# SIMULATION AND OPTIMIZATION OF AMMONIA SYNTHESIS LOOP

A THESIS

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### CERTIFICATION OF THESIS WORK

We, the undersigned, certify that MUHAMMAD ABDUL MUQEEM, candidate for the degree of Master of Science in Engineering (Chemical) has presented his thesis on the subject "SIMULATION AND OPTIMIZATION OF AMMONIA SYNTHESIS LOOP", that the thesis is acceptable in form and content, and that the student demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on 22nd June, 1988.

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# ABSTRACT

Simulation model (pseudo homogeneous one-dimensional) based on Temkin-Pyzhev kinetic expression for Uhde three bed quench reactor has been developed. The present model was developed based on the configuration of an ongoing fertilizer plant in the country. Kinetic-parameters of the rate expression and the deactivation parameters for catalyst ageing were calculated using steady-state plant data collected over three years period at an interval of two weeks using parameter estimation techniques. Values of the kinetic parameters were comparable to those reported in the literature. The deactivation parameters showed that deactivation of the synthesis catalyst was extremely small with time, which was consistent with the plant experience. The model was simulated under different operating conditions. The operating variables considered are recycle ratio, quench temperature, $H_2/N_2$ ratio and inert level in the fresh feed. Simulation studies indicate that the optimum operating conditions lies in the range: $H_2/N_2$ ratio - 2.50 to 3.25, inerts in fresh feed - 0.001 to 0.02, recycle ratio - 3.5 to 4.0 and quench temperature - 480°K to 500°K.

Simulation studies alone cannot indicate the values of the operating variables which will result in optimum operation of the plant. Suitable models of other equipments in the ammonia synthesis loop were formulated. The whole synthesis loop was optimized by changing the above four variables one at a time i.e., using perturbation type optimization technique. Finally the whole loop was optimized using complex Box method. The conditions for designing the synthesis loop based on the minimum operating cost is found to be: $H_2/N_2$ ratio = 2.55, inerts in fresh feed = 0.0023, recycle ratio = 3.24, quench temperature = 499.9°K.

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# CHAPTER 1

# INTRODUCTION

Catalytic synthesis of ammonia is a well known chemical process having importance in Bangladesh. Of the two important types of reactors, the shell and tube type and the quench type, the latter is used in the Urea Fertilizer Factories at Ghorasal and Ashuganj. This type of reactor is being increasingly used in fertilizer industries because of their simplicity in construction and ease in operation and maintenance (Hossain, 1981).

Modelling, simulation and optimization are three interlinked activities in chemical process engineering. Based on a mathematical model for a system, the simulation will involve the behaviour of the reactor under given conditions of feed and operating conditions and optimization would involve the search for conditions of operation to minimize the operating cost of the system or maximize the return from the system.

Simulation studies would attempt to predict the performance of a given physical system based on a mathematical model for the system. In so doing, the performance of the plant can be predicted at various operating conditions and effects of varying operating conditions can be studied. This allows better operating conditions to be adopted resulting in improved performance of the plant. Simulation studies also provide information on the control and stability of the plant.

Optimization is the collective process of finding the set of conditions required to achieve the best result from a given situation (Beveridge and Schechter, 1970). Almost any problem in the design, operation of industrial processes can be reduced in the final analysis to the problem of determining the largest or smallest value of a function of several variables i.e. to an optimization problem. There are two types of optimization: structural and parametric. Parametric optimization is performed when the plant is in operation, where certain parameters are adjusted to increase the performance of the plant. On the other hand, structural optimization, which has been done in this work, is used in the design phase when a new plant is going to be designed. In the last part of this work, the ammonia synthesis loop has been optimized using constrained Box method (Box, 1965) to minimize the annual operating cost of the loop. By this study a set of optimum operating variables has been found out. The variables considered in this study are $H_2/N_2$ ratio, recycle ratio, inerts in the feed and quench temperature.

# CHAPTER II

# LITERATURE REVIEW

## 2.1 Introduction

The catalytic synthesis of ammonia from nitrogen and hydrogen is one of the most successful application of chemical technology for the benefit of mankind. Thermodynamic and kinetic considerations suggest operating at a high pressure, at a high temperature and in the presence of a catalyst, in order to combine nitrogen with hydrogen under industrially economic conditions.

Wealth of information exist in the literature on all aspects of ammonia synthesis reaction; much more are stored in the files of industrial research laboratories as classified documents (Vancini, 1971). Extensive literature survey has been done by Hossain (1981). This has been updated and is given in Appendix II.

## 2.2 The Synthesis Reaction

The synthesis of ammonia from nitrogen and hydrogen is a reversible exothermic equilibrium reaction:

$$\tfrac{1}{2}\ N_2(g) + 3/2\ H_2(g) \rightleftharpoons NH_3(g) - \Delta H \qquad (2.1)$$

Direct determination of heat of reaction and equilibrium over wide ranges of temperature and pressure is in practice time consuming, delicate and expensive. Therefore, indirect methods are used, which are based on thermodynamic data such as free energy, heat of formation, specific heat capacity, entropy, P-V-T relationship, etc. which are experimentally obtainable and values are available in the literature (Vancini, 1971 and Hossain, 1981).

Various expressions for heat of reaction is available in literature given by different workers. The expressions varied widely and as generally no specific conditions were given it was rather difficult to choose an expression to use in the present work.

The equation for specific heat capacity of nitrogen, hydrogen and ammonia are mostly given in the form $C_p = a+bT+cT^2+dT^3$. For these three gases the values used in this work for the constants a,b,c and d were taken from Reid, Sherwood and Prausnitz (1977).

The expression for viscosity and thermal conductivities of gases varies with temperature and pressure as shown by Reid et al. (1977).

Many workers have evaluated the equilibrium constant as a function of temperature. They have expressed the expression in temperature for various temperature ranges. In the present work, the most widely used expression by the workers Dyson and Simon (1968), Gaines (1977), Rase (1977) and Shah (1967) have been used for equilibrium calculations.

Extensive studies of the catalytic synthesis of ammonia on iron suggest that nitrogen adsorption on the catalyst surface is the rate controlling step (Vancini 1971). Temkin and Pyzhev (1939) derived a rate equation for ammonia synthesis, which brought order among kinetic data and helped correlating kinetic expressions. Temkin-Pyzhev (T-P) equation is given in the following form:

$$r = k_1 P_{N_2} [P_{H_2}^3 / P_{NH_3}^2]^{\alpha} - k_2 [P_{NH_3}^2 / P_{H_2}^3]^{\beta} \qquad (2.2)$$

There are some limitations regarding the exponents $\alpha$ and $\beta$. Many workers reports the value of 0.5 for $\alpha$. Nielsen (1968) recommended a value of 0.75 for $\alpha$ in the T-P equation and he also reports that $\alpha$ depends on the process conditions. In this work a modified form of the T-P equation has been used using activities instead of partial pressure and $\alpha$ having a value of 0.5 (Rase, 1977). Many other expressions for rate equation have been given by various workers (Hossain, 1981).

Active metal used in the synthesis catalyst is Fe. Promoters are used for better catalytic action. Most common promoters used in synthesis catalyst are $Al_2O_3$ and $K_2O$. $Al_2O_3$ increases the surface area and prevents sintering of the surface area. $K_2O$ neutralizes the acid character of $Al_2O_3$, decreases the electron work function of iron and increases the ability to chemisorb nitrogen. Artificial magnetite is mainly used for catalyst preparation. The reduction of the catalyst can be carried out in the synthesis column, and then start producing ammonia with adjusting the pressure and spatial velocity. But the most economic, safest and practical method consists of oxidizing the catalyst surface with a nitrogen stream containing 0.1 - 0.2% $O_2$ at a pressure 2-5 kg/cm$^2$ and at temperature lower than 150$^\circ$C.

## 2.3 Simulation Models

Mathematical modelling is the mathematical representation of a physical system. Its ultimate aim is to predict the process behaviour under different sets of operating condition for working out a better strategy to control the process. Mathematical modelling costs less money and time (Hussain, 1986). Mathematical models for simulation studies have been developed by many workers. Singh and Saraf (1979) carried out simulation studies for ammonia synthesis reactors having adiabatic catalyst beds as well as autothermal reactors. They used a modified T-P equation and value of $\alpha$ from Guacci (1977). They obtained the temperature and ammonia concentration profile along the bed and in all cases, comparison with plant data and simulation result shows very good agreement. Gaines (1977) also developed a steady state model for a quench type ammonia converter and studied the effects of process variables. He proposed a simple method for optimum temperature control to obtain better efficiency from his results. Other workers (Baddour et al., 1965) have worked on TVA converters. Lutschutenkow et al. (1978) investigated the reactor sensitivity to changes in perturbation and control variables over a broad operating range. They also estimated and analyzed the reactor properties and showed them as a basis for structural and parametric synthesis of the control system.

The above studies clearly reveal that simulation is a useful tool to obtain informations on the performance of an ammonia synthesis reactor.

## 2.4 Parameter Estimation

Parameters of the kinetic expression reported in literature differ widely in their values. So, to find the different parameters applicable to the operating conditions of the present study, parameter estimation was done. Plant data of ammonia synthesis loop from Zia Fertilizer Factory was collected twice in a week over a period of three years when the plant was operating near steadily. The data were screened by doing a mass balance around the reactor. Data points which gave more than 10% error were discarded. In this way, 47 data points were selected. The objective function was the absolute difference between the actual (plant) ammonia produced and ammonia formed using Temkin-Pyzhev rate expression. The difference of this function over 47 data points was minimized within specified domain of the constraints (parameters) using constrained complex Box (Box, 1965) method.

Initially using the constraints and random numbers, a complex was formed and the function is evaluated at each of the vertices of the complex. The point giving maximum function value is modified using the method of reflection. In this way the complex gets modified and the above process continues until the standard deviation of the function values at all complex points satisfies any specified convergence criteria. The final complex points are taken as the optimum parameter value.

## 2.5 Optimization Methods

Almost any problem in the design, operation of industrial process can be reduced in the final analysis to the problem of determining the largest or smallest value of a function of several variables, i.e. to an optimization problem. The optimum seeking methods are also known as mathematical programming techniques. There are various methods in mathematical programming: nonlinear programming, linear programming, geometric programming, quadratic programming, dynamic programming etc.

In the present study, complex Box (Box, 1965) method was used for optimization study. It falls in the nonlinear programming category. In the Box method, a geometric space is formed using the constraint and random numbers to find the constrained minimum point. At each of the vertices the function is evaluated and the vertex giving the largest function value is discarded. This point is improved by the process of reflection. Each time the worst point of the current complex is replaced by a new point, the complex gets modified and test for convergence is made. Convergence has attained when the standard deviation of the function value becomes sufficiently small for all the vertices of the current complex.

This method does not require derivatives of the objective function and constraints to find the minimum point, and hence it is computationally very simple.

## 2.6 Process Costing

Process costing of different equipments in the synthesis loop, e.g. reactor, heat exchangers, compressor, separator has been done using the methods outlined in Peter and Timmerhaus (1980).

Reactor costs has been calculated assuming it as a pressure vessel. Using diameter and height of the actual converter, the weight of the vessel has been determined using suitable correlations from Peter and Timmerhaus (1980) and given in Appendix IV. From the weight the cost of the vessel has been calculated. Using suitable Lang factors, this cost has been transformed into installed cost of the equipment. In the same manner, installed cost of the separator has been calculated.

Process costing of the gas compressors has been done using appropriate equations from Peter and Timmerhaus (1980) and given in Appendix IV. Assuming multistage and isentropic compression, power required to compress the gas for a specific compression ratio has been calculated and from there cost of the compressor has been determined. In the same way as described above, Lang factors have been used.

For heat exchangers, heat load of the exchangers have been calculated. From the heat load and overall heat transfor co-efficient, the heat transfer surface area has been calculated. Based on this area, cost of the heat exchanger has been estimated. Again appropriate Lang factors have been used to find the installed cost of the heat exchanger.

# CHAPTER III

## PARAMETER ESTIMATION

Parameters used in the rate expression reported in the literature varied widely. Moreover, no catalyst activity decay function was available. So, parameter study was done to find the different rate parameters pertinent to the present operating conditions and catalyst properties. Rate parameters for ammonia synthesis were updated using plant data from Zia Fertilizer Factory. Plant data were collected twice in a week over a period of three years when the plant was operating near steadily. After collection, the data were screened by doing a mass balance around the reactor; those points which gave more than 10% error were discarded. In this way 47 data points were selected. The objective function was expressed as a constrained optimization problem:

$$F_{op} = \sum_{j=1}^{m} \mathrm{Abs}[r_j - f(t)\ ff_j(P, T_{av}, y_i)] \qquad (3.1)$$

where,

$r_j$ = measured rate for ammonia synthesis reaction

m = number of data points available

$ff_j(P, T_{av}, y_i)$ = rate expression

$$= A*10^{15} \exp(-D*10^4/RT)\,[ff_j'(P, T_{av}, y_i)]$$

f(t) = catalyst activity decay function in bed

$= (1-B) + Be^{-Ct}$

P = Partial pressure in bed

$T_{av}$ = average temperature

$y_i$ = mole fraction of component i.

The parameters A,B,C and D in the rate expression were determined by employing an optimization technique e.g., constrained Box method (Box, 1965), by minimizing the values of the function $F_{op}$ within specified domain over 47 data points. Three different attempts were made to determine the parameters. First, inlet conditions (of reactor) were used to find the parameters so that the plant data and model result match. But the ammonia production and inert mole fraction in the recycle gas did not match. Secondly, average conditions (inlet and outlet of reactor) were used to find a better match. The difference between actual ammonia production and estimated production using average plant values for temperature, pressure and compositions in modified Temkin-Pyzhev rate equation was minimized using Box method. A reasonably better match was found for three randomly selected plant data points. This method was finally accepted for further study. Lastly, another attempt was made by integrating the rate equation using plant data and bed inlet temperatures and finding the ammonia production. The difference between this estimated ammonia production and actual (plant) ammonia production was tried to minimize using Box method. But this method could not be used due to the shortage of computer time.

The values of A,B,C and D found are given in Table 3.1.

## TABLE 3.1

Values of the Parameters

| Parameter | Estimated value | Literature value |
|---|---|---|
| A | 0.1499977E+02 | 1.7698-5.162E+14 (43,78) |
| B | 0.1415377E-05 | - |
| C | 0.9017344E+00 | - |
| D | 0.4216922E+05 | 3.9057E+04 - 4.2953E+04 (43,78 |

### Catalyst Activity Decay

The expression for catalyst activity decay function is

$$f(t) = (1 - B) + Be^{-Ct} \tag{3.2}$$

From the value of B and C and from figure 3.1 it is evident that the decay is extremely negligible. There may be several reasons for this: firstly, the catalyst is robust and the time span which was considered was small enough to be effective in seeing the activity decay of the synthesis catalyst; secondly, the activity of the catalyst of the whole reactor was taken into account, so, although some bed or part of it may be deactivated, the overall deactivation of the reactor catalyst becomes insignificant. Thirdly, the reactor may be overdesigned. It can be mentioned, however, that under normal operating conditions the ageing of an ammonia synthesis catalyst is rather slow. The catalyst is also well protected against poisoning, and very long lifetimes with almost constant performance can be achieved (de Lasa, 1986).

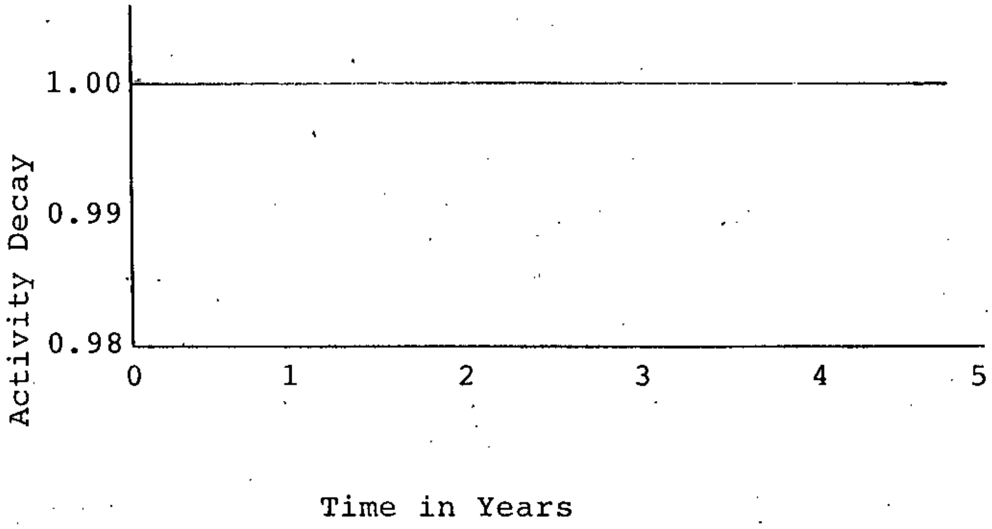

Fig. 3.1: Activity Decay in Bed

Better parametric estimation can be obtained if each catalyst bed is considered in separate manner. A comparison of plant data and model results is given in Table 3.2.

TABLE 3.2

Comparison of plant data and model results

(process conditions are the same as in Table 4.1 of Chapter IV)

| Recycle gas composition (mole frac.) | $N_2$ | $H_2$ | $NH_3$ | $CH_4$ | Ar | $NH_3$ produced (kmol/sec) |
|---|---|---|---|---|---|---|
| Plant data | 0.1950 | .6311 | .0280 | .1122 | .0337 | 0.6262 |
| Model result | 0.2073 | .6481 | .0124 | .1057 | .0265 | 0.6219 |
| Bed temperature (°K) | Bed 1 | | Bed II | | Bed III | |
| | In | Out | In | Out | In | Out |
| Plant data | 684 | 777 | 734 | 786 | 748 | 786 |
| Model result | 691 | 735 | 724 | 787 | 761 | 788 |

Temperature and pressure corrected plant data are given in Appendix V.

Better match could be achieved by modifying the objective function taking into account the absolute differences between actual and calculated temperature of each bed as has been suggested by Hussain (1986).

# CHAPTER IV

## SIMULATION

### 4.1 Synthesis Loop and Converter

A schematic diagram of the ammonia synthesis loop is shown in figure 4.1. From the ammonia recovery unit a small fraction of $H_2$-$N_2$-$NH_3$ and inert mixture is purged to limit the inert buildup in the synthesis loop. Rest of the gas mixture is recycled. This gas is total feed to the converter. This converter feed gas is split into three main fractions: one fraction is used for shell cooling and enters at the top section of the annulus, the other fraction is preheated in the exchanger and is again split into two fractions. One fraction is used as quench in the quenching zones, and the other fraction enters the bottom of the shell. The top annulus fraction and the bottom fraction mixes and rises through a central tube to the top of the catalyst bed and again mixes with a fraction of the quench gas. These three fractions together comprises the feed to first bed and flows downward through the catalyst beds.

The converter is a three-bed-quench reactor as shown in figure 4.2; the first bed is followed by two quench zones and beds, each containing a larger quantity of catalyst. The hot gases from the third bed is subsequently cooled in a converter heat exchanger, in a waste heat boiler, a process gas heat exchanger, several water coolers, a cold exchanger. After cold exchanger it

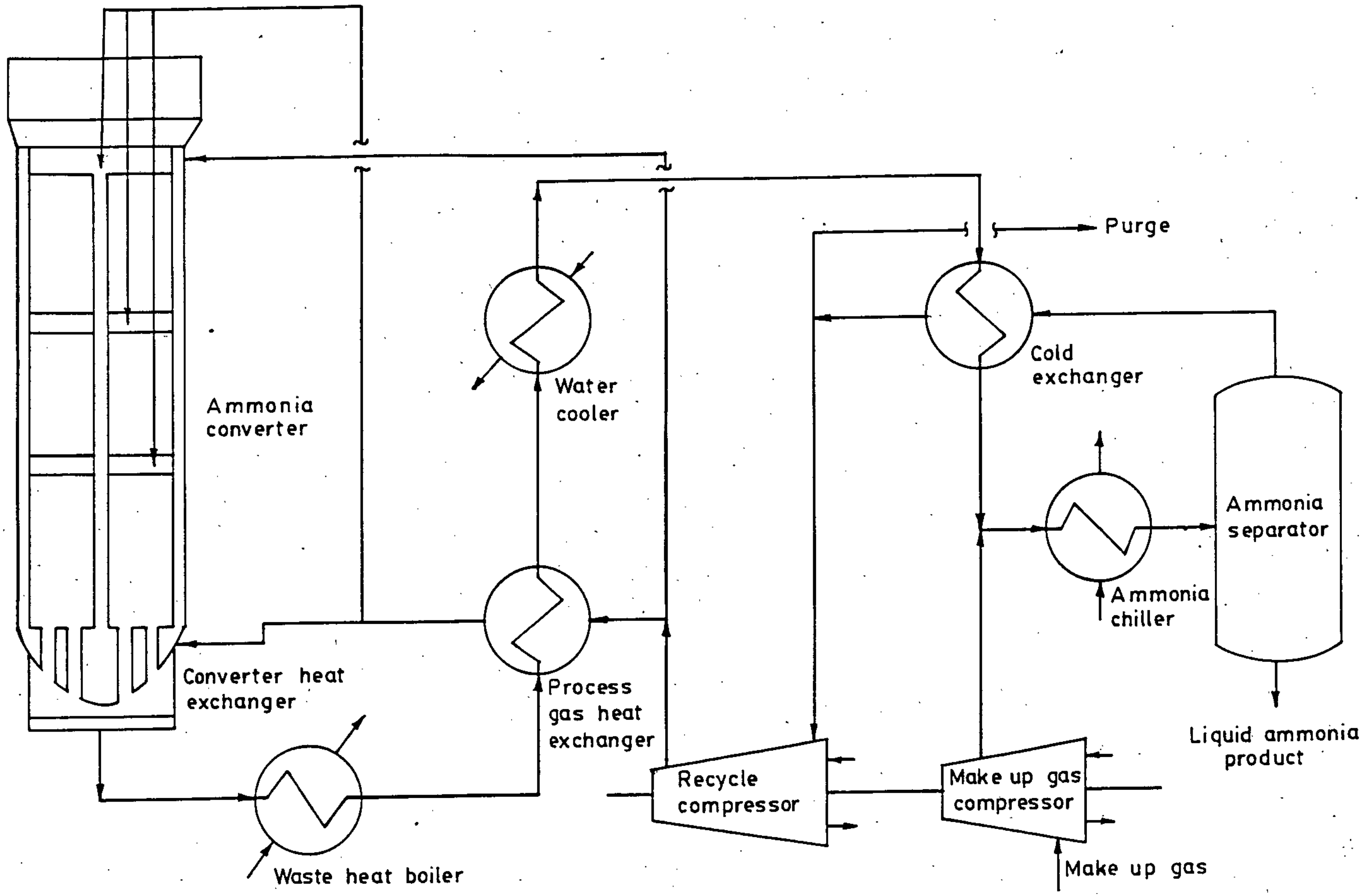

FIG. 4.1 SCHEMATIC DIAGRAM OF AMMONIA SYNTHESIS LOOP.

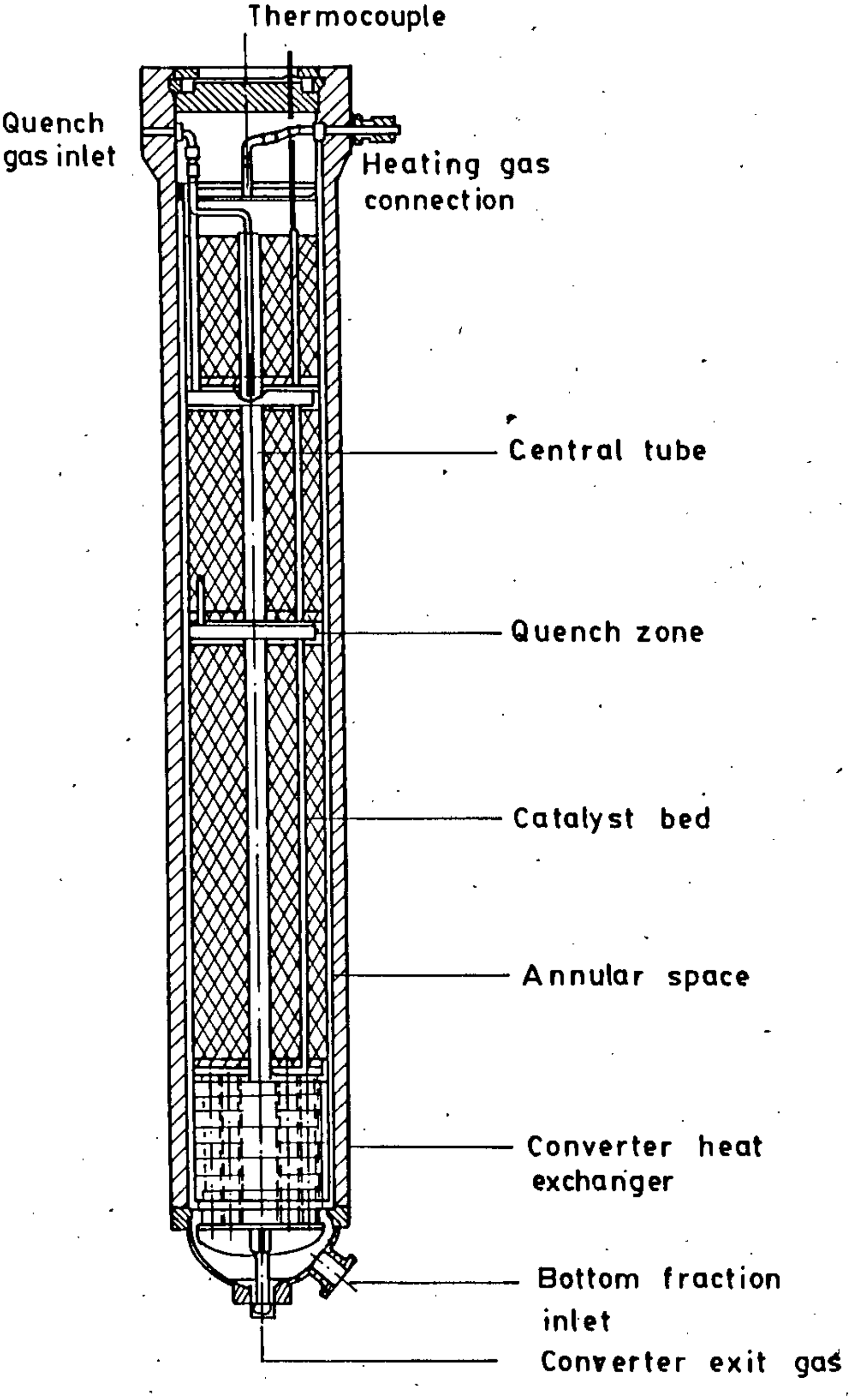

FIG. 4.2 AMMONIA CONVERTER.

is mixed with fresh makeup gas and finally cooled in an ammonia chiller using liquid ammonia refrigerant. After condensation of ammonia it is separated in a separator and the uncondensed gas is recycled.

