SSE1+SEA
       SEA1=ERAM1*ERAM1;SSE6=SSE6+SEA1;SSE7=SSE7+SSE1+SSE3+SSE5
       SSE8=SSE8+SSE2+SSE4+SSE6
       SSE=SSE+SSE1+SSE5
C      PRINT 7039,SSE,SSE1,SSE2,SSE3,SSE4,SSE5,SSE6,SSE7,SSE8
C      WRITE(3,7061),SSE,SSE1,SSE2,SSE3,SSE4,SSE5,SSE6,SSE7,SSE8
7039   FORMAT(9E11.3)
7061   FORMAT(7E11.3)
       IF(ITYPE.NE.2)GO TO 7041
       TYPE 7039,SSE,SSE1,SSE2,SSE3,SSE4,SSE5,SSE6,SSE7,SSE8
7041   CONTINUE
       IF(IOL2.EQ.1)GO TO 209
       N2LEP=LPOBJN(MJK1)
       IF(ITYP11.NE.1)N2LEP=1
```

```
      IF(M.NE.1)GO TO 7081
      SES=SSE;SES1=SSE1;SES2=SSE2;SES3=SSE3;SES4=SSE4;SES5=SSE5
      SES6=SSE6;SES7=SSE7;SES8=SSE8
7081  CONTINUE
      CALL FUNOBJ(OBJF,M,N2LEP,PATD,OBLPN(ILPS2)
      1,SSE,SSE1,SSE2,SSE3,
      1SSE4,SSE5,SSE6,SSE7,SSE8,SES,SES1,SES2,SES3,SES4
      1,SES5,SES6,SES7,SES8,OBJF32)
      CALL FUNOBJ(OBJF3,M,LPOBJN(MJK1),PATD,OBLPN(ILPS2)
      1,SSE,SSE1,SSE2,SSE3,
      1SSE4,SSE5,SSE6,SSE7,SSE8,SES,SES1,SES2,SES3,SES4
      1,SES5,SES6,SES7,SES8,OBJF31)
      CALL FUNOBJ(OBJF4,M,NOBLP1,PATD,OBLPN(ILPS2)
      1,SSE,SSE1,SSE2,SSE3,
      1SSE4,SSE5,SSE6,SSE7,SSE8,SES,SES1,SES2,SES3,SES4
      1,SES5,SES6,SES7,SES8,OBJF33)
      GO TO 209
299   APATD(MJK1)=0.0;PATD1=0.0;PATD=0.0;IM8=1;MLPK1=MLPK1+1
      M107=M107+1;SALP2(M107,M)=0.0;STLP2(M107,M)=0.0
      M107=M107+1;SALP2(M107,M)=0.0;STLP2(M107,M)=0.0
      IF(LPOBJN(MJK1).NE.1)GO TO 4441
      OBJF(M)=0.0
      GO TO 4442
4441  OBJF(M)=ABCD2
4442  CONTINUE
      IF(IOL2.EQ.1)GO TO 764
      IF(J5.EQ.0)GO TO 764
      GO TO 1703
  719 CONTINUE
      IF(OBJF(M).EQ.ABCD2)GO TO 761
761   CONTINUE
      IF(OBJLPN(M).NE.0.0)IOPT2=3
     IF(IOPT2.EQ.3) GO TO 92
     IF(M.GT.1) GO TO 785
      IF(M1LP.GT.1)GO TO 4440
      IF(M8LP.GT.1)GO TO 4440
   92 VFT(M)=VFTN(MJK1)
```

```
      RATIO(M)=RATION(MJK1)
        FC1(M)=FC1N(MJK1);FC2(M)=FC2N(MJK1)
      FC3(M)=FC3N(MJK1)
      FC4(M)=FC4N(MJK1)
      FC5(M)=FC5N(MJK1)
      FD22(M)=FD22N(MJK1);FD33(M)=FD33N(MJK1)
       FD44(M)=FD44N(MJK1);PF(M)=PFN(MJK1)
      TF(M)=TFN(MJK1);VCAT(M)=VCATN(MJK1)
      DBED2(M)=DBED2N(MJK1);DBED3(M)=DBED3N(MJK1)
      HLL(M)=HLLN(MJK1);UAR(M)=UARN(MJK1);UAH(M)=UAHN(MJK1)
      FF1(M)=FF1N(MJK1);FD55(M)=FD55N(MJK1)
        G1=VFT(M);G3=RATIO(M);G5=FC3(M);G7=FC4(M);G9=FC5(M);G11=FD22(M)
        G13=FD33(M);G15=FD44(M);G17=PF(M);G19=TF(M);G21=VCAT(M)
        G23=DBED2(M);G25=DBED3(M);G27=HLL(M);G29=UAR(M);G31=UAH(M)
```

```
      G33=FD55(M)
 4440 CONTINUE
      I26=M
      M3LP=1
      CALL PCONV(I26,M3LF,AQX)
 785  CONTINUE
      IF(M.LT.ND2PL)GO TO 98
      NOPTM=M
      GO TO 1709
   98 IF(IOPT2.EQ.3) GO TO 602
      NCOLD=12
      IF(IOL2.EQ.1)NCOLD=1
      CALL PNEXT(NVLPI,NCOLD,M,AQX,ISIGPL)
      IF(NVLPI.GT.NVARI)GO TO 755
      SSE=0.0;SSE1=0.0;SSE2=0.0;SSE3=0.0;SSE4=0.0;SSE5=0.0
      SSE6=0.0;SSE7=0.0;SSE8=0.0
      IF(IOPT8-2)1844,1808,1817
 1709 CONTINUE
      ISIGPL=1;ND7PL=1
      IF(IOL2.EQ.1)GO TO 7704
      DO 8701 I=1,M
      OBJF2(I)=OBJF(I)*OBJF32
 8701 CONTINUE
C     IF(NOBJLP(MJK1).LT.2)GO TO 8761
C     DO 8761 L=1,NVARI
C     AQX8(M1LP,L)=AGX(NOPTM,L)
C8761 CONTINUE
      PRINT 866,OBJF31,OBJF33,(I,PF(I),TF(I),VFT(I),RATIO(I)
      1,FC3(I),FC4(I),FC5(I),FD44(I),FD22(I),FD33(I)
      2,VCAT(I),OBJF2(I),OBJF3(I),OBJF4(I),
      2DBED2(I),DBED3(I),HLL(I),UAR(I),UAH(I)
      2,FD55(I),AQX(I,18),AQX(I,19),AQX(I,20),I=1,M)
      WRITE(3,7049),(I,TPRD,PF(I),TF(I),VFT(I),RATIO(I)
      1,FC3(I),FC4(I),FC5(I),FD44(I),FD22(I),FD33(I)
      2,VCAT(I),OBJF2(I),
      2DBED2(I),DBED3(I),HLL(I),UAR(I),UAH(I)
      2,FF1(I),I=1,M)
```

```
 7049 FORMAT(I3,F5.2,2F6.1,F9.1,F4.1,F5.2,F6.2,F5.2,3F6.3,F5.1
      1,F7.1/2F5.2,F6.2,F6.1,F7.1,F5.2)
      IF(IOP201.NE.1)GO TO 7027
      PRINT 7014,((STLP(J,I),SALP(J,I),J=1,M106),
      1(STLP2(J,I),SALP2(J,I),J=1,M107),I=1,M)
      WRITE(3,7051),((STLP(J,I),SALP(J,I),J=1,M106),
      1(STLP2(J,I),SALP2(J,I),J=1,M107),I=1,M)
      IF(ITYPE.NE.2)GO TC 7015
      TYPE 7014,((STLP(J,I),SALP(J,I),J=1,M106),
      1(STLP2(J,I),SALP2(J,I),J=1,M107),I=1,M)
 7015 CONTINUE
      PRINT 7016,((AZ11PL(J,I),J=1,MSLP),(AZ14PL(J,I),J=1,MSLP1)
      1,(AZ15PL(J,I),J=1,MSLP2),I=1,M)
      WRITE(3,7052),((AZ11PL(J,I),J=1,MSLP),(AZ14PL(J,I),J=1,MSLP1)
      1,(AZ15PL(J,I),J=1,MSLP2),I=1,M)
      IF(ITYPE.NE.2)GO TC 7017
      TYPE 7016,((AZ11PL(J,I),J=1,MSLP),(AZ14PL(J,I),J=1,MSLP1)
      1,(AZ15PL(J,I),J=1,MSLP2),I=1,M)
 7017 CONTINUE
      PRINT 7018,((AZ12PL(J,I),J=1,MSLP),I=1,M)
      WRITE(3,7053),((AZ12PL(J,I),J=1,MSLP),I=1,M)
      IF(ITYPE.NE.2)GO TC 7019
      TYPE 7018,((AZ12PL(J,I),J=1,MSLP),I=1,M)
 7019 CONTINUE
      PRINT 7020,((AZ2PL(J,I),AZ3PL(J,I),J=1,MSLP3),I=1,M)
      WRITE(3,7054),((AZ2PL(J,I),AZ3PL(J,I),J=1,MSLP3),I=1,M)
      IF(ITYPE.NE.2)GO TC 7021
      TYPE 7020,((AZ2PL(J,I),AZ3PL(J,I),J=1,MSLP3),I=1,M)
 7021 CONTINUE
      PRINT 7022,((AZ4PL(J,I),AZ5PL(J,I),AZ6PL(J,I),AZ7PL(J,I),
      1J=1,MSLP4),I=1,M)
      WRITE(3,7055),((AZ4PL(J,I),AZ5PL(J,I),AZ6PL(J,I),AZ7PL(J,I),
      1J=1,MSLP4),I=1,M)
      IF(ITYPE.NE.2)GO TC 7023
      TYPE 7022,((AZ4PL(J,I),AZ5PL(J,I),AZ6PL(J,I),AZ7PL(J,I),
      1J=1,MSLP4),I=1,M)
 7023 CONTINUE
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      PRINT 7024,((AZ8PL(J,I),J=1,MSLP5),I=1,M)
      WRITE(3,7056),((AZ8PL(J,I),J=1,MSLP5),I=1,M)
      IF(ITYPE.NE.2)GO TO 7025
      TYPE 7024,((AZ8PL(J,I),J=1,MSLP5),I=1,M)
7025  CONTINUE
      PRINT 7026,((AZ9PL(J,I),J=1,MSLP6),I=1,M)
      WRITE(3,7057),((AZ9PL(J,I),J=1,MSLP6),I=1,M)
      IF(ITYPE.NE.2)GO TO 7027
      TYPE 7026,((AZ9PL(J,I),J=1,MSLP6),I=1,M)
7027  CONTINUE
      IF(ITYPE.NE.2)GO TO 884
      TYPE 866,OBJF31,OBJF33,(I,PF(I),TF(I),VFT(I),RATIO(I)
      1,FC3(I),FC4(I),FC5(I),FD44(I),FD22(I),FD33(I)
      2,VCAT(I),OBJF2(I),OBJF3(I),OBJF4(I),
      2DBED2(I),DBED3(I),HLL(I),UAR(I),UAH(I)
      2,FD55(I),AQX(I,18),AQX(I,19),AQX(I,20),I=1,M)
866   FORMAT(/2X,'OPTIMISATION RESULTS:'/2X
      1,'S.',29X,'DATA SET',29X,'MAXIMUM AMMONIA'/
      12X,'NO.',65X,'PRODUCTION RATE'/70X,'(TONS PER DAY)'/
      12X,F12.4,2X,F12.4/
      1(1X,I3,2X,2F6.1,F9.1,F4.1,F5.2,F6.2,F5.2,3F6.3,F5.1
      1,6X,F7.1,11X,F12.4,2X,F12.4/6X,2F5.2,F6.2,F6.1,F7.1,F6.3,F11.8,
      1F11.8,F8.4)/)
884   ISM=1;M=NOPTM
      PRINT 1712,OBJF2(M),PF(M),TF(M),FF1(M),VFT(M),FC1(M)
      1,FC2(M),FC3(M),FC4(M),FC5(M),FD55(M),FD44(M),FD22(M),FD33(M)
      2,VCAT(M),DBED2(M),DBED3(M),HLL(M),UAR(M),UAH(M)
      IF(ITYPE.NE.2)GO TO 704
      TYPE 1712,OBJF2(M),PF(M),TF(M),FF1(M),VFT(M),FC1(M)
      1,FC2(M),FC3(M),FC4(M),FC5(M),FD55(M),FD44(M),FD22(M),FD33(M)
      2,VCAT(M),DBED2(M),DBED3(M),HLL(M),UAR(M),UAH(M)
1712  FORMAT(/2X,'OPTIMUM PRODUCTION RATE OF AMMONIA(TONS PER DAY)='
      1,F10.2/2X,'OPTIMUM PARAMETERS:'/2X,'PRESSURE(ATM)='
      2,F8.2,8X,',FEED TEMPERATURE(K)=',F8.2
      3,',CATALYST ACTIVITY FACTOR=',F5.2/2X,
      4'FEED FLOW RATE(NORMAL CUBIC METER/HOUR)=',F10.2/2X,
      5'FEED COMPOSITION(MOLE %):HYDROGEN=',
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      6F8.2,',NITROGEN=',F8.2,',AMMONIA=',F8.2,',METHANE=',F8.2,
      7',ARGON=',F8.2/2X,'COLD SHOT DISTRIBUTION:',
      7'HEAT EXCHANGER EXIT(SHELL SIDE)=',F8.3,',FIRST BED='
      8,F8.3,',SECOND BED=',F8.3,',THIRD BED=',F8.3/2X,
      9'CATALYST VOLUME(CUBIC METER)=',F8.2,2X,
     A',CATALYST DISTRIBUTION:BED1:BED2:BED3=1.00:'
     B,F5.2,':',F5.2/2X,'EXTERNAL PREHEATER VOLUME(CUBIC METER)='
     C,F8.2/2X,
     D'HEAT EXCHANGE CAPACITIES IN CAL/(SEC)(K)(CUBIC METER):INTERNAL=
     E',F8.2,',EXTERNAL=',F8.2/)
      GO TO 704
7704  CONTINUE
      PRINT 7705,(AQX(NOPTM,J),J=18,20),OBJF2(NOPTM)
      PRINT 7706,(I,(AQX(I,J),J=18,20),OBJF2(I),I=1,M)
      PRINT 7707,(I,PFN(I),TFN(I),FF1N(I),VFTN(I),FC1N(I),
      1FC2N(I),FC3N(I),FC4N(I),FC5N(I),VCATN(I),HLLN(I),
      1UARN(I),UAHN(I),FD55N(I),FD44N(I),FD22N(I),FD33N(I),DBED2N(I),
      1DBED3N(I),I=1,M5)
      IF(ITYPE.NE.2)GO TO 5204
      TYPE 7707,(I,PFN(I),TFN(I),FF1N(I),VFTN(I),FC1N(I),
      1FC2N(I),FC3N(I),FC4N(I),FC5N(I),VCATN(I),HLLN(I),
      1UARN(I),UAHN(I),FD55N(I),FD44N(I),FD22N(I),FD33N(I),DBED2N(I),
      1DBED3N(I),I=1,M5)
      TYPE 7706,(I,(AQX(I,J),J=18,20),OBJF2(I),I=1,M)
      TYPE 7705,(AQX(NOPTM,J),J=18,20),OBJF2(NOPTM)
7705  FORMAT(2X,'DATA VALIDATION RESULTS:OPTIMUM PARAMETERS OF REACTION
      1RATE:'/2X,'PARA1=',F8.4,',PARA2=',F11.8,',PARA3=',F8.4,':',
      111X,'SUM OF SQUARES(AVG.)=',F12.4/)
7706  FORMAT(2X,'S.',17X,'DATA SET',41X,'SUM OF SQUARES OF ERROR IN BE
      1/2X,'NO.',65X,'TEMP. AND AMMONIA EXIT MOLE(%) BETWEEN'/70X,
      1'COMPUTED RESULTS AND PLANT DATA(AVG.)'/(1X,I3,
      12X,F8.4,2X,F11.8,2X,F8.4,40X,F12.4/))
7707  FORMAT(2X,'PLANT DATA SET:'/(2X,
      1'DATA SET NO.=',I3/2X,'FEED PRESS.(ATM)=',F8.2,2X,
      1',FEED TEMP.(K)=',F8.2,',CATALYST ACTIVITY FACTOR=',F5.2,
      12X,',FEED FLOW RATE(NM3/HR)=',F10.2/2X,
      1'FEED COMPOSITION(MOLE%):H2=',F8.2,',N2=',F8.2,',NH3=',F8.2,
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             1',CH4=',F8.2,',A=',F8.2/2X,'CATALYST VOL(M3)=',F7.2,2X,
             1',EXT.PREHEATER VOL(M3)=',F7.2,2X,',HEAT EXCHANGE CAPACITIES,CA
             1 K M3:INTERNAL=',F8.1,',EXTERNAL=',F8.1/2X,
             1'COLD SHOT DISTRIBUTION:',
             7'HEAT EXCHANGER EXIT(SHELL SIDE)=',F8.3,',FIRST BED='
             1,F8.3,',SECOND BED=',F8.3,',THIRD BED=',F8.3/2X,
             1'CATALYST DISTRIBUTION:BED1:BED2:BED3:1.00:',F5.2,':',F5.2))
             GO TO 5204
704          CONTINUE
             IF(NOBJLP(MJK1).GE.12)GO TO 701
C            IF(M.GT.1)GO TO 8761
             IF(M1LP.GT.1)GO TO 8761
             IF(M8LP.GT.1)GO TO 8761
             DO 8761 L=1,NVARI
             AQX8(1,L)=AQX(1,L);AQX9(1,L)=AQX(1,L)
8761         CONTINUE
             OBJF8(M1LP)=OBJF3(NOPTM)
             OBJF5(M1LP)=OBJF4(NOPTM)
             IF(OBJF31.EQ.0.0)GO TO 697
             OBJF82(M1LP)=OBJF3(NOPTM)*OBJF31
             GO TO 698
697          OBJF82(M1LP)=OBJF3(NOPTM)
698          CONTINUE
             M1LP=M1LP+1;M=1;NOPTM=0;NVLPI=0
             IF(NOBJLP(MJK1).GE.2)GO TO 205
      701 IF(MJK1.GE.M5)GO TO 204
           MM1=MM1+1;IM=IM+1;MJK1=MJK1+1;M1LP=1;NV1LP=0;NOPTM1=0
             ISIPL2=1;ND7PL=1;M8LP=1
             IF(IOL2.EQ.1)GO TO 205
             IF(NOBJLP(MJK1).GE.2)GO TO 205
             IF(IOP201.NE.1)GO TO 601
           READ(8,*)PARA1,PARA2,PARA3,PARA4,IOP26,ICP29,
             1IHH1,IHH2,IHH3,IHH4,W11,W11L,W11H,J5,M81,M15,M16,M161,
             1K7,K8,C71,C72,C73,C74,
          2UV,C2,IOPT2,ICSIZE,IOPT3,IOPT8,IOPT1,IOPT4,NUMBP
             PRINT 758
             IF(ITYPE.NE.2)GO TO 794
```

```
            TYPE 758
758         FORMAT(2X,'ADDITIONAL DATA FOR SUBSEQUENT SET:'/)
794          PRINT *,PARA1,PARA2,PARA3,PARA4,IOP26,IOP29,
            1IHH1,IHH2,IHH3,IHH4,W11,W11L,W11H,J5,M81,M15,M16,M161,
            1K7,K8,C71,C72,C73,C74,FF,
         2UV,C2,IOPT2,ICSIZE,IOPT3,IOPT8,IOPT1,IOPT4,NUMBP
            IF(ITYPE.NE.2)GO TO 601
          TYPE *,PARA1,PARA2,PARA3,PARA4,IOP26,IOP29,
            1IHH1,IHH2,IHH3,IHH4,W11,W11L,W11H,J5,M81,M15,M16,M161,
            1K7,K8,C71,C72,C73,C74,FF,
         2UV,C2,IOPT2,ICSIZE,IOPT3,IOPT8,IOPT1,IOPT4,NUMBP
601         IF(IOPT2.EQ.1)GO TO 205
            IF(M.GT.1)IOPT2=3
          GO TO 205
602         IF(M.EQ.NDPTS)GO TO 755
            M=M+1
            IF(OBJLPN(M).EQ.0.0)GO TO 701
            PATD=OBJLPN(M);MJK1=MJK1+1;APATD(MJK1)=PATD;PATD1=PATD
            IM8=1;MLPK1=MLPK1+1;OBJF(M)=PATD
            GO TO 719
            M3LP=1;I26=0
1835        I26=I26+1
            CALL PCONV(I26,M3LP,AQX)
            IF(I26.LT.M)GO TO 1835
2600        CONTINUE
            GO TO 755
209         GO TO 800
764         IF(MJK1-M5)206,728,204
728         IF(IOPT2-2)204,1907,719
204         IF(IOL2.NE.1)GO TO 5204
            IF(MLPK1.EQ.M5)GO TO 5214
            OBJF2(M)=SSE/(M5-MLPK1);MJK1=1
            IF(OBJF2(1).EQ.0.0)GO TO 692
            OBJF(M)=-OBJF2(M)/OBJF2(1)
            GO TO 693
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RS APPENDIX-B

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692     OBJF(M)=-OBJF2(M)
693     CONTINUE
        ML1KP=M5-MLPK1
        SSE=SSE/ML1KP;SSE1=SSE1/ML1KP;SSE2=SSE2/ML1KP;SSE3=SSE3/ML1KP
        SSE4=SSE4/ML1KP;SSE5=SSE5/ML1KP;SSE6=SSE6/ML1KP;SSE7=SSE7/ML1KP
        SSE8=SSE8/ML1KP
        IF(M.NE.1)GO TO 92
        SES=SSE;SES1=SSE1;SES2=SSE2;SES3=SSE3;SES4=SSE4;SES5=SSE5
        SES6=SSE6;SES7=SSE7;SES8=SSE8
        GO TO 92
5214    MJK1=1;OBJF2(M)=100*OBJF2(1);OBJF(M)=-100.0
        GO TO 92
1907    GO TO 719
710     CONTINUE
        IF(IOL2.EQ.1)GO TO 701
        M=1
        GO TO 701
206     IF(IOPT2-2)710,1907,719
800     IF(IOPT4.EQ.2)GO TO 1703
      M1K1=1
      IF(IOPT2.NE.1) GO TO 605
      GO TO 614
605     CONTINUE
614     IF(IOPT2.NE.1)GO TO 620
      GO TO 1703
620     CONTINUE
1703    IF(ISM.EQ.1)GO TO 764
        IF(IOL2.EQ.1)GO TO 764
755   CONTINUE
854     CONTINUE
        N2LEP=LPOBJN(MJK1)
        IF(ITYP11.NE.1)N2LEP=1
        CALL FUNOBJ(OBJF,M,N2LEP,PATD,OBLPN(ILPS2)
        1,SSE,SSE1,SSE2,SSE3,
        1SSE4,SSE5,SSE6,SSE7,SSE8,SES,SES1,SES2,SES3,SES4
        1,SES5,SES6,SES7,SES8,OBJF32)
        CALL FUNOBJ(OBJF3,M,LPOBJN(MJK1),PATD,OBLPN(ILPS2)
```