## 4.2 Simulation Model

The mathematical model for the ammonia synthesis section was developed assuming:

1. Steady state.
2. No temperature and concentration gradient in the radial direction of the reactor i.e. temperature and concentration uniform at any cross section.
3. No axial diffusion of mass transfer.
4. Global rate expressions for ammonia synthesis reaction was used neglecting heat and mass transfer within the catalyst and also from bulk phase to the catalyst surface; though an effectiveness factor was used.
5. Momentum balance in the reactor was neglected. Pressure drop in each catalyst bed was calculated using average values of inlet and outlet conditions.
6. Liquid ammonia product was free from any dissolved gases.
7. Temperatures of the annular and central tube gas mixture was assumed constant.

### 4.2.1 Model Equation and Method of Solution

The various physical and chemical processes taking place in the reactor can be described mathematically by performing mass balance for $NH_3$ and also an overall energy balance over a differential section of catalyst, $\Delta w$ (Bird et al., 1960), shown in figure 4.3.

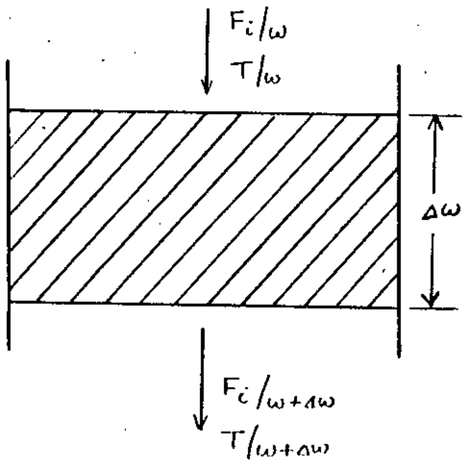

Fig. 4.3: Schematic diagram of differential catalyst section of weight $\Delta w$ in the reactor.

Mass balance:

$$\frac{dF_{NH_3}}{dW} = r_1 \qquad (4.1)$$

where, $dW$ = differential amount of catalyst in bed, kg

$dF_{NH_3}$ = differential molar flow of ammonia in bed, kmole/s

$r_1$ = rate of formation of ammonia,
kmole ammonia/(kg cat.-s)

$$r_1 = f(t)(\eta)(2k)(\psi)\left(K^2 \frac{a_{N_2} a_{H_2}^{3/2}}{a_{NH_3}} - \frac{a_{NH_3}}{a_{H_2}^{3/2}}\right) \qquad (4.2)$$

$f(t)$ = Catalyst activity decay function in bed

$$= (1 - B) + Be^{-Ct} \qquad (4.2a)$$

$$2k = A*10^{15}\exp(-D*10^{4}/RT) \qquad (4.3)$$

$\psi$ = area of 6-10 mm catalyst particle / area of 3-6 mm catalyst particle
(on which original data was based)

$$= 7.5 \text{ m}^2/\text{gm}/8.6 \text{ m}^2/\text{gm} = 0.87 \qquad (4.4)$$

$$\eta = b_o + b_1T + b_2X + b_3T^2 + b_4X^2 + b_5T^3 + b_6X^3 \qquad (4.5)$$

X = molar flow of $NH_3$/(molar flow of $NH_3$
+ 2*molar flow of $N_2$) (4.6)

$$a_j = f_j = y_j \; \nu_j P \qquad (4.7)$$

t = time, year

$N_2$ and $H_2$ consumed in producing $NH_3$ is related by

$$\Delta n_{NH_3} = -3/2 \;\; \Delta n_{H_2} = -\tfrac{1}{2} \;\; \Delta n_{N_2} \qquad (4.8)$$

The outlet gas from one bed is quenched to give inlet value for the next bed.

Energy balance:

$$\frac{dT}{dw} = \frac{r_1(-\Delta H)}{\Sigma F_i C_{pi}} - \frac{U_1 \quad D_{cntb}(T - T_{cntb})}{0.25\ D_b^2\ \rho_{cat}\ \Sigma F_i C_{pi}} - \frac{U_2 \quad D_{anuls}(T - T_{anuls})}{0.25\ D_b^2 \rho_{cat} \Sigma F_i C_{pi}} \qquad \ldots\ldots \qquad (4.9)$$

These two coupled first order non-linear differential equations were solved by a variable step-size fourth order Runge-Kutta-Gill method (Carnahan et al., 1969) with initial conditions at

$w = 0$ (at top of the bed), $F_i = F_{io}$ and $T = T_o$

The flow of other components were determined from stoichiometry of the reactions involved for each $\Delta w$. At the end of each bed, a fraction of the reactant gases (cold shot) was added, then the composition and temperature of the gas mixture were calculated from an overall mass and heat balance in the quenching zone; the above steps were repeated for each subsequent bed.

## 4.3 Algorithm for Simulation of a 3-Bed Quench Cooling Ammonia Reactor

### 4.3.1 Input data

1. Composition of the fresh makeup feed gas.
2. Fresh makeup feed rate, recycle ratio.

3. Initial estimate of recycle compositions, separator operating pressure and temperature, approximate crude product compositions to determine initial recycle compositions.
4. Ammonia production rate and its specifications.
5. Average operating pressure of the reactor.
6. Amount of catalyst used in different beds.
7. Fractions of total feed used in different beds as feed/ cold shot.
8. Catalyst properties.
9. Parameters used for Wegestein convergence accelerating technique.

### 4.3.2 Algorithm

1. The flow and compositions of reactor total feed were determined from flow and compositions of fresh feed and recycle.
2. The amount of feed used in the first bed was calculated.
3. For first bed at point w of the bed:
    - (a) Rate of ammonia synthesis was calculated.
    - (b) Differential equations (4.1), (4.9) were solved by a variable step-size fourth order Runge-Kutta-Gill method.
    - (c) Molal flow rates of other components over $\Delta w$, were calculated from reaction stoichiometry.
    - (d) The above steps are repeated until the first bed was completed.

4. The quench at the inlet of the bed II was added and the composition of the mixed feed was determined and from the heat balance the temperatuere of the gas mixture at the inlet of bed II was also determined.
5. Steps 3 and 4 were continued through bed II and bed III.
6. At the outlet of the last bed the fraction of ammonia in the product was calculated and the mole fraction of ammonia and other gases in the recycle were also estimated.
7. The amount of crude ammonia to be condensed and its compositions were calculated.
8. The amount of recycle and its composition, and the purge rate were calculated.
9. Assumed and calculated recycle compositions were compared and the sum of absolute difference for each component in the recycle was calculated.
10. Convergence criteria was checked.
11. If the convergence criteria was not satisfied, multiple Wegestein accelerating technique was applied to the individual component of recycle and the new recycle composition was calculated and then returned to step 1.

## 4.4 Results and Discussions

In order to study the effect of process variables upon ammonia production, concentration profile and catalyst bed temperature profile, a large volume of work has to be done. The study is most conveniently done by selecting a set of operating conditions typical to the operating conditions of an Ammonia plant and it will be referred to as base case simulation. The effect of process variables are studied by varying the operating condition from the base case. The operating variables considered in this investigation are inert content in feed, $H_2/N_2$ ratio in feed, recycle ratio, quench temperature. The model was used to simulate an operating ammonia reactor producing around 1000 tonne ammonia/day. Operating data are given in Table 4.1.

TABLE 4.1

Data for base case simulation

| | |
|---|---|
| Makeup feed gas rate | : 1.391 kmol/s |
| Makeup gas composition(mole fraction): | |
| $N_2$ | : 0.2460 |
| $H_2$ | : 0.7401 |
| $NH_3$ | : 0.0 |
| $CH_4$ | : 0.0113 |
| Ar | : 0.0026 |
| Catalyst : Haldor-Topsoe iron based | |
| Size : KM - 16; 6-10 mm (28.72 $m^3$) | |
| AM 1-3: 8-12 mm (0.84 $m^3$) | |
| KM 1-16:16-23 mm (0.84 $m^3$) | |
| Equivalent diameter | : 0.008 m |
| Bed porosity | : 0.293 |
| Catalyst bulk density | : 2700 $kg/m^3$ |

Catalyst used in different beds($m^3$):

Bed (1) : 4.4

Bed (2) : 8.8

Bed (3) :17.2

Reactor : Uhde 3-bed quench reactor

Height : 15.5 m

Inside diameter : 2 m

Central tube diameter : 0.203 m

Recycle ratio (recycle/makeup feed, mole/mole) : 4.0

Cold shot temperature : 463 K

Distribution of mixed feed/cold shot in beds :

Bed (1) : 0.2

Bed (2) : 0.25

Bed (3) : 0.55

Separator operating pressure : 28161 kPa

Separator operating temperature : 268 K

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## 4.5 Effects Of Different Variables On Reactor Performance

The model was used to examine the effects of some important variables e.g., recycle ratio, $H_2/N_2$ ratio, inerts ($CH_4$+Ar) in makeup feed, quench temperature on reactor performance.

### 4.5.1 Base Case

Figures 4.4 to 4.6 give the results of base case simulation with a comparison with plant data. Figure 4.4 and 4.5 show the concentration and temperature profile in the reactor. Figure 4.6 shows how the bed temperature changes with conversion. The dip in temperature is due to the introduction of quench gas which also results in a decrease in ammonia concentration.

### 4.5.2 Effect of $H_2/N_2$ ratio

Usually in an ammonia synthesis reactor, stoichiometric ratio of nitrogen and hydrogen is used. Calculations have been carried out at two other ratios 2.5 and 3.5 and the results are shown in figure 4.7 and 4.8. There is some reduction in performance of the reactor as the $H_2/N_2$ ratio is raised from 2.5 to 3.5. The optimum ratio is around 2.5 which agrees with Nielsen (1968) and Gaines (1977) for a quench type converter.

### 4.5.3 Effect of Inerts

Figures 4.9 and 4.10 shows the effect of inerts on the performance of the reactor. The effect is quite pronounced. The

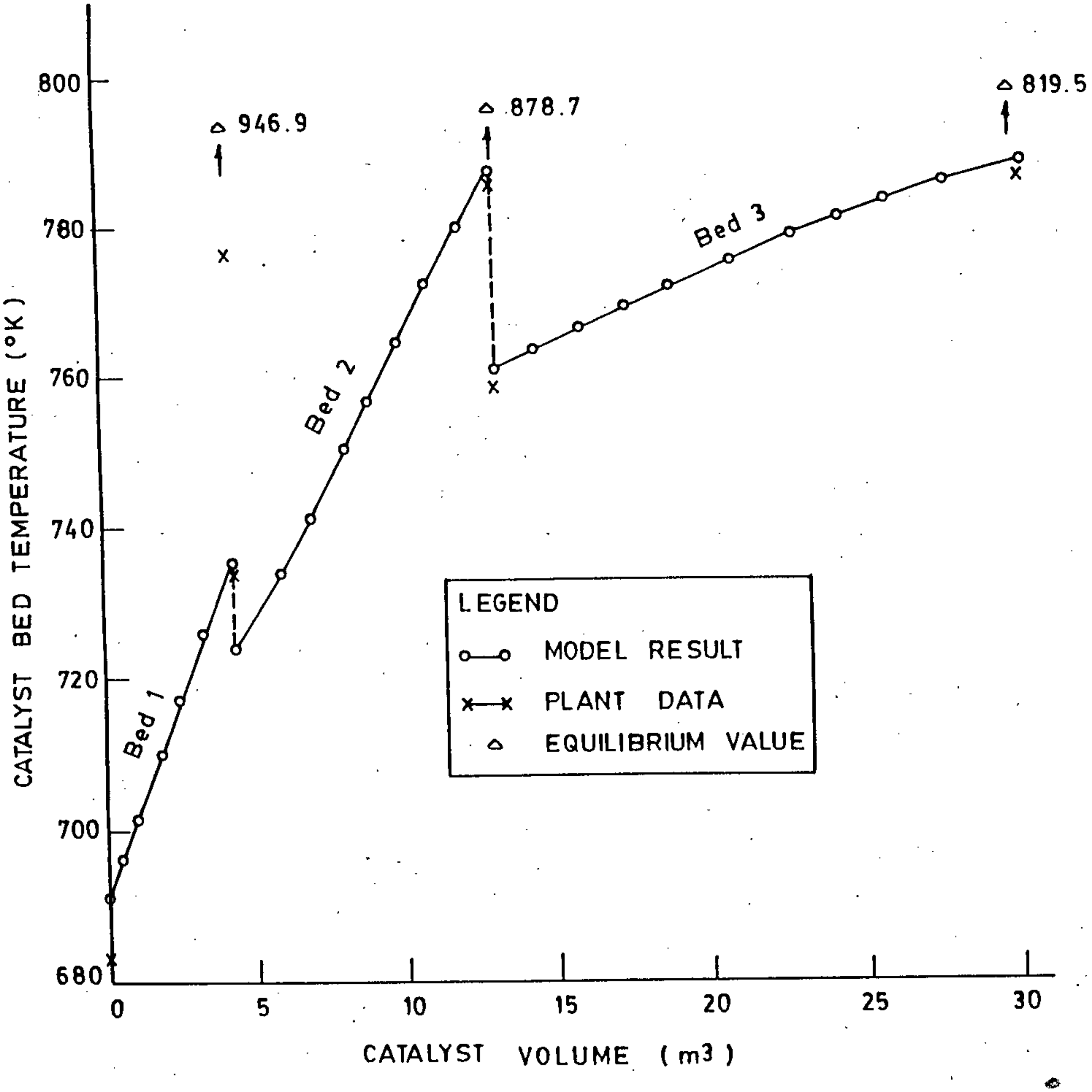

FIG. 4.4 TEMPERATURE PROFILE ALONG CATALYST BED LENGTH.

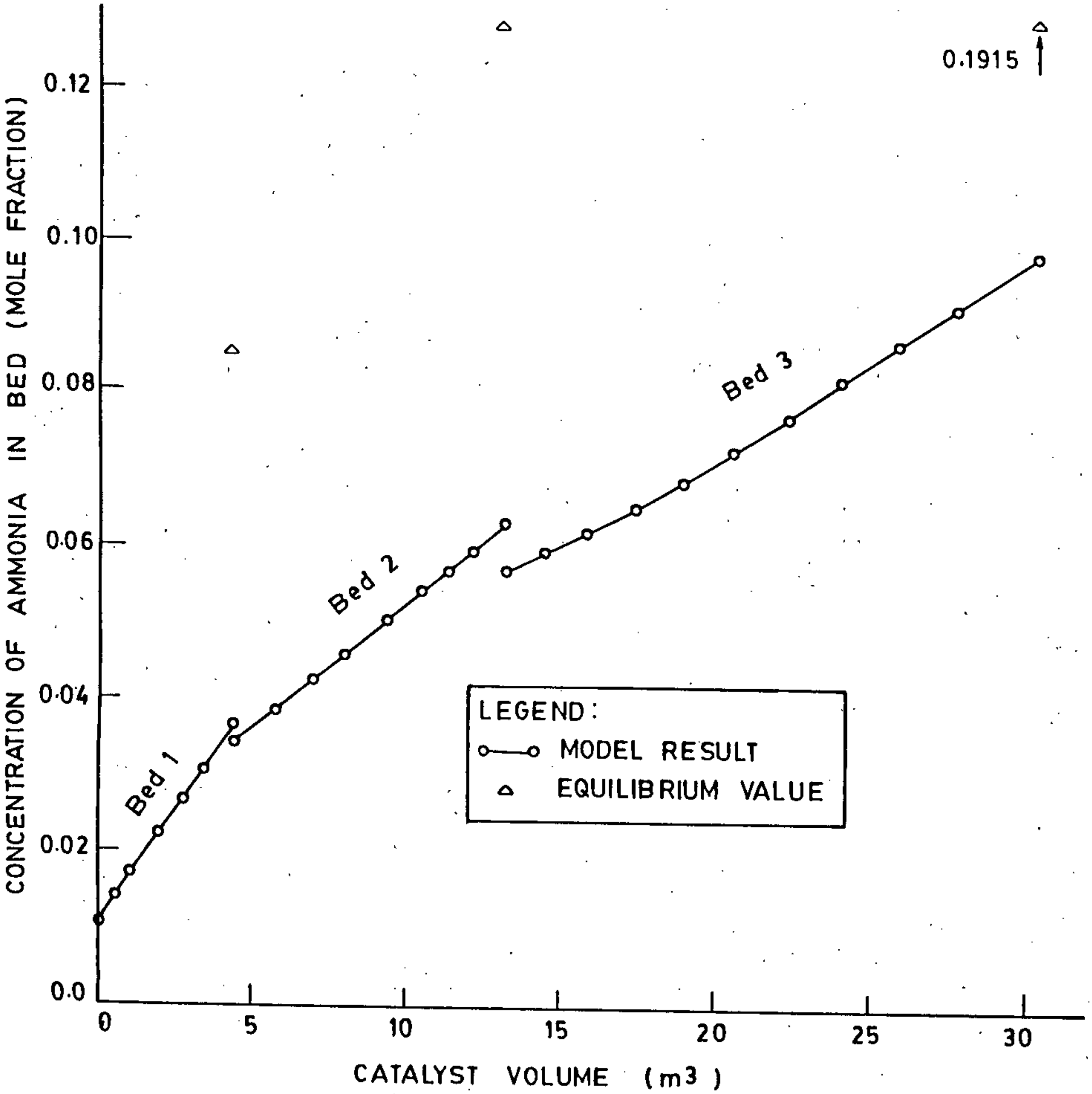

FIG. 4.5 CONCENTRATION PROFILE OF AMMONIA ALONG CATALYST BED LENGTH.

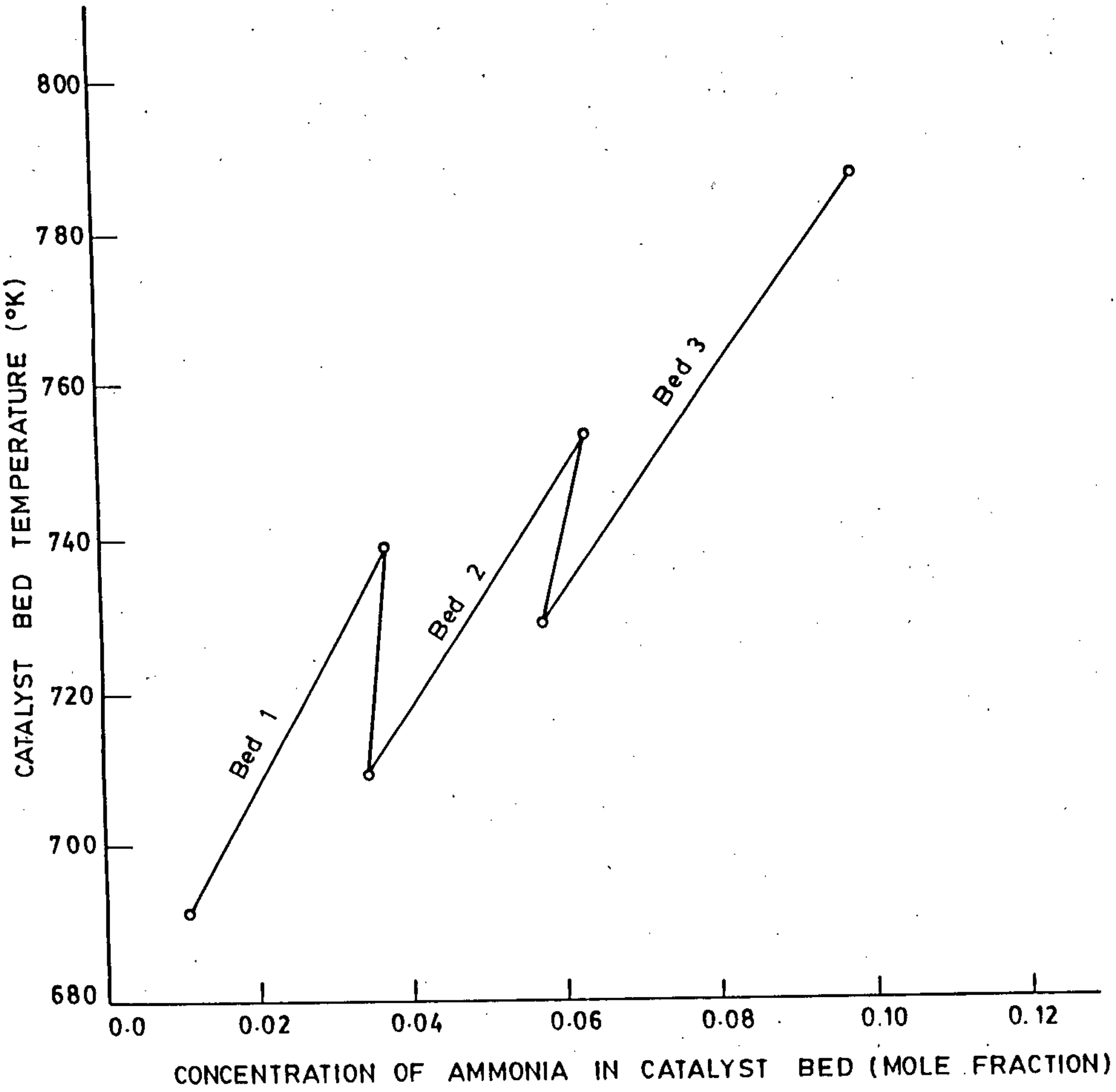

FIG. 4.6 TEMPERATURE AND CONCENTRATION OF AMMONIA IN CATALYST BED (MODEL RESULT).

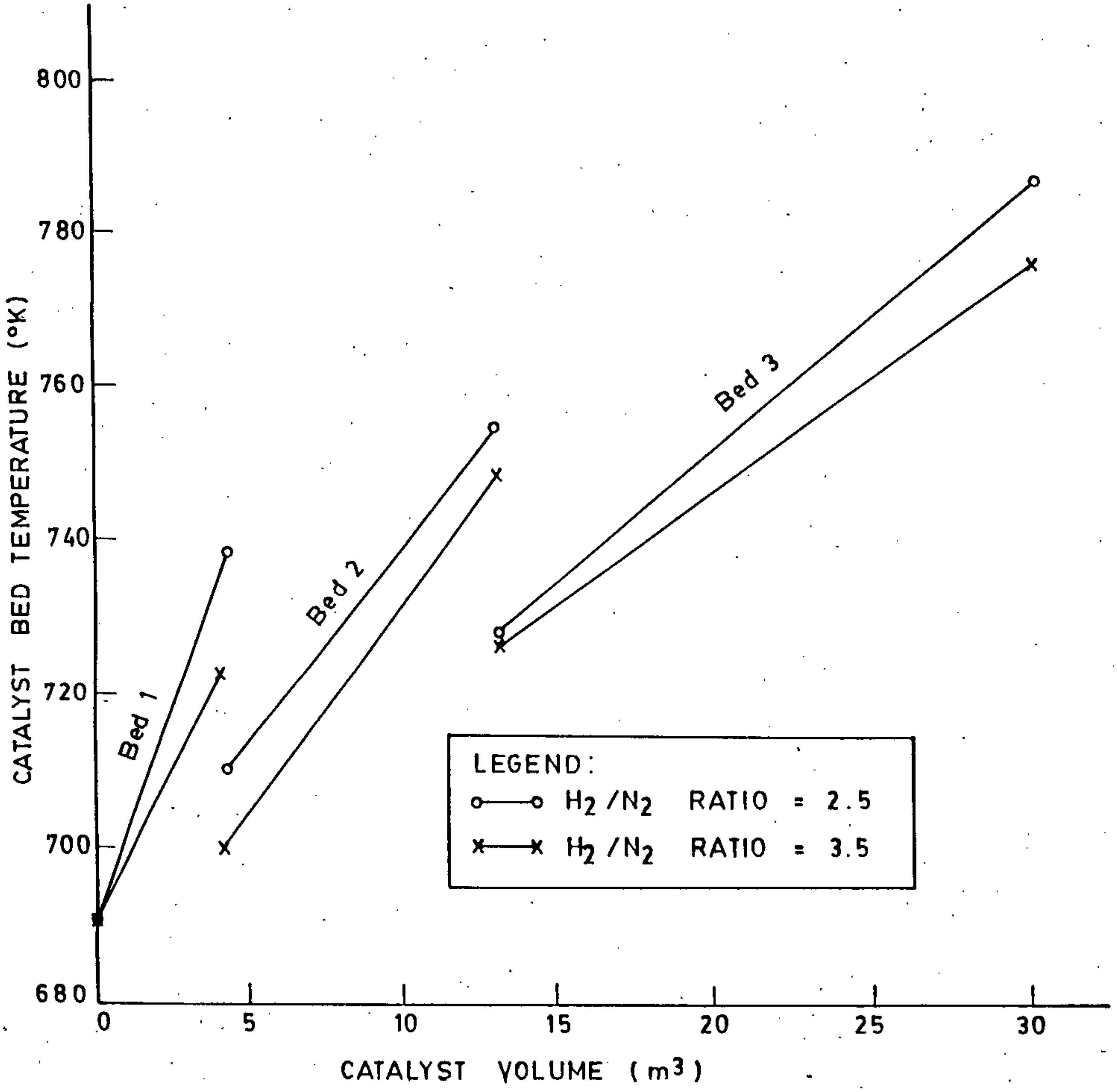

FIG. 4.7 EFFECT OF HYDROGEN-NITROGEN RATIO IN THE FRESH FEED ON THE CATALYST BED TEMPERATURE PROFILE.