```
             1,SSE,SSE1,SSE2,SSE3,
             1SSE4,SSE5,SSE6,SSE7,SSE8,SES,SES1,SES2,SES3,SES4
             1,SES5,SES6,SES7,SES8,OBJF31)
             CALL FUNOBJ(OBJF4,M,NOBLP1,PATD,OBLPN(ILPS2)
             1,SSE,SSE1,SSE2,SSE3,
             1SSE4,SSE5,SSE6,SSE7,SSE8,SES,SES1,SES2,SES3,SES4
             1,SES5,SES6,SES7,SES8,OBJF33)
       857 CALL OPTIMA(OBJF,M,AGX,AQX1,IOPT8,NVARI,AC2,NLEV,
             1NOPTM,TOL8,NMAX1,NDPTS,XLPX,
             1OBLPF,NLN8,ALPC1,YLPN,IOL8P)
             SSE=0.0;SSE1=0.0;SSE2=0.0;SSE3=0.0;SSE4=0.0;SSE5=0.0
             SSE6=0.0;SSE7=0.0;SSE8=0.0
             IF(NOPTM.NE.0)GO TO 1709
             NDPTS2=NDPTS*NDLPS
             IF(M.GE.ND2PL)GO TO 881
           ISM=ISM+1 ; IM=1
             IF(IOPT8-2)1844,1808,1817
     881     NOPTM=NMAX1;M=M-1
             GO TO 1709
      1808 CALL INTEGR(AQX,NVARI,M)
           GO TO 862
      1817 CALL MLEVEL(AQX,NVARI,AQX1,M,NLEV)
             GO TO 862
     1844    CONTINUE
     862     CONTINUE
             I26=M
             M3LP=2
             CALL PCONV(I26,M3LP,AQX)
             IF(M.LE.NDPTS)GO TO 7224
             CALL ACOMP(LPIK,AQX,M,NVARI)
             IF(LPIK.EQ.0)GO TO 7224
             OBJF3(M)=OBJF3(LPIK);OBJF4(M)=OBJF4(LPIK)
             OBJF(M)=OBJF(LPIK);PATD=OBJF(LPIK)*OBLPN(ILPS2);LPIK=0
             IF(ISM.EQ.1)GO TO 764
           GO TO 857
     C     OUTPUT STATEMENTS PROGRAM
       404 PRINT 403,IJ1,IJ2,IJ3,IJ4
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      IF(ITYPE.NE.2)GO TC 405
     TYPE 403,IJ1,IJ2,IJ3,IJ4
403 FORMAT(/1X,57X,6HSTART  //   44X,6HDATE: ,I3,2H.,,I3,2H.,,I5,9H; R
   1UN NO. ,I3   //   2X, 62HNAME OF THE STUDENT(PART TIME):SUDHINDRA
   2NATH SINHA,LECTURER    //   2X,81HDEPARTMENT OF CHEMICAL ENGINEERI
   3NG,UNIVERSITY OF ROORKEE,ROORKEE(U.P.),PIN 247667    //2X,'PHD THE
   4SIS PROBLEM :  'STABILITY ANALYSIS AND OPTIMIZATION OF A MULTIBED
      8QUENCH REACTOR FOR AMMONIA SYNTHESIS '/
   5        /2X,'PHD.THESIS SUPERVISOR: DR.SHANT KUMAR SARAF,SC.D.(M.I
   6.T.,U.S.A.),PROFESSOR,DEPTT.OF CHEM.ENGG.,UNIVERSITY OF ROORKEE'
   7//)
     GO TO 405
407 CONTINUE
      IF(ITYPE8.NE.1)GO TO 287
      IF(M.EQ.1) GO TO 632
     IF(IOPT2-2)632,638,647
647 IF(M.GT.NDPTS) GO TO 638
632 PRINT 408,XW,UV,VFTN(MJK1),FC1N(MJK1),FC2N(MJK1),FC3N(MJK1),
   1FC4N(MJK1),FC5N(MJK1),AFD4,AFD2,AFD3,AFD01,ZC1,ZC2,ZC3,HCL,RUAI
      IF(ITYPE.NE.2)GO TC 806
     TYPE  408,XW,UV,VFTN(MJK1),FC1N(MJK1),FC2N(MJK1),FC3N(MJK1),
   1FC4N(MJK1),FC5N(MJK1),AFD4,AFD2,AFD3,AFD01,ZC1,ZC2,ZC3,HCL,RUAI
     GO TO 806
638 PRINT408,XW,UV,VFT(M),FC1(M),FC2(M),FC3(M),FC4(M)
      1,FC5(M),AFD4,AFD2,AFD3,AFD01,ZC1,ZC2,ZC3,
   2HCL, RUAI
      IF(ITYPE.NE.2)GO TC 806
     TYPE 408,XW,UV,VFT(M),FC1(M),FC2(M),FC3(M),FC4(M)
      1,FC5(M),AFD4,AFD2,AFD3,AFD01,ZC1,ZC2,ZC3,
   2HCL, RUAI
408 FORMAT(  2X,'FEED : PRESSURE(ATM)=',F7.1, ';TEMP.(K)=',F7.1
   1//2X,'VOLUMETRIC FLOW RATE OF TOTAL FEED(NORMAL CUBIC METER/HOUR)=
   2',F10.1//2X,'FEED COMPOSITION(MOLE%):'/2X,'HYDROGEN',
   35X,F8.2/2X,'NITROGEN',5X,F8.2/2X,'AMMONIA',6X,F8.2/2X,'METHANE',
   46X,F8.2/2X,'ARGON',8X,F8.2//2X,'COLD SHOT DISTRIBUTION:FIRST BED='
   5,F6.3,',SECOND BED=',F6.3,',THIRD BED=',F6.3,';EXTERNAL PREHEATER
   6FEED=',F6.3//       2X,
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     7'CATALYST SPLIT IN CUBIC METER:  FIRST BED=',
     8F7.1,12H,SECOND BED=,F7.1,11H,THIRD BED=,F7.1   /  2X,40HHEAT EXCH
     9ANGER TUBE SIDE VOLUME(CU.MR.)=,F7.1/2X,52HRATE OF HEAT TRANSFER/(
     ATEMP.DIFFERENCE)FOR REACTOR=  ,      F7.1     )
 806 PRINT807,HUAI ,F
        IF(ITYPE.NE.2)GO TO 287
      TYPE 807,HUAI ,F
 807 FORMAT(2X,42HHEAT TRANSFER CAPACITY FOR HEAT EXCHANGER=,
     1F8.1,42H CAL./(SEC)(K)(CU.MR.OF TUBE SIDE VOLUME) /2X,
     225HCATALYST ACTIVITY FACTOR=  ,F5.2/)
      GO TO 287
401     IF(IOL2.EQ.1)GO TO 1874
        IF(M81.EQ.1)GO TO 875
1874    CONTINUE
        IF(IOP12.EQ.1)GO TC 566
        JJ1=J1-1;JJ2=J1-2
        PRINT 560,((I,QR1AV(I,K1),WRXN(I,K1),WRXNS(I,K1),RINTL(I,K1),
        1SINTL(I,K1),I=1,JJ2,M162),JJ1,QR1AV(JJ1,K1),WRXN(JJ1,K1),
        1WRXNS(JJ1,K1),RINTL(JJ1,K1),SINTL(JJ1,K1),K1=1,3)
        IF(ITYPE.NE.2)GO TC 566
        TYPE 560,((I,QR1AV(I,K1),WRXN(I,K1),WRXNS(I,K1),RINTL(I,K1),
        1SINTL(I,K1),I=1,JJ2,M162),JJ1,QR1AV(JJ1,K1),WRXN(JJ1,K1),
        1WRXNS(JJ1,K1),RINTL(JJ1,K1),SINTL(JJ1,K1),K1=1,3)
560     FORMAT(3X,'I',3X,'RATEAV',5X,'DRT',2X,'SUM DRT',1X,'INTEGRAL',
        11X,'SUM INTGL'/(I5,5E9.2,I4,5E9.2))
566     IF(IOP11.EQ.1)GO TO 321
        IF(ITYPE8.NE.1)GO TO 321
      IF(IOPT3.EQ.1) GO TO 452
875   PRINT 406,((AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),ATH(M1,K1),
     1ACX(M1,K1),ACT(M1,K1),ACTH(M1,K1),M1=M15
        2,M12(K11),M16),K1=K7,K5,K8)
        IF(ITYPE.NE.2)GO TO 416
      TYPE 406,((AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),ATH(M1,K1),
     1ACX(M1,K1),ACT(M1,K1),ACTH(M1,K1),M1=M15
        2,M12(K11),M16),K1=K7,K5,K8)
 406 FORMAT(  1X,24X,44HREACTOR CONVERSION AND TEMPERATURE PROFILES  //
     1    11X,'REACTOR ',5X,8HPRESSURE,4X,'  AMMONIA '  ,5X,
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     29HBED TEMP.,2X,9HPREHEATER,3X,42HDIFF.IN VALUE OBTAINED AND LAST I
     3TERATION     /     3X,'BED VOLUME(PERCENT)',3X,5H(ATM),5X,'     (MOL
     4E )' ,5X,10H(DEGREE K),2X,8HTEMP.(K),3X,10HCONVERSION,5X,9HBED TEM
     5P. ,5X,15HPREHEATER TEMP.       //(4X,F10.2,10X,F8.2,3X,F10.3,5X,
     6F8.1,3X,F8.1,4X,F10.6,4X,F10.6,8X,F10.6    /  ))
416     IF(IOPT1.EQ.2)GO TO 321
      PRINT 1701,((AZP(M1,K1),AXE(M1,K1),AXEN(M1,K1),AXRM(M1,K1),AXRMN
     1(M1,K1),M1=M15,M12(K11),M16),K1=K7,KL51,K8)
        IF(IOLP8.EQ.2)GO TO 587
C       PRINT 593,(((AXE2(MLPK,M1,K1),AXRM2(MLPK,M1,K1),MLPK=1,4),
C       1M1=M15,M12(K11),M16),K1=K7,KL51,K8)
C593    FORMAT(2X,7X,'XE1',7X,'XRM1',7X,'DXE1',7X,'DXRM1',
C       16X,'XE2',8X,'XRM2',6X,'DXE2',7X,'DXRM2'/(2X,8F11.4))
587     IF(ITYPE.NE.2)GO TO 321
      TYPE 1701,((AZP(M1,K1),AXE(M1,K1),AXEN(M1,K1),AXRM(M1,K1),AXRMN
     1(M1,K1),M1=M15,M12(K11),M16),K1=K7,KL51,K8)
        IF(IOLP8.EQ.2)GO TO 321
C       TYPE 593,(((AXE2(MLPK,M1,K1),AXRM2(MLPK,M1,K1),MLPK=1,4),
C       1M1=M15,M12(K11),M16),K1=K7,KL51,K8)
      GO TO 321
452    PRINT 458,((AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),ATH(M1,K1),
     1 M1=M15,M12(K11),M161),(AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),
     2 ATH(M1,K1),M1=M12(K11),M12(K11)),K1=K7,K5,K8)
        IF(ITYPE.NE.2)GO TO 461
        TYPE 458,((AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),ATH(M1,K1),
     1 M1=M15,M12(K11),M161),(AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),
     2 ATH(M1,K1),M1=M12(K11),M12(K11)),K1=K7,K5,K8)
  458 FORMAT(1X,24X,'REACTOR CONVERSION AND TEMPERATURE PROFILES:'
     1//3X,'REACTOR CATALYST',5X,'PRESSURE',4X,'    AMMONIA',5X,
     2'BED TEMP.',2X,'PREHEATER'/3X,'BED VOLUME(PERCENT)',3X
     3,'(ATM)',5X,'     (MOLE )',5X,'(DEGREE K)',2X,'TEMP.(K)'//
     4(4X,F10.2,10X,F8.2,3X,F10.3,5X,F8.1,3X,F8.1/))
461     IF(IOPT1.EQ.2)GO TO 321
1727    PRINT 1701 ,((AZP(M1,K1),AXE(M1,K1),AXEN(M1,K1),AXRM(M1,K1),
        1AXRMN(M1,K1),M1=M15,M12(K11),M161),K1=K7,KL51,K8)
        IF(IOLP8.EQ.2)GO TO 596
C       PRINT 593,(((AXE2(MLPK,M1,K1),AXRM2(MLPK,M1,K1),MLPK=1,4),
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C        1M1=M15,M12(K11),M16),K1=K7,KL51,K8)
596      IF(ITYPE.NE.2)GO TO 321
          TYPE 1701 ,((AZP(M1,K1),AXE(M1,K1),AXEN(M1,K1),AXRM(M1,K1),
         1AXRMN(M1,K1),M1=M15,M12(K11),M161),K1=K7,KL51,K8)
         IF(IOLP8.EQ.2)GO TO 321
C        TYPE 593,(((AXE2(MLPK,M1,K1),AXRM2(MLPK,M1,K1),MLPK=1,4),
C        1M1=M15,M12(K11),M16),K1=K7,KL51,K8)
1701   FORMAT(4X,'BED VOL.',  16X,'EQUILIBRIUM',  20X,'CONVERSION'/
      13X,'(PERCENT)',  16X,'CONVERSION',  21X,'AT MAXIMUM RATE'/  23X,
      2'HYDROGEN', 3X,'MOLE % AMMONIA',  9X,'HYDROGEN' ,  4X,'MOLE % AMMO
      3NIA'//(2X,F10.2,  9X,F10.3,  5X,F10.3,  6X,F10.3,  5X,F10.3/))
       GO TO 321
138      CONTINUE
         IF(IOP12.EQ.1)GO TO 565
         JJ1=J1-1;JJ2=J1-2
         PRINT 560,((I,QR1AV(I,K1),WRXN(I,K1),WRXNS(I,K1),RINTL(I,K1),
         1SINTL(I,K1),I=1,JJ2,M162),JJ1,QR1AV(JJ1,K1),WRXN(JJ1,K1),
         1WRXNS(JJ1,K1),RINTL(JJ1,K1),SINTL(JJ1,K1),K1=1,3)
         IF(ITYPE.NE.2)GO TO 565
         TYPE 560,((I,QR1AV(I,K1),WRXN(I,K1),WRXNS(I,K1),RINTL(I,K1),
         1SINTL(I,K1),I=1,JJ2,M162),JJ1,QR1AV(JJ1,K1),WRXN(JJ1,K1),
         1WRXNS(JJ1,K1),RINTL(JJ1,K1),SINTL(JJ1,K1),K1=1,3)
565      IF(IOP11.EQ.1)GO TO 209
         IF(ITYPE8.NE.1)GO TO 209
         IF(IOPT3.EQ.1)GO TO 139
       PRINT 406,((AZP(M1,K1),AP(M1,K1),ANX(M1,K1),
      1AT(M1,K1),ATH(M1,K1),ACX(M1,K1),ACT(M1,K1),ACTH(M1,K1), M1=M15,
      2M12(K11),M16),K1=K7,K5,K8)
         IF(ITYPE.NE.2)GO TO 209
        TYPE 406,((AZP(M1,K1),AP(M1,K1),ANX(M1,K1),
      1AT(M1,K1),ATH(M1,K1),ACX(M1,K1),ACT(M1,K1),ACTH(M1,K1), M1=M15,
      2M12(K11),M16),K1=K7,K5,K8)
         GO TO 209
139     PRINT 458,((AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),ATH(M1,K1),
      1 M1=M15,M12(K11),M161),(AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),
      2 ATH(M1,K1),M1=M12(K11),M12(K11)),K1=K7,K5,K8)
         IF(ITYPE.NE.2)GO TO 209
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      TYPE 458,((AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),ATH(M1,K1),
     1 M1=M15,M12(K11),M161),(AZP(M1,K1),AP(M1,K1),ANX(M1,K1),AT(M1,K1),
     2 ATH(M1,K1),M1=M12(K11),M12(K11)),K1=K7,K5,K8)
      GO TO 209
421     TPRD=XW-AP(M12(K5),K5)
        IF(ITYPE8.NE.1)GO TO 260
        PRINT 423,M7,W1,DELT1,(K1,ANX(1,K1)
        1,AXEN(1,K1),AXRMN(1,K1),AX(1,K1),AT(1,K1),ATH(1,K1)
        1,EFZI8(1,K1)
        1,QR1B(1,K1),ALPS8(K1),AXMAX(K1),ATMAX(K1),ATHMAX(K1)
        1,ANX(M12(K1),K1),AXEN(M12(K1),K1),AXRMN(M12(K1),K1)
        1,AX(M12(K1),K1),AT(M12(K1),K1)
        1,ATH(M12(K1),K1),EFZI8(M12(K1),K1)
        1,QR1B(M12(K1),K1),EFZIA(K1),PDROP(K1)
        1,AP(M12(K1),K1),K1=1,KL51)
        IF(HL.EQ.0.0)GO TO 8427
        PRINT 707,AT(1,K5),ATH(1,K5),AT(M12(K5),K5),
        1ATH(M12(K5),K5),PDROP(K5),AP(M12(K5),K5),TPRD
8427    CONTINUE
        IF(ITYPE.NE.2)GO TO 260
        TYPE 423,M7,W1,DELT1,(K1,ANX(1,K1)
        1,AXEN(1,K1),AXRMN(1,K1),AX(1,K1),AT(1,K1),ATH(1,K1)
        1,EFZI8(1,K1)
        1,QR1B(1,K1),ALPS8(K1),AXMAX(K1),ATMAX(K1),ATHMAX(K1)
        1,ANX(M12(K1),K1),AXEN(M12(K1),K1),AXRMN(M12(K1),K1)
        1,AX(M12(K1),K1),AT(M12(K1),K1)
        1,ATH(M12(K1),K1),EFZI8(M12(K1),K1)
        1,QR1B(M12(K1),K1),EFZIA(K1),PDROP(K1)
        1,AP(M12(K1),K1),K1=1,KL51)
        IF(HL.EQ.0.0)GO TO 260
        TYPE 707,AT(1,K5),ATH(1,K5),AT(M12(K5),K5),
        1ATH(M12(K5),K5),PDROP(K5),AP(M12(K5),K5),TPRD
  423 FORMAT(1X,14HITERATION NO.=,I2,52H,ASSUMED INTERNAL PREHEATER OUTL
     1ET STREAM TEMP.(K)=  ,F6.1,1X,',CAL.AND GIVEN FEED TEMP.DIFF.(K)='
     2,F7.1/16X,'NH3 MOLE',7X,'H2 FR.',1X,'BED',
        25X,'SHELL',3X,'EFF.',8X,'RATE',8X,'MAXIMA IN BED' /
        211X,'ACTUAL EQU. MAX.RATE',1X,'CONV.'
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     2,2X,'TEMP,K',2X,'TEMP,K',2X,'FACTOR'
     2,12X,' VOL.',2X,'H2 FR.CONV.',2X,'BED T(K)'
     2,2X,'SHELL T(K)'/(
     22X,'BED NO.=',I3 /2X,'INLET',3X,F6.3
     2,1X,F6.3,1X,F6.3,1X,F6.3,1X,F7.1,1X,F7.1
     2,1X,F7.3,1X,E10.3,1X,F6.2,3X,F8.3,5X,F7.1,2X,F7.1/2X,'EXIT'
     2,4X,F6.3,1X,F6.3,1X,F6.3,1X,F6.3
     2,1X,F7.1,1X,F7.1,1X,F7.3,1X,E10.3
     2/2X,'AVERAGE EFFECTIVENESS FACTOR=',F8.3
     2,2X,',BED PRESSURE DROP(ATM)=',F8.2,2X,
     2',EXIT PRESSURE(ATM)=',F8.2))
 707 FORMAT(2X,'HEAT EXCHANGER:'/2X,
     2'INLET',31X,F7.1,1X,F7.1/2X,'EXIT',32X,F7.1,1X,F7.1/
     22X,'TUBE SIDE PRESSURE DROP(ATM)=',F8.2,2X,',EXIT PRESSURE(ATM)=
     2,F8.2,',TOTAL PRESSURE DROP(ATM)=',F8.2)
    GO TO 260
 424 TPRD=XW-AP(M12(K5),K5)
     IF(ITYPE8.NE.1)GO TO 1260
     PRINT 423,M7,W2,DELT2,(K1,ANX(1,K1)
     1,AXEN(1,K1),AXRMN(1,K1),AX(1,K1),AT(1,K1),ATH(1,K1)
     1,EFZI8(1,K1)
     1,QR1B(1,K1),ALPS8(K1),AXMAX(K1),ATMAX(K1),ATHMAX(K1)
     1,ANX(M12(K1),K1),AXEN(M12(K1),K1),AXRMN(M12(K1),K1)
     1,AX(M12(K1),K1),AT(M12(K1),K1)
     1,ATH(M12(K1),K1),EFZI8(M12(K1),K1)
     1,QR1B(M12(K1),K1),EFZIA(K1),PDROP(K1)
     1,AP(M12(K1),K1),K1=1,KL51)
     IF(HL.EQ.0.0)GO TO 8429
     PRINT 707,AT(1,K5),ATH(1,K5),AT(M12(K5),K5),
     1ATH(M12(K5),K5),PDROP(K5),AP(M12(K5),K5),TPRD
8429 CONTINUE
     IF(ITYPE.NE.2)GO TO 1260
     TYPE 423,M7,W2,DELT2,(K1,ANX(1,K1)
     1,AXEN(1,K1),AXRMN(1,K1),AX(1,K1),AT(1,K1),ATH(1,K1)
     1,EFZI8(1,K1)
     1,QR1B(1,K1),ALPS8(K1),AXMAX(K1),ATMAX(K1),ATHMAX(K1)
     1,ANX(M12(K1),K1),AXEN(M12(K1),K1),AXRMN(M12(K1),K1)
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      1,AX(M12(K1),K1),AT(M12(K1),K1)
      1,ATH(M12(K1),K1),EFZI8(M12(K1),K1)
      1,QR1B(M12(K1),K1),EFZIA(K1),PDROP(K1)
      1,AP(M12(K1),K1),K1=1,KL51)
      IF(HL.EQ.0.0)GO TO 1260
      TYPE 707,AT(1,K5),ATH(1,K5),AT(M12(K5),K5),
      1ATH(M12(K5),K5),PDROP(K5),AP(M12(K5),K5),TPRD
    GO TO 1260
427   TPRD=XW-AP(M12(K5),K5)
      IF(ITYPE8.NE.1)GO TO 1520
      PRINT 423,M7,W3,DELT3,(K1,ANX(1,K1)
      1,AXEN(1,K1),AXRMN(1,K1),AX(1,K1),AT(1,K1),ATH(1,K1)
      1,EFZI8(1,K1)
      1,QR1B(1,K1),ALPS8(K1),AXMAX(K1),ATMAX(K1),ATHMAX(K1)
      1,ANX(M12(K1),K1),AXEN(M12(K1),K1),AXRMN(M12(K1),K1)
      1,AX(M12(K1),K1),AT(M12(K1),K1)
      1,ATH(M12(K1),K1),EFZI8(M12(K1),K1)
      1,QR1B(M12(K1),K1),EFZIA(K1),PDROP(K1)
      1,AP(M12(K1),K1),K1=1,KL51)
      IF(HL.EQ.0.0)GO TO 8430
      PRINT 707,AT(1,K5),ATH(1,K5),AT(M12(K5),K5),
      1ATH(M12(K5),K5),PDROP(K5),AP(M12(K5),K5),TPRD
8430  CONTINUE
      IF(ITYPE.NE.2)GO TO 1520
      TYPE 423,M7,W3,DELT3,(K1,ANX(1,K1)
      1,AXEN(1,K1),AXRMN(1,K1),AX(1,K1),AT(1,K1),ATH(1,K1)
      1,EFZI8(1,K1)
      1,QR1B(1,K1),ALPS8(K1),AXMAX(K1),ATMAX(K1),ATHMAX(K1)
      1,ANX(M12(K1),K1),AXEN(M12(K1),K1),AXRMN(M12(K1),K1)
      1,AX(M12(K1),K1),AT(M12(K1),K1)
      1,ATH(M12(K1),K1),EFZI8(M12(K1),K1)
      1,QR1B(M12(K1),K1),EFZIA(K1),PDROP(K1)
      1,AP(M12(K1),K1),K1=1,KL51)
      IF(HL.EQ.0.0)GO TO 1520
      TYPE 707,AT(1,K5),ATH(1,K5),AT(M12(K5),K5),
      1ATH(M12(K5),K5),PDROP(K5),AP(M12(K5),K5),TPRD
    GO TO 1520
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     71 PRINT 74,M7,K11,J1,AT(MQ1,K11),AX(MQ1,K11),ATH(MQ1,K11)
          IF(ITYPE.NE.2)GO TO 67
        TYPE 74,M7,K11,J1,AT(MQ1,K11),AX(MQ1,K11),ATH(MQ1,K11)
     74 FORMAT(1X,14HITERATION NO.= ,I3,21H,CATALYST BED NUMBER= ,I3,
       115H,BED POINT NO.= ,I5,
          2',BED TEMP.AT THIS POINT IS BELOW MINIMUM DESIRED(K)=' ,
       3F8.1//2X,'AT THIS PT.FR. CONVERSION OF HYDROGEN= ', F8.3,
       4'SHELL SIDE TEMP.(K)=' ,F8.1/2X,'THEREFORE SWITCHING TO NEXT ITERA
       5TION BY ASSUMING ANOTHER TEMPERATURE'/)
        GO TO 67
     72 PRINT 74,M7,K11,J1,AT(MQ1,K11),AX(MQ1,K11),ATH(MQ1,K11)
          IF(ITYPE.NE.2)GO TO 68
        TYPE 74,M7,K11,J1,AT(MQ1,K11),AX(MQ1,K11),ATH(MQ1,K11)
        GO TO 68
     73 PRINT 74,M7,K11,J1,AT(MQ1,K11),AX(MQ1,K11),ATH(MQ1,K11)
          IF(ITYPE.NE.2)GO TO 69
        TYPE 74,M7,K11,J1,AT(MQ1,K11),AX(MQ1,K11),ATH(MQ1,K11)
        GO TO 69
    231 FORMAT(   1X,56X,7HTHE END     )
   5204 PRINT 231
        TYPE 231
        STOP
        END
        SUBROUTINE FEEDT(TF,W1,F,H1,H2,H3,H4,VW,C71,C72,C73,C74,BHA31,
       1BHA32,BHA33,BHA34,CHA31,CHA32,CHA33,CHA34,J,K1    )
C       SUBROUTINE NO. 1 FOR CALCULATION OF FEED TEMPERATURE TO AMMONIA SYN
C       REACTOR
        DIMENSION AZ(210,4),AP(210,4),AX(210,4),AT(210,4),ATH(210,4),
       1ACX(210,4),ACT(210,4)
          1,ACTH(210,4),EFZI8(210,4),EFZIA(8),QR1B(210,4)
          1,QR1AV(210,4),WRXN(210,4),WRXNS(210,4),RINTL(210,4),SINTL(210,4)
       2,ANX(210,4),AZP(210,4),AXMAX(8),ATMAX(8),ATHMAX(8),ALPS8(8)
       3,AXE(210,4),AXRM(210,4),AXEN(210,4),AXRMN(210,4),M12(20),PDROP(8)
C         2,AXE2(4,310,4),AXRM2(4,310,4)
        COMMON/CB1/F1,F2,F3,F4,F5,LQQ,ITYPE,PARA1,PARA2,PARA3
          1,PARA4,IOP26,IOP29,FLPF
          1/CB2/AZ,AP,AX,AT,ATH,AXMAX
```