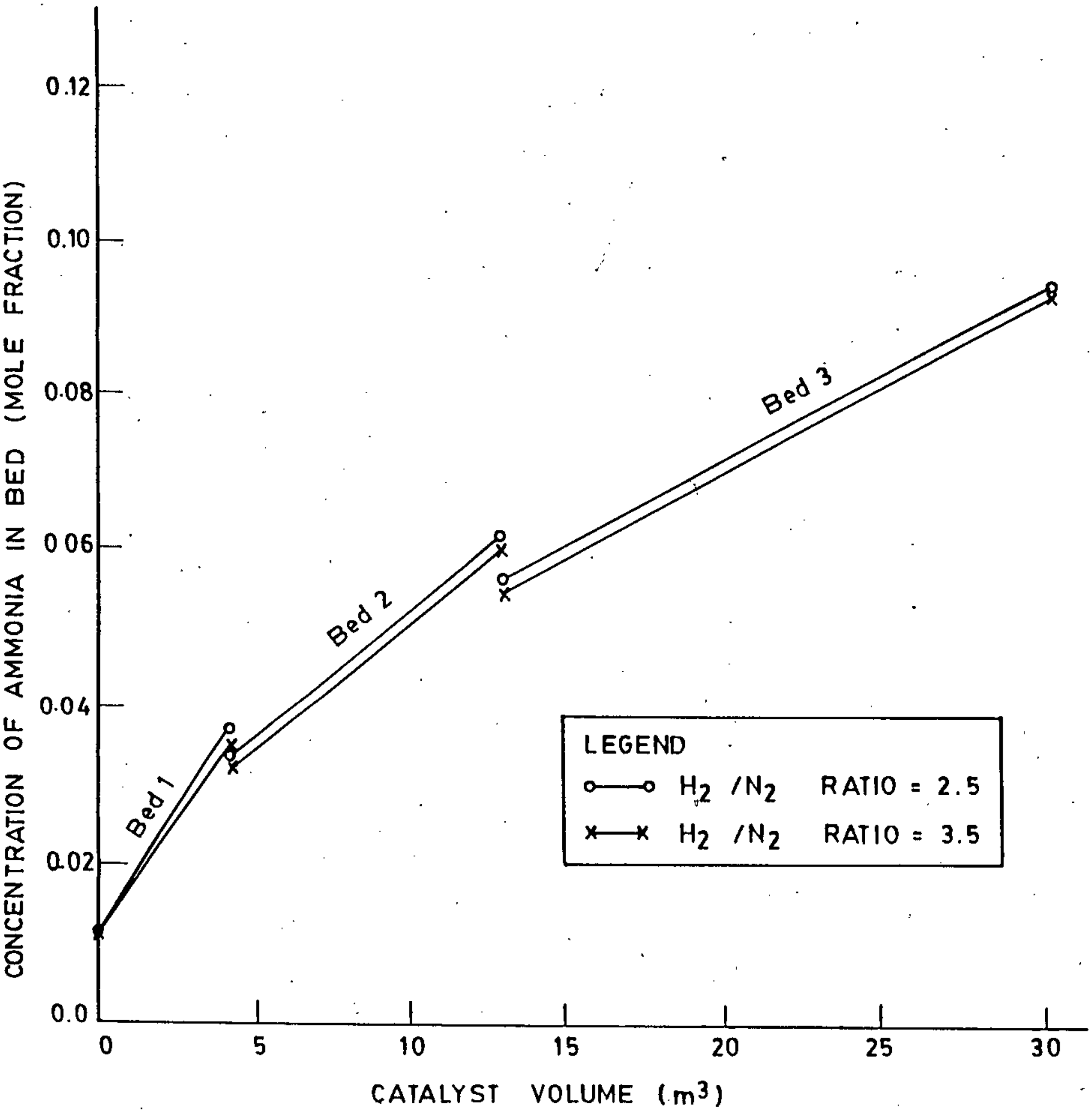

FIG. 4.8 EFFECT OF HYDROGEN-NITROGEN RATIO IN THE FRESH FEED ON THE AMMONIA CONCENTRATION PROFILE IN THE REACTOR.

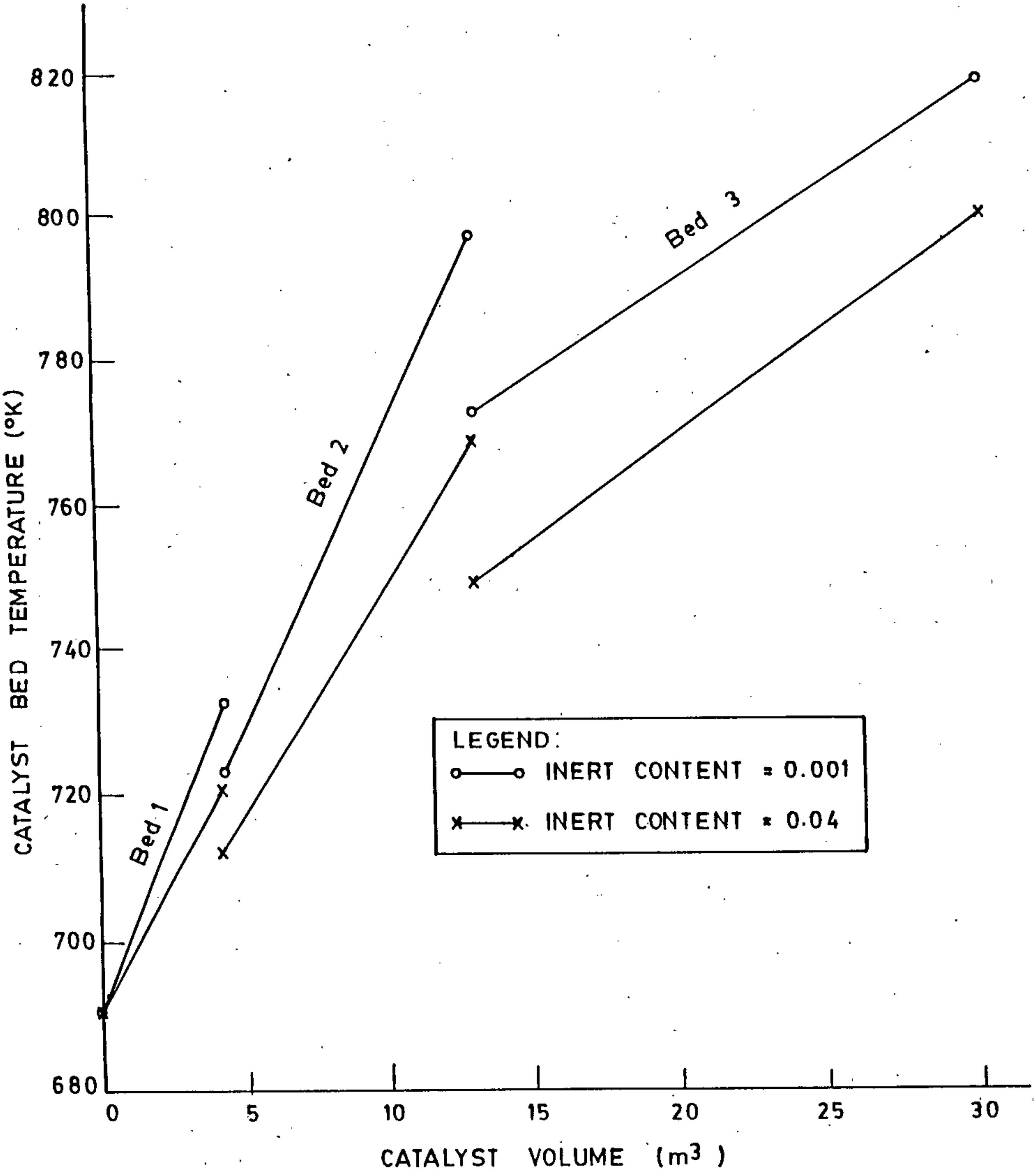

FIG. 4.9 EFFECT OF INERTS (METHANE+ ARGON) IN THE FRESH FEED ON THE CATALYST BED TEMPERATURE PROFILE.

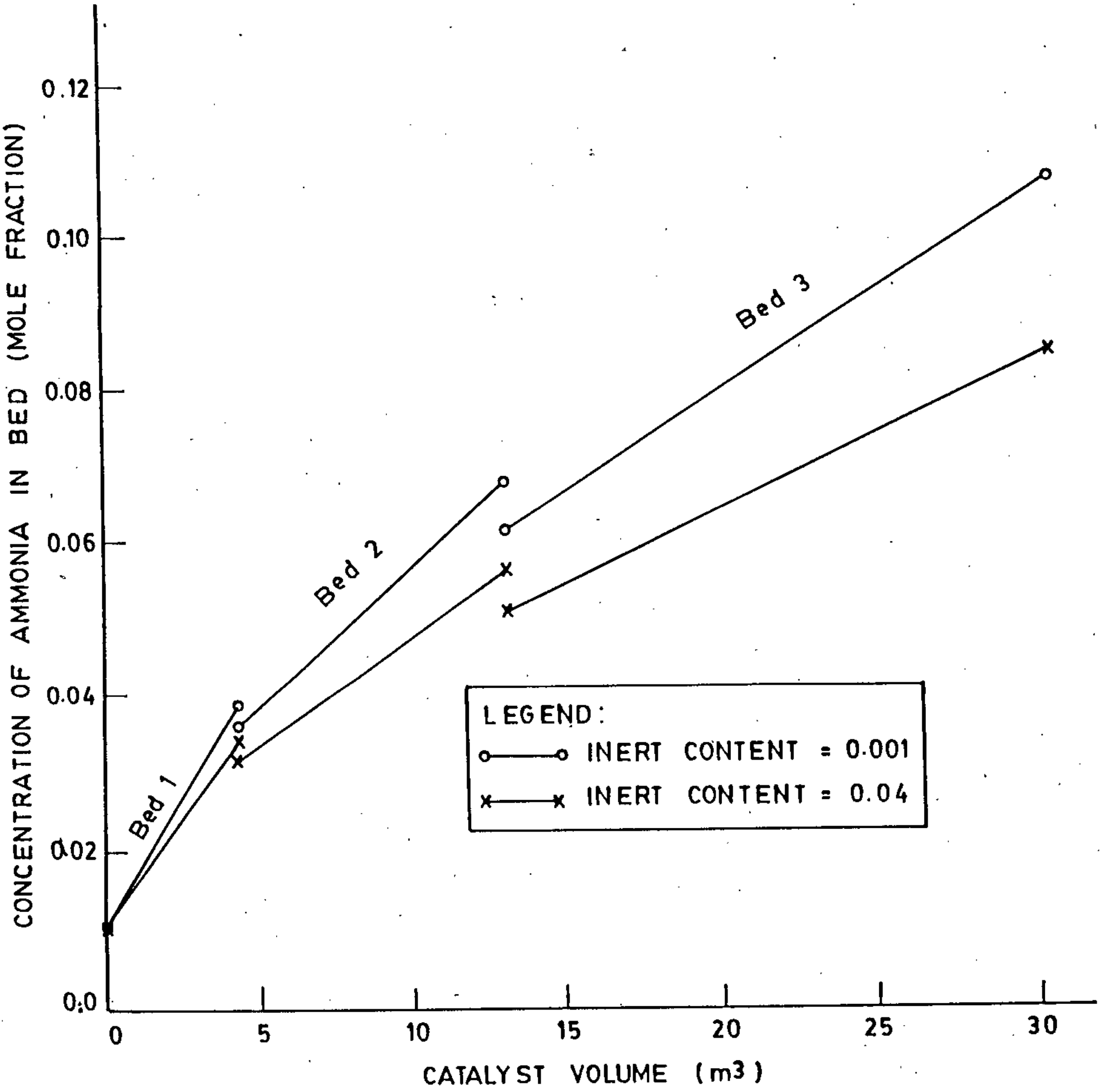

FIG. 4.10 EFFECT OF INERTS (METHANE + ARGON) IN THE FRESH FEED ON THE AMMONIA CONCENTRATION PROFILE IN THE REACTOR.

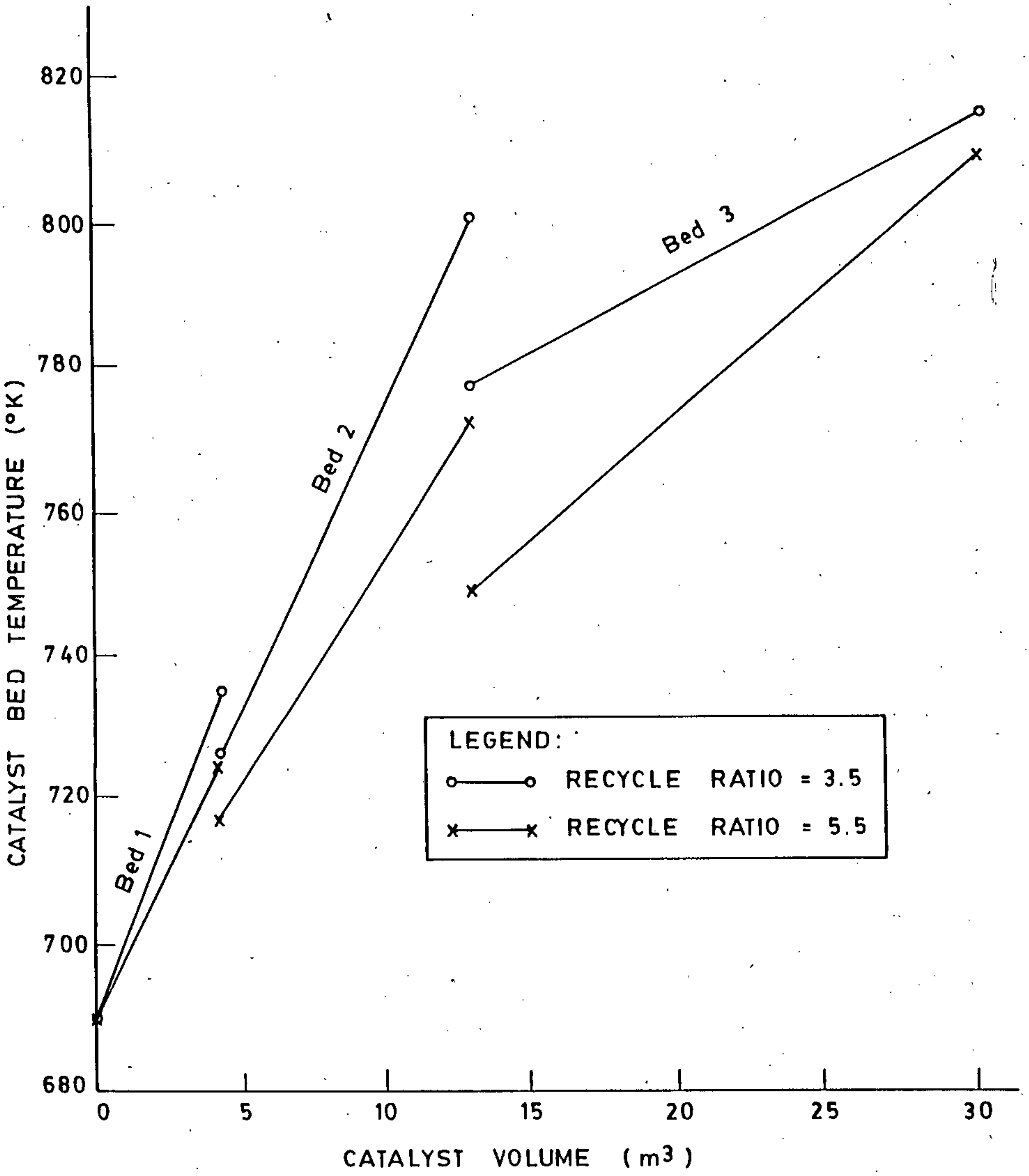

FIG. 4.11 EFFECT OF RECYCLE RATIO ON THE CATALYST BED TEMPERATURE PROFILE.

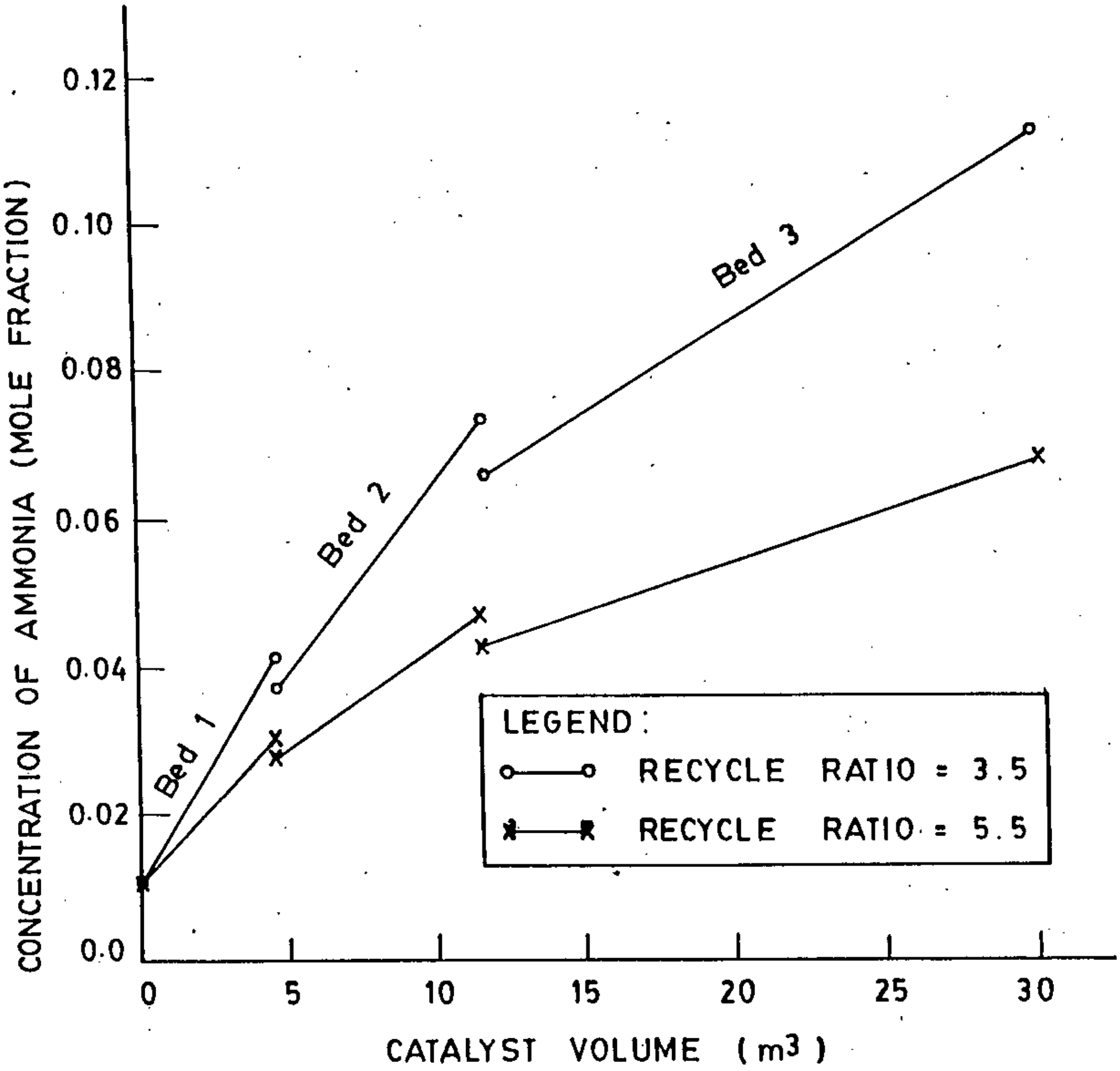

FIG. 4.12 EFFECT OF RECYCLE RATIO ON THE AMMONIA CONCENTRATION PROFILE IN THE REACTOR.

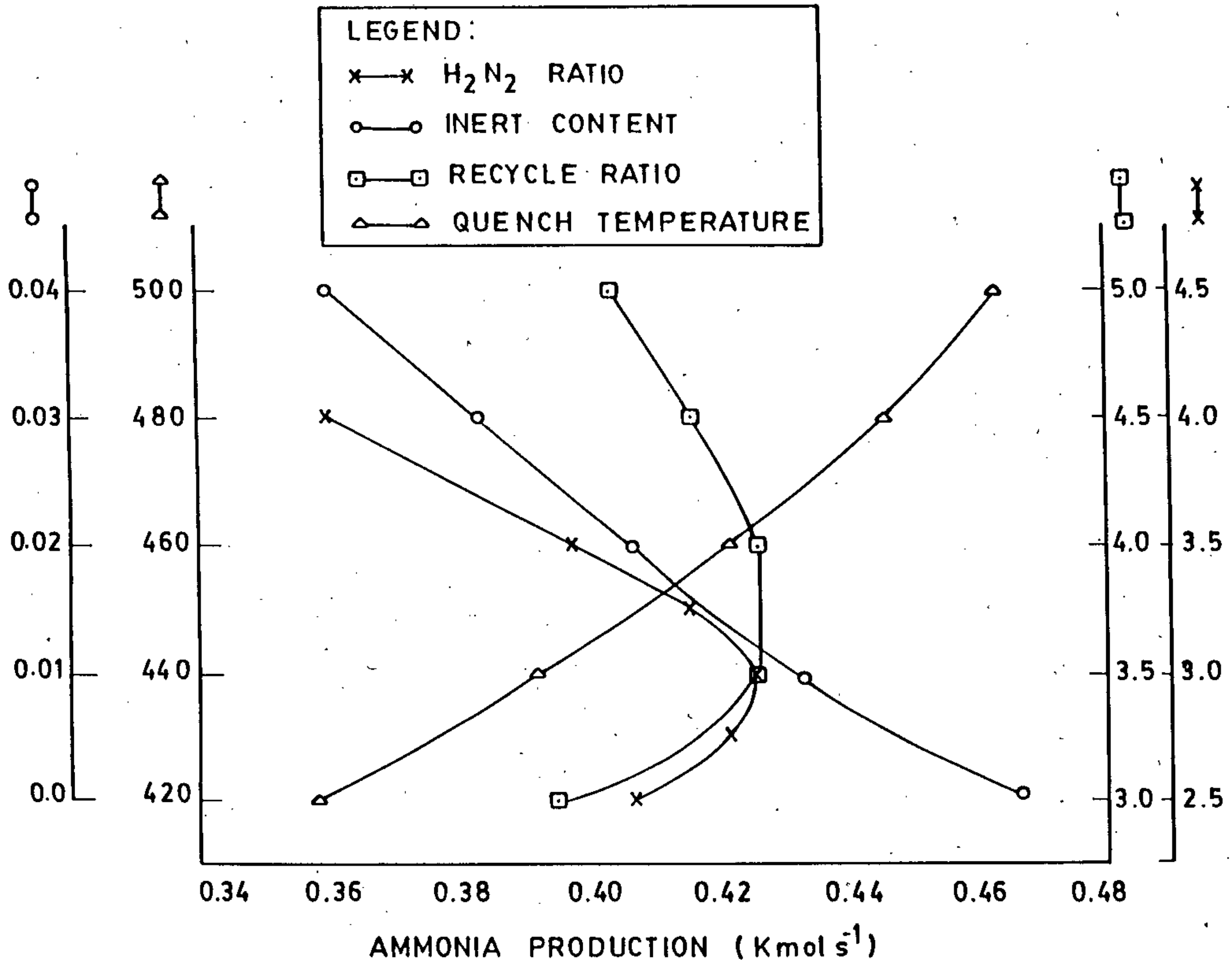

FIG. 4.13 EFFECT OF $H_2/N_2$ RATIO IN THE FRESH FEED, INERTS (METHANE + ARGON) IN THE FRESH FEED, RECYCLE RATIO AND QUENCH TEMPERATURE ON THE AMMONIA PRODUCTION.

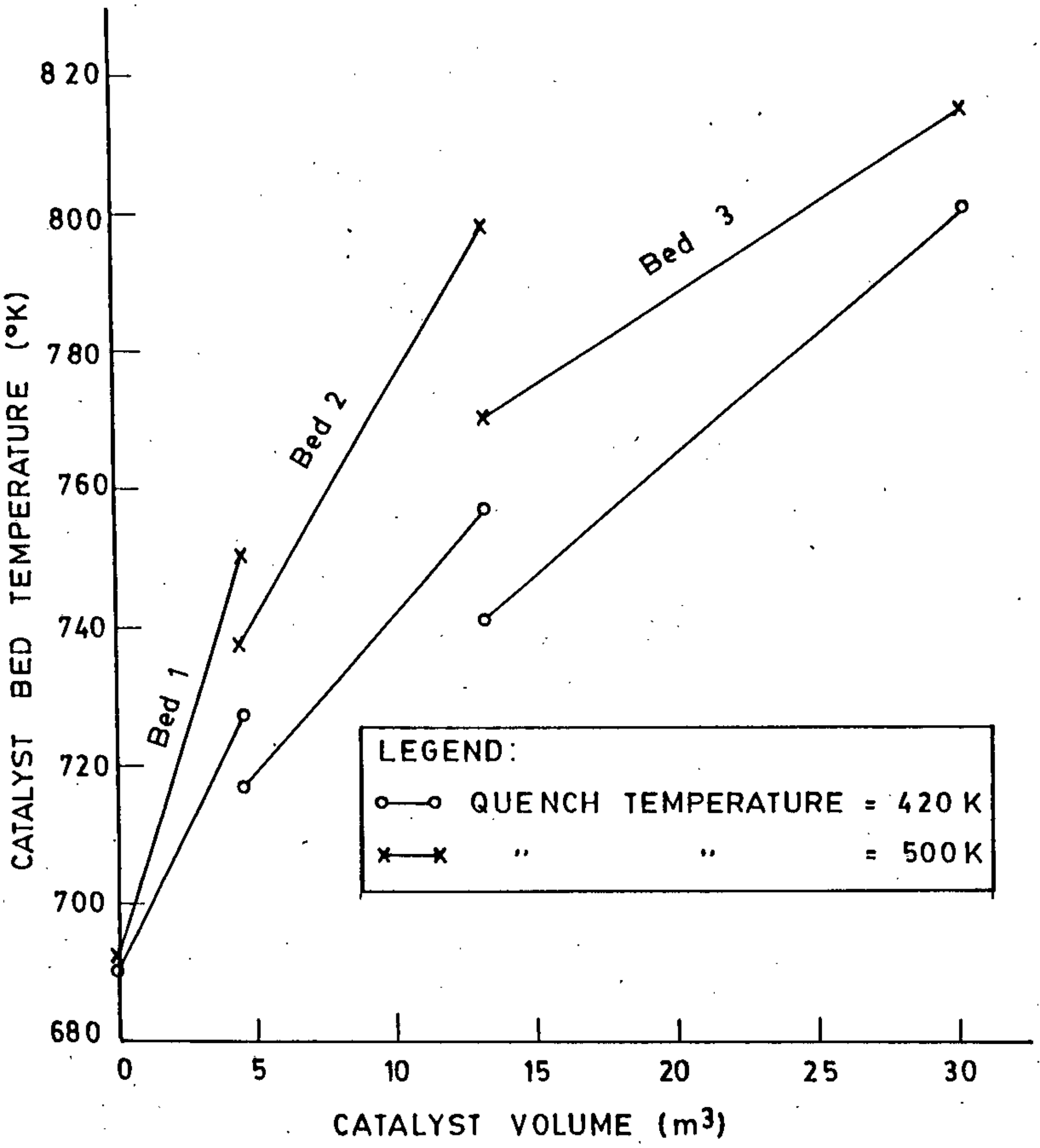

FIG. 4.14 EFFECT OF QUENCH TEMPERATURE ON THE CATALYST BED TEMPERATURE PROFILE.

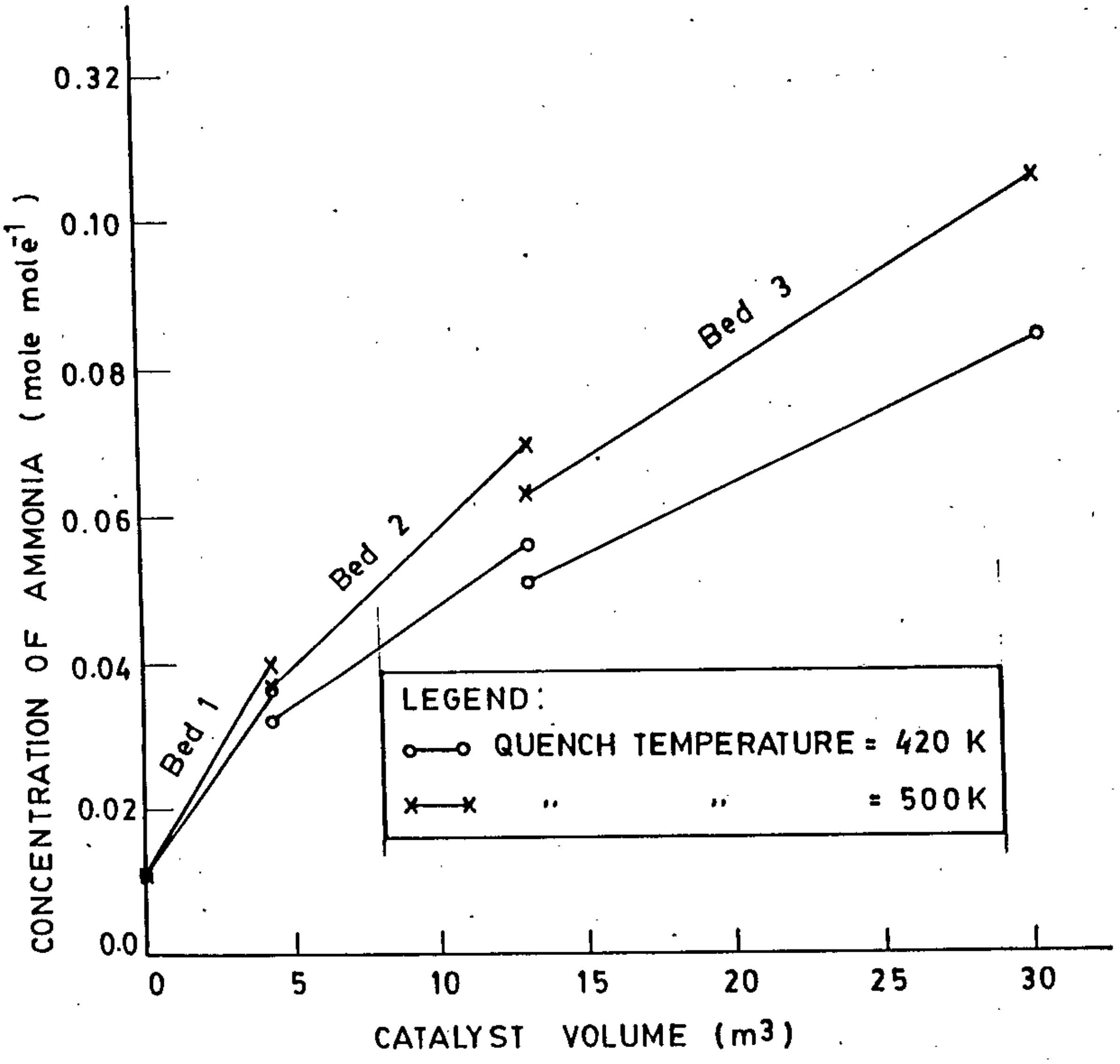

FIG. 4.15 EFFECT OF QUENCH TEMPERATURE ON THE AMMONIA CONCENTRATION PROFILE IN THE REACTOR.

temperature and concentration levels are much reduced as the inert content is raised from 0.001 to 0.04. Similar effect is reported by Hussain (1986).

### 4.5.4 Effect of Recycle Ratio

Figures 4.11, 4.12 and 4.13 shows the effect of recycle ratio on reactor performance. Initially $NH_3$ production increases with recycle ratio and then decreases as the recycle ratio is increased further as shown in figure 4.13. The temperature level and ammonia concentration level decreases as the recycle ratio is increased from 3.5 to 5.5.

### 4.5.5 Effect of Quench Temperature

Figures 4.14 and 4.15 shows the effect of quench temperature on temperature and concentration profiles. Both temperature and concentration level increases with the increase in quench temperature from 420°K to 500°K which indicates that the reaction temperature is still very far away from equilibrium temperature as is evident from figure 4.4 and the increase in quench temperature favours the synthesis reaction.

### 4.6 Limitations of the model and suggestions for further work

The model have been developed assuming no temperature gradient in the radial direction. But the temperature does not remain uniform at any cross section as heat is exchanged with the gas in the annular shell and with the gas in the central tube. For improvement of the model and results obtained, the radial temperature and concentration gradient may be considered.

Liquid ammonia product was assumed to be free of any dissolved gases. But this assumption is valid at low pressure (ideal conditions). At high pressure, some amount of gases dissolves in liquid ammonia and this phenomena has to be considered for a better approach to the real case. A realistic separator calculation technique is shown in the Appendix I .

The thermodynamic properties were calculated using expressions which are functions of temperatures only, But at high pressures, the effect of pressure on properties has to be considered to account for realistic approach to actual phenomena.

The heat exchanger module (Subroutine HEATEX) was written in such a way that of the four temperatures (two shell side and two tube side), three must be specified. So these three constraints made the application of the module limited. Also approximate heat transfer coefficients and fouling factors were used for heat transfer surface area calculations. Therefore, the module has to be modified to overcome these limitations.

In the module PREL, the temperatures of the stream rising through the central tube and of the stream going downward through the shell was assumed constant; which are actually not true. Realistic temperature profiles have to be found out so that the actual temperature of the two streams can be calculated throughout the length of the reactor.

In the parametric study only the sum of absolute differences between calculated rate and the actual rate is used to estimate the parameters in the rate expression. As a result reasonable match of temperature profiles could not be achieved. Better match could be achieved by modifying the objective function taking into account the absolute differences between actual and calculated temperature of each bed as has been suggested by Hussain (1986).

# CHAPTER V

# OPTIMIZATION

## 5.1 Introduction

Simulation studies alone cannot be used to predict the performance of a process in varying operating condition because in any process certain costs are involved. For example, in an Ammonia plant, ammonia production increases as the inert content in the feed is decreased. So simulation studies will favour low inert content in feed; but this low inert will cause high reforming cost. So, for design and operation of chemical plants optimization has to be done where the operating cost is minimized or the return from the system is maximized.

Current systems for the computer-aided flowsheeting and optimization of chemical processes are based on the sequential-modular approach. However, there are serious drawbacks to this approach that are today increasingly recognized. For these drawbacks there has been considerable interest in developing alternatives to the sequential-modular approach. Two promising alternatives are the equation-based approach and the simultaneous-modular approach (Chen and Stadtherr, 1985).

In its most fundamental form, the process flowsheeting and optimization problem can be regarded as one of solving a large system of nonlinear equations. The different approaches to process flowsheeting differ most fundamentally in their approach to solving this set of simultaneous equations. The equation system can generally be thought of as consisting of three types of equations (Chen and Stadtherr, 1985):

- Model equations, including process unit models and physical property models
- Flowsheet connection equations that indicate how the units are connected together in the flowsheet
- Specifications

## 5.2 Main Assumptions in this Optimization

(i) Base temperature for heat balance was taken as 298°K.

(ii) Appropriate Lang factors were used to convert equipment cost to total cost.

(iii) Capital cost and all utility costs were updated to 3rd quarter of 1984 using Marshall and Swift all industry cost indexes (Chemical Engg., Nov. 26, 1984).

(iv) 20% of total fixed capital investment was included as the annual capital charge in the annual operating cost of the system.

(v) The costs of all the vessels, e.g. reactors, separators, etc. were calculated assuming them as pressure vessels.

(vi) When actual model production was different from the required production, then fixed capital costs were adjusted using 6/10th rule (Peter and Timmerhaus, 1980) whereas utility costs were adjusted proportionately comparing actual production to the required production.

(vii) Steam generating efficiency of the boiler was taken as 75%.

Cost data and other relevant data for optimization are given in Table 5.1.

TABLE 5.1

Cost data (in US dollars for the year 1979) and other relevant data for this optimization study. (Peter and Timmerhaus, 1980; Backhurst and Harker, 1983; Rase, 1977; Wham, 1981).

---

Cost data:

Steam (high pressure, more than 500 kPa) = $4.21*10^{-3}$ \$/Kg

Steam (low pressure, less than 500 kPa ) = $2.10*10^{-3}$ \$/Kg

Electricity (purchased) = 0.05 \$/KWH

Cooling water = $2.65*10^{-5}$ \$/Kg

$NH_3$ refrigerant = 1.00 \$/Kg

Catalyst = 1.50 \$/ton of ammonia

Other relevant data:

Marshall and Swift all industry cost indexes: (Peter and Timmerhaus, 1980; Chemical Engg., Nov. 26, 1984)

For the year, 1979 = 561

For the 3rd quarter of 1984 =811.2

Lang factors:

For reactors = 5.6

For boilers = 5.6

For heat exchangers = 3.5

For separators = 4.0

For compressors = 2.5

---

## 5.3 Ammonia Synthesis Loop Optimization

The ammonia reactor module described in chapter IV, along with modules of pressure vessels, heat exchangers, separators, and of compressors have been used to optimize the annual operating cost of the ammonia synthesis loop of a 1000 tonne/day ammonia plant on the basis of the following assumptions;

(i) A 3-bed quench reactor (dimensions given in table 4.1 of chapter IV) was used.

(ii) All the studies have been started with a fixed feed rate of 1.391 kmol/s (compositions given in table 4.1 of Chap. IV).

(iii) Fixed heat transfer coefficients from Bell (1983) were used in heat exchanger calculations.

(iv) The reactor exit gas was used in the converter heat exchanger to increase the temperature of the gas used in the cooling of the shell.

(v) Annual operating cost($) was determined using the following expression:-

$$C_{anopa} = C_{fr} + C_{fch} + C_{fwhb} - C_{swhb} + C_{fph} + C_{fwc} + C_{opwc} + C_{fac} + C_{opac} + C_{fsp} + C_{fcm} + C_{mnc} + C_{opc}$$

where,

$C_{fr}$ = annual fixed cost of the ammonia reactor, \$

$C_{fch}$ = annual fixed cost of the converter heat exchanger, \$

$C_{fwhb}$ = annual fixed cost of the waste heat boiler, \$

$C_{swhb}$ = annual recovered steam cost from the waste heat boiler, \$

$C_{fph}=$ = annual fixed cost of the process gas heat exchanger, \$

$C_{fwc}$ = annual fixed cost of water cooler, \$

$C_{opwc}$ = annual operating cost of water cooler, \$

$C_{fac}$ = annual fixed cost of ammonia chiller, \$

$C_{opac}$ = annual operating cost of ammonia chiller, \$

$C_{fsp}$ = annual fixed cost of the separator, \$

$C_{fcm}$ = annual fixed cost of the compressors, \$

$C_{mnc}$ = annual maintenance cost of the compressors, \$

$C_{opc}$ = annual operating cost of the compressors, \$

$C_{anopa}$ = total annual operating cost of the Ammonia synthesis loop section of a 1000 tonne/day plant.

## 5.4 Results and Discussions

For a fixed rate, the following four variables were chosen for optimization of the ammonia synthesis loop system:

(i) $H_2/N_2$ ratio in the fresh feed

(ii) Recycle ratio

(iii) Inert ($CH_4$+Argon) contents in the fresh feed

(iv) Quench temperature.

This optimization study was divided into two parts; in the first part the effects of different variables on the annual operating cost was studied, while in the second part a Box constrained optimization technique (Box, 1965; Kuester et al., (1973) was used to find the optimum operating conditions.

### 5.4.1 Part I

The effect of $H_2/N_2$ ratio in the feed on the annual operating cost of the ammonia synthesis loop

The effect of $H_2/N_2$ ratio on the annual operating cost of the ammonia synthesis loop is shown in figure 5.1 for two levels of steam cost (process conditions are the same as in table 4.1 of Chapter IV).

It is evident from figure 5.1 that:

------- The minimum annual operating cost lies near a $H_2/N_2$ ratio of 3 (close to optimum ratio of 2.57) for all cases considered. Similar result is reported by Hussain (1986).

- The annual operating cost is a strong function of steam cost because steam cost is a major cost item in the annual operating cost.

## The effect of recycle ratio in feed on the annual operating cost of the ammonia synthesis loop

The effect of recycle ratio in feed on the annual operating cost of the ammonia synthesis loop is shown in figure 5.2 for two levels of steam cost (process conditions are the same as in table 4.1 of Chapter IV).

It is evident from figure 5.2 that:

- Annual operating cost of the ammonia synthesis loop decreases with the decrease in recycle ratio.
- The reactor should be operated at the minimum possible recycle ratio.

## The effect of inert ($CH_4$+Argon) in makeup feed on annual operating cost of the ammonia synthesis loop

The effect of inert contents in the makeup feed on the annual operating cost of the ammonia synthesis loop is shown in figure 5.3 for two levels of steam cost (process conditions are the same as shown in table 4.1 of Chapter IV).

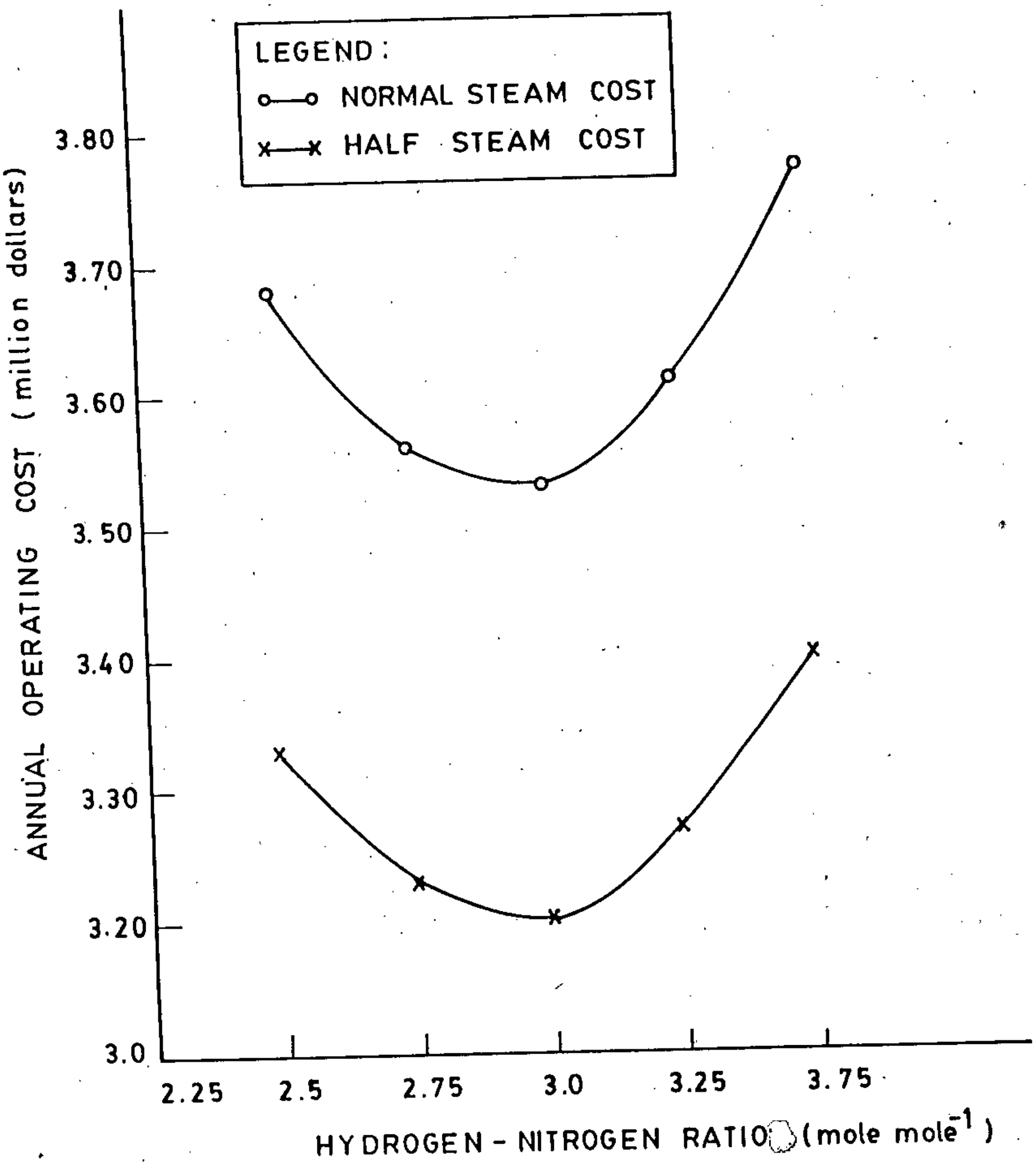

FIG. 5.1 EFFECT OF HYDROGEN - NITROGEN RATIO ON THE ANNUAL OPERATING COST.

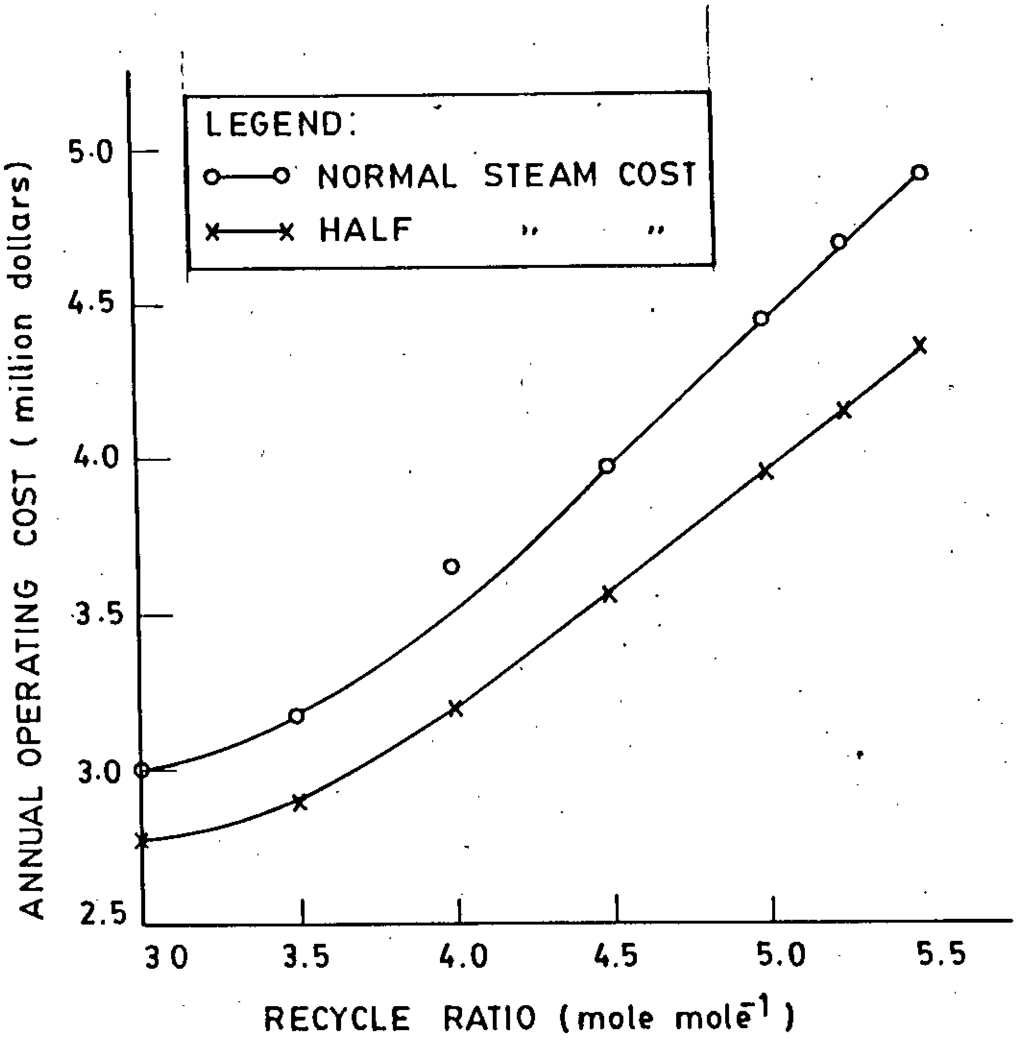

FIG. 5.2 EFFECT OF RECYCLE RATIO ON THE ANNUAL OPERATING COST.

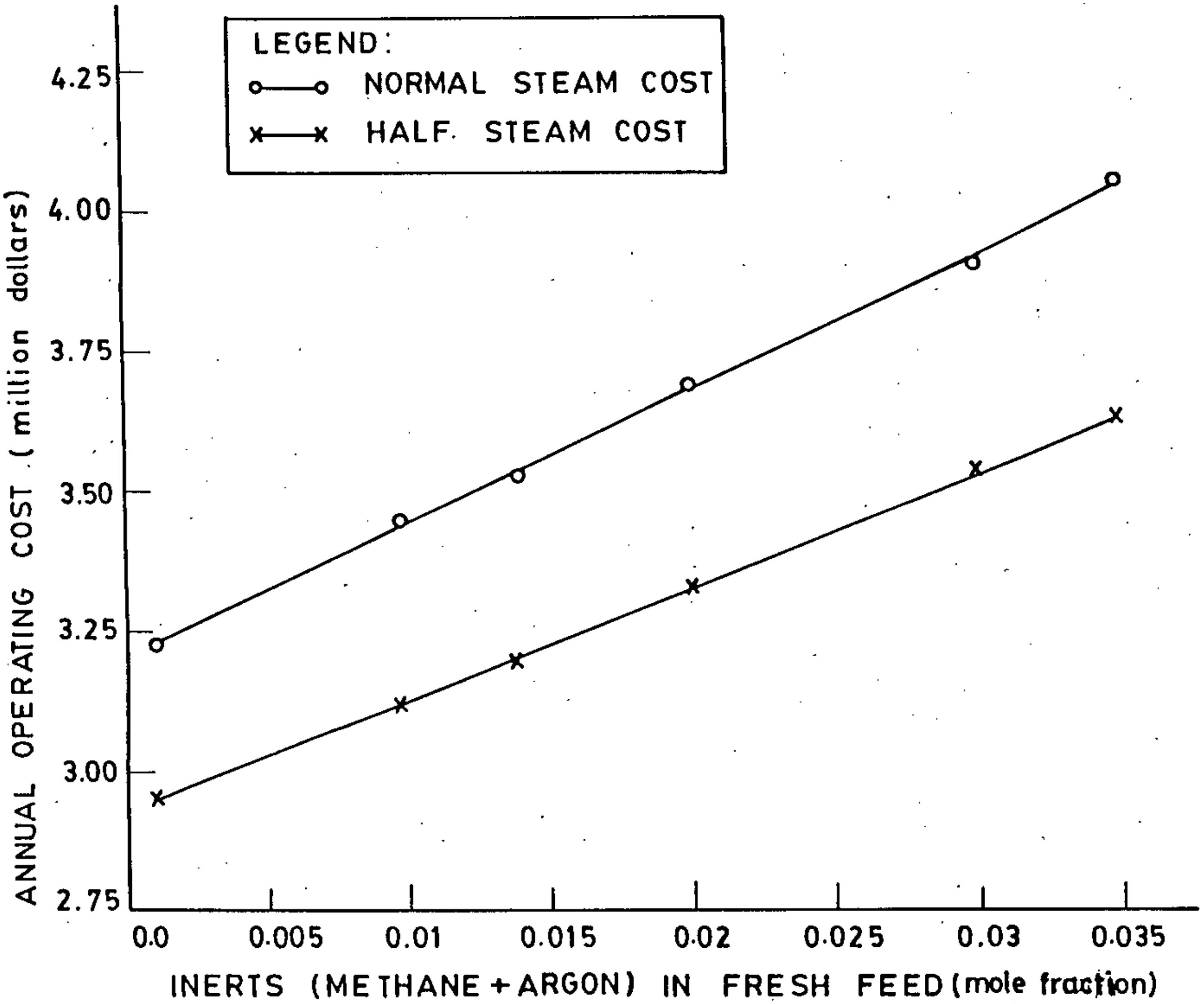

FIG. 5.3 EFFECT OF INERTS IN FRESH FEED ON THE ANNUAL OPERATING COST.

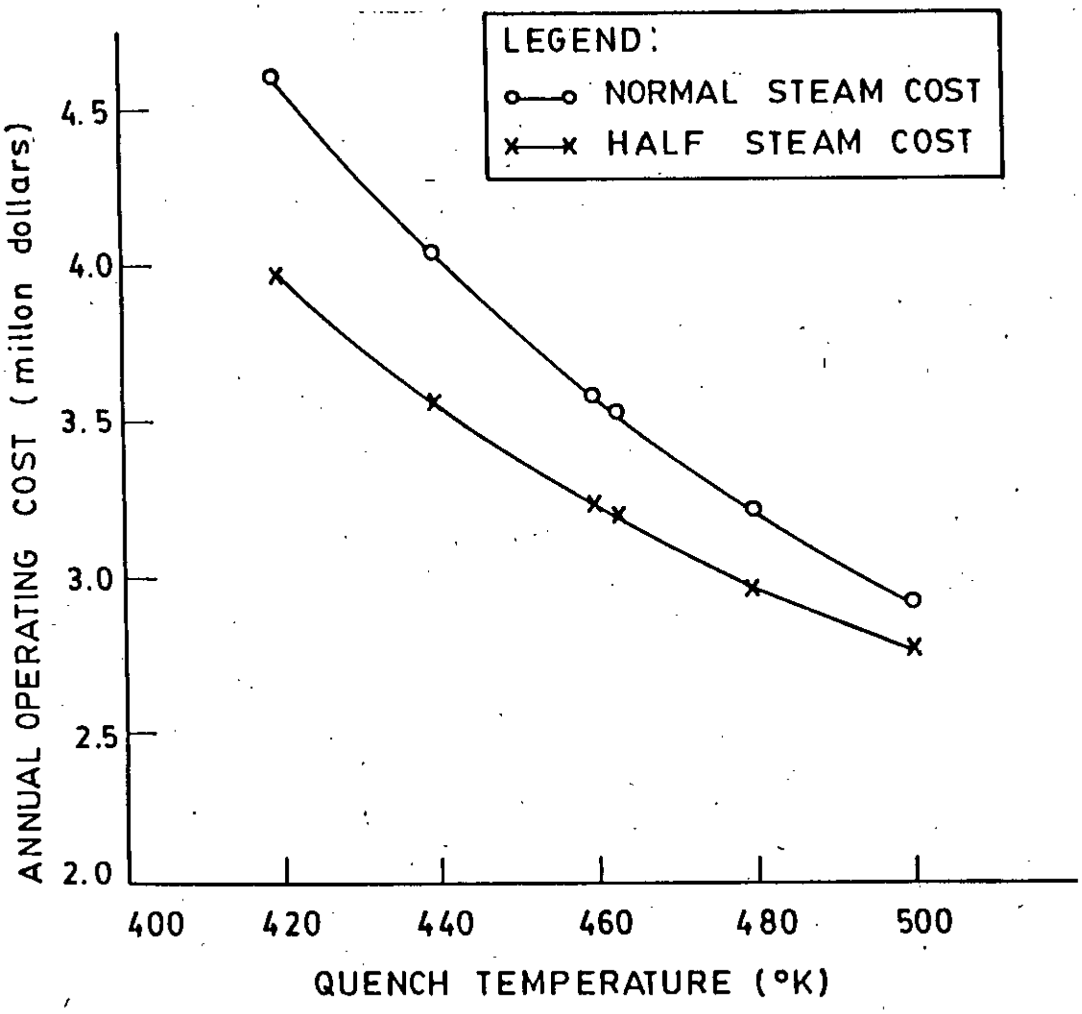

FIG. 5.4 EFFECT OF QUENCH TEMPERATURE ON THE ANNUAL OPERATING COST.

It is evident from figure 5.3 that:

- ----- Annual operating cost of the ammonia synthesis loop decreases monotonically with decrease in inert contents since reforming costs are not considered.