```
     1,ATMAX,ATHMAX,ALPS8,W11L,QR1AV,AXE2,AXRM2
     1,WRXN,WRXNS,RINTL,SINTL,EFZI8,QR1B,EFZIA,PDROP,IOL1/CB3/
   1AFD1,AFD2,AFD3,AFD4,Z1,Z2,Z3,HL,XW,UV,C4,RUA,HUA,C5,C61,C62,M15,K7
   2,FI11,FI12,FI13,FI21,FI22,FI23,FI31,FI32,FI33,FI41,FI42,FI43,M1,
   3FI51,FI52,FI53,PH1,PH2,PB11,S2,S11,S12,FTF1,S112,S122,AR1,AR2,
   4AR3,AR4,AR5,Q11,Q21,Q31,Q41,Q51,Q12,Q22,Q32,Q42,Q52,
     5IEL2P,UARLP,K5,KL51,IOPT3,AFD0,
   5Q13,Q23,Q33,Q43,Q53,HA11,HA21,HA31,HA41,HA51,HA61,HA71,HA12,M16,
   6HA22,HA32,HA42,HA52,HA62,HA72,HA13,HA23,HA33,HA43,HA53,HA63,K8,
   7HA73,HA14,HA24,HA34,HA44,HA54,HA64,HA74,NZ1,NZ2,NZ3,NZ4,MZ1,MZ2,
   8MZ3,MZ4,HAA21,HAA22,HAA23,HAA24,AHA21,AHA22,AHA23,AHA24,BHA21,
   9BHA22,BHA23,BHA24,HAB21,HAB22,HAB23,HAB24,AHA31,AHA32,AHA33,AHA34
   A/CB4/ANX,ZTI,PAM,AZP/CB5/LK,AN3T1,ZCTV/CB20/ACX,ACT,ACTH
   B/CB6/AXE,AXRM,AXEN,AXRMN,M12/CB7/ICSIZE,IOPT1,EFFAH,EFFAL
     1/CB9/FFL,RHNL,XINCL,XINCL2,TOL81,PHYL,PNIL,PAML,DELE
     1,DELM,IOL8,M88,IOP11,IOL81
      M1=1
      K1=1
      K3=1
      LK=1
C     CALCULATION OF FIRST REACTOR BED CONVERSION AND TEMPRATURE PROFILE
      ZCTV=0.
      UA1=RUA
      AX(M1,K1)=0.0
      ATH(M1,K1)=W1
        TB1=ATH(M1,K1)
C     CALCULATION FOR MIXTURE TEMPERATURE ENTERING FIRST BED
      XB12=0.0
      IF(AFD4)21,22,21
   22 TB=ATH(M1,K1)
      GO TO 23
   21 CALL MTEMP(TB,W1,F1,AR1,AR2,AR3,AR4,AR5,Q11,Q21,Q31,Q41,Q51,
     1XB12,PB11,UV,C4,IOP26)
   23 AP(M1,K1)=PB11
      C6=C61*(AFD1+AFD4)**1.8
C     CALCULATION FOR REACTOR PROFILES BY MILNE PREDICTOR CORRECTOR METH
C     NUMERICAL INTEGRATION
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```
      IF(IOPT3.NE.1) GO TO 110
110   CALL RNUMI(M1,K1,K3,TB,AFD1,NZ1,MZ1,HA11,HA21,HAA21,AHA21,BHA21,
     1HA31,HA41,HA51,HA61,HA71,FI11,FI21,FI31,FI41,FI51,Z1,HL,H1,C6,
     2VW,C71,UA1,F,PH1,HAB21,AHA31,BHA31,CHA31,J,TB1   )
107      IF(LQQ.EQ.2)GO TO 800
         IF(AT(M1,K1)-W11L)11,11,12
C     CALCULATION FOR SECOND BED PROFILES
   12 IF(K5.LE.1)GO TO 800
440      IF(Z2.NE.0.0)GO TO 431
         K5=K5-1;KL51=KL51-1
         GO TO 14
431      IF(IEL2P.NE.1)GO TO 452
         LK=2;UA1=RUA*UARLP
452      TH12=AT(M1,K1)
      PB1=AP(M1,K1)
      XB12=AX(M1,K1)
      IF(AFD2)24,25,24
   25 TB=AT(M1,K1)
      GO TO 26
   24 CALL MTEMP(TB,TH12,F1,FI11,FI21,FI31,FI41,FI51,Q12,Q22,Q32,
     1Q42,Q52,XB12,PB1,UV,C4,IOP26)
   26 C6=((S112-FTF1*XB12)*(AFD1+AFD4))**1.8*C61
      ZCTV=Z1;TB1=ATH(M1,K1)
      IF(IOPT3.NE.1) GO TO 119
119       CALL RNUMI(M1,K1,K3,TB,AFD1,NZ2,MZ2,HA12,HA22,HAA22,AHA22,
     1BHA22,HA32,HA42,HA52,HA62,HA72,FI12,FI22,FI32,FI42,FI52,Z2,
     2HL,H2,C6,VW,C72,UA1,F,PH1,HAB22,AHA32,BHA32,CHA32,J,TB1   )
116      IF(LQQ.EQ.2)GO TO 800
         IF(AT(M1,K1)-W11L)11,11,14
C     CALCULATION OF THIRD BED REACTOR PROFILES
   14 IF(K5-2)800,461,462
461      IF(Z2.NE.0.0)GO TO 800
462      CONTINUE
         IF(Z3.NE.0.0)GO TO 404
         K5=K5-1;KL51=KL51-1
         GO TO 15
404      XB12=AX(M1,K1)
```

```
      PB1=AP(M1,K1)
      TH12=AT(M1,K1)
      IF(AFD3)27,28,27
   28 TB=AT(M1,K1)
      GO TO 29
   27 CALL MTEMP(TB,TH12,F1,FI12,FI22,FI32,FI42,FI52,Q13,Q23,Q33,Q43,
     1Q53,XB12,PB1,UV,C4,ICP26)
   29 C6=((S122-FTF1*XB12)*(AFD1+AFD4))**1.8*C61
      ZCTV=Z2+Z1;TB1=ATH(M1,K1)
      IF(IOPT3.NE.1)GO TO 128
128   CALL RNUMI(M1,K1,K3,TB,AFD1,NZ3,MZ3,HA13,HA23,HAA23,AHA23,BHA23,
     1HA33,HA43,HA53,HA63,HA73,FI13,FI23,FI33,FI43,FI53,Z3,HL,H3,C6,
     2VW,C73,UA1,F,PH1,HAB23,AHA33,BHA33,CHA33,J,TB1  )
125     IF(LQQ.EQ.2)GO TO 800
        IF(AT(M1,K1)-W11L)11,11,15
C     CALCULATION OF HEAT EXHANGER PROFILES
   15 IF(K5-2)800,470,471
470     IF(Z2.NE.0.0)GO TO 800
        IF(Z3.NE.0.0)GO TO 800
        GO TO 468
467     IF(Z3.EQ.0.0)GO TO 468
        IF(Z2.EQ.0.0)GO TO 468
        GO TO 800
471     IF(K5.LE.3)GO TO 467
468     IF(HL.NE.0.0)GO TO 425
        K5=K5-1
        GO TO 800
425     UA11=HUA
        FI10=F1*AFD1;FI20=F2*AFD1;FI30=F3*AFD1;FI40=F4*AFD1
        FI50=F5*AFD1;Q101=-F1*AFD0;Q201=-F2*AFD0;Q301=-F3*AFD0
        Q401=-F4*AFD0;Q501=-F5*AFD0;PB12=PH2;AFD11=AFD1-AFD0
        XB12=0.0;TH12=ATH(M1,K1)
        IF(AFD0)200,201,200
201     TB1=ATH(M1,K1)
        GO TO 202
 200      CALL MTEMP(TB1,TH12,F1,FI10,FI20,FI30,FI40,FI50,
        1Q101,Q201,Q301,Q401,Q501,
```

```
     1XB12,PB12,UV,C4,IOP26)
202     CONTINUE
      TB=AT(M1,K1)
      C6=C62
      LK=2
      ZCTV=Z1+Z2+Z3
      IF(IOPT3.NE.1) GO TO 137
137   CALL RNUMI(M1,K1,K3,TB,AFD11,NZ4,MZ4,HA14,HA24,HAA24,AHA24,BHA24,
     1HA34,HA44,HA54,HA64,HA74,FI13,FI23,FI33,FI43,FI53,HL,HL,H4,C6,
     2VW,C74,UA11,F,PH2,HAB24,AHA34,BHA34,CHA34,J,TB1     )
   11 TF=ATH(M1,K1)
C       PRINT *,IOPT3,LOQ,UA1,UA11
800   RETURN
      END
      SUBROUTINE RNUMI (M1,K1,K3,TB,FD1,NL,M2,HA1,HA2,HAA2,AHA2,BHA2,
     1HA3,HA4,HA5,HA6,HA7,FI1,FI2,FI3,FI4,FI5,Z1,HL,H,C6,VW,C7,UA1,F,
     2PH,HAB2,AHA3,BHA3,CHA3,J,TB1  )
C     SUBROUTINE NO.2 FOR NUMERICAL INTEGRATION OF AMMONIA SYNTHESIS REAC
C     DIFFERENTIAL EQUATIONS BY MILNE PREDICTOR AND CORRECTOR METHOD
      DIMENSION WX(310),WT(310),WTH(310),P(310),T(310),TH(310),
     1AZ(210,4),AP(210,4),AX(210,4),AT(210,4),ATH(210,4),ACX(210,4),
     2ACT(210,4),ACTH(210,4),XN(310),TN(310),THN(310),Z(310),X(310),
     3CX(310),CT(310),CTH(310),AXMAX(8),ATMAX(8),ATHMAX(8)
     4,ANX(210,4),AZP(210,4),ALPS8(8),SINTL(210,4),RINTL(210,4)
        4,QR1AV(210,4),WRXN(210,4),PDROP(8),AELP2(4,2),
        4WRXNS(210,4),EFZI8(210,4),QR1B(210,4),EFZIA(8),EFFZI(310)
     5,XE(310),XRM(310),AXE(210,4),AXRM(210,4),AXEN(210,4)
        6,AXRMN(210,4),M12(20),QR1(310),QHR3(310),QAK(310),QAKF(310),
        7QAKR(310),QAN1(310),QAN2(310),QAN3(310),QAN4(310),QAN5(310)
C       4AXE2(4,310,4),AXRM2(4,310,4)
      COMMON/CB1/F1,F2,F3,F4,F5,LOQ,ITYPE,PARA1,PARA2,PARA3
        1,PARA4,IOP26,IOP29,FLPF
        1/CB2/AZ,AP,AX,AT,ATH,AXMAX
        1,ATMAX,ATHMAX,ALPS8,W11L,QR1AV,AXE2,AXRM2
        1,WRXN,WRXNS,RINTL,SINTL,EFZI8,QR1B,EFZIA,PDROP,IOL1
     1/CB4/ANX,ZTI,PAM,AZP/CB5/LK,AN3T,ZCTV
        2/CB20/ACX,ACT,ACTH
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     2/CB9/FFL,RHNL,XINCL,XINCL2,TOL81,PHYL,PNIL,PAML,DELE,DELM
    3,IOL8,M88,IOP11,IOL81/CB7/ICSIZE,IOPT1,EFFAH,EFFAL
     3/CB8/AKR,AK,AKF,ABLP8,ITYP,ZIF/CB6/AXE,AXRM,AXEN,AXRMN,M12
     4/CB35/QR1,QHR3,QAK,QAKF,QAKR,QAN1,QAN2,QAN3,QAN4,QAN5,EFFZI
      AB11=0.666667*FI1 ; FIT=FI1+FI2+FI3+FI4+FI5
      AZ1=Z1;WRXS=0.0;SINT=0.0;SEFZI=0.0
      I=1;LP17=1;ITYP=ITYPE
      Z(I)=0.0
      P(I)=AP(M1,K1)
      X(I)=AX(M1,K1);ABLP8=FI2-F1*0.3333333*AX(M1,K1)
      T(I)=TB
      TH(I)=TB1
      IF(K3-1)302,301,302
  302 K1=K1+1
  301 M1=1
      J=I
      AZ(M1,K1)=Z(I)
      AZP(M1,K1)=(Z(I)+ZCTV)*ZTI
      AP(M1,K1)=P(I)
      AX(M1,K1)=X(I)
      AT(M1,K1)=T(I)
      ACX(M1,K1)=0.0
      ACT(M1,K1)=0.0
      ACTH(M1,K1)=0.0
      ANX(M1,K1)=PAM
      IF(T(J)-W11L)304,304,303
  303 ATH(M1,K1)=TH(I)
      CALL DEV(I,WX,WT,WTH,P,T,TH,X,FD1,
     1FI1,FI2,FI3,FI4,FI5,F,AZ1,HL,UA1,PH)
        IF(LQQ.EQ.2)GO TO 800
        IF(LK.EQ.2)GO TO 206
      IF(IOPT1.NE.1)GO TO 206
      CALL CONV(X,XE,XRM,P,T,J,AELP2)
      AXE(M1,K1)=XE(J)
      AXRM(M1,K1)=XRM(J)
      CALL AMMC(AN3E,AN3MR,AB11,FI3,FIT,XE,XRM,J)
      AXEN(M1,K1)=AN3E
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```
      AXRMN(M1,K1)=AN3MR
C       DO 704 LQ2P=1,4
C       AXE2(LQ2P,M1,K1)=AELP2(LQ2P,1)
C       AXRM2(LQ2P,M1,K1)=AELP2(LQ2P,2)
704     CONTINUE
206      ANX(M1,K1)=AN3T
      HC6=C6*H
      Z(I+1)=H
      P(I+1)=P(I)-HC6
      X(I+1)=X(I)+H*WX(I)
      T(I+1)=T(I)+H*WT(I)
      TH(I+1)=TH(I)+H*WTH(I)
    4 J=I+1
      IF(T(J)-W11L)304,304,305
  305 CALL DEV(J,WX,WT,WTH,P,T,TH,X,FD1,
     1FI1,FI2,FI3,FI4,FI5,F,AZ1,HL,UA1,PH      )
        IF(X(J).LT.0.0)LQQ=2
        IF(LQQ.EQ.2)GO TO 800
      TN(I+1)=T(I)+HA1*(WT(J)+WT(I))
      XN(I+1)=X(I)+HA1*(WX(J)+WX(I))
      THN(I+1)=TH(I)+HA1*(WTH(J)+WTH(I))
      CX(I+1)=(XN(I+1)-X(I+1))
      CT(I+1)=(TN(I+1)-T(I+1))
      CTH(I+1)=(THN(I+1)-TH(I+1))
      X(I+1)=XN(I+1)
      T(I+1)=TN(I+1)
      TH(I+1)=THN(I+1)
      IF(ABS (CX(I+1))-VW*0.01)1,1,4
    1 IF(ABS(CT(I+1))-VW)5,5,4
    5 IF(ABS(CTH(I+1))-VW)3,3,4
    3 M1=M1+1
        IF(LK.EQ.2)GO TO 8
        IF(LP17.EQ.2)GO TO 422
        IF(X(J).GT.X(J-1))GO TO 431
        AXMAX(K1)=X(J-1);ATMAX(K1)=T(J-1);ATHMAX(K1)=TH(J-1)
        ALPS8(K1)=(Z(J-1)+ZCTV)*ZTI;LP17=2
        GO TO 431
```