- ----- The reactor should be operated at the minimum possible inert content.

<u>The effect of quench temperature on the annual operating cost of the ammonia synthesis loop</u>

The effect of quench temperature on the annual operating cost of the ammonia synthesis loop is shown in figure 5.4 for two levels of steam cost (process conditions are the same as in table 4.1 of Chapter IV).

It is evident from figure 5.4 that:

- ----- Annual operating cost of the ammonia synthesis loop decreases with the increase in quench temperature and at higher temperatures the effect is less significant. It indicates that equilibrium temperature is far away from the reaction temperature.

- ---- The minimum point couldnot be reached because the quench temperature cannot be raised beyond 500 K due to program limitations.

### 5.4.2 Part II

The parameter values used in the Box constrained optimization are given in Table 5.2. The original program of the Box optimization technique is in Kuester et al. (1973). The tree structure of the computer program is given in figure 5.5. Computer programmes are given in Appendix III.

TABLE 5.2

Parameters used in Box constrained optimization study

---

No. of variables : 4

No. of constraints : 4

Total no. of points in the complex : 10

Reflexion parameter ( $\alpha$ ) : 1.3

Convergence parameter ( $\beta$ ) : 0.1

Explicit constraints violation correction terms

$\delta_1$(for $H_2/N_2$ ratio in fresh feed) = 0.001

$\delta_2$(for recycle ratio) = 0.001

$\delta_3$(for inert contents in fresh feed) = 0.001

$\delta_4$(for quench temperature ) = 0.1

Convergence parameter( $\gamma$ ) : 4

Feasible starting point :

$H_2/N_2$ ratio = 3.0

Recycle ratio = 4.0

Inert in fresh feed = 0.0139

Quench temperature (°K) = 463.0

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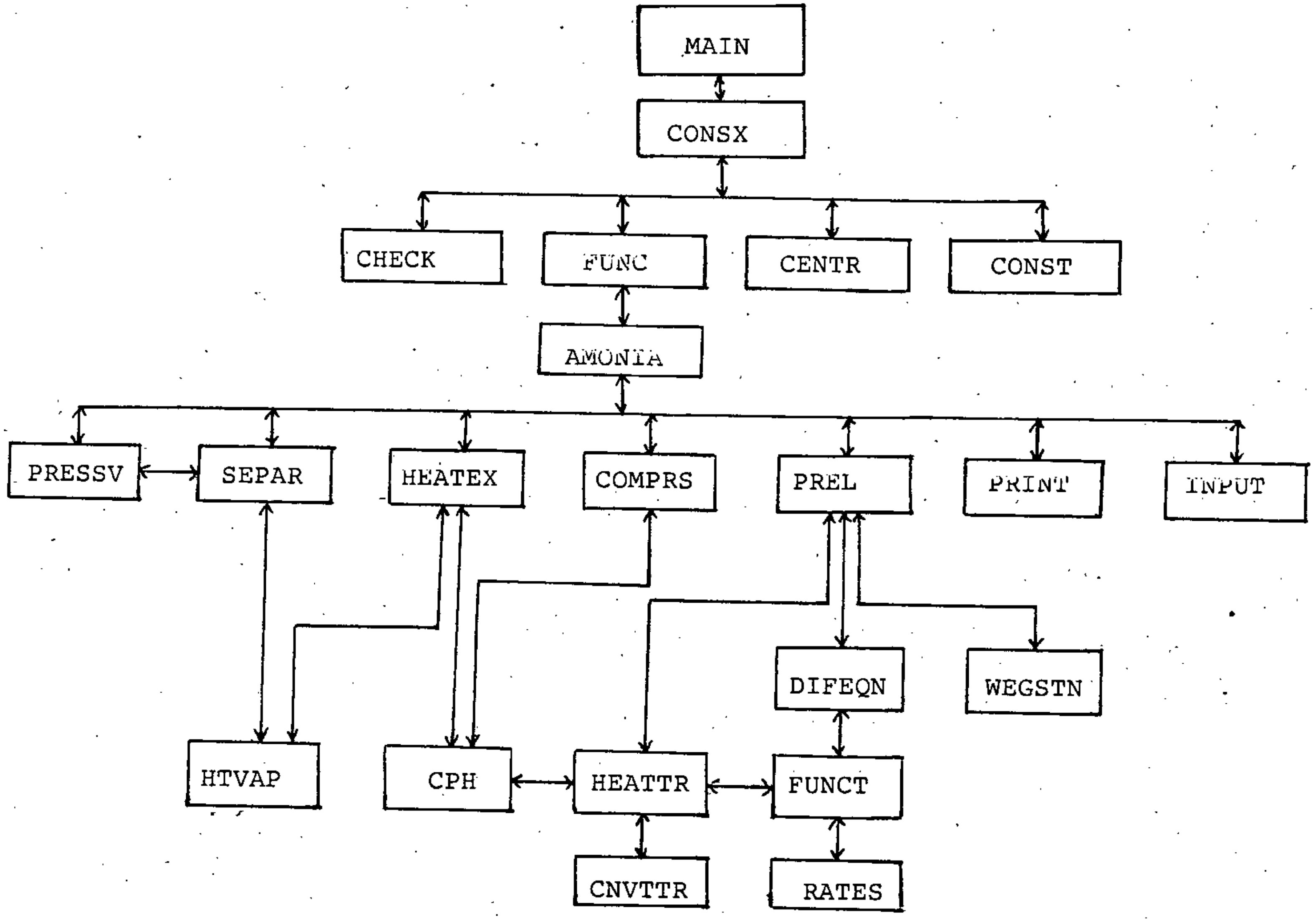

FIG. 5.5: TREE STRUCTURE OF THE OPTIMIZATION COMPUTER PROGRAM

Problem statement

Maximize $- C_{anopa}$ ($H_2/N_2$ ratio in fresh feed, recycle ratio, inert contents in fresh feed, quench temperature)

subject to,

$2.5 \leqq H_2/N_2 \text{ ratio} \leqq 4.0$

$3.5 \leqq \text{Recycle ratio} \leqq 5.5$

$0.001 \leqq \text{Inert contents} \leqq 0.04$

$420.0 \leqq \text{Quench temperature} \leqq 500.0$

The problem statement was run on an IBM 4331 computer with the results given in Table 5.3.

TABLE 5.3

Results of optimization study of ammonia synthesis loop

| | Case I Normal cost data from table 5.1 | Case II Half the steam cost, all other costs are same as in Case I | Case III Half the steam and double the catalyst, all cost are same as in Case I |
|---|---|---|---|
| Minimum annual operating cost(million $/yr) | 2.80 | 2.72 | 3.08 |
| Optimum operating conditions: | | | |
| $H_2/N_2$ ratio: | 2.55 | 2.57 | 2.57 |
| Recycle ratio: | 3.24 | 3.11 | 3.11 |
| Inert contents ($CH_4$+Argon) in feed: | 0.0023 | 0.00955 | 0.00955 |
| Quench temperature(°K): | 499.9 | 499.9 | 499.9 |

It is evident from Table 5.3 that:

------ Catalyst cost is the most predominant item of the annual operating cost of the ammonia synthesis loop system.

---- As the steam cost is halved and the catalyst cost is doubled, optimum conditions move towards higher $H_2/N_2$ ratio.

## 5.5 Limitations

Merits and demerits of both perturbation type (studying the effects of one variable at a time on objective function) and partial optimization are briefly mentioned below:

Merits

(i) These studies give a good idea of trends of change of the objectives e.g. operating cost, profit etc. of the system under consideration with different variables, and thereby help in finding the important variables and their ranges worthy of further study using formal optimization techniques

(ii) The results of perturbation type optimization study can be used to check the final converged solutions of formal optimization studies, because sometimes formal optimization techniques may converge to totally wrong values depending on the initial starting conditions, convergence criterion etc.

(iii) Because of comparatively less execution times, these studies can be used to check the robustness and reliability of individual modules of the system; which are essential for large plant optimization.

Demerits

(i) As the number of variables increase and their domain range increase, it can become very difficult to pinpoint the optimum operating conditions of a system by simply performing purturbation type optimization and also it becomes difficult to keep track of different results.

(ii) There are dangers of partial optimization, because optimum operating conditions in one part of the plant donot usually give optimum conditions for other parts of the plant.

## 5.6 Suggestions for further work

In order to get better and realistic optimum operating conditions of the Ammonia synthesis loop the whole Ammonia synthesis plant comprising of natural gas reforming, shift conversion, $CO_2$ absorption and desorption and methanation should be optimized at a time.

# NOMENCLATURE

| | |
|---|---|
| a, b, c, d | coefficients in the heat capacity equation |
| $A_i$, $B_i$, $C_i$ | constants used in calculation of activity coefficients of component i |
| $A'$ | heat transfer area per foot of exchanger, $ft^2/ft$ |
| A | heat exchange area, $m^2$ |
| $A_1$, $B_1$, $C_1$ | correction terms in eq. (2.31) |
| $a_{N_2}$, $a_{H_2}$, $a_{NH_3}$ | activity of components $N_2$, $H_2$, $NH_3$ respectively, atm |
| $b_i$ | constant in eq. (4.5) |
| $B_{oi}$, $B_{oj}$ | BWR constants for i or j |
| $B_{om}$ | BWR mixture constant |
| $C_1$, $C_2$, $C_3$, $C_4$ | constants in eq. (2.30) |
| C | circumference of riser, m |
| $C'$ | circumference of catalyst section, m |
| $C_{orr}$ | a term as defined in eq. (2.42) |
| $C_p$ | specific heat of reaction mixture, kcal/(kmole °K) |
| $C_{pa}$ | specific heat of ammonia, kcal/(kmole °K) |
| $C_{po}$ | molal heat capacity of the feed gas, Btu/(lbmole °F) |
| $C_{pi}$ | heat capacity of component i, kcal/(kmole °K) |
| $C_{pg}$ | specific heat of feed gas, kcal/(kmole °K) |
| $D_b$ | bed diameter, m |
| $D_{shell}$ | shell diameter, m |
| $D_{anuls}$ | diameter of the annular section |

| | |
|---|---|
| | = $(D_{shell} - D_b)$, m |
| $D_{cntb}$ | diameter of the central tube, m |
| $E$ | activation energy, cal/gmole |
| $F_i$ | molar flow of component i, kmole/s |
| $f_{N_2}$, $f_{H_2}$, $f_{NH_3}$ | fugacity of $N_2$, $H_2$, $NH_3$ respectively atm |
| $f^\circ_{N_2}$, $f^\circ_{H_2}$, $f^\circ_{NH_3}$ | standard state fugacity of $N_2$, $H_2$, $NH_3$ respectively, atm |
| $\Delta F^\circ$ | free energy change at standard state cal/gmole |
| $G$ | mass velocity, kg/(hr-m$^2$) |
| $g_j$ | mass fraction of component j |
| $g_{jo}$ | mass fraction of component j at inlet |
| $\Delta H$ | heat of reaction, cal/gmole |
| $\Delta H_{fo}$ | heat of formation of ammonia at standard state, cal/gmole |
| $(\Delta H_f)_{N_2}$, $(\Delta H_f)_{H_2}$, $(\Delta H_f)_{NH_3}$ | heat of formation of $N_2$, $H_2$, $NH_3$ respectively, cal/gmole |
| $I$ | constant in eq. (2.29) |
| $K$ | thermodynamic equilibrium constant |
| $K_p$ | equilibrium constant in partial pressure units |
| $K_p^*$ | synthesis equilibrium constant at zero pressure |
| $K_a$ | equilibrium constant in terms of activities |
| $K$ | equilibrium constant in terms of fugacities |
| $k$ | rate constant of catalyst reduction reaction |

| | |
|---|---|
| $k'$ | thermal conductivity of catalyst basket insulation, kcal/(m-hr-°K) |
| $k_1$ | rate constant for ammonia formation |
| $k_2$ | rate constant for ammonia decomposition |
| $k_i$ | thermal conductivity of component i, kcal/(m-hr-°K) |
| L | length of reactor, ft |
| $M_i$ | molecular weight of component i, kg/kmole |
| n | moles of gas |
| P | pressure, atm |
| $P_{ci}$ | critical pressure of component i,atm |
| $p_{N_2}$, $p_{H_2}$, $p_{NH_3}$ | partial pressure of $N_2$, $H_2$, $NH_3$ respectively, atm |
| R | gas constant,1.987 gm cal/(gmole °K) |
| r | rate of formation of ammonia, kmole $NH_3$/(kg catalyst-s) |
| $r'$ | rate of reduction of catalyst |
| S | total heat transfer area, $m^2$ |
| $S_m$ | as defined in eq. (2.25) |
| T | temperature, °K |
| $T_{anuls}$ | temperature in annulus, °K |
| $T_b{}^*$ | base temperature for enthalpy =537°R |
| $T_{cntb}$ | temperature in the central tube, °K |
| $T_c$ | normalized catalyst section temperature |
| $T_{ci}$ | critical temperature of component i, °K |
| $T_g$ | temperature of gas in cooling tubes, °K |

| | |
|---|---|
| $T_r$ | temperature in riser, °K |
| $T_{ri}$ | reduced temperature of component i, $T/T_{ci}$ |
| $T_t$ | normalized empty tube section temperature |
| $T_{top}^*$ | top temperature, °K |
| $T_s$ | temperature on shell side of exchanger, °K |
| $U$ | overall heat transfer coefficient, kcal/(m-hr-°K) |
| $V$ | catalyst volume, $m^3$ |
| $V_o$ | space velocity, $hr^{-1}$ |
| $W$ | weight of catalyst, kg |
| $x_{3,eq}$ | equilibrium ammonia concentration |
| $y_{N_2}$, $y_{H_2}$, $y_{NH_3}$ | mole fraction of $N_2$, $H_2$, $NH_3$ respectively |
| $y_{int}$ | mole fraction of inerts |
| $Z$ | compressibility factor |

## GREEK LETTERS

| | |
|---|---|
| $\alpha$, $\beta$ | exponents in T-P equation |
| $\gamma_i$ | activity coefficient of component i |
| $\sigma$ | sensitivity as defined by eq. (2.74) |
| $\mu_i$ | viscosity of component i, kg/(m-s) |
| $\eta$ | effectiveness factor |
| $\psi$ | pressure correction term |
| $\rho_{cat}$ | bulk density of catalyst, $kg/m^3$ |
| $\nu_{N_2}$, $\nu_{H_2}$, $\nu_{NH_3}$ | fugacity coefficients of $N_2$, $H_2$, $NH_3$ respectively |

## Other terms

| | |
|---|---|
| $\Sigma$ | summation term |

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# APPENDIX I

## Vapour-Liquid Equilibrium Relationship in Presence of Other Gases

Ammonia is industrially synthesized in a variety of systems incorporating converters of various designs, which operate either at low pressures, 15200 to 30400 kPa (150-300 atm), or at higher pressures upto 60800 kPa (600 atm). In such systems, besides ammonia other components are present, viz., unconverted $H_2$ and $N_2$ and small amounts of $CH_4$ and Ar.

In the modelling and simulation of such an industrial synthesis loop, vapour-liquid equilibrium relationships are needed in a range of 293-333 K and 2026 to 60800 kPa (20-600 atm). Temperatures in this range are more than the critical temperatures of $N_2$, $H_2$, Ar and $CH_4$ and less than the critical temperature of $NH_3$. Hence only $NH_3$ will condense at these conditions and the liquid $NH_3$, in equilibrium with the gaseous phase, will contain some amount of each of the above components dissolved in it.

In the present study, the liquid $NH_3$ from the separator was considered to be free of any dissolved gases for simplicity of calculations. But actually it is not true. For realistic calculations, the vapour-liquid equilibrium relationship for ammonia in presence of other gases must be considered. The method is outlined below.

At equilibrium, fugacity of each component in both the liquid and vapour phases should be equal giving

$$f_i^V = f_i^L \qquad \text{(I-1)}$$

Both the vapour and liquid phases will be nonideal at the conditions under consideration. In the liquid phase, $NH_3$ is the solvent (subcritical) and the other components are solute (supercritical). With the vapour pressure of $NH_3$ as the reference pressure, fugacity of $NH_3$ in this phase is given by

$$f_1{}^L = \gamma_1 x_1 f^{P_1^s}_{pure,1} \quad \exp \left[ \int_{P_1^s}^{P} \frac{\bar{v}_1}{RT} \, dP \right] \qquad (I\text{-}2)$$

and the fugacity of each solute by

$$f_i{}^L = \gamma_i{}^* x_i H^{P_i^s}_{i,1} \quad \exp \left[ \int_{P_i^s}^{P} \frac{\bar{v}_i{}^\infty}{RT} \, dP \right] \quad (i=2,\ldots,5) \qquad (I\text{-}3)$$

The vapour phase fugacity of each component is

$$f_i{}^V = \phi_i y_i P \qquad (i=1,\ldots,5) \qquad (I\text{-}4)$$

The solvent ($NH_3$) activity coefficient is given by

$$\ln\gamma_1 = v_{c,1} \left[ \sum_i \frac{x_i v_{c,i}}{\sum_j x_j v_{c,j}} \alpha_{ii,1}{}^{½} \right]^2 \qquad (I\text{-}5)$$

and for solute component by

$$\ln \gamma_i{}^* = v_{c,i} \left[ \sum_j \frac{x_j v_{c,j}}{\sum_k x_k v_{c,k}} \alpha_{jj,1}{}^{½} - 2\alpha_{ii,1}{}^{½} \right] \sum_j \frac{x_j v_{c,j}}{\sum_k x_k v_{c,k}} \alpha_{jj,1}{}^{½} \qquad (I\text{-}6)$$

The self-interaction constants of solute i in $NH_3$, $\alpha_{ii,1}$, as obtained from binary solubility data are filled by Alesandrini et al. (1972) by the following type of equation in the range 253-378 K

$$\ln\alpha_{ii,1} = A + B/T + C/T^2 \qquad (I\text{-}7)$$

The pressure correction term for the fugacity of solvent $NH_3$ in the liquid phase is given by

$$\int_{P_1^s}^{P} \frac{\bar{v}_1}{RT} \, dP = \frac{v_1{}^s}{6RT\beta_1{}^s} \left[ \{1 + 7\beta_1{}^s(P - P_1{}^s)\}^{6/7} - 1 \right] \qquad (I\text{-}8)$$

where the saturated-liquid compressibility of $NH_3$, $\beta_1{}^s$, is calculated using the Chueh-Prausnitz (1969) equation as follows

$$\beta_1{}^s = \frac{v_{c,1}}{RT_{c,1}} (1 - 0.89\omega_1{}^{½}) \exp(6.9547 - 76.2853T_{R,1} +$$

$$191.306T_{R,1}^2 - 203.5472T_{R,1}^3 + 82.7631T_{R,1}^4) \quad (I-9)$$

The pressure coreection term for the fugacity of each solute component in the liquid phase is given by

$$\int_{P_1^s}^{P} \frac{\bar{v}_i^{\infty}}{RT}\, dP = \int_{P_1^s}^{P} \frac{\bar{v}_i^{\infty s}}{RT} [1 + 7\bar{\beta}_i^{\infty s}(P - P_1^s)]^{-1/7}\, dP \qquad (I-10)$$

in which partial compressibility of the solute component i at infinite dilution, $\bar{\beta}_i^{\infty s}$, is given by Alesandrini et al. (1972) based on the pseudocritical relationships of Gunn-Prausnitz (1958); this reduces to

$$\bar{\beta}_i^{\infty s} = \beta_1^s + \frac{v_1^s}{\bar{v}_i^{\infty s}} \lim_{x_i \to 0} \left[ \frac{HJ}{G}\frac{\delta F}{\delta x_i} - \frac{FHJ}{G^2}\frac{\delta G}{\delta x_i} + \frac{FJ}{G}\frac{\delta H}{\delta x_i} + \frac{FH}{G}\frac{\delta J}{\delta x_i} \right]_{T,n_j} \qquad (I-11)$$

In equation (I-11)

$$F = \sum_i x_i v_{c,i} \qquad (I-12)$$

$$G = R \sum_i x_i T_{c,i} \qquad (I-13)$$

$$H = 1 - 0.89( \sum_i x_i \omega_i)^{1/2} \qquad (I-14)$$

$$J = \exp[6.5947 - 76.2853(T/\sum_i x_i T_{c,i}) + 191.306(T/\sum_i x_i T_{c,i})^2 - 203.5472(T/\sum_i x_i T_{c,i})^3 + 86.7631(T/\sum_i x_i T_{c,i})^4 \qquad (I-15)$$

In pressure correction term in equation (I-2) and (I-3) experimental data on partial molar liquid volumes, $\bar{v}_1$ and $\bar{v}_i^{\infty}$, are required, which are rare for the binary systems and almost nonexistant for the multicomponent systems. Hence, an empirical correlation by Wada (1949) is used for calculating the partial molar volumes; for use in this correlation, the saturated liquid $NH_3$ molar volumes at different temperatures as given in the International Critical Tables (1926) are filled by the following equation

$$v_1^s = 78.986133 - 0.43363766T + 0.00087587742T^2 \qquad \text{(I-16)}$$

For further use in the Wada correlation, in order to calculate partial molar volume, $\overline{v}_i^{\infty}$, at infinite dilution in $NH_3$, $\overline{v}_i^{\infty s}$ values are required at pressure $P_1^s$ and system temperature T; these are reported by Alesandrini et al. (1972) in the range 253-378 K, which are correlated as follows

$$\overline{v}_i^{\infty s} = A + BT + CT^2 + DT^3 + ET^4 \quad (i=2,....,5) \qquad \text{(I-17)}$$

The constant of equation (I-17) are given in Table I-1.

Table I-1

Coefficients of Equation (I-17)

| | A | B | C*10⁻² | D*10⁻⁴ | E*10⁻⁷ |
|---|---|---|---|---|---|
| $v_2^{\infty s}$ | 193.19389 | 2.4116593 | 0.84695638 | 0.10233027 | 0 |
| $v_3^{\infty s}$ | -203.39420 | 2.4117042 | -0.84697111 | 0.10233186 | 0 |
| $v_4^{\infty s}$ | 483.54588 | -6.4121276 | 3.4018649 | -0.80038523 | 0.71411916 |
| $v_5^{\infty s}$ | 413.8843 | -5.3940156 | 2.9121251 | -0.69651858 | 0.63228243 |

The Henry's constants for various components, $H^{P^s}_{i,1}$, for use in equation (I-3) are correlated by Alesandrini et al. (1972) in the range 253-378 K in the similar way as equation (I-7).

The relation for calculating the fugacity coefficient of any component i including $NH_3$, based on the Redlich-Kwong equation is reproduced fron the work of Prausnitz (1969)

$$\ln\phi_i = \ln\left(\frac{v_m}{v_m - b_m}\right) + \frac{b_i}{v_m - b_m} - \frac{2\sum_j a_{ij}y_j}{b_m R T^{1.5}} \ln\left(\frac{v_m + b_m}{v_m}\right) + \frac{a_m b_i}{b_m^2 R T^{1.5}}\left[\ln\frac{v_m + b_m}{v_m} - \frac{b_m}{v_m + b_m}\right] - \ln\left(\frac{P v_m}{RT}\right)$$

(I-18)

Alesandrini et al. (1972) proposed to calculate

$$a_m = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j a_{ij} \qquad \text{(I-19)}$$

in which for those pairs were neither i nor j is ammonia

$$a_{ij} = \sqrt{(a_i a_j)} \qquad \text{(I-20)}$$

The $b_m$ is computed as originally proposed by Redlich and Kwong (1949), i.e.

$$b_m = \sum_{i=1}^{n} b_i y_i \qquad \text{(I-21)}$$

For $NH_3$, $\Omega_{a1}$ is calculated from

$$\Omega_{a1} = -0.39788936 + 0.0023754678T \qquad \text{(I-22)}$$

and $\Omega_{b1} = 0.0867$. For other components

$$a_i = \frac{0.4278R^2 T_{c,i}^{2.5}}{P_{c,i}} \qquad \text{(I-23)}$$

$$b_i = \frac{0.0867RT_{c,i}}{P_{c,i}} \qquad \text{(I-24)}$$

Furthermore, for use in equation (I-2), fugacity of the saturated liquid $NH_3$, $f^{P_1^s}_{pure,1}$, is given as follows

$$f^{P_1^s}_{pure,1} = P_1^s \left[ \exp \left\{ \ln\left( \frac{RT}{P_1^s} \right) \ln(v - b_1) + \frac{b_1}{v - b_1} + \frac{a_1}{RT^{1.5}} \left\{ \frac{1}{b_1} \ln\left( \frac{v}{v + b_1} \right) - \frac{1}{v + b_1} \right\} \right\} \right] \qquad \text{(I-25)}$$

Nomenclature

A = coefficient in eq. (I-7) or (I-17)

$a_i$, $a_j$ = defined in eq. (I-23), (cm³/gmol)² atm K½, for component i or j

$a_{ij}$ = defined by eq. (I-20)

$a_m$ = value of a for vapour mixture, eq. (I-19)

B = coefficient in eq. (I-7) or (I-19)

$b_i$ = defined by eq. (I-24), $cm^3$/gmol

$b_m$ = value of b for vapour mixture, eq. (I-21)

C = coefficient in eq. (I-7) or (I-17)

D = coefficient in eq. (I-17)

E = coefficient in eq. (I-17)

F = defined by eq. (I-12)

$f_i^L$ = fugacity of component i in the liquid phase, atm

$f_i^V$ = fugacity of component i in the vapour phase, atm

$f^{P_1^*}_{pure,1}$ = fugacity of pure saturated liquid $NH_3$, atm

G = defined by eq. (I-13)

H = defined by eq. (I-14)

$H^{P_1^*}_{i,1}$ = Henry's constant of component i in $NH_3$ at saturation pressure of $NH_3$, atm

i = component designation index: 1, $NH_3$; 2, $N_2$; 3, $H_2$; 4, Ar; 5, $CH_4$

J = defined by eq. (I-15)

j = same as i

$n_i$, $n_j$ = number of moles of component i or j

P = pressure, atm

$P_{c,i}$, $P_{c,j}$ = critical pressure of component i or j, atm

$P_1^*$ = saturation pressure of $NH_3$, atm

R = gas constant, (atm $cm^3$)/(gmol-K)

T = temperature, K

$T_{c,i}$, $T_{c,j}$ = critical temperayre of component i or j, K

$T_{R,1}$ = reduced temperature of $NH_3$

v = molar volume, $cm^3$/gmol

$v_{c,i}$, $v_{c,j}$ = critical molar volume of component i or j, $cm^3$/gmol

$v_1^*$ = molar volume of saturated liquid $NH_3$, $cm^3$/gmol

$v_m$ = molar volume of the mixture, cm$^3$/gmol

$\bar{v}_1$ = partial molar volume of $NH_3$, cm$^3$/gmol

$\bar{v}_1^{\infty}$ = partial molar volume of component i for infinite dilution in $NH_3$, cm$^3$/gmol

$\bar{v}_i^{\infty s}$ = partial molar volume of component i for infinite dilution in $NH_3$ at saturation temperature of $NH_3$, cm$^3$/gmol

$x_i$, $x_j$ = mole fraction of component i or j in liquid phase

$y_i$, $y_j$ = mole fraction of component i or j in vapour phase

Z = compressibility factor

<u>Greek Letters</u>

$\alpha_{ii,1}$, $\alpha_{jj,1}$ = self-interaction constant of molecule i or j in the environment of molecule 1

$\beta_1^s$ = saturated liquid compressibility of $NH_3$

$\bar{\beta}_i^{\infty s}$ = partial compressibility of component i at infinite dilution

$\gamma_1$ = activity coefficient of solvent $NH_3$

$\gamma_i^*$ = activity coefficient of solute i

$\phi_i$ = fugacity coefficient of component i

$\Omega_{a1}$ = defined by eq. (I-22) $NH_3$

$\Omega_{b1}$ = defined as 0.0867 for $NH_3$

$\omega$ = accentric factor

# APPENDIX II

# LITERATURE SURVEY

## 2.1 Introduction

The catalytic synthesis of ammonia from nitrogen and hydrogen is one of the most successful application of chemical technology for the benefit of mankind. Thermodynamic and kinetic considerations suggest operating at a high pressure, at a high temperature and in the presence of a catalyst, in order to combine nitrogen with hydrogen under industrially economic conditions.

Wealth of information exist in the literature on all aspects of ammonia synthesis reaction; much more are stored in the files of industrial research laboratories as classified documents (Hossain, 1981 and Vancini, 1971). In the present survey of literature, attention was focused on the following aspects of the ammonia synthesis reaction system.

a. Thermodynamic
b. Kinetics
c. Catalysis
d. Reactors and Reactor Models

## 2.2 Thermodynamics of Ammonia Synthesis Reaction

The synthesis of ammonia from nitrogen and hydrogen is a classical industrial example of a reversible exothermic equilibrium reaction:

$$1/2N_2(g) + 3/2H_2(g) \rightleftharpoons NH_3(g) - \Delta H \tag{2.1}$$

$$K = \frac{a_{NH_3}}{a_{N_2}^{1/2}\, a_{H_2}^{3/2}} \tag{2.2}$$

Direct determination of heat of reaction and equilibrium over wide ranges of temperature and pressure is in practice delicate, time consuming and expensive. Therefore, indirect methods are used, which are based on thermodynamic data such as free energy, heat of formation, specific heat capacity, entropy, P-V-T relationship, etc. which are experimentally obtainable and values are available in the literature (Hossain, 1981 and Vancini, 1971). This review gives a survey of the measurements and correlations used to determine values of the thermodynamic properties of nitrogen, hydrogen, ammonia and equilibrium conversion for ammonia synthesis. The effect of process variables on the equilibrium yield are also discussed. Out of a large number of correlations available for calculating different thermodynamic properties, attempt have been made to come up with a recommended set in order to carry out the simulation studies in the work.

### 2.2.1 Heat of Reaction

Nielsen (1968) reports the direct determination of the heat of reaction of ammonia synthesis carried out by Haber. At 1 atm. and 0°C Haber found $\Delta H = -11,000$ cal/mole and at 1 atm.

and 600°C $\Delta H = -13{,}000$. Lewis and Randall (1923) gives an expression for $C_p$ which together with the Haber's data leads to the following equation for $\Delta H$ at atmospheric pressure:

$$\Delta H = -9{,}500 - 4.96T - 0.000575T^2 + 0.0000017T^3 \qquad (2.3)$$

Heats of reaction at higher pressures have been calculated by various authors. Gillespie and Beattie (1930) have calculated

$\Delta H$ and $\Delta S$ at 0°C and 1 atm. on the basis of constants obtained from their equilibrium data. On this basis and the Beattie Bridgeman equation of state, they arrive at the following equation for the determination of $\Delta H$ at different pressures and temperatures:

$$\Delta H = -(0.54526 + 840.609/T + 459.734*10^6/T^3)\,P - 5.34685T$$
$$- 0.2525*10^{-3}T^2 + 1.692*10^{-6}T^3 - 9157.09$$

$$\ldots\ldots \qquad (2.4)$$

Table 2.1 gives the values of heat of reaction at 500°C and pressures obtained by earlier workers.

TABLE 2.1

Values of ΔH in the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3 - 2\,\Delta H$ at 500°C and different pressures

| Pressure in atm. | Gillespie and Beattie (1930) | Kazarnovskii and Karapet'yants. (1941) Without correction for heat of mixing | Kazarnovskii and Karapet'yants. (1941) Corrected for differential heat of mixing. Dilute solution. | Kazarnovskii Corrected for heat of mixing 17.6% $NH_3$-20.6% $N_2$-61.8% $H_2$ end-product (1945) |
|---|---|---|---|---|
| 1 | -12,660 | -12,893 | -12,893 | -12893 |
| 100 | -12,920 | -13,149 | -13,121 | -13,040 |
| 200 | - | -13,413 | -13,293 | -13,182 |
| 300 | -13,450 | -13,708 | -13,411 | -13,210 |
| 400 | | -14,023 | -13,555 | -13,045 |
| 500 | | -14,275 | -13,650 | -12,895 |
| 600 | -14,240 | -14,493 | -13,741 | |
| 700 | | -14,702 | -13,842 | |
| 800 | | -14,903 | -13,943 | -13,257 |
| 900 | | -15,098 | -14,048 | |
| 1000 | -15,290 | -15,280 | -14,145 | -13,595 |

Using the heat of reaction data presented by Kazarnovskii (1945) for the formation of a mixture containing 17.6% $NH_3$ in a 3:1 $H_2$:$N_2$ mixture, Gaines (1977) derived the following expression for heat of reaction in Btu/lbmole of $NH_3$ formed:

$$\begin{aligned}\Delta H = {} & -23840.37 + (P - 300)(1.08 + (P - 300) * (0.01305 \\ & +(P - 300)(0.83502*10^{-5} + (P - 300)(0.65934*10^{-7})))) \\ & +4.5(1391 - T) \qquad (2.5)\end{aligned}$$

More recently Shah (1979) use the following equation:

$$\begin{aligned}(\Delta H)_{T,P} = {} & - 9184 - 7.2949T + 0.34996*10^{-2}T^2 + .03356*10\ T \\ & - 0.11625*10^{-9}T^4 - (6329.3 - 3.1619P) + (14.3595 \\ & + 4.4552*10^{-3}T)P - T^2(8.3395*10^{-3} + 1.928*10^{-6}P) \\ & - 51.21 + 0.14215P \qquad (2.6)\end{aligned}$$

In this work, the following expression for heat of reaction have been used:

$$\Delta H = (\Delta H_f)_{NH_3} - 1.5(\Delta H_f)_{H_2} - 0.5(\Delta H_f)_{N_2} \qquad (2.7)$$

### 2.2.2 Specific Heat of Hydrogen, Nitrogen and Ammonia

Granet (1954) gives a chart showing the specific heat of hydrogen as a function of pressure and temperature at pressure from 1 atm. to 700 atm. and temperatures from 0°C to 800°C.

Granet and Kass (1953) report the specific heat of nitrogen at pressures from 1 atm. to 140 atm. and temperatures from 40°C to 800°C.

The specific heat of ammonia is given by Grahl (1953) at pressures between 0 atm. to 1,000 atm. and temperatures from 0°C to 400°C.

Harrison and Kobe (1953) derived empirical constants for heat capacity equation for ammonia. The constants for the equations of the form $C_p = a+bT+cT^2+dT^3$, for the heat capacity of ammonia are as follows:

TABLE 2.2

Values of constants for calculating specific heats

| Temperature °K | a | $b*10^3$ | $C*10^6$ | $d*10^9$ | %Av. deviation | %Max. |
|---|---|---|---|---|---|---|
| 233 - 1500 | 6.0864 | 8.8116 | 1.5055 | -- | 0.55 | 1.48 |
| 233 - 1500 | 6.5846 | 6.1251 | 2.3663 | 1.5981 | 0.36 | -- |
| -40 - 1200 | 8.3810 | 7.9891 | 7.9891 | -1.5055 | -- | -- |
| -40 - 1200 | 8.4017 | 7.0601 | 1.0567 | -1.5981 | -- | -- |

--------

In calculating ΔH and ΔF, Vancini (1971) used linear expressions for heat capacities as:

for $N_2$ : $C_p = 6.5 + 0.001T$ (2.8a)

for $H_2$ : $C_p = 6.5 + 0.009T$ (2.8b)

for $NH_3$: $C_p = 6.7 + 0.0063T$ (2.8c)

The following expressions were reported by Brayant (1933) and Kobe and Harrison (1954) for specific heat at 1 atm. from 0°C to 2000°C.

for $H_2$ : $C_p = 6.5 + 0.00071T$ (2.9a)

$C_p = 6.85 + 0.00028T + 0.22*10^{-6}T^2$ (2.9b)

for $N_2$ : $C_p = 6.76 + 0.000606T + 0.13*10^{-6}T^2$ (2.10a)

$C_p = 6.30 + 0.001819T + 0.345*10^{-6}T^2$ (2.10b)

For ammonia specific heat equation are available for two ranges:

$C_p = 7.561 + 0.00373T + 1.4*10^{-6}T^2$ (from 0°C-500°C) (2.11a)

$C_p = 5.92 + 0.0893T - 1.764*10^{-6}T^2$ (from 0°C-2000°C) (2.11b)

The following constants were reported by Hougen, Watson and Ragatz (1959).

## TABLE 2.3

Values of constants for calculating specific heats

| Gas | a | $b*10^2$ | $c*10^5$ | $d*10^9$ |
|---|---|---|---|---|
| $H_2$ | 6.952 | -0.04567 | 0.09563 | -0.2079 |
| $N_2$ | 6.903 | -0.03753 | 0.1930 | -0.6861 |

Shah (1967) used the following heat capacity equation for $NH_3$

$$C_{pa} = 6.5846 - 0.61251*10^{-2}T + 0.23663*10^{-5}T^2 - 1.5981*10^{-9}T^3 + 96.1678 - 0.067571P + (-0.2225 + 1.6847*10^{-4}P)T + (1.289*10^{-4} - 1.0095*10^{-7}P)T^2 \quad .. \quad (2.12)$$

Gaines (1977) in calculating mixture heat capacities and enthalpies used BWR equation of state. Table 2.4 containes pure component constants used to compute mixture constants; only constant $B_{om}$ is computed from:

$$B_{om} = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j (B_{oi}^{0.333} + B_{oj}^{0.333})^3 \qquad (2.13)$$

In this work, the following expressions have been used for heat capacities of $N_2$, $H_2$, $NH_3$ respectively (Reid and Sherwood, 1977):

## Table 2.4

## BWR CONSTANTS[a]

| | Nitrogen | Argon | Methane | Ammonia | Hydrogen |
|---|---|---|---|---|---|
| $A$ | 0.0312319 | 0.0288358 | 0.0494 | 0.10354029 | 0.0008108534 |
| $A_o$ | 0.872086 | 0.823417 | 1.855 | 3.789282 | 0.18267058 |
| $b$ | 0.0032351 | 0.00215289 | 0.00338004 | 0.0007195852 | 0.01092708 |
| $B_o$ | 0.0281066 | 0.0222852597 | 0.0426 | 0.051646121 | 0.026812097 |
| $c * 10^{-6}$ | 0.000547364 | 0.0007982437 | 0.002545 | 0.00015753298 | 0.00000355307 |
| $C_o * 10^{-6}$ | 0.00781375 | 0.01314125 | 0.02257 | 0.1785709 | 0.00009996711 |
| $\alpha$ | 0.0000709232 | 0.00003558895 | 0.000124359 | 0.000004652178 | 0.0000893277 |
| $\gamma$ | 0.0045 | 0.0023382711 | 0.006 | 0.019805156 | 0.002576974 |

( a = Units L/gm mol atm K )

for $N_2 : C_p = 7.44 - .324*10^{-2}T + 0.64*10^{-5}\ T^2 - 2.79*10^{-9}T^3$

.... (2.14a)

for $H_2 : C_p = 6.483+0.2215*10^{-2}T-0.3298*10^{-5}T^2+1.826*10^{-9}T^3$

..... (2.14b)

for $NH_3 : C_p = 6.524+0.5692*10^{-2}T+0.4078*10^{-5}T^2-2.83*10^{-9}T^3$

### 2.2.3 Viscosity and Thermal conductivity of Reactants

Absolute viscosity and thermal conductivity of hydrogen as a function of temperature are given by Granet (1954) and of nitrogen by Granet and Kass (1953).

Comings and Egly (1940) present method for the prediction of viscosity at high pressures from the viscosity at atmospheric pressures. Thermal conductivity and dynamic viscosity at 1 kg/cm² and higher pressures for ammonia have been reported by Groenier (1961) and shown by Vancini (1971) in diagrams.

Reid and Sherwood (1977) suggested methods to calculate mixture viscosities and thermal conductivities. Pure component viscosities are computable from Chapman and Enskog equation. These are also obtainable from Wilke's method applying Dean and Stiel pressure correction (Nielsen, 1968).

Pure component thermal conductivities are computed as suggested by Bromley (Dodge, 1944). Mixture thermal conductivities are computed by Lindsay and Bromley and corrected for pressure by equations of Stiel and Thodos (Reid and Sherwood, 1977).

In this work, the following expressions have been used for viscosities and thermal conductivities of $N_2$, $H_2$ and $NH_3$:

$$\text{Viscosity:} \quad \mu_i = \frac{3.5 \cdot M_i^{\frac{1}{2}} P_{ci}^{2/3} T_{ri}}{T_{ci}^{1/6} [1 + .36 T_{ri} (T_{ri} - 1)]^{1/6}} * 10^{-7} \qquad (2.15)$$

$$\text{Thermal conductivity} : k_i = \mu_i / M_i \; (C_{pi} + 2.48) \qquad ..... \; (2.16)$$

## 2.2.4 P-V-T Relationship and Compressibility Factors

In industrial synthesis of ammonia, where high pressure is used, the ideal gas law does not hold good. One way to take the nonideality into consideration is to introduce the compressibility factor into the equation of state.

$$PV = nZRT \qquad (2.17)$$

Values of the compressibility factor for a 3:1 hydrogen-nitrogen mixture at 10°C and various pressures are given in Table 2.5. The generalized compressibility charts for pure gases are given in Dodge (1944).

TABLE 2.5

Compressibility factors for a 3:1 $H_2$:$N_2$ mixture at 10°C

| Pressure (atm.) | Compressibility factor (Z) |
|---|---|
| 100 | 1.08 |
| 200 | 1.15 |
| 300 | 1.21 |
| 400 | 1.28 |

---------------

Compressibility factors for ammonia gas has been reported by Beattie (1930).

Any appreciable content of methane or argon, and more pronouncedly of ammonia, will decrease the compressibility factor listed above. Compressibility chart for hydrogen and inert gases has been reported by Maslan and Littman (1953).

Bennett and Dodge (1950) have measured compressibility factors of mixtures of hydrogen and nitrogen above 1000 atm. and have found that at these high pressures hydrogen-nitrogen mixtures follow the additive law.

Nelsen and Obert (1950) present two sets of generalized compressibility charts. Othmer and Chen (1966) have outlined a method for determination of the compressibility factor of a gas mixture of two or more gases and compared the results by this method with experimental P-V-T data.

### 2.2.5 Equilibrium of Ammonia Synthesis Reaction

The thermodynamic equilibrium for this reaction can be calculated from the equation

$$-\Delta F^\circ/T = R\ln K \tag{2.18}$$

The free energy change for the reaction can be calculated from the free energy function of the products and reactants.

$$\frac{\Delta F^\circ}{T} = \left[\frac{F^\circ - H^\circ}{T} + \frac{(\Delta H_f^\circ)_o}{T}\right]_{\text{Products}} - \left[\frac{F^\circ - H^\circ}{T}\right]_{\text{Reactants}} \quad \ldots\ldots \tag{2.19}$$

The heat of formation at 0°K, $(\Delta H_f^\circ)_o$ can be calculated from the heat of formation and the enthalpies $H-H_o^\circ$, of ammonia, nitrogen and hydrogen at 298.16°K as 9,374 cal/gmol. However, better agreement of the calculated and experimental equilibrium constants was found when $(\Delta H_f^\circ) = -9{,}254$ cal/gmol a value determined experimentally by Stephensen and Macmohan (1939). Harrison and Kobe (1953) calculated the equilibrium constant based on the best available data. Their calculated values are given in Table 2.6. A graph of logK vs. reciprocal of absolute temperature doesnot give a straight line. They obtained the following expression for the equilibrium constant based on a method to give a minimum percentage deviation in the temperature range of 500-1300°K;

$$\log K = 2250.322/T - 0.85340 - 1.51049 \log T - 25.8987*10^{-5}T + 14.8961*10^{-8}T^2 \quad .. \quad (2.20)$$

Dyson and Simon (1968), Gaines (1977) and Shah (1967) used the equation of Gillespie and Beattie:

$$\log K = - 2.691122 \log T - 5.519265*10^{-5}T + 1.848863*10^{-7}T^2 + 2001.6/T + 2.6899 \quad (2.21)$$

TABLE 2.6

Equilibrium constants for Ammonia Synthesis

| T,°K | Log K | K |
|---|---|---|
| 298.16 | 2.83062 | 677.0 |
| 300.00 | 2.78246 | 606.0 |
| 400.00 | 0.75038 | 5.628 |
| 500.00 | -0.52178 | 0.3008 |
| 600.00 | -1.39940 | 0.03987 |
| 700.00 | -2.04342 | 0.009048 |
| 800.00 | -2.53646 | 0.009048 |
| 900.00 | -2.92783 | 0.001181 |
| 1000.00 | -3.24477 | 0.0005692 |

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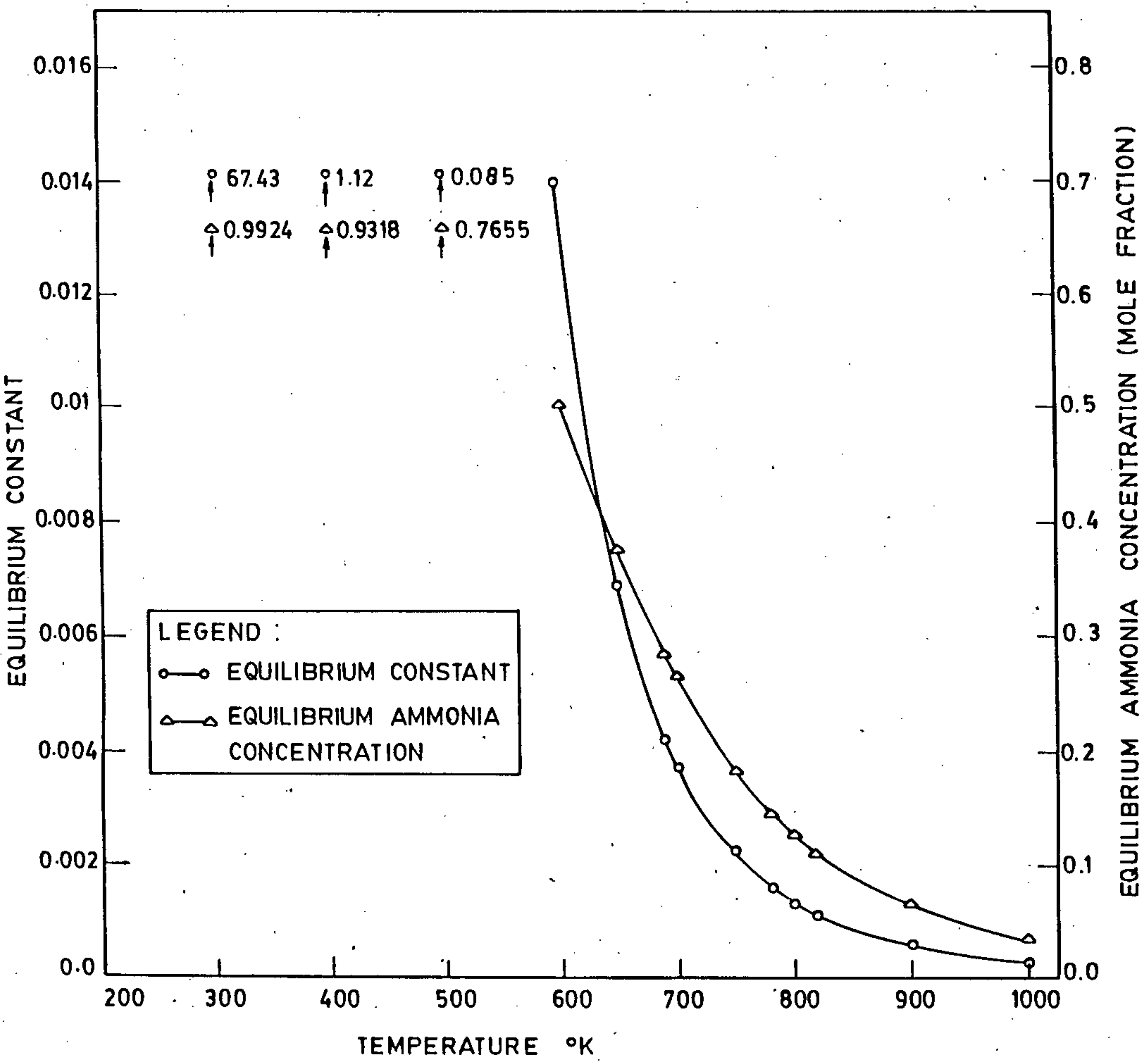


FIG. 2.1 VARIATION OF EQUILIBRIUM CONSTANT (EQ II.21) AND EQUILIBRIUM AMMONIA CONCENTRATION WITH TEMPERATURE. ($H_2/N_2$ = 3:1, P = 300 atm.)

The equilibrium constant is related to partial pressures and fugacity coefficient in the following way:

$$K = \frac{\alpha_{NH_3}}{\alpha_{N_2}^{1/2}\ \alpha_{H_2}^{3/2}} = \frac{(f/f^\circ)NH_3}{(f/f^\circ)N_2^{1/2}(f/f^\circ)H_2^{3/2}} = K_f$$

$$\text{or, } K = \frac{\nu_{NH_3}}{\nu_{N_2}^{1/2} * \nu_{H_2}^{3/2}} * \frac{P_{NH_3}}{P_{N_2}^{1/2} * P_{H_2}^{3/2}} \qquad (2.22)$$

$$\text{Or, } K = K_\nu * K_p \qquad (2.23)$$

The thermodynamic constant K in terms of fugacity coefficients $\nu$, for $N_2$, $H_2$ and $NH_3$ can be read directly or calculated from the generalized chart by Hougen and Watson (1959). This can also be calculated from the formulae reported by Cooper (1967) and Newton (1935).

$$\nu_{NH_3} = 0.1438996 + 0.2028538*10^{-2}T - 0.4487672*10^{-3}P - .1142945 *10^{-5}T^2 + 0.2761216*10^{-6}P^2 \qquad (2.24a)$$

$$\nu_{N_2} = 0.93431737 + 0.3101804*10^{-3}T + 0.295896*10^{-3}P - 0.2707279 *10^{-6}T^2 + 0.4775207*10^{-6}P^2 \qquad (2.24b)$$

$$\nu_{H_2} = \exp[e^{(-3.8402T^{0.125}+0.541)}P - e^{(-0.1263T^{0.5}-15.98)}P^2$$

$$+ 300e^{(-0.011901T-6.941)}(e^{-P/300} - 1)] \qquad (2.24c)$$

Activity coefficients of the reactants can also be calculated on the basis of Gillespie and Beattie equation:

$$RT\ln \gamma_i = [(B_i - A_i/RT - C_i/T^3P)P + (A_i^{0.5} - S_m)^2/RT]\ P \qquad \ldots\ldots \qquad (2.25)$$

The numerical coefficients are:

| $i$ | $A_i$ | $B_i$ | $C_i*10^{-4}$ |
|---|---|---|---|
| $H_2$ | 0.1975 | 0.02096 | 0.0504 |
| $N_2$ | 1.3445 | 0.05046 | 0.420 |
| $NH_3$ | 2.3930 | 0.34150 | 476.98 |
| Ar | 1.2907 | -- | -- |
| $CH_4$ | 2.2769 | -- | -- |
| He | 0.0216 | -- | -- |

$R = 0.08206$ and

$$S_m = \sum_{i=1}^{n} y_i A_i^{0.5}$$

$y_i$ are the mole fractions of the components including inert.

The equilibrium constant K is related to the heat of reaction through Van't Hoff's equation

$$d\ln K/dT = \Delta H/RT^2 = \Delta H_o/RT^2 + 1/RT^2 \int \Delta C_p \, dT \qquad (2.26)$$

$$\Delta C_p = \Delta a + \Delta bT + \Delta cT^2$$

where, $\Delta a = a_{NH_3} - (0.5a_{N_2} + 1.5a_{H_2})$

with similar expressions for $\Delta b$ and $\Delta c$.

Integrating,

$$\ln K = -\Delta H_o/RT + (\Delta a/R)\ln T + (\Delta b/2R)T + (\Delta c/6R)T^2 + C \qquad \ldots\ldots \quad (2.27)$$

where C is the constant of integration which can be evaluated from known value of K at any temperature. Thus

$$\ln K_p = -\ln K_\nu - (\Delta H_o/RT) + (\Delta a/R)\ln T + (\Delta b/2R)T + (\Delta c/6R)T^2 + C \qquad \ldots\ldots \quad (2.28)$$

This is the general but approximate equation of the equilibrium constant $K_p$ at any pressure and temperature and where the specific heat coefficients, $\Delta a$, $\Delta b$, $\Delta c$ are in any case at 1 atm. The equation is sufficiently reliable for a priori theoretical calculations upto about 400 atm.

The values of $K_p$, as obtained by means of accurate experimental measurements are given in Table 2.7 for the most common operating conditions. These data are sufficiently adequate for the industrial conditions of pressure and temperature. For further information on these semi-empirical equations and diagrams, nomograph on $K_p$ of synthesis reaction, references are given (Vancini, 1971).

TABLE 2.7

Values of $K_p$ for the reaction: $1/2N_2(g) + 3/2H_2(g) \rightleftharpoons NH_3(g)$

| Pressures (atm) | Temperatures (°C)<br>325 | 350 | 400 | 450 | 500 |
|---|---|---|---|---|---|
| 1 | 0.0401 | 0.0266 | 0.0129 | 0.00664 | 0.00382 |
| 100 | - | - | 0.0137 | 0.0072 | 0.00403 |
| 300 | - | - | - | 0.0088 | 0.00498 |
| 600 | - | - | - | 0.0130 | 0.00561 |
| 1000 | - | - | - | 0.0233 | 0.00985 |

--------

The equilibrium constant is determined to calculate the equilibrium ammonia yield at any temperature and pressure, usually a higher yield is desirable though it involves operation at very high pressures. A yield between 20-30% is desirable and less than 15% is undesirable.