```
422     IF(AXMAX(K1).GE.X(J))GO TO 431
        AXMAX(K1)=X(J);ATMAX(K1)=T(J);ATHMAX(K1)=TH(J)
        ALPS8(K1)=(Z(J)+ZCTV)*ZTI
431      IF(IOPT1.NE.1)GO TO 8
        IF(IOP11.EQ.1)GO TO 8
      CALL CONV(X,XE,XRM,P,T,J,AELP2)
      AXE(M1,K1)=XE(J)
      AXRM(M1,K1)=XRM(J)
      CALL AMMC(AN3E,AN3MR,AB11,FI3,FIT,XE,XRM,J)
      AXEN(M1,K1)=AN3E
      AXRMN(M1,K1)=AN3MR
C       DO 710 LQ2P=1,4
C       AXE2(LQ2P,M1,K1)=AELP2(LQ2P,1)
C       AXRM2(LQ2P,M1,K1)=AELP2(LQ2P,2)
710     CONTINUE
    8 CONTINUE
      AX(M1,K1)=X(I+1)
      AT(M1,K1)=T(I+1)
      ATH(M1,K1)=TH(I+1)
      ACT(M1,K1)=CT(I+1)
      ACX(M1,K1)=CX(I+1)
      ACTH(M1,K1)=CTH(I+1)
      AZ(M1,K1)=Z(I+1)*0.000001
      AZP(M1,K1)=(Z(I+1)+ZCTV) *ZTI
      ANX(M1,K1)=AN3T
      AP(M1,K1)=P(I+1)
      X(I+2)=X(I+1)+HA1*(3.0*WX(J)-WX(I))
      T(I+2)=T(I+1)+HA1*(3.0*WT(J)-WT(I))
      TH(I+2)=TH(I+1)+HA1*(3.0*WTH(J)-WTH(I))
        Z(I+2)=Z(I+1)+H
      P(I+2)=P(I+1)-HC6
      WXI1=HAB2*WX(I+1)
      WXI2=HA2*WX(I)
      WTI1=HAB2*WT(I+1)
      WTI2=HA2*WT(I)
      WTHI1=HAB2*WTH(I+1)
      WTHI2=HA2*WTH(I)
```

```
   12 J=I+2
      IF(T(J)-W11L)304,304,306
  306 CALL DEV(J,WX,WT,WTH,P,T,TH,X,FD1,
     1FI1,FI2,FI3,FI4,FI5,F,AZ1,HL,UA1,PH        )
        IF(X(J).LT.0.0)LQQ=2
        IF(LQQ.EQ.2)GO TO 800
      XN(I+2)=X(I+1)+HAA2*WX(J)+WXI1-WXI2
      TN(I+2)=T(I+1)+HAA2*WT(J)+WTI1-WTI2
      THN(I+2)=TH(I+1)+HAA2*WTH(J)+WTHI1-WTHI2
      CX(I+2)=(XN(I+2)-X(I+2))
      CT(I+2)=(TN(I+2)-T(I+2))
      X(I+2)=XN(I+2)
      CTH(I+2)=(THN(I+2)-TH(I+2))
      T(I+2)=TN(I+2)
      TH(I+2)=THN(I+2)
      IF(ABS(CX(I+2))-VW*0.01)11,11,12
   11 IF(ABS(CT(I+2))-VW)14,14,12
   14 IF(ABS(CTH(I+2))-VW)15,15,12
   15 M1=M1+1
        IF(LK.EQ.2)GO TO 17
        IF(LP17.EQ.2)GO TO 425
        IF(X(J).GT.X(J-1))GO TO 434
        AXMAX(K1)=X(J-1);ATMAX(K1)=T(J-1);ATHMAX(K1)=TH(J-1)
        ALPS8(K1)=(Z(J-1)+ZCTV)*ZTI;LP17=2
        GO TO 434
425     IF(AXMAX(K1).GE.X(J))GO TO 434
        AXMAX(K1)=X(J);ATMAX(K1)=T(J);ATHMAX(K1)=TH(J)
        ALPS8(K1)=(Z(J)+ZCTV)*ZTI
434      IF(IOPT1.NE.1)GO TO 17
        IF(IOP11.EQ.1)GO TC 17
      CALL CONV(X,XE,XRM,P,T,J,AELP2)
      AXE(M1,K1)=XE(J)
      AXRM(M1,K1)=XRM(J)
      CALL AMMC(AN3E,AN3MR,AB11,FI3,FIT,XE,XRM,J)
      AXEN(M1,K1)=AN3E
      AXRMN(M1,K1)=AN3MR
C       DO 713 LQ2P=1,4
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C         AXE2(LQ2P,M1,K1)=AELP2(LQ2P,1)
C         AXRM2(LQ2P,M1,K1)=AELP2(LQ2P,2)
713       CONTINUE
17        AX(M1,K1)=X(J)
        AT(M1,K1)=T(J)
        ATH(M1,K1)=TH(J)
        ACT(M1,K1)=CT(J)
        ACTH(M1,K1)=CTH(J)
        ACX(M1,K1)=CX(J)
        AZ(M1,K1)=Z(J)*0.000001
        AZP(M1,K1)=(Z(J)+ZCTV)*ZTI
        ANX(M1,K1)=AN3T
        AP(M1,K1)=P(J)
        X(I+3)=X(I+2)+AHA2*WX(I+2)-BHA2*WX(I+1)+HAA2*WX(I)
        T(I+3)=T(I+2)+AHA2*WT(I+2)-BHA2*WT(I+1)+HAA2*WT(I)
        TH(I+3)=TH(I+2)+AHA2*WTH(I+2)-BHA2*WTH(I+1)+HAA2*WTH(I)
        Z(I+3)=Z(I+2)+H
        P(I+3)=P(I+2)-HC6
        WXN1=BHA3*WX(I+2)
        WXN2=CHA3*WX(I+1)
        WXN3=HA3*WX(I)
        WTN1=BHA3*WT(I+2)
        WTN2=CHA3*WT(I+1)
        WTHN1=BHA3*WTH(I+2)
        WTN3=HA3*WT(I)
        WTHN2=CHA3*WTH(I+1)
        WTHN3=HA3*WTH(I)
     22 J=I+3
        IF(T(J)-W11L)304,304,307
    307 CALL DEV(J,WX,WT,WTH,P,T,TH,X,FD1,
       1FI1,FI2,FI3,FI4,FI5,F,AZ1,HL,UA1,PH)
          IF(X(J).LT.0.0)LQQ=2
          IF(LQQ.EQ.2)GO TO 800
        XN(I+3)=X(I+2)+AHA3*WX(I+3)+WXN1-WXN2+WXN3
        TN(I+3)=T(I+2)+AHA3*WT(I+3)+WTN1-WTN2+WTN3
        THN(I+3)=TH(I+2)+AHA3*WTH(I+3)+WTHN1-WTHN2+WTHN3
        CX(I+3)=(XN(I+3)-X(I+3))
```

```
      CT(I+3)=(TN(I+3)-T(I+3))
      CTH(I+3)=(THN(I+3)-TH(I+3))
      X(I+3)=XN(I+3)
      T(I+3)=TN(I+3)
      TH(I+3)=THN(I+3)
      IF(ABS(CX(I+3))-VW*0.01)21,21,22
   21 IF(ABS(CT(I+3))-VW)23,23,22
   23 IF(ABS(CTH(I+3))-VW)24,24,22
   24 M1=M1+1
        IF(LK.EQ.2)GO TO 26
        IF(LP17.EQ.2)GO TO 416
        IF(X(J).GT.X(J-1))GO TO 440
        AXMAX(K1)=X(J-1);ATMAX(K1)=T(J-1);ATHMAX(K1)=TH(J-1)
        ALPS8(K1)=(Z(J-1)+ZCTV)*ZTI;LP17=2
        GO TO 440
416     IF(AXMAX(K1).GE.X(J))GO TO 440
        AXMAX(K1)=X(J);ATMAX(K1)=T(J);ATHMAX(K1)=TH(J)
        ALPS8(K1)=(Z(J)+ZCTV)*ZTI
440      IF(IOPT1.NE.1)GO TO 26
        IF(IOP11.EQ.1)GO TC 26
      CALL CONV(X,XE,XRM,P,T,J,AELP2)
      AXE(M1,K1)=XE(J)
      AXRM(M1,K1)=XRM(J)
      CALL AMMC(AN3E,AN3MR,AB11,FI3,FIT,XE,XRM,J)
      AXEN(M1,K1)=AN3E
      AXRMN(M1,K1)=AN3MR
C       DO 719 LQ2P=1,4
C       AXE2(LQ2P,M1,K1)=AELP2(LQ2P,1)
C       AXRM2(LQ2P,M1,K1)=AELP2(LQ2P,2)
719     CONTINUE
   26 CONTINUE
      AX(M1,K1)=X(J)
      AT(M1,K1)=T(J)
      ATH(M1,K1)=TH(J)
      ACT(M1,K1)=CT(J)
      ACTH(M1,K1)= CTH(J)
       ACX(M1,K1)=CX(J)
```

```
      AZ(M1,K1)=Z(J)*0.000001
      AZP(M1,K1)=(Z(J)+ZCTV)*ZTI
      ANX(M1,K1)=AN3T
      AP(M1,K1)=P(J)
      L11=1
      K=1
  101 X(K+4)=X(K)+HA4*WX(K+2)+HA5*(WX(K+3)-2.0*WX(K+2)+WX(K+1))
      T(K+4)=T(K)+HA4*WT(K+2)+HA5*(WT(K+3)-2.0*WT(K+2)+WT(K+1))
      TH(K+4)=TH(K)+HA4*WTH(K+2)+HA5*(WTH(K+3)-2.0*WTH(K+2)+WTH(K+1))
      Z(K+4)=Z(K+3)+H
      P(K+4)=P(K+3)-HC6
      IF(L11-1) 25,89,25
   25 X(K+4)=X(K+4)+CX(K+3)
      T(K+4)=T(K+4)+CT(K+3)
      TH(K+4)=TH(K+4)+CTH(K+3)
   89 L11=2
      WXK1=HA6*WX(K+3)
      WTK1=HA6*WT(K+3)
      WTHK1=HA6*WTH(K+3)
      WXK2=WXK1/3.0
      WXK3=HA7*WX(K+2)
      WTK2=WTK1/3.0
      WTK3=HA7*WT(K+2)
      WTHK2=WTHK1/3.0
      WTHK3=HA7*WTH(K+2)
   29 J=K+4
      IF(T(J)-W11L)304,304,308
  308 CALL DEV(J,WX,WT,WTH,P,T,TH,X,FD1,
     1FI1,FI2,FI3,FI4,FI5,F,AZ1,HL,UA1,PH)
        IF(X(J).LT.0.0)LQQ=2
        IF(LQQ.EQ.2)GO TO 800
      XN(K+4)=X(K+2)+WXK1+HA7*WX(K+4)-WXK2+WXK3
      TN(K+4)=T(K+2)+WTK1+HA7*WT(K+4)-WTK2+WTK3
      THN(K+4)=TH(K+2)+WTHK1+HA7*WTH(K+4)-WTHK2+WTHK3
      CX(K+4)=(XN(K+4)-X(K+4))
      CT(K+4)=(TN(K+4)-T(K+4))
      X(K+4)=XN( K+4)
```

```
      CTH(K+4)=(THN(K+4)-TH(K+4))
      T(K+4)=TN(K+4)
      TH(K+4)=THN(K+4)
      IF(ABS(CX(K+4))-VW*0.01)31,31,29
   31 IF(ABS (CT(K+4))-VW)32,32,29
   32 IF(ABS(CTH(K+4))-VW)33,33,29
33      IF(LK.EQ.2)GO TO 38
        IF(LP17.EQ.2)GO TO 407
        IF(X(K+4).GT.X(K+3))GO TO 542
        AXMAX(K1)=X(K+3);ATMAX(K1)=T(K+3);ATHMAX(K1)=TH(K+3)
        ALPS8(K1)=(Z(K+3)+ZCTV)*ZTI;LP17=2
        GO TO 542
407     IF(AXMAX(K1).GE.X(J))GO TO 542
        AXMAX(K1)=X(J);ATMAX(K1)=T(J);ATHMAX(K1)=TH(J)
        ALPS8(K1)=(Z(J)+ZCTV)*ZTI
542     IF(IOPT1.NE.1)GO TO 38
        IF(IOP11.EQ.1)GO TO 38
      CALL CONV(X,XE,XRM,P,T,J,AELP2)
      AXE((M1+1),K1)=XE(J)
      AXRM((M1+1),K1)=XRM(J)
      CALL AMMC(AN3E,AN3MR,AB11,FI3,FIT,XE,XRM,J)
      AXEN((M1+1),K1)=AN3E
      AXRMN((M1+1),K1)=AN3MR
C       DO 722 LQ2P=1,4
C       AXE2(LQ2P,(M1+1),K1)=AELP2(LQ2P,1)
C       AXRM2(LQ2P,(M1+1),K1)=AELP2(LQ2P,2)
722     CONTINUE
   38 M3=K+4
      M4=M2*(M1-3)
      IF(M3-M4)34,34,35
   35 M1=M1+1
      AZ(M1,K1)=Z(M3) *0.000001
      AP(M1,K1)=P(M3)
      AX(M1,K1)=X(M3)
      AT(M1,K1)=T(M3)
      ATH(M1,K1)=TH(M3)
      ACX(M1,K1)=CX(M3)
```