Larson and Dodge (1923) have suggested the following empirical equation for correlating the equilibrium constant with temperature:

$$\log K_p^{1/2} = -2074.8T^{-1} + 2.4943 \log T + \beta T - 1.8564*10^{-7}T^2 + I \qquad (2.29)$$

Coefficients β and I vary with pressures as given in Table 2.8:

TABLE 2.8

Variation of β and I with pressure

| Pressures (atm.) | β | I |
|---|---|---|
| 10 | 0 | -1993 |
| 30 | $0.34*10^{-5}$ | -2021 |
| 50 | $1.256*10^{-4}$ | -2090 |
| 100 | $1.256*10^{-4}$ | -2113 |
| 300 | $1.256*10^{-4}$ | -2206 |
| 600 | $1.085*10^{-3}$ | -3059 |
| 1000 | $2.6833*10^{-3}$ | -4473 |

---------

The equation that gives the equilibrium constants most closely approaching the experimental data appears to have been developed by Gillespie and Beattie (1930) from an equation proposed by Beattie and Bridgeman. This equation separates the effects of temperature and pressure as follows:

$$\log \frac{K_p}{K_p^*} = P\ [C_1T^{-1}+C_2T^{-4} + C_3T^{-2}(\Sigma x_iA_i^{1/2}) + C_4T^{-2}(\Sigma x_iA_i^{1/2})^2] \quad \ldots \quad (2.30)$$

where $C_i$ = numerical coefficients according to the subscript, $x_i$ = mol% of component i in the gaseous mixture, $A_i$ = the Beattie - Bridgeman coefficient for component i, and $K_p^*$ = the equilibrium constant extrapolated to P=0 and thus depending only on temperature. Winchester and Dodge (1956) have shown that this equation applies for pressures upto 3500 atm. However, it is seldom used because of the complicated computations.

In this work Eq. (2.21) was used for equilibrium calculations.

### 2.2.6 Equilibrium Conversion

A nomograph for determining equilibrium ammonia percentages in the pressure range upto 330 atm. has been given by Tour (1921). In this nomograph, only the effect of temperature is considered and therefore, it should not be used when accurate values are required.

In the presentation given by Kjaer (1958) the effects of temperature and pressure on $K_p$ are separated. The pressure independent part of the equilibrium constant is expressed exactly and explicity as a function of temperature. The actual equilibrium constant $K_p$ is expressed as

$$\log K_p = \log K_p^* + P(A_1 B_1 + C_1) \qquad (2.31)$$

$K_p^*$ is the equilibrium constant at ideal conditions (zero pressure) and its value is calculated from equation (2.21).

The correction term $A_1$ is:

$$A_1 = 1.419487 x_{3,eq}^2 + 2.838990 x_{3,eq} + 1.269225$$

and two temperature dependent factors $B_1$ and $C_1$ are:

$$B_1 = 38.76816/T^2$$

$$C_1 = 0.1191849/T + 25122730/T^4$$

Having $K_p$ from equation (2.31) $x_{3,eq}$ is calculated from:

$$\frac{x_{3,eq}}{(1-x_{3,eq})^2} = (27/16)\, PK_p = D$$

$$\text{or, } x_{3,eq} = \frac{2D - (\sqrt{1 + 4D} - 1)}{2D} \qquad (2.32)$$

Successive approximation is applied to find $x_{3,eq}$. The convergence is very fast as the pressure dependent term is rather small.

Vancini (1971) calculated the equilibrium ammonia yield using the definition of $K_p$. The expression for equilibrium ammonia percentage becomes

$$x_{3,eq} = \frac{K_p P}{K_p P(1 - x_{3,eq}) + 3.08} \qquad (2.33)$$

which can be solved by trial. Usually not more than two trials are required.

Table 2.9 gives the values of $x_{3,eq}$ at different pressures and temperatures, as obtained by applying successively equation (2.33).

TABLE 2.9

Equilibrium yields (in %) of $NH_3$ at different pressures and temperatures (as determined after expansion upto ambient pressure)

| Temperature | Pressures (atm.) | | | | |
|---|---|---|---|---|---|
| (°C) | 10 | 100 | 300 | 600 | 1000 |
| 200 | 50.66 | 81.54 | 89.94 | 95.37 | 98.29 |
| 300 | 14.73 | 52.04 | 70.96 | 84.21 | 92.55 |
| 400 | 3.85 | 25.37 | 48.18 | 66.17 | 79.80 |
| 500 | 1.21 | 10.51 | 25.80 | 42.32 | 57.47 |
| 600 | 0.49 | 4.53 | 12.84 | 24.04 | 31.43 |
| 700 | 0.25 | 2.18 | 7.28 | 12.60 | 12.87 |

------------

This table shows two fundamental facts:

(i) For the same pressure conditions the ammonia equilibrium yield decreases with increasing temperature, because the ammonia formation is hindered by increasing temperature.

(ii) Under equal temperature conditions the equilibrium yield increases with increasing pressure. This is due to two simultaneous causes: the increase of $K_p$ with pressure and the decrease of reaction volume, half of volume of ammonia being produced from one volume of gas mixture.

Nielsen (1968) has tabulated the values of equilibrium constant using Gillespie-Beattie equation for a stoichiometric mixture of nitrogen and hydrogen between pressure 100 atm. and 800 atm. at interval of 100 atm. and temperatures between 344°C and 600°C.

## 2.3 Kinetics of Ammonia Synthesis

### 2.3.1 Reaction Mechanism and Rate Limiting Step

Extensive studies of the catalytic synthesis of ammonia on iron suggest that the reaction occurs through surface imine radicals and comprise the following elementary steps (Hossain, 1981):

$$\begin{aligned}
&N_2(g) + 2X \longrightarrow 2N.X \\
&H_2(g) + 2X \longrightarrow 2H.X \\
&N.X + H.X \longrightarrow NH.X + X \\
&NH.X + H.X \longrightarrow NH_2.X + X \\
&NH_2.X + H.X \longrightarrow NH_3.X + X \\
&NH_3.X \longrightarrow NH_3(g) + X
\end{aligned} \tag{2.34}$$

One of the main questions on the fundamentals of the ammonia synthesis is the problem of finding the rate-determining step of the overall reaction.

If the synthesis reaction is homogeneous, its activation energy is about 55,000 kcal/kmol whereas the corresponding free energy change is 6,900 kcal/kmol. Thermodynamically the synthesis reaction is not feasible, because the free energy change is positive. That is why it requires a high temperature and use of a catalyst to obtain a reasonable reaction rate.

The equilibrium between ammonia synthesis catalyst and nitrogen is particularly delicate: if the catalyst-N bond is too strong, there is formation of a stable complex; if it is too weak, no atomic N is formed and therefore no reaction takes place. Stable nitrides are formed by Li, Ca, Al, Ti, V and Cr, which are therefore not suitable catalysts; Mn and Fe form stable nitrides only under conditions of very high pressures and temperature.

As hydrogen chemisorption only will not yield ammonia, an ammonia synthesis catalyst should mainly chemisorb nitrogen; nitrogen is more stable than hydrogen as evident by a comparison of the free energy changes required to dissociate $N_2$ and $H_2$ at 25°C and 1 atm. Therefore common hydrogenation catalysts Pt, Pd, Ni and Cu donot catalyze the synthesis. Pure Fe chemisorbs nitrogen fairly well. Attempts to explain the synthesis reaction by means of the formation of intermediate compounds, of the nitride type have not been successful.

From the heat of dissociation value reported by Kistiakowsky et al. (1951) and heat of adsorption value by Emmett and Brunauer (1933), the bonding energy is of the order of 130 kcal per chemisorbed nitrogen atom. This can be compared with the bond dissociation energies in $NH_2$-H of 104 kcal/kmol, in NH-H of 88 kcal/kmol and in N-H of 88 kcal/kmol, as calculated by Attshuller (1954). Thus analysis of the energetics of the different steps lend support to the postulate that the activated chemisorption of nitrogen is the slowest step in the overall reaction because nitrogen has a strong bond between its atoms (Vancini, 1971).

Both nitrogen chemisorption and ammonia synthesis occur at almost the same temperature. $H_2$ chemisorption occur at a lower temperature and therefore $H_2$ chemisorption only cannot cause the ammonia synthesis reaction. $H_2$ and $N_2$ are chemisorbed by Fe as atoms and therefore hydrogenation of N atoms to $NH_3$ is possible. The combination of nitrogen and hydrogen in the adsorption phase requires an activation energy of about 9,500 kcal/kmol of $N_2$ (Vancini, 1971).

Emmett and Brunauer (1933, 1934) proved that the rate of chemisorption of nitrogen on Fe catalyst is equal to the formation of a corresponding amount of $NH_3$ on this catalyst. Kozhenova and Kagan (1940) proved that the hydrogenation reaction is faster than the chemisorption of $N_2$.

Tylor and Jungers (1935) investigated the exchange between ammonia and deuterium on $K_2O-Al_2O_3$ promoted Fe catalyst.

$$2NH_3 + 3D_2 \rightleftharpoons 2ND_3 + 3H_2$$

The reaction occurs at room temperature and no reaction occurs at about 300°C. The exchange reaction proceeds right to $ND_3$ as analysed by spectroscopy. Therefore at high temperature neither the chemisorption of $H_2$ nor the addition of last H atom to $NH_2$ is rate determining in ammonia synthesis.

All these facts and postulates suggest that, neither the adsorption of $H_2$ nor the desorption of $NH_3$ can be ratedetermining step. Cosequently the assumption that one of the slowest step in the whole heterogeneous reaction of ammonia synthesis is the chemisorption of nitrogen on uniform or on a heterogeneous surface, the coverage of the surface consisting of adsorbed NH in equilibrium with $H_2$ and $NH_3$, is the obvious starting point for further investigations (Hossain, 1981).

### 2.3.2 Temkin-Pyzhev Equation

Temkin and Pyzhev (1939) derived a rate equation for ammonia synthesis, which brought order among kinetic data and helped correlating kinetic expressions. The following were introduced in course of their derivation:

(i) The rate of activated chemisorption of $N_2$ on the surface of the catalyst is the rate controlling step; from this it follows that the adsorbed $N_2$ is in equilibrium with $H_2$ and $NH_3$ in the gas phase.

(ii) The adsorption and desorption rates are described by the Temkin isotherm, which is based on a linear variation of activated energy of adsorption and heat of adsorption with the fraction of available surface covered.

(iii) The $N_2$ adsorption phenomena is not affected by the presence of varying amounts of $H_2$ and $NH_3$.

Temkin-Pyzhev equation (T-P equation) is given in the following form:

$$r = k_1 P_{N_2} [P_{H_2}^{3} / P_{NH_3}^{2}]^{\alpha} - k_2 [P_{NH_3}^{2} / P_{H_2}^{3}]^{\beta} \qquad (2.35)$$

where, r = the conversion rate, i.e, the difference between synthesis and decomposition rates,

$k_1, k_2$ = rate constants for synthesis and decomposition, respectively,

$\alpha, \beta$ are constants so that $\alpha + \beta = 1$

## 2.3.3 Limitation of Temkin-Pyzhev Equation and its Modification

The equation may be discussed in terms of three main points. The first of these is the exponents $\alpha$ and $\beta$. Temkin and Pyzhev suggest the value of $\alpha$ approximately equal to 0.5 for ammonia synthesis on doubly promoted iron catalysts. However, no general agreement on a constant value of $\alpha$ has been obtained by various other investigators. Brill (1951) found values of $\alpha$ of 0.6-0.7 to give the best agreement with experimental data for an unpromoted, a singly and doubly promoted catalyst. Nielsen (1968) reports that Livshits and Sidorov (1952) found good agreement with $\alpha = 0.5$. He also reports that $\alpha$ depends on the process conditions and it should vary at different points along the axes of an industrial converter. Finally he recommended a value of 0.75 for $\alpha$ in the T-P equation to give better agreement of his experimental data and data of industrial reactors.

One other point to be mentioned in the T-P equation is the analysis of Bokhoven et al. (1955). These authors evaluated experimental results of the literature and concluded that concerning the dependency of space velocity and $H_2:N_2$ ratio the T-P equation is reasonably satisfactory upto 500 atm. pressures. But the rate constants are in most cases pressure dependent.

Temkin (1950) introduced a correction term to eliminate the dependence of k on pressure and presented this equation in the modified form in terms of fugacities instead of partial pressure.

$$r = \Psi [k_1 f_{N_2} (f_{H_2}^{3} / f_{NH_3}^{2})^{\alpha} - k_2 (f_{NH_3}^{2} / f_{H_2}^{3})^{\beta} ] \qquad (2.36)$$

where, $\psi$ = correction term = exp $(\alpha \bar{V}_s - \bar{V}_a)P/RT$

$\bar{V}_s$ = partial molal volume of $N_2$ activated complex adsorbed

$\bar{V}_a$ = partial molal volume of $N_2$ adsorbed

P = pressure

T = temperature

Livshits and Sidorov (1952) used this equation and found rate constants to remain independent of pressure upto 400 atm. Nielsen, Hansen and Kjaer (1964) also did not find any pressure dependence of the rate constants within 150-300 atm. However, Mills and Bennett (1959) found little effect of this correction term in studying the reaction rates of ammonia synthesis over doubly promoted iron catalyst at 400°C and 450°C and at pressures upto 1,000 atm.

At zero or very low ammonia partial pressure, T-P equation breaks down, as it would give infinite rate. It has been shown that at low pressure far removed from equilibrium the rate is dependent on the partial pressure of nitrogen as well as arbitrary pressure of ammonia involving molecular adsorption of nitrogen and reaction with gaseous hydrogen.

$$N_2(g) + X \rightleftharpoons N_2.X$$

$$N_2.X + H_2(g) \rightleftharpoons N_2H_2.X$$

$$N_2H_2.X + H_2(g) \rightleftharpoons N_2H_4.X$$

$$N_2H_4.X + H_2(g) \rightleftharpoons 2NH_3.X$$

$$2NH_3.X \rightleftharpoons 2NH_3(g) + X \qquad \text{(II.37)}$$

The rate equation based on the above mechanism reduces to the following equation for very low concentration of ammonia.

$$r = k_1 P_{H_2}^{0.5} . P_{N_2}^{0.5} \qquad \text{(II.38)}$$

Nielsen (1968) rules out the possibility of molecular adsorption and suggest a different mechanism assuming atomic adsorption of nitrogen as well as hydrogen and rate determining step is the reaction between N and H. The rate equation derived on the basis of above mechanism is

$$r = k_1 \frac{P_{N_2}^{0.5} \; P_{H_2}^{0.5}}{1 + K_{N_2} P_{N_2}^{0.5} + K_{H_2} P_{H_2}^{0.5}} \qquad (2.39)$$

This reduces to equation (2.38) when adsorption constants $K_{H_2}$ and $K_{N_2}$ are very small.

### 2.3.4 Evaluation of Rate Constants

The reaction rate constants $k_1$ of T-P equation has been discussed in Nielsen (1968) in detail. Nielsen analyzed his data and obtained the following values of the constants.

$$k_1 = k_o \exp(-E/RT) P^{k_2}$$

$$k_o = 8.57*10^{11}$$

$$E = 45055 \pm 1493$$

$$k_2 = -0.33 \pm 0.17 \qquad (2.40)$$

It is also evident that the rate constant decreases with increase of pressure. This was reported by Livshits and Sidorov (1952) as found from investigations with original T-P equation.

But analysis with pressure influence i.e., with equation (2.40) showed that $k_o$ was independent of pressure upto 300 atm.

and showed a small decrease at higher pressures. The relation between $k_1$ and $k_o$ is given by

$$k_1 = k_o\left(\frac{a_{NH_3}^{2}}{a_{H_2}^{3}}\right)^{\beta} e^{-(\bar{V}_a - \alpha\bar{V}_s)P/RT} \tag{2.41}$$

Kjaer (1958) discussed the influence of other factors, particularly of the temperature on the rate constant. He suggested an equation of the form

$$k_1 = C_{orr}.k_{450}\,\mathfrak{F}(A.t) \tag{2.42}$$

$C_{orr}$ is the product of the factors due to the influence of pressure, inerts, poisons, aging and catalyst particle size. $\mathfrak{F}(A.t)$ is the temperature correction factor and is usually expressed in exponential form.

Dyson and Simon (1968) found the reverse rate constant explicitly as a function of temperature and recommended its application for ammonia synthesis rate at pressures 150-300 atm. with commercial catalysts.

$$k_2 = 8.849*10^{15}\exp(-80{,}899/RT) \tag{2.43}$$

Guacci (1977) et al. obtained different coefficients in rate constant equation for various catalysts and gave the following equations for two specific catalysts.

For Montecatini Catalyst:

$$k_2 = \exp(2.303*14.7102-39{,}057/RT)$$

For Haldor-Topsoe Catalyst:

$$k_2 = \exp(2.303*15.2059-42{,}893/RT)$$

### 2.3.5 Decomposition of Ammonia

The T-P equation can be also used satisfactorily for ammonia decomposition; experimental data gives a value

$$\alpha = 0.724$$

But Love and Emmett (1942) showed that the assumption that adsorption and desorption of $N_2$ are uninfluenced by adsorbed $H_2$ and NH does not hold good for ammonia decomposition on only $Al_2O_3$ promoted catalyst. And T-P equation turns out to be valid unless a negative value for $\alpha$ is assumed which cannot be acceptable. However, for a doubly promoted iron the relationship is

$$- dP_{NH_3}/dt = k_2(P_{NH_3}^{2} / P_{H_2}^{3})^{0.3} \qquad (2.44)$$

For ammonia decomposition, a number of other kinetic equations have been proposed. Winter (1931) found a rate expression for ammonia decomposition on iron catalyst:

$$- dP_{NH_3}/dt = k_2 \, P_{NH_3}^{0.9} \, / \, P_{H_2}^{1.5} \qquad (2.45)$$

Several other authors agree in the equation

$$r = k_2 P_{NH_3}^{m} / p_{H_2}^{n} \qquad (2.46)$$

m and n vary between 0.9-2.2 and 0.25-1.5, respectively.

Takezawa and Toyoshima (1966) have determined the rate of decomposition of ammonia over a well reduced doubly promoted iron catalyst. They found a decomposition rate

$$- dP_{NH_3}/dt = k_2 (P_{NH_3}/P_{H_2}^{1.5})^{0.48} \text{ (at 420°C)} \qquad (2.47)$$

$$- dP_{NH_3}/dt = k_2 (P_{NH_3}/P_{H_2}^{0.5})^{0.75} \text{ (at 479°C)} \qquad (2.48)$$

They concluded with the comment that the rate determining step changes with temperature as evident in the rate expression.

### 2.3.6 Other Mechanisms for Ammonia Synthesis

Ozaki, Taylor and Boudart (1960) have proposed a new mechanism of ammonia synthesis. Their kinetic experiments include the effect of pressure and isotope on the synthesis rate. They concluded that the rate determining step is the chemisorption of $N_2$ on a uniform or non-uniform surface and the covered surface consists of adsorbed (NH) in equilibrium with hydrogen and ammonia in gas phase. However, the state of the surface determines the relative amounts of adsorbed (N) and (NH). They also found the observed rate constant to be identical for hydrogen and deuterium. Nielsen, Kjaer and Hansen (1964) mentioned that this above fact proves that hydrogen is not a reaction partner in the slowest step of the synthesis.

Considering the nitrogen adsorption to be the slowest step, the authors determined a rate equation, out of those proposed by Ozaki et al. (1960) to give the best agreement with experimental measurements on ammonia synthesis at industrial conditions.

Boudart (1962) and earlier Ozaki et al. (1960) derived the various rate equations for ammonia synthesis. The equations are

$$\text{Uniform surface,}\quad r = \overset{\underline{N}}{\frac{k_1P_{N_2}}{[1 + KP_{NH_3}/P_{H_2}^{1.5}]^2}}; \quad r= \overset{\underline{NH}}{\frac{k_1P_{N_2}}{[1+K'P_{NH_3}/P_{H_2}]^2}} \qquad \text{--------(2.49, 2.50)}$$

$$\text{Non-uniform surface,}\quad r = \frac{k_1P_{N_2}}{[1 + K_oP_{NH_3}/P_{H_2}^{1.5}]^{2\alpha}}; \quad r= \frac{k_1P_{N_2}}{[1+K'_oP_{NH_3}/P_{H_2}]^{2\alpha}} \qquad \text{------- (2.51, 2.52)}$$

The above equations are derived on the assumption that the two site chemisorption of nitrogen is the rate-determining, but different with respect to the energy spectrum of the surface and the main species occupying the surface at synthesis conditions.

Nielsen et al. (1964) combined the four expressions into one and formulated a rate equation by introducing $\alpha$ and w. The equation takes the form:

$$r = \frac{k_1 P_{N_2}}{(1 + K_3 \; P_{NH_3}/P_{H_2}{}^{w})^{2\alpha}} \qquad (2.53)$$

Substituting activities for partial pressures and introducing the equilibrium constant of the synthesis reaction, the final form to be used in kinetic analysis is as follows:

$$r = \frac{k_1 \; a_{N_2} - k_2 \; a_{NH_3}^2 \; / a_{H_2}^3}{(1 + k_3 \; a_{NH_3}/a_{H_2}{}^{w})^2} \qquad (2.54a)$$

$$= \frac{k_2 (a_{N_2} \; K_a{}^2 - a_{NH_3}/a_{H_2}{}^3 \;)}{(1 + k_3 \; a_{NH_3}/a_{H_2}{}^{w})^2} \qquad (2.54b)$$

The rate constant $k_2$ and the adsorption equilibrium constant $K_3$ are functions of temperature. w is a new parameter and $\alpha$ has its original meaning. The temperature dependence is introduced through the equations:

$$k_2 = k_{2o} \exp \; (-E_2/RT) \qquad (2.55a)$$

$$k_3 = K_{3o} \exp(-E_3/RT) \qquad (2.55b)$$

All the values of the unknown coefficients have been found and given in tabular form by Nielsen et al. (1964). As reported, w assumes a value in the range 1.44-1.56, and the best value correlating the experiments is w = 1.50. This disproves (NH) radicals as the main species on the surfaces as it could happen when w = 1.0.

The equation (2.54b) reduces to original T-P equation with a best value of $\alpha$ of about 0.75.

The rate constant was found to be independent of pressure and it is so as the activities instead of partial pressures were used.

It is also reported that the apparent energy of activation is 42,300 kcal/kmol for use in T-P equation with $\alpha = 0.64$.

In this work, the Temkin-Pyzhev equation for rate expression (2.35) have been used.

### 2.3.7 Heat Transfer Resistances

#### Axial temperature profile:

By the analysis of the kinetic data from the isothermal reactor used by Nielsen et al. (1968) it was found that in most cases the temperature recorded in all the thermocouples in the bed was within 5°C. A weighted mean of the temperatures gives sufficient accuracy for isothermal condition. But in runs at high pressure and at high space velocity, the deviation was as high as 17°C.

## Radial temperature profiles:

Radial temperature differences are small whether the catalyst bed is cylindrical or ringshaped as reported by Nielsen (1968). It was found that if the heat transfer to the catalyst support grid is considered, the over-temperature at the center should be around 5°C. Usually a bed diameter to pellet diameter of at least ten is used to reduce the radial gradients of temperature, velocity and composition (Hossain, 1981).

## Temperature profile in Catalyst particle:

As the synthesis reaction is exothermic heat flows from the catalyst particle to the surrounding gases. Due to the flow of heat a radial temperature profile exists between the surface of the catalyst particles to their centers. These temperature gradients depend on the thermal conductivity of the catalyst particles. With an already calculated value of 3 kcal/m-hr-°C for thermal conductivity, temperature profile was estimated by Nielsen (1968). As reported in the result an appreciable over-temperature of the particles as compared with the surrounding fluid existed in the inlet zones where reaction rate is high. The temperature difference is small at a short distance into the bed and in conversion measurements these are of little consequence.

### 2.3.8 Mass Transfer Resistances

The industrial solid catalysts possess high activity and the restriction of the overall reaction rate by the finite diffusion velocity of reactants and products through the pores of the solid becomes more and more important. A summary of this aspect of the kinetics of heterogeneous catalysts is given by Wheeler (1951).

Two phenomena are characteristic for a restricted interdiffusion velocity:

(1) With increasing particle size, the activity of the catalyst decreases.
(2) In general Arrhenius plot is straight, but in the temperature zone where the diffusion rate restrict the reaction rate, the Arrhenius plot shows a bend.

Earlier work suggested that under the usual conditions ammonia synthesis reaction is too slow to be retarted by internal diffusion. This belief is supported by the results of some old experiments at 100 atm. reported by Bokhoven (1955) where Larson and Tour (1922) failed to find any influence of particle size on catalyst activity.

As reported by Bokhoven (1955), estimations by Wagner (1944) show that under industrial conditions (300 atm., 450°C, particle size 5-10 mm) restriction by internal diffusion is probable. On account of this, it was suggested that at high pressure, surface migration of the chemisorbed molecules or radicals contributes considerably to the diffusion rate through the porous catalyst.

Bokhoven and Raayan (1954) reported the results of extensive study on this subject. The results show both the phenomena mentioned above, which are characteristic of diffusional retardation. It was found that the retardation by internal diffusion decreases by increasing pressure.

The method of Wagner (1944) was reported and used to calculate the effectiveness factor, the ratio of the experimental rate constant and rate constant in absence of diffusional retardation. This ratio depends on the dimensionless number $kR^2/D_{eff}$, where k is pseudo first order reaction rate constant, R is the particle radius and $D_{eff}$ is the effective diffusivity. Comparison of the values of effectiveness factor show that this restriction is more pronounced at low pressure (upto 300 atm.) rather than at high pressure (with size upto 10 mm).

These conclusions and observations are based on laboratory studies. It is necessary that one should be aware of the possibility of retardation of the rates in industrial converters, where more favourable conditions for retardation of rates exists with the gases being less pure and the catalyst being much less active.

Lastly, it may be concluded that the Temkin-Pyzhev equation gives a reasonably representative picture of the kinetics of ammonia synthesis on a good number of catalysts especially on the technically important $Al_2O_3$-$K_2O$ promoted iron catalysts.

## 2.4 Catalysis

### 2.4.1 Active Metal Catalysts

The catalysts proposed for the synthesis of ammonia by catalytic combination of nitrogen and hydrogen are mainly the metals of groups V and VIII of the periodic table (Vancini, 1971). The first investigator was Haber, the contact materials he investigated were Uranium, Ruthenium, Osmium, Cerium, Iron, Manganese, Nickel, Tungsten, Palladium and Platinum. Most of them follows Temkin-Pyzhev equation and hence the mechanism of action is the same as for the iron catalyst. Of these Osmium and Uranium gave the most promising results technically. But these noble metals are not available in plenty and have no significance as a catalyst.

Two companies, Badische Anilin Soda Fabric (BASF) and Fixed Nitrogen Research Laboratory played pioneering role in the development of catalyst for ammonia synthesis. From the results of BASF, 30 different metals were found suitable for the technical production of ammonia (Vancini, 1971). However only pure Fe, Co, Mo and W were industrially important. There are also mixtures of these metals which are suitable for commercial yields, for example Fe:Mo=1:1 catalyst.

### 2.4.2 Promoters

After years of persistant effort in experimentation with metals it was found that no metal possesses all the properties of a practical catalyst. Better catalytic action has been affected (i) by mixing certain active metals, and (ii) by adding small quantities of inert substance to the active metals. The BASF suggested the inert substances as oxides, hydroxides or salts of alkaline earths and the rare earth metals. The fixed Nitrogen Research Laboratory mentioned the oxides of aluminium, silicon, zirconium, cerium or thorium. In all the investigations multicomponent promoters were found superior and the best. The most common catalyst for ammonia synthesis was iron with a combination of $Al_2O_3$ and $K_2O$ promoters (Catalyst Handbook, 1970).