```
      ACT(M1,K1)=CT(M3)
      ACTH(M1,K1)=CTH(M3)
      AZP(M1,K1)=(Z(J)+ZCTV)*ZTI
      ANX(M1,K1)=AN3T
   34 IF(K-NL)191,192,192
  191 K=K+1
      GO TO 101
  192 K3=K3+1
        IF(LK.EQ.2)GO TO 309
        IF(LP17.EQ.2)GO TO 309
        ALPS8(K1)=(Z(K+4)+ZCTV)*ZTI;AXMAX(K1)=X(K+4)
        ATMAX(K1)=T(K+4);ATHMAX(K1)=TH(K+4);LP17=1
C       PRINT *,IOPT1,LQO,((AZP(I,J),AT(I,J),ATH(I,J),I=1,M1),J=1,K1)
      GO TO 309
  304   M1=M1+1
      AT(M1,K1)=T(J)
      AX(M1,K1)=X(J)
      ATH(M1,K1)=TH(J)
        IF(IOL1.NE.2)GO TO 309
        PRINT 935,F1,F2,F3,F4,F5,(N,X(N),T(N),TH(N),P(N),QAN1(N),QAN2(N),
        1QAN3(N),QAN4(N),QAN5(N),QR1(N),QHR3(N),QAK(N),QAKF(N),QAKR(N),
        2WX(N),WT(N),WTH(N),N=1,J)
        IF(ITYPE.NE.2)GO TO 309
```

```
          TYPE 935,F1,F2,F3,F4,F5,(N,X(N),T(N),TH(N),P(N),QAN1(N),QAN2(N),
          1QAN3(N),QAN4(N),QAN5(N),QR1(N),QHR3(N),QAK(N),QAKF(N),QAKR(N),
          2WX(N),WT(N),WTH(N),N=1,J)
    935   FORMAT(2X,5F10.1/(2X,I5,F10.3,8F10.1/2X,8E10.3/))
    309   M12(K1)=M1;JJ1=J-1;LP17=1
          PDROP(K1)=P(1)-P(J)
          IF(IOP11.NE.1)GO TO 701
        CALL CONV(X,XE,XRM,P,T,J,AELP2)
        AXE(M1,K1)=XE(J)
        AXRM(M1,K1)=XRM(J)
        CALL AMMC(AN3E,AN3MR,AB11,FI3,FIT,XE,XRM,J)
        AXEN(M1,K1)=AN3E
        AXRMN(M1,K1)=AN3MR
C         DO 728 LQ2P=1,4
C         AXE2(LQ2P,M1,K1)=AELP2(LQ2P,1)
C         AXRM2(LQ2P,M1,K1)=AELP2(LQ2P,2)
    728   CONTINUE
    701   IF(LK.EQ.2)GO TO 800
          DO 830 I=1,JJ1
          EFZI8(I,K1)=EFFZI(I)
          QR1B(I,K1)=QR1(I);SEFZI=EFFZI(I)+SEFZI
          WRXN(I,K1)=(QR1(I+1)-QR1(I))*2.016/(T(I+1)-T(I))
          WRXNS(I,K1)=WRXN(I,K1)+WRXS;WRXS=WRXNS(I,K1)
          QR1AV(I,K1)=(QR1(I+1)+QR1(I))*1.008
          IF(QR1AV(I,K1).NE.0.0)GO TO 557
          RINTL(I,K1)=1.0E8
          GO TO 566
    557   RINTL(I,K1)=WRXN(I,K1)*(X(I+1)-X(I))/(QR1AV(I,K1)*QR1AV(I,K1))
    566   SINTL(I,K1)=RINTL(I,K1)+SINT;SINT=SINTL(I,K1)
    830   CONTINUE
          EFZI8(J,K1)=EFFZI(J);EFZIA(K1)=(SEFZI+EFFZI(J))/J
    800 RETURN
        END
        SUBROUTINE DEV(I,WX,WT,WTH,P,T,TH,X,FD1,
       1FI1,FI2,FI3,FI4,FI5,F,AZ1,HL,UA1,PH)
C       SUBROUTINE NO.3 FOR CALCULATION OF DERIVATIVE VALUES FROM AMMONIA
C       SYNTHESIS REACTOR
```

```
C     EQUATIONS FOR NUMERICAL INTEGRATION
      DIMENSION WX(310),WT(310),WTH(310),P(310),T(310),TH(310),X(310)
     1,QR1(310),QHR3(310),QAK(310),QAKF(310),QAKR(310),QAN1(310),
     2QAN2(310),QAN3(310),QAN4(310),QAN5(310),EFFZI(310)
      COMMON/CB1/F1,F2,F3,F4,F5,LQQ,ITYPE,PARA1,PARA2,PARA3
     1,PARA4,IOP26,IOP29,FLPF
     1/CB5/LK,AN3T,ZCTV
     2/CB7/ICSIZE,IOPT1,EFFAH,EFFAL/CB8/AKR,AK,AKF,ABLP8,ITYP,EFFAC
     3/CB35/QR1,QHR3,QAK,QAKF,QAKR,QAN1,QAN2,QAN3,QAN4,QAN5,EFFZI
      PP=P(I);ITYP=ITYPE
      TT=T(I)
      THH=TH(I)
      AB=F1*X(I)
      AN1=FI1-AB
      AB1=0.33333*AB
      AN2=FI2-AB1
      AN3=FI3+0.66667*AB
C     EFFECTIVENESS FACTOR EFFECT
        IF(LK.EQ.2)GO TO 314
      IF(ICSIZE.EQ.2)GO TO 305
      ETA=AN3/(AN3+2.0*AN2)
      CALL ZIFA(EFFAC,PP,TT,ETA,BLP1,BLP2,BLP3,BLP4,BLP5,BLP6)
        EFFZI(I)=EFFAC
        IF(EFFAC.GE.EFFAH)GO TO 107
        IF(EFFAC.LE.EFFAL)EFFAC=EFFAL
        GO TO 314
107     EFFAC=EFFAH
      GO TO 314
  305 EFFAC=1.0
  314 CONTINUE
      AN4=FI4
      AN5=FI5
      ANT=AN1+AN2+AN3+AN4+AN5
        ANTI=1/ANT;Y1=AN1*ANTI;Y2=AN2*ANTI;Y3=AN3*ANTI;Y13=Y1/Y3
        Y13S=Y13*Y13;ALPHA=PARA3*0.5;Y13P=Y1*Y13S*PP;Y13PA=Y13P**ALPHA
      AN3T=100.*Y3
      IF(LK.EQ.2) GO TO 202
```

```
          TT11=TT-273.0
    201   IF(IOP29-2)404,407,408
    407   HR3=-10906.0-(5.293-(3.429E-3-2.01E-6*TT11)*TT11)*TT11
          GO TO 422
    408   HR3=-(0.54526+(840.609+459.734E6/(TT*TT))/TT)*PP-
          1(5.34685+(.2525E-3-1.69167E-6*TT)*TT)*TT-9157.09
          GO TO 422
    404  HR3=-15564.51+(7.0646-(14.8399E-03-(3.3563E-07-1.1625E-10*TT)*
        1TT)*TT)*TT-PP*(3.01975-(4.4552E-03-1.928E-06*TT)*TT)
         AK=EXP  (0.50327*(9184.0/TT-7.2949*ALOG (TT)+(3.4966E-03+
        1(1.6781E-07-3.875E-11*TT)*TT)*TT+23.05))
          GO TO 416
    422   AK17=(2250.322/TT-C.8534-0.656*ALOG(TT)-(2.58987E-4-
          11.48961E-7*TT)*TT)
          AK=10**AK17
    416   CONTINUE
        AKF=(1.7343-8.143E-04*PP+
          1(5.714E-07*PP-2.6714E-03+2.0E-06*TT)*TT)*PARA4
          AKKF=AK/AKF;AKSQ=AKKF*AKKF
        PANT=PP*Y1
        IF(PP)11,11,15
     15 IF(PANT)11,11,12
     11 PRINT 14,PANT,PP
          IF(ITYPE.NE.2)GO TO 35
        TYPE 14,PANT,PP
     14 FORMAT(1X,5HPANT= ,E15.6,10H,PRESSURE= ,F10.4   /)
    35    LQQ=2
          GO TO 800
     12 SPANT=SQRT(PANT)
        AKR=((300.0/PP)**0.63)*EXP (-24092.2*(PARA2/TT)+(33.5566/PARA1))
        R11=29.4204*(AKSG*PP*Y2-1/Y13P)*Y13PA*F*AKR*1.0E-06
          R1=R11*EFFAC
        B7=-0.666667*HR3*R1
        GO TO 203
    202 R1=0.0
        B7=0.0
    203 WX(I)=R1/F1;UALP1=UA1*FLPF**0.8
```

```
      B4=-UALP1*(TT-THH)
      B1=B7+B4
      CALL HEATC (CP1,Cp2,CP3,CP4,CP5,PP,TT,IOP26     )
      B2=AN1*CP1+AN2*CP2+AN3*CP3+AN4*CP4+AN5*CP5
      WT(I)=B1/B2
      CALL HEATC (CP1,Cp2,CP3,CP4,CP5,PH,THH,IOP26)
      B3=FD1*(F1*CP1+F2*CP2+F3*CP3+F4*CP4+F5*CP5    )
      WTH(I)=B4/B3
        QR1(I)=R1;QHR3(I)=HR3;QAK(I)=AK;QAKF(I)=AKF;QAKR(I)=AKR
        QAN1(I)=AN1;QAN2(I)=AN2;QAN3(I)=AN3;QAN4(I)=AN4;QAN5(I)=AN5
800   RETURN
      END
C     SUBROUTINE NO.4 FOR CALCULATION OF MIXTURE STREAM TEMPERATURE BY TR
C     AND ERROR TECHNIGUE
      SUBROUTINE MTEMP(TB21,TB12,F1,R11,R22,R33,R44,R55,Q1,Q2,Q3,Q4,Q5,
     1XB12,PB1,UV,C4,IOP26)
      I=1;C41=0.5
      RT=R11+R22+R33+R44+R55-0.666667*F1*XB12
      QT=Q1+Q2+Q3+Q4+Q5
      W1=(RT*TB12+QT*UV)/(RT+QT)
  192 TB21=W1
      CALL TEMP(AT1,F1,R11,R22,R33,R44,R55,Q1,Q2,Q3,Q4,Q5,XB12,PB1,
     1TB12,TB21,UV,IOP26)
      DELT1=AT1-W1
      IF(ABS(DELT1)-C41) 151,151,191
  191 IF(I-1)153,152,153
  152 W2=AT1
134       TB21=W2
      CALL TEMP(AT2,F1,R11,R22,R33,R44,R55,Q1,Q2,Q3,Q4,Q5,XB12,PB1,
     1TB12,TB21,UV,IOP26)
      DELT2=AT2-W2
      IF(ABS(DELT2)-C41)154,154,153
  153 DW12=(W1-W2)
      I=I+1
      IF(DELT1)1,151,5
    1 IF(DELT2)2,154,7
    5 IF(DELT2)7,154,2
```

```
      2 IF(ABS(DELT1)-ABS(DELT2))161,161,162
    161 W2=W1+DW12
        GO TO 134
    162 W1=W2-DW12
        GO TO 192
      7 W3=W2+(W1-W2)*ABS(DELT2)/(ABS(DELT2)+ABS(DELT1))
          IW3=W3*100.0+0.5;W3=IW3*0.01
        TB21=W3
        CALL TEMP(AT3,F1,R11,R22,R33,R44,R55,Q1,Q2,Q3,Q4,Q5,XB12,PB1,
       1TB12,TB21,UV,IOP26)
        DELT3=AT3-W3
        IF(ABS(DELT3)-C41)170,170,188
    170 TB21=AT3
        GO TO 155
    188 IF(DELT3)11,170,35
     11 IF(DELT2)17,154,26
     35 IF(DELT2)26,154,17
     17 W2=W3
        DELT2=DELT3
        GO TO 7
     26 W1=W3
        DELT1=DELT3
        GO TO 7
    154 TB21=AT2
        GO TO 155
    151 TB21=AT1
    155 RETURN
        END
        SUBROUTINE TEMP(T,F1,R11,R22,R33,R44,R55,Q1,Q2,Q3,Q4,Q5,XB12,
       1PB1,TB12,TB21,UV,IOP26)
C       SUBROUTINE NO. 5 FOR CALCULATION OF MIXTURE TEMPERATURE FROM ENTHAL
C       BALANCE
        XBF1=F1*XB12
        R1=R11-XBF1
        R2=R22-0.33333*XBF1
        R3=R33+0.66667*XBF1
        R4=R44
```

```
      R5=R55
      CALL HEATC(CP1,CP2,CP3,CP4,CP5,PB1,TB12,IOP26   )
      C1=TB12*(R1*CP1+R2*CP2+R3*CP3+R4*CP4+R5*CP5      )
      CALL HEATC(CP1,CP2,CP3,CP4,CP5,PB1,UV,IOP26       )
      C2=UV*(Q1*CP1+Q2*CP2+Q3*CP3+Q4*CP4+Q5*CP5 )
      CALL HEATC(CP1,CP2,CP3,CP4,CP5,PB1,TB21,IOP26     )
      C3=(R1+Q1)*CP1+(R2+Q2)*CP2+(R3+Q3)*CP3+(R4+Q4)*CP4+(R5+Q5)*CP5
      T=(C1+C2)/C3
      RETURN
      END
      SUBROUTINE HEATC(CP1,CP2,CP3,CP4,CP5,P,T,IOP)
C     SUBROUTINE NO. 6 FOR CALCULATION OF HEAT CAPACITY AT GIVEN TEMPERAT
C     AND PRESSURE
        T11=T-273.0
        IF(IOP-2)2,3,8
3       CP3=8.497+(8.001E-3-1.764E-6*T11)*T11
        GO TO 17
2      CP3=102.7524-(21.63767E-02-(13.12707E-05-1.5981E-09*T)*T)*T-
     1P*(6.7571E-02-(1.6847E-04-1.009514E-07*T)*T)
17      CP1=6.952-(4.576E-04-(9.563E-07-2.079E-10*T)* T)*T
      CP2=6.903-(3.753E-04-(1.93E-06-6.861E-10*T)*T)*T
      CP4=4.750+(1.2E-02+(3.03E-06-2.63E-09*T)*T)*T
        GO TO 11
8       CP3=8.497+(8.001E-3-1.764E-6*T11)*T11
C       CPNH2=8.62+(0.002+7.2E-9*TT11)*TT11
        CP2=6.822+(1.631E-3-0.345E-6*T11)*T11
C       CPN2=6.815+(317E-4+5.3E-8*TT11)*TT11
        CP1=6.919+(0.218E-3+0.279E-6*T11)*T11
C       CPH2=6.5+0.0009*TT11
        CP4=3.00+(0.0228-4.8E-6*T)*T
11      CP5=4.9675
      RETURN
      END
C     SUBROUTINE NO. 21
C     RUNGE KUTTA FOURTH ORDER NUMERICAL INTEGRATION
C     METHOD. ERROR IS APPROXIMATELY FIFTH POWER OF H.
C     SUBROUTINE NO.7 FOR CALCULATION OF EFFECTIVE
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```
C      NESS FACTOR OF LARGER SIZE CATALYST
C      PARTICLES OF 6MM AND 10 MM
       SUBROUTINE ZIFA(ZIF,P,T,ETA,B1,B2,B3,B4,B5,B6)
```

```
      IF(P-150.0)20,26,35
   35 IF(P-225.0)20,26,47
   47 IF(P-300.0)71,26,71
   26 CB0=1 ; CB1=1 ; CB2=1 ; CB3=1 ; CB4=1 ; CB5=1 ; CB6=1
      IF(P-225)44,56,80
   44 B0=-17.539096*CB0 ; B1=0.07697849*CB1
      B2=6.900548*CB2 ; B3=-1.08279E-4*CB3
      B4=-26.42469*CB4 ; B5=4.927648E-8*CB5
      B6=38.93727*CB6
      GO TO 200
   56 B0=-8.2125534*CB0 ; B1=0.03774149*CB1
      B2=6.190112*CB2 ; B3=-0.5354571E-4*CB3
      B4=-20.86963*CB4; B5=2.379142E-8*CB5
      B6=27.88403*CB6
      GO TO 200
   80 B0=-4.6757259*CB0 ; B1=0.02354872*CB1
      B2=4.687353*CB2 ; B3=-0.3463308E-4*CB3
      B4=-11.28031*CB4 ; B5=1.540881E-8*CB5
      B6=10.46627*CB6
      GO TO 200
   20 CB0=2.06351463-0.007090097*P ; CB1=2.019427635-0.006796184*P
      CB2=1.205907125-0.001372714*P ;CB3=2.010967778-0.006739785*P
      CB4=1.420444667-0.002802964*P ; CB5=2.03437015-0.0068958*P
      CB6=1.567746018-0.003784973*P
      GO TO 44
   71 CB0=4.025692759-0.010085642*P;CB1=3.410792604-0.008035975*P
      CB2=2.282394563-0.004274648*P;CB3=3.184342831-0.007281142*P
      CB4=4.400374635-0.011334582*P;CB5=3.176056425-0.007253521*P
      CB6=7.656721067-0.02218907*P
      GO TO 80
  200 ZIF=B0+(B1+(B3+B5*T)*T)*T+(B2+(B4+B6*ETA)*ETA)*ETA
      RETURN
      END
C     SUBROUTINE NO. 8 FOR CALCULATION OF
C     CONVERSION AT EQUILIBRIUM AND MAXIMUM
C     REACTION RATE AT CONVERGED VALUES IN THE
C     CATALYST BED
```

```
      SUBROUTINE CONV(XACT,XE,XRM,P,T,I,AELP2)
      DIMENSION XACT(310),XE(310),XRM(310),XY(310),P(310),
     1T(310),ADELP(4),AELP2(4,2),RATE(800)
      COMMON/CB8/AKR,AK,AKF,ABLP8,ITYPE,ZIF
     1/CB9/FF,RATIO,XINCL,XINCL2,TOL8,FC1,FC2,FC3,DELE,DELM
     1,IOL8,M88,IOP11,ICL81
     1/CB26/CONSL7,CONSL8,SCONL8,TWTH,PP,TT,DAKR,DAK,DAKF,RAKKF
      REAL KC1,KC2,KC3
      J=1;PP=P(I)  ; TT=T(I)
      RAKKF=AK/AKF ; SRAF=RAKKF*RAKKF
      CONP=1.29904*PP ; MC=1 ; KC1=CONP*RAKKF
       CONSL7=29.4204*AKR*FF/PP**0.5;CONSL8=PP*RAKKF
       SCONL8=CONSL8*CONSL8;TWTH=2/3
       Y3F=1.5*(100-FC3)/FC1;Y1F=225*FC3/(FC1*FC1)
  278 IF(MC.EQ.1) GO TO 287
      KC1=KC3
  287 AKC1=KC1+1
      BKC1=2*KC1+Y3F
      CKC1=KC1-Y1F
      AKCK=4*AKC1*CKC1
      BKSQ=BKC1*BKC1
      IF(AKCK.GT.BKSQ) GO TO 305
      ROOT=(BKSQ-AKCK)**0.5
       AKC2=2*AKC1;ROOT2=ROOT/AKC2
       BKC2=BKC1/AKC2;BKROOT=BKC2+ROOT2
C      IF(BKROOT.LT.1.0)GO TO 35
       IF(BKC2.LE.ROOT2)GO TO 35
       LXY=(BKC2-ROOT2)*10000+0.5;XY(I)=LXY*0.0001
       IF(IOL81.NE.1)GO TO 1109
       PRINT 1101,XY(I)
       TYPE 1101,XY(I)
 1109  CONTINUE
 1101  FORMAT(F7.3)
       GO TO 26
 35    LXY=(BKC2+ROOT2)*10000+0.5;XY(I)=LXY*0.0001
       IF(IOL81.NE.1)GO TO 1118
       PRINT 1101,XY(I)
```

```
            TYPE 1101,XY(I)
      1118  CONTINUE
            IF(XY(I).GT.1.0)GO TO 305
      26    IF(MC.EQ.2)GO To 350
          XE(I)=XY(I)
          GO TO 332
      350 XRM(I)=XY(I)
            IF(RATIO.NE.3.0)GO TO 443
      C     IF(ZIF.NE.1.0)GO TO 443
          GO TO 377
      443   CONTINUE
            GO TO 458
      305 PRINT 308,PP,TT
            IF(ITYPE.NE.2)GO TO 107
          TYPE 308,PP,TT
      308 FORMAT(2X,'PRESSURE(ATM)=',F10.3,8X,',TEMPERATURE(K)=',F10.3/)
      107     IF(MC.EQ.2) GO TO 800
          PRINT 809
            IF(ITYPE.NE.2)GO TO 116
          TYPE 809
      809 FORMAT(2X,'CONVERSION AT EQUILIBRIUM IS COMING COMPLEX/NEGATIVE OR
         1ZERO.'/)
      116   XE(I)=0.0
          GO TO 332
      800 PRINT 818
            IF(ITYPE.NE.2)GO TO 125
          TYPE 818
      818 FORMAT(2X,'CONVERSION AT MAXIMUM RATE IS COMING COMPLEX/NEGATIVE O
         1R ZERO.'/)
      125   XRM(I)=0.0
          GO TO 377
      332   CONTINUE
            IF(RATIO.EQ.3.0)GO TO 431
      458   ABC=1;XLPE=XY(I)
            IF(MC.EQ.2)GO To 1100
      C     XLPE=XACT(I);ABC=-1
      1100  XEL=(1-ABC*XINCL2)*XLPE
```

```
C         XINCL2=(XE(I)-XRM(I))*0.2
          CALL LMINP(XEL,MC,ADELP,RATE,LMP)
          IF(MC.EQ.2)GO TO 440
          XE(I)=XEL
          DO 530 LP=1,4
  530     AELP2(LP,1)=ADELP(LP)
          GO TO 431
  440     XRM(I)=XEL
          DO 533 LP=1,4
  533     AELP2(LP,2)=ADELP(LP)
          GO TO 377
    431 MC=2
          TINV=1/TT
        DAKR=24092.2*AKR*TINV*TINV
        DAK=AK*0.50327*(3.4966E-3-TINV*(9184.0*TINV+7.2949)+
          1TT*(3.3562E-7-TT*11.625E-11))
        DAKF=5.714E-7*PP+4.0E-6*TI-2.6714E-3
        KC2=2.0*AKR*RAKKF*(DAK-RAKKF*DAKF)/(AKF*DAKR)+SRAF
        KC3=CONP*KC2**0.5
        GO TO 278
    377 CONTINUE
          IF(IOL81.NE.1)GO TO 1105
          PRINT 1106,((AELP2(LP,LP1),LP=1,4),LP1=1,2),
         2(RATE(LP),LP=1,LMP)
          TYPE 1106,((AELP2(LP,LP1),LP=1,4),LP1=1,2),
         2(RATE(LP),LP=1,LMP)
  1106    FORMAT(8F7.3,6E11.3/)
  1105    CONTINUE
          RETURN
        END
C SUBROUTINE NO.9
C         SUBROUTINE NO. 10
        SUBROUTINE COMPA(DELT,T,J,J1)
        DIMENSION DELT(800),T(800)
        I=1;J1=0
     26 IF(ABS(T(J)-T(I)).EQ.0.0)GO TO 35
        I=I+1
```

```
      IF(I.EQ.J) GO TO 44
      GO TO 26
   35 T(J)=T(I)
      DELT(J)=DELT(I)
      J1=I
      GO TO 53
   44 DELT(J)=8.0
   53 RETURN
      END
      SUBROUTINE OPTIMA(OBJF,M,X,X1,IOP,NV,
     1AC2,NLEV,NOPTM,TOL8,NMAX1,NDPTS,X8,
     2OBJ,NN8,AC1,YN,ILP)
C     SUBROUTINE NO.11 FOR COMPLEX SEARCH TECHNIQUE
      DIMENSION OBJF(50),X(50,20),X1(20,20),
     1OBJ(20),X8(20,20),NLEV(20),X8N(20)
        CALL MAXMIL(OBJF,M,OBMAX1,
        1OBMAX2,OBMIN,NMAX1,NMAX2,NMIN,NDPTS,ILP)
      IF(M.GT.NDPTS) GO TO 251
32    IN=0;IK=0;NN8=1;AC1=AC2;LP=0;NDPT1=NDPTS-1
260     DO 17 L=1,NDPTS
        IF(L.EQ.NMIN)GO TO 17
        LP=LP+1
        OBJ(LP)=OBJF(L)
        DO 17 K=1,NV
        X8(LP,K)=X(L,K)
17      CONTINUE
        OBJ(NDPTS)=OBJF(NMIN)
        DO 116 K=1,NV
116     X8(NDPTS,K)=X(NMIN,K)
125     CONTINUE
  278 CALL NPOINT(IN,OBMIN,OBJ,X8,NV,NN8,AC1
        1,NOPTM,TOL8,OBMAX1,OBMAX2,NMAX1,NMIN,NDPTS)
        IF(NN8.NE.1)GO TO 440
        YN=OBJ(NDPTS)
440     CONTINUE
        IF(NOPTM.NE.0)GO TO 71
        M=M+1
```

```
      DO 74 K=1,NV
   74 X(M,K)=X8(NDPTS,K)
        GO TO 80
  251 CONTINUE
  206 OBJ(NDPTS)=OBJF(M)
      DO 233 K=1,NV
  233 X8(NDPTS,K)=X(M,K)
        IF(OBJ(NDPTS).LE.YN)GO TO 125
        NN8=1;AC1=AC2;LP=0;NDPT1=NDPTS-1
        CALL MIN(OBJ,NDPTS,OBMIN,NMIN)
        DO 143 K=1,NV
143     X8N(K)=X8(NMIN,K)
        DO 134 L=1,NDPTS
        IF(L.EQ.NMIN)GO TO 134
        LP=LP+1
        IF(L.EQ.LP)GO TO 134
        OBJ(LP)=OBJ(L)
        DO 134 K=1,NV
        X8(LP,K)=X8(L,K)
134     CONTINUE
        OBJ(NDPTS)=OBMIN
        DO 890 K=1,NV
890     X8(NDPTS,K)=X8N(K)
        GO TO 125
   80 OBJF(M)=0.0
   71 RETURN
      END
      SUBROUTINE NPOINT(IN,YN,Y,X,N,N1,AC
        1,NOPTM,TOL8,YMAX1,YMAX2,NMAX1,NMIN,NDPTS)
      DIMENSION Y(20),X(20,20)
C     SUBROUTINE NO.12 FOR NEXT OPTIMISATION POINT
      I=0;NOPTM=0;NDPT1=NDPTS-1;XMEAN=0.0
227     CONTINUE
      IF(N1-2)38,47,56
   38 CONTINUE
   65 I=I+1;XMEAN=0.0
        DO 332 L=1,NDPT1
```

```
332     XMEAN=X(L,I)+XMEAN
        XMEAN=XMEAN/NDPT1
        X(NDPTS,I)=XMEAN+(XMEAN-X(NDPTS,I))*AC
      IF(I.LT.N) GO TO 65
      N1=N1+1
      IN=3
      GO TO 80
   47 AC=-0.5*AC
      GO TO 38
   56 AC=0.5*AC
      GO TO 38
80      CONTINUE
        IF((YMAX1-YMAX2).GT.TOL8)GO TO 233
        NOPTM=NMAX1
233     CONTINUE
      RETURN
      END
      SUBROUTINE INTEGR(X,N,M)
      DIMENSION X(50,20),IX(20)
C     SUBROUTINE NO.13 FOR MAKING REAL VARIABLES
C     TO ITS NEAREST ROUNDED OFF VALUE
        DO 8 K=1,17
        IX(K)=X(M,K)*100+0.5;X(M,K)=IX(K)*0.01
8       CONTINUE
      RETURN
      END
      SUBROUTINE MLEVEL(X,N,X1,M,N1)
      DIMENSION X(50,20),X1(20,20),N1(20)
C     SUBROUTINE NO.14 FOR MAKING VARIABLES TO
C     THEIR NEAREST SPECIFIED LEVEL
C     FEED DATA THROUGH DATA FILE'DA17.DAT'
C     IN DESCENDING ORDER,SAY 20,15,10,SO ON.
        J=1;K=1;LP1=1
80      IF(X(M,J)-X1(K,J))26,29,29
26      IF(K.GE.N1(J))GO TO 11
        K=K+1;LP1=2
      GO TO 80
```

```
29       IF(LP1.EQ.1)GO TO 11
         LP1=1
       IF(ABS(X(M,J)-X1((K-1),J)).GE.
      1ABS(X(M,J)-X1(K,J)))GO TO 11
         X(M,J)=X1((K-1),J)
         GO TO 74
11       X(M,J)=X1(K,J)
74       IF(J.GE.N)GO TO 53
         J=J+1;K=1;LP1=1
       GO TO 80
53       RETURN
       END
C        SUBROUTINE NO. 15
       SUBROUTINE ACOMP(IK,X,M,N)
       DIMENSION X(50,20)
       J=1
    35 I=1
    17 IF(X(M,I).EQ.X(J,I)) GO TO 8
       J=J+1
       IF(J.GE.M) GO TO 71
       GO TO 35
     8 I=I+1
       IF(I.GT.N) GO TO 80
       GO TO 17
    71 IK=0
       GO TO 89
    80 IK=J
    89 RETURN
       END
C      SUBROUTINE NO. 16
       SUBROUTINE MINMAX(X,N,XMAX,XMIN,NDIM)
       DIMENSION X(NDIM)
       J=1 ; A=X(1)
       DO 26 J=2,N
       IF(A.GE.X(J)) GO TO 26
       A=X(J)
    26 CONTINUE
```

```
      XMAX=A
      I=1
      A1=X(1)
      DO 80 J=2,N
      IF(A1.LE.X(J))GO TO 80
      A1=X(J)
   80 CONTINUE
      XMIN=A1
      RETURN
      END
C     SUBROUTINE NO. 17
      SUBROUTINE AMMC(AN3E,AN3MR,AB1,FI3,FIT,XE,XRM,I)
      DIMENSION XE(310),XRM(310)
        COMMON/CB9/FF,RATIO,XINCL,XINCL2,TOL8,FC1,FC2,FC3,DELE,DELM
         1,IOL8,M88,IOP11
      J=1 ; X=XE(I)
   17 AB2=2*FC1*X/3
      AN3T1=100*(FC3+AB2)/(100-AB2)
      IF(J.GE.2)GO TO 26
      AN3E=AN3T1
      X=XRM(I)
      J=2
      GO TO 17
   26 AN3MR=AN3T1
      RETURN
      END
C     SUBROUTINE NO.18
      SUBROUTINE FLOWR(F1,F2,F3,F4,F5,VFT,FC1,FC2,FC3,FC4,I)
      C1=1.1355E-4
      C2=1.1135E-4
      C3=1.1349E-4
      C4=1.1351E-4
      C5=1.136E-4
      IF(I.EQ.2)GO TO 26
   17 CONTINUE
      FC5=100.0-(FC1+FC2+FC3+FC4)
        FCLP=FC1/C1+FC2/C2+FC3/C3+FC4/C4+FC5/C5
```

```
        FTC=100*VFT/FCLP
      IF1=FTC*FC1+0.5
      F1=IF1
      IF2=FTC*FC2+0.5
      F2=IF2
      IF3=FTC*FC3+0.5
      F3=IF3
      IF4=FTC*FC4+0.5
      F4=IF4
      IF5=FTC*FC5+0.5
      F5=IF5
      GO TO 80
   26 IVFT=0.01*((F1/C1)+(F2/C2)+(F3/C3)+(F4/C4)+(F5/C5))+0.5
      VFT=IVFT
        FTC=0.01*(F1+F2+F3+F4+F5)
   35 IFC1=100*F1/FTC+0.5
      FC1=IFC1/100
      IFC2=100*F2/FTC+0.5
      FC2=IFC2/100
      IFC3=100*F3/FTC+0.5 ; FC3=IFC3/100
      IFC4=100*F4/FTC+0.5 ; FC4=IFC4/100
      FC5=100.0-(FC1+FC2+FC3+FC4)
80      RETURN
      END
C     SUBROUTINE NO. 19

C  SUBROUTINE NO. 20
        SUBROUTINE FUNCBJ(X,M,N1,P,P1,S,S1,S2,S3,S4,S5,S6,S7,S8
        1,S20,S21,S22,S23,S24,S25,S26,S27,S28,G)
        DIMENSION X(50)
        IF(N1-2)2,3,7
7       IF(N1-4)8,11,12
12      IF(N1-6)17,80,21
21      IF(N1-8)26,29,30
30      IF(N1-10)35,38,38
2       G=P1
        IF(P1.EQ.0.0)GO TO 44
```

```
      X(M)=P/P1
      GO TO 20
44    X(M)=P
      GO TO 20
3     G=S21
      IF(S21.EQ.0.0)GO TO 45
      X(M)=-S1/S21
      GO TO 20
45    X(M)=-S1
      GO TO 20
8     G=S22
      IF(S22.EQ.0.0)GO TO 46
      X(M)=-S2/S22
      GO TO 20
46    X(M)=-S2
      GO TO 20
11    G=S23
      IF(S23.EQ.0.0)GO TO 47
      X(M)=-S3/S23
      GO TO 20
47    X(M)=-S3
      GO TO 20
17    G=S24
      IF(S24.EQ.0.0)GO TO 48
      X(M)=-S4/S24
      GO TO 20
48    X(M)=-S4
      GO TO 20
80    G=S25
      IF(S25.EQ.0.0)GO TO 50
      X(M)=-S5/S25
      GO TO 20
50    X(M)=-S5
      GO TO 20
26    G=S26
      IF(S26.EQ.0.0)GO TO 51
      X(M)=-S6/S26
```

```
           GO TO 20
     51    X(M)=-S6
           GO TO 20
     29    G=S27
           IF(S27.EQ.0.0)GO TO 53
           X(M)=-S7/S27
           GO TO 20
     53    X(M)=-S7
           GO TO 20
     35    G=S28
           IF(S28.EQ.0.0)GO TO 52
           X(M)=-S8/S28
           GO TO 20
     52    X(M)=-S8
           GO TO 20
     38    G=S20
           IF(S20.EQ.0.0)GO TO 56
           X(M)=-S/S20
           GO TO 20
     56    X(M)=-S
     20    RETURN
           END
C       SUBROUTINE NO. 21
        SUBROUTINE MIN(X,N,XMIN,NMIN)
        DIMENSION X(20)
        I=1;NMIN=1
        A1=X(1)
        DO 80 J=2,N
        IF(A1.LE.X(J))GO TO 80
        A1=X(J)
          NMIN=J
     80 CONTINUE
        XMIN=A1
        RETURN
        END
C       SUBROUTINE NO. 22
        SUBROUTINE MAXMIL(X,N,XMAX1,XMAX2,
```

```
       1XMIN,NMAX1,NMAX2,NMIN,NDPTS,ILP)
     DIMENSION X(50)
       NMAX=1;LP=1;NMAX1=1;NDLP=NDPTS+2
53     I=1
       IF(LP.EQ.1)GO TO 56
       IF(NMAX.EQ.1)I=I+1
56     A=X(I);II1=I+1
     DO 26 J=II1,N
       IF(J.EQ.NMAX1)GO TO 26
     IF(A.GE.X(J)) GO TO 26
     A=X(J);NMAX=J
  26 CONTINUE
       IF(LP.NE.1)GO TO 35
     XMAX1=A;NMAX1=NMAX;LP=2
       GO TO 53
35     XMAX2=A;NMAX2=NMAX
     I=1;NMIN=1
       IF(ILP.EQ.1)GO TO 101
       IF(N.LE.NDLP)I=I+1
101    CONTINUE
     A1=X(I);II1=I+1;NMIN=I
     DO 80 J=II1,N
     IF(A1.LE.X(J))GO TO 80
     A1=X(J);NMIN=J
  80 CONTINUE
     XMIN=A1
     RETURN
     END
C   SUBROUTINE NO.23
       SUBROUTINE LMINP(TB21,MC,DELP2,R11,LMP)
       DIMENSION ADELT(800),ATH12(800),DELP2(4),R11(800)
       COMMON/CB9/FF,RATIC,XINCL,XINCL2,C4,FC1,FC2,FC3,DELE,DELM
       1,IOL8,M88,IOP11,ICL81
       1/CB8/AKR,AK,AKF,ABLP8,ITYPE,ZIF/CB26/CONSL7,CONSL8
       1,SCONL8,TWTH,P,T,DAKR,DAK,DAKF,RAKKF
       LMP=1;I=0;ATLP=1.0;C41=0.0008
     W1=TB21
```

```
192      I=I+1
         IF(W1.GT.ATLP)W1=2.0*ATLP-W1
         IF(W1.LT.0.0)W1=-W1
         ATH12(I)=W1
         IF(I.EQ.1)GO TO 224
         CALL COMPA(ADELT,ATH12,I,LP)
         IF(LP.NE.0)GO TO 227
224       CALL DELTAP(DELT1,W1,MC,R11(LMP),LMP)
         GO TO 233
227      DELT1=ADELT(LP)
233      ADELT(I)=DELT1
C        IF(IOL81.NE.1)GO TO 323
         IF(I.GE.M88)GO TO 151
323       IF(ABS(DELT1)-C41) 151,151,191
  191 IF(I-1)153,152,153
  152 W2=W1*XINCL
134       TB21=W2
         I=I+1
         IF(W2.GT.ATLP)W2=2*ATLP-W2
         IF(W2.LT.0.0)W2=-W2
         ATH12(I)=W2
         CALL COMPA(ADELT,ATH12,I,LP)
         IF(LP.NE.0)GO TO 236
200       CALL DELTAP(DELT2,W2,MC,R11(LMP),LMP)
         GO TO 242
236      DELT2=ADELT(LP)
242      ADELT(I)=DELT2
C        IF(IOL81.NE.1)GO TO 314
         IF(I.GE.M88)GO TO 154
314       IF(ABS(DELT2)-C41)154,154,153
  153 DW12=(W1-W2)*2.0
209       IF(DELT1)1,151,5
    1 IF(DELT2)2,154,7
    5 IF(DELT2)7,154,2
    2 IF(ABS(DELT1)-ABS(DELT2))161,161,162
  161 W2=W1+DW12
      GO TO 134
```

```
  162 W1=W2-DW12
      GO TO 192
    7 W3=W2+(W1-W2)*ABS(DELT2)/(ABS(DELT2)+ABS(DELT1))
      TB21=W3
        I=I+1;ATH12(I)=W3
        CALL COMPA(ADELT,ATH12,I,LP)
        IF(LP.NE.0)GO TO 245
      CALL DELTAP(DELT3,W3,MC,R11(LMP),LMP)
        GO TO 251
245     DELT3=ADELT(LP)
251     ADELT(I)=DELT3
C       IF(IOL8.NE.1)GO TO 206
        IF(I.GE.M88)GO TO 305
206      IF(ABS(DELT3)-C41)170,170,188
  170 TB21=W3
      GO TO 155
  188 IF(DELT3)11,170,35
   11 IF(DELT2)17,154,26
   35 IF(DELT2)26,154,17
   17 W2=W3
      DELT2=DELT3
      GO TO 7
   26 W1=W3
      DELT1=DELT3
      GO TO 7
305     TB21=W3
        GO TO 155
  154 TB21=W2
      GO TO 155
  151 TB21=W1
155     CONTINUE
        DELP2(1)=ATH12(I);DELP2(2)=ADELT(I);DELP2(3)=ATH12(I-1)
        DELP2(4)=ADELT(I-1)
      RETURN
      END
C  SUBROUTINE NO.24
        SUBROUTINE DELTAP(DELTA,XEL,MC,R1,LMP)
```

```
      COMMON/CB9/FF,RATIO,XINCL,XINCL2,TOL8,FC1,FC2,FC3,DELE,DELM
      1,IOL8,M88,IOP11,ICL81
      1/CB8/AKR,AK,AKF,ABLP8,ITYPE,ZIF/CB26/CONSL7,CONSL8
      1,SCONL8,TWTH,P,T,DAKR,DAK,DAKF,RAKKF
      FC1XE=FC1*XEL;FLPC=100-TWTH*FC1XE;FLPCI=1/FLPC
      FC1LP=FC1*FLPCI*FLPCI;Y1=FLPCI*(FC1-FC1XE)
      Y2=FLPCI*(FC2-FC1XE/3);Y3L=FC3+TWTH*FC1XE
      Y3=Y3L*FLPCI;Y15P=Y1**1.5;Y1BY3=Y15P/Y3
      IF(MC.EQ.2)GO TO 17
      DELTA=1-1/(CONSL8*Y1BY3*(Y2**0.5))
      DELE=DELTA
      GO TO 260
17    CONTINUE
C     GO TO 44
260   ETA=Y3/(Y3+2*Y2)
      CALL ZIFA(ZIF,P,T,ETA,B1,B2,B3,B4,B5,B6)
      DZIT=B1+(2*B3+3*B5*T)*T
44    SCONLP=SCONL8*Y1BY3*Y2;R1=CONSL7*(SCONLP-1/Y1BY3)*ZIF
      LMP=LMP+1
      IF(MC.NE.2)GO TO 26
      DRT=R1*DAKR/AKR+2*CONSL7*SCONLP*(DAK-RAKKF*DAKF)/AK
C     GO TO 47
      DELTA=1+R1*DZIT/(ZIF*DRT);DELM=DELTA
      GO TO 26
47    DELTA=DRT;DELM=DELTA
26    CONTINUE
C     TYPE 11,XEL,DELTA
C     PRINT 11,XEL,DELTA
C11   FORMAT(2F8.3)
      RETURN
      END
C  SUBROUTINE NO.25
      SUBROUTINE PCONV(I26,N,AQX)
      DIMENSION AQX(50,20),LPAQX(50),AQXLP(2,50),A(20),A1(20)
      COMMON/CB74/AQXLP,A2,A22,A3,A23,A4,A24,A5,A25,A6,A26,A7,A27,
      1A8,A28,A9,A29,A10,A30,A11,A31,A12,A32,A13,A33,A14,A34,A15,
      1A35,A16,A36,A17,A37,A18,A38,A19,A20,A21,FDLIM
```

```
      A(1)=A2;A(2)=A3;A(3)=A4;A(4)=A5;A(5)=A6;A(6)=A7;A(7)=A8
      A(8)=A9;A(9)=A10;A(10)=A11;A(11)=A12;A(12)=A13;A(13)=A14
      A(14)=A15;A(15)=A16;A(16)=A17;A(17)=A18;A(18)=A19;A(19)=A20
      A(20)=A21;A1(1)=A22;A1(2)=A23;A1(3)=A24;A1(4)=A25;A1(5)=A26
      A1(6)=A27;A1(7)=A28;A1(8)=A29;A1(9)=A30;A1(10)=A31;A1(11)=A32
      A1(12)=A33;A1(13)=A34;A1(14)=A35;A1(15)=A36
      A1(16)=A37;A1(17)=A38
      M=I26;A1(18)=1.0;A1(19)=1.0;A1(20)=1.0
      IF(N.NE.1)GO TO 200
      DO 53 I=1,20
      IF(A1(I).EQ.0.0)GO TO 152
      AQX(I26,I)=A(I)/A1(I)
      GO TO 53
152   AQX(I26,I)=A(I)
53    CONTINUE
      GO TO 80
200   CONTINUE
862   DO 515 L=1,17
      LPAQX(L)=AQX(M,L)*1000+0.5;AQX(M,L)=LPAQX(L)*0.001
      IF(AQX(M,L).LT.AQXLP(1,L))GO TO 521
      AQX(M,L)=AQXLP(1,L)
      GO TO 515
521   IF(AQX(M,L).GT.AQXLP(2,L))GO TO 515
      AQX(M,L)=AQXLP(2,L)
515   CONTINUE
      LPAQX(18)=AQX(M,18)*10000+0.5;AQX(M,18)=LPAQX(18)*0.0001
      LPAQX(19)=AQX(M,19)*1000000+0.5;AQX(M,19)=LPAQX(19)*0.000001
      LPAQX(20)=AQX(M,20)*10000+0.5;AQX(M,20)=LPAQX(20)*0.0001
      DO 62 I=1,20
      IF(A1(I).EQ.0.0)GO TO 155
      A(I)=AQX(I26,I)*A1(I)
      GO TO 62
155   A(I)=AQX(I26,I)
62    CONTINUE
      FD24=A(6)+A(7)+A(8)+A(17)
      IF(FD24.LE.FDLIM)GO TO 92
      FD24I=100.0*FDLIM/FD24
```

```
      IFD11=A(17)*FD24I;A(17)=IFD11*0.01
      IF(A1(17).EQ.0.0)GO TO 161
      AQX(I26,17)=A(17)/A1(17)
      GO TO 164
161   AQX(I26,17)=A(17)
164   CONTINUE
      IFD22=A(6)*FD24I
      A(6)=IFD22*0.01
      IFD33=A(7)*FD24I
      A(7)=IFD33*.01
      A(8)=FDLIM-A(6)-A(7)-A(17)
      DO 170 I=6,8

      IF(A1(I).EQ.0.0)GO TO 165
      AQX(M,I)=A(I)/A1(I)
      GO TO 170
165   AQX(M,I)=A(I)
170   CONTINUE
92    CONTINUE
      A2=A(1);A3=A(2);A4=A(3);A5=A(4);A6=A(5);A7=A(6);A8=A(7)
      A9=A(8);A10=A(9);A11=A(10);A12=A(11)
      A13=A(12);A14=A(13);A15=A(14)
      A16=A(15);A17=A(16);A18=A(17);A19=A(18);A20=A(19);A21=A(20)
80    RETURN
      END
C  SUBROUTINE NO.26
      SUBROUTINE PNEXT(N1,N3,N4,X,ISIG)
      DIMENSION F(17,20),X(50,20)
      COMMON/CB71/N2,F,M1,ILP
      IF(ISIG.NE.1)M1=2

2     N1=N1+1
      IF(N1.GT.N2)GO TO 8
      IF(F(N3,N1).EQ.0.0)GO TO 2
      N4=N4+1
      DO 3 L=1,N2
      IF(L.NE.N1)GO TO 7
```

```
      X(N4,L)=X(1,L)+F(N3,N1)*ISIG
      IF(ILP.NE.1)ISIG=-ISIG
      GO TO 3
7     X(N4,L)=X(1,L)
3     CONTINUE
      IF(ILP.EQ.1)GO TO 8
      IF(M1.NE.2)N1=N1-1
      M1=1
8     RETURN
      END
C  THE END OM
```