Such catalyst

(i) increases the production of ammonia without further expenditure of energy for compression or circulation of the reaction gases.

(ii) makes possible to operate the process at low temperature. This prolongs the life of the catalysts.

(iii) is capable of maintaining a high efficiency as the pressure is increased.

(iv) simplifies the heat interchange problem, because the conversion is high and heat production is also in large proportion/amount.

(v) can be operated at pressures as high as 1500 atmospheres without suffering any appreciable lowering of efficiency.

Of the three known iron oxides, the spinal FeO, $Fe_2O_3$ yields an efficient synthesis catalyst when promoters are added. It is found in nature as magnetite and can be used directly in the syn-reaction after reduction. The mixture of oxides obtained by coprecipitation from the hydroxide is less effective. The oxides increase the catalytic activity of pure reduced iron (Vancini, 1971). Effects of two promoters are given below:

$Al_2O_3$

(i) increases the surface of $\alpha$ -iron 10-20 times;

(ii) prevents sintering and stabilizes the surface area; and

(iii) also prevents the loss of other oxide ($K_2O$) by strong bonding

$K_2O$

(i) neutralizes the acid character of $Al_2O_3$;

(ii) decreases the electron work function of iron and increases the ability to chemisorb nitrogen;

(iii) acts as a promoter only with $Al_2O_3$ and at high pressures;

(iv) favours the chemisorption of $NH_3$ at slower rate than $N_2$ chemisorption and prevents it from the rate determining step; and

(v) acts as inhibitor at low pressures or without $Al_2O_3$.

How promoters increase the catalytic activity is understandable from higher $NH_3$ yields obtainable at various promoter combinations are given below:

Pressure = 100 atm.

Temperature = 450°C

Spatial velocity = 5000 $Nm^3/(m^3\text{-hr})$

| | |
|---|---|
| Pure Fe from reduced magnetite | 5% |
| Fe + 0.4% $K_2O$ | 3% |
| Fe + 1.3% $Al_2O_3$ | 9% |
| Fe + 1.3% $Al_2O_3$ + 0.4% $K_2O$ | 13% |

Molybdenum is a poor iron promoter whereas Cu and Ni are inhibitors.

Increasing the amount of added promoters (a) increases resistances of the catalyst to sintering; (b) increases the catalytic activity upto a maximum followed by a decrease; and (c) reduces mechanical resistance of catalyst.

At temperatures and pressures above 550°C and 350 atm., a total of at least 5% $Al_2O_3$ + $K_2O$ whereas at lower temperatures and pressures 2% $Al_2O_3$ + 1% $K_2O$ are mixed for desired conversion (Bridger et al., 1947).

The effect of adding different types of oxides on catalytic activity are presented in Table 2.10 (Vancini, 1971).

## TABLE 2.10

Activity Decay of Catalyst

| Addition (2% of $Fe_3O_4$) | Soon after reduction | after many hours of operation |
|---|---|---|
| $Li_2O$ | 2.3 | 2.2 |
| $Na_2O$ | 3.2 | 3.3 |
| $K_2O$ | 2.8 | 2.9 |
| $Cs_2O$ | 1.3 | 1.3 |
| $B_2O$ | 2.5 | 2.3 |
| $M_gO$ | 3.9 | 3.0 |
| CaO | 1.6 | 0.7 |
| SrO | 1.3 | 0.6 |
| BaO | 1.6 | 0.9 |
| $B_2O_3$ | 4.3 | 1.2 |
| $Al_2O_3$ | 4.7 | 4.6 |
| $La_2O_3$ | 3.4 | 3.3 |
| $SiO_2$ | 4.9 | 4.3 |
| $ThO_2$ | 4.6 | 4.4 |
| $ZrO_2$ | 4.9 | 4.7 |
| $CeO_2$ | 4.6 | 4.4 |

Resistance to sintering can be obtained by adding either of the promoters CaO, $SiO_2$, MgO or $Cr_2O_3$ (Nielsen, 1952). However this method of obtaining resistance to sintering is at the expense of catalytic activity and should therefore be used only at high temperatures.

### 2.4.3 Physical Properties

The important characteristics of the promoted iron catalysts are (a) surface area (b) mean pore size and (c) pore size distribution. Surface area is determined either by (i) B.E.T. method or (ii) method based on sedimentation rate, gas permeability, X-ray diffraction, use of microscope or use of radioactive gases. The mean pore size and pore size distribution are determined by standard techniques such as nitrogen adsorption method or mercury penetration method.

The catalyst size for ammonia synthesis is determined by the consideration of (a) a good diffusion rate inside the catalyst pores; (b) the space inside the catalyst basket between the thermocouple protective covering and the cooling tubes should be well packed; (c) the pressure drop of the mixture should be smaller, the lower the operating pressure, and (d) the tendency to break and form dust should be hindered. (a) and (b) lead to the choice of a small catalyst size, (c) and (d) lead to the opposite choice.

Usually the catalyst size in industrial reactors having operating pressures 300 $Kg/cm^2$ is 8-15 mm, at 600-800 $Kg/cm^2$ it drops to 4-8 mm and in laboratory reactors it is reduced to 1-4 mm (Vancini, 1971).

### 2.4.4 Mechanism of Catalysis

The promoted iron catalyst is formed by very minute crystals of pure α -iron; the promoters are scattered in the crystal lattice, covering more than half of the surface. The promoters give an insulating protection to the crystals and reduces the physical structure. They can also occupy the interstices occupied by the oxygen atoms of the original magnetite.

The activity of the active centers vary both with time and space from a maximum to minimum, depending on the rate and degree of chemisorption. Hydrogen and nitrogen are chemisorbed as atoms by active centers; the mechanism of action of the iron catalyst may be represented by the following (Vancini, 1971):

$$:N:::N: \rightleftharpoons 2.\ddot{N}._{ads}$$

$$H:N \rightleftharpoons 2H._{ads}$$

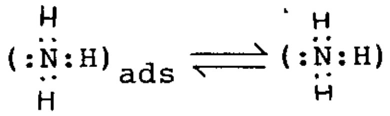
$$(.\ddot{N}.\ )_{ads} + H._{ads} \rightleftharpoons (.\underset{\cdot}{\ddot{N}}:H)_{ads}$$

$$(.\underset{\cdot}{\ddot{N}}:H)_{ads} + H._{ads} \rightleftharpoons (.\underset{\cdot\cdot}{\overset{H}{\ddot{N}}}:H)_{ads}$$

$$(.\underset{\cdot\cdot}{\overset{H}{\ddot{N}}}:H)_{ads} + H._{ads} \rightleftharpoons (:\underset{H}{\underset{\cdot\cdot}{\overset{H}{\ddot{N}}}}:H)_{ads} \qquad (2.56a)$$

.dot indicate the valence electrons

The desorption reaction is given by:



$$(:\underset{H}{\overset{H}{\ddot{N}}}:H)_{ads} \rightleftharpoons (:\underset{H}{\overset{H}{\ddot{N}}}:H) \qquad (2.56b)$$

## 2.4.5 Preparation of Catalyst

The properties of an ammonia catalyst of the iron type may be modified by adding promoters or other foreign materials to it; therefore close control of chemical composition and accurate method of preparation are necessary for an active product. The preparation of a promoted catalyst involves two steps:

(1) the preparation of an iron oxide combined with suitable promoters and

(2) its reduction by hydrogen.

The second step is done by $H_2$-$N_2$ mixture prepared for the synthesis reaction. The second step is easier; the first step involves the real problem.

Magnetite is mainly used for catalyst preparation. The characteristics of magnetite are:

(i) It is spinel in structure with elementary cell containing 32 oxygen ions, forming octahedral and tetrahedral interstices.

(ii) Half the $Fe^{+3}$ is distributed in 16 octahedral interstices and an equal number of $Fe^{+2}$ is distributed in 8 tetrahedral interstices.

(iii) Heat of formation according to the reaction:

$$3Fe(s) + 2O_2(g) \longrightarrow Fe_3O_4(s)$$

$$\Delta H_f{}^\circ = -266{,}700 \text{ kcal/kmol}$$

(iv) Free energy of formation:

$$\Delta F^\circ = -242{,}500 \text{ kcal/kmol}$$

Both natural and artificial magnetite can be used for $NH_3$ synthesis catalyst; but the latter contains less impurities and gives the most satisfactory results. It can be obtained by burning pure iron in an oxygen atmosphere. The iron oxide is then fused with promoter under rigid control on chemical composition of the oxide mixture. The oxide cannot be melted in any crucible; even refractory materials get contaminated. The method so far suggested consists in fusing in a protecting bed of the same material, promoters are readily added to the iron oxide in this fusion.

To obtain the spinel structure, two iron oxides $Fe_2O_3$, FeO must be grinded and remelted at about 1500°C in an electric induction furnace. The structure is stabilized by cooling in steam bath.

Finally crystallised iron is obtainable by reducing ferrocyanide complexes. Iron metal thus formed consists of $\alpha$ -Fe with little $\gamma$ -Fe and its activity is fairly good.

### 2.4.6 Reduction of Catalyst

Magnetite is reduced to pure iron by hydrogen (in practice by $N_2 + 3H_2$) according to the reaction

$$1/4Fe_3O_4(s) + H_2(g) \rightarrow 3/4Fe(s) + H_2O(g) \qquad (2.57)$$

$\Delta H = 8500$ kcal/kmol

TABLE 2.11

Equilibrium constants for the reaction : $K_p = p_{H_2O}/p_{H_2}$

| Temperature (°C) | $K_p$ |
|---|---|
| 200 | 0.013 |
| 300 | 0.044 |
| 400 | 0.107 |
| 500 | 0.214 |

The reaction towards the right is little influenced by pressure and greatly influenced by temperature as the reaction is endothermic. During reduction a linear increase in surface area and pore volume occurs. The reaction is carried out with hydrogen in very large excess and at condition far away from equilibrium and the rate is very high. The empirical rate equation (Hall et al., 1950) is

$$r' = k\ (O)^{2/3} \qquad (2.58)$$

where (O) is the oxygen content in the partially reduced catalyst.

The value of k is reduced by promoters especially by $K_2O + Al_2O_3$. The reduction is enhanced by the addition of copper and nickel oxides, which also reduces the activity. Reaction is carried out at low pressures (50 $kg/cm^2$) and at high spatial velocity (above 5000 $Nm^3/hr\text{-}m^3$). The latter condition decreases the formation of water vapour and thus prevents the synthesis reaction from inhibition and the catalyst from poisoning.

The reduction rate and the activity are increased by increasing spatial velocity. At the advanced stage of the reaction, the temperature is raised to increase the rate considerably; however, the maximum value is lower than the synthesis temperature. The pressure can be lower or higher and the $N_2 + 3H_2$ should be as free from moisture as possible.

A typical data on reduction of an iron catalyst with promoters $Al_2O_3 + K_2O$ is given below (Vancini, 1971):

| | |
|---|---|
| Pressure | 100-200 $kg/cm^2$, in systems at moderate pressure<br>300-400 $kg/cm^2$, in systems at higher pressure |

| | |
|---|---|
| Temperature | 24 hr at 300-350°C<br>24 hr at 350-400°C<br>then for a few days at 340-450°C |
| Spatial velocity | 48 hr at 5,000 $Nm^3/(hr\text{-}m^3)$<br>(or as high as possible)<br>then at 10,000 $Nm^3/(hr\text{-}m^3)$<br>(or as high as possible) |

Under the above conditions, the reduction is not lower than 95%; the catalyst weight loss is 25%.

The reduction can be carried out in the synthesis column, and then start producing ammonia with adjusting the pressure and spatial velocity. However, the economic method is to run the reduction reaction separately and dry the mixture over activated alumina before adding to the catalyst. This is again unfortunate because of the pyrophoric nature of the reduced catalyst. It can be made non-pyrophoric by passing $NH_3$ over it at 450°C (Burnett et al., 1953). Another method involves passing a mixture of $N_2 + 3H_2$, with 0.2 - 0.5% air over the catalyst. A third method is to keep the catalyst at 200°C for a while under $N_2$ stream. But the safest and most practical method consists of oxidizing the catalyst surface with a nitrogen stream containing 0.1 - 0.2% $O_2$ at a pressure 2-5 $kg/cm^2$ and at temperature lower than 150°C.

## II.5 Reactors and Reactor Models

In the synthesis process of ammonia different types of reactors are used, each characterized by its working pressure and temperature, space velocity, flow pattern and heat transfer arrangement. The following are the types of ammonia reactors (Hossain, 1981):

1. Quench Converter
2. T.V.A. Converter
3. NEC Converter
4. Fauser-Montecatini Converter
5. Haber-Bosch-Mittasch Converter
6. Mt. Cenis Converter
7. Uhde Converter
8. Casale Converter
9. Radial Flow Converter
10. Claude Converter

### II.5.1 Reactor Models

Mathematical modelling is the mathematical representation of a physical system. Its ultimate aim is to predict the process behaviour under different sets of operating conditions for working out a better strategy to control the process. Mathematical modelling costs less money and time (Hussain, 1986). Mathematical models for simulation studies have been developed by many workers. Singh and Saraf (1979) carried out simulation studies for ammonia synthesis reactors having adiabatic catalyst beds as well as authothermal reactors. A workable method to calculate diffusion effects within the catalyst pores has been developed. Suitable rate equations have been selected to describe the ammonia synthesis rate over the catalysts of different make. The simulation model gives an insight into the physical and chemical process in the reactor. A method to evaluate the effectiveness factor is developed and used in the model calculations.

The authors used a modified form of the Temkin equation.

$$r_{NH_3} = k_2[K^2 f_{N_2} (f_{H_2}^{\ 2}/f_{NH_3}^{\ 3})^{\alpha} - (f_{NH_3}^{\ 2}/f_{H_2}^{\ 3})^{1-\alpha}] \qquad (2.59)$$

They used the values of $\alpha$ and expression for $k_2$ from the published work of Guacci (1977). The values used for Montecatini- Edison Catalyst:

$\alpha = 0.55$, $E_2 = 39057$ kcal/kmol

$k_2 = \exp(2.303*14.7102-39057/RT)$

and for Haldor - Topsoe Catalyst:

$\alpha = 0.692$, $E_2 = 42983$ kcal/kmol

$k_2 = \exp(2.303*15.2059-42953/RT)$

The rate expressions are extended for large size industrial catalyst particles (6-12mm) by taking account of the diffusion effects. The authors solved for the following models of ammonia synthesis reactor, Figure 2.2 shows the schematic diagram of the reactors.

### Adiabatic Catalyst Bed

Material balance equation is

$$dx/dV = \eta\, r_{NH_3}/G \tag{2.60}$$

Heat balance equation is

$$dT/dV = (-\Delta H/C_p)\ (\eta\, r_{NH_3}/G) \tag{2.61}$$

x is the extent of reaction defined by

$$g_j = g_{jo} + \alpha_j\, m_j\, x \tag{2.62}$$

### Nonadiabatic Catalyst Bed

Material balance equation (2.60) holds for this case also. The heat balance is described by the equations:

$$dT_g/dV = UA(T-T_g)/G\bar{C}_{pg} \quad \ldots\ldots \tag{2.63}$$

$$dT/dV = (-\Delta H/C_p)(\eta\, r_{NH_3}/G) - UA(T-T_s)/G\bar{C}_p$$

$$= (-\Delta H/C_p)\ (\eta\, r_{NH_3}/G) - (dT_g/dV)(\bar{C}_{pg}/\bar{C}_p) \tag{2.64}$$

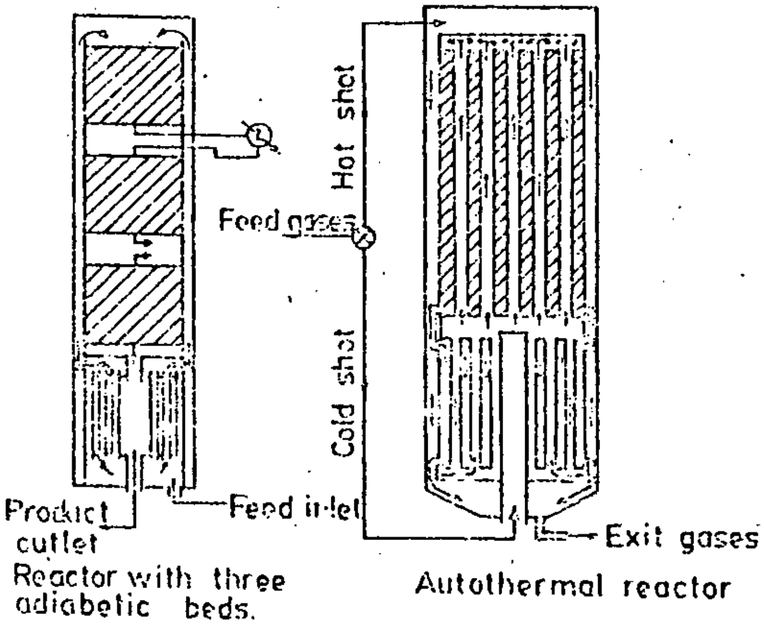


Figure 2.2 Schematic diagrams of a three-bed reactor and an autothermal reactor for synthesis of ammonia.

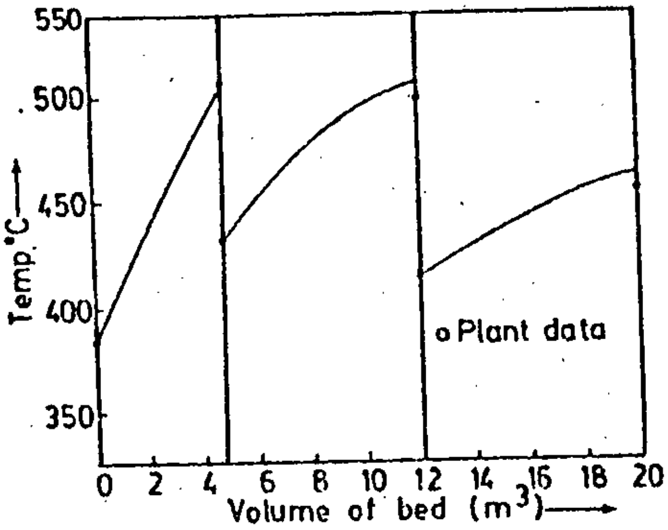


Figure 2.3 Temperature profile in a triple-bed ammonia synthesis reactor.

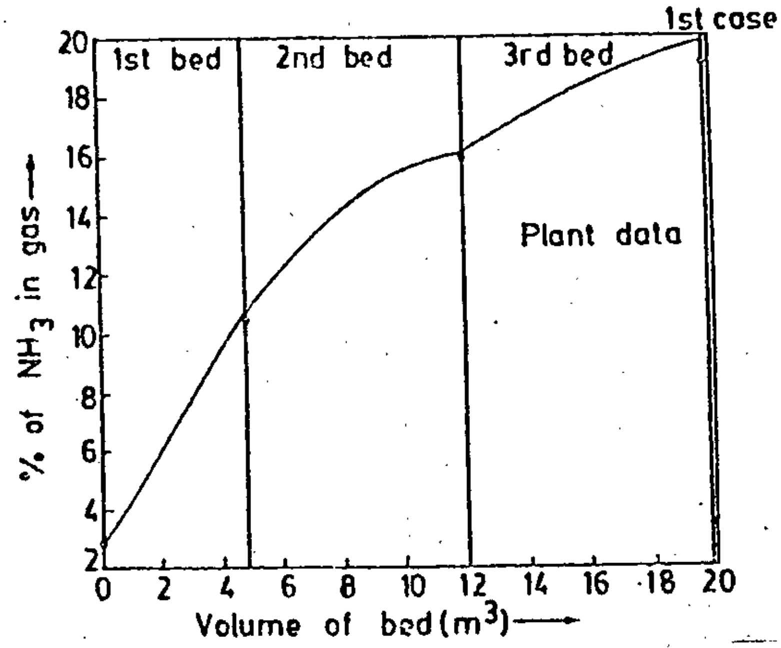


Figure 2.4 Ammonia concentration profile in a triple-bed synthesis reactor.

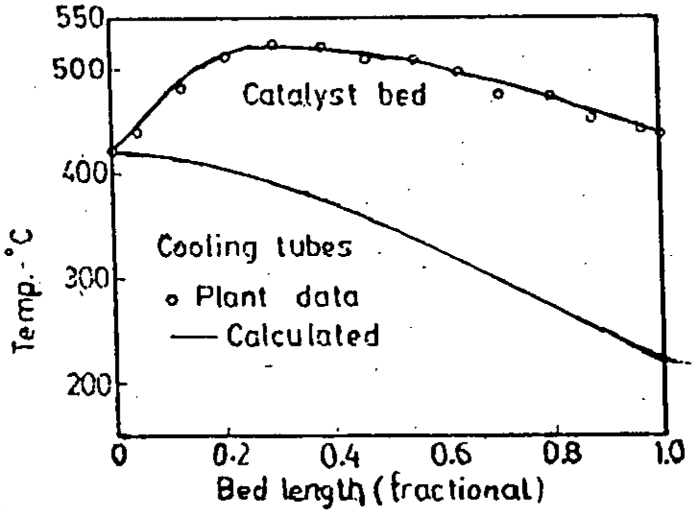


Figure 2.5 Temperature of synthesis gas in catalyst bed and cooling tubes along the length.

U used in this work is 400 kcal/(hr-in$^2$-°C). The equilibrium constant K is obtained from the Gillespie and Beattie equation (1930). The fugacity coefficients are calculated by means of the Cooper's (1967) expression for nitrogen and hydrogen and by Newton's (1935) expression for ammonia.

Each adiabatic reactor has three catalyst beds. The results are presented in figures 2.3 and 2.4 in terms of temperature and ammonia percent profile along the beds. The temperature profile for autothermal reactors are shown in fig.2.5. In al cases, comparison with plant data and simulation model shows very good agreement.

Gaines (1977) developed a steady-state model for a quench-type ammonia converter and studied the effects of process variables upon converter efficiency over large range of operating conditions. Process variables investigated were pressure, catalyst activity, space velocity, $H_2$-$N_2$ ratio, feed temperature, concentration of inerts and ammonia in converter feed. A substantial improvement in converter efficiency is possible by maintaining optimal temperatures and this value may be determined from effluent concentration and equilibrium concentration. Finally they proposed a simple method for optimum temperature control to obtain better efficiency. A schematic diagram of the converter is shown in figure 2.6. Figure 2.7 gives a block diagram representation.

The equilibrium constant is calculated from equation (2.21) and activity coefficients used to calculate activities are computed from equation (2.25). The reverse rate constant is

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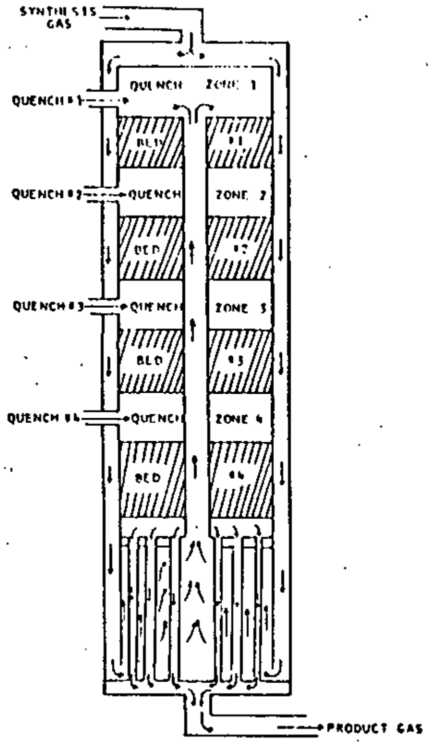

Figure 2.6 Synthesis converter.

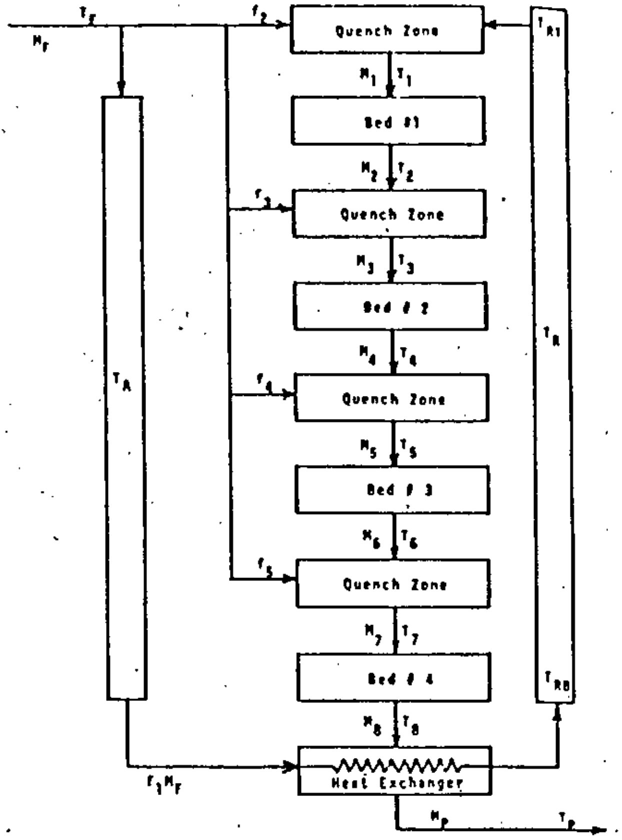

Figure 2.7 Block diagram of synthesis converter.

computed from equation (2.43). Material and energy balance are developed on the basis of the following assumptions:

(i) the catalyst section is nearly adiabatic,

(ii) the radial temperature distribution is nearly uniform,

(iii) the velocity profile in the bed is uniform, as the bed diameter is much larger than the catalyst diameter,

(iv) the pressure varies linearly with the fraction of catalyst traversed.

## Material Balance

The hydrogen consumed in a differential element of a catalyst bed is given by

$$F_1 dx_1 = rAdZ \tag{2.65}$$

Component flow equations are

$$F_{c1} = F_1(1-x_1)$$

$$F_{c2} = F_2 - F_1 x_1/3$$

$$F_{c3} = F_3 + 2F_1 x_1/3$$

$$F_{c4} = F_4, \; F_{c5} = F_5 \tag{2.66}$$

## Energy Balance

The converter may be divided into three sections: catalyst beds, quench zones and heat exchanger. The energy balance equations for a differential element of catalyst bed involves four heat terms:

$$dQ_{reaction} + dQ_{gas} + dQ_{riser} + dQ_{annulus} = 0$$

$$-\frac{2}{3}\Delta HF_1 dx_1 - F_1 C_p dT - UC(T - T_r)dZ + k'\ C'\ \frac{(T - T_a)}{dZ} = 0$$

$$\text{---------} \qquad (2.67)$$

The energy balance for the reacted gas in the shell side of the heat exchanger is

$$F_C C_p dT_s = UA'\ (T_s - T_t)dZ \qquad (2.68)$$

The energy balance for the feed gas in the heat exchanger tubes is

$$f_1 F_1 C_p dT_t = -UA'\ (T_s - T_t)\ dZ \qquad (2.69)$$

Gaines has given an algorithm to solve the set of equations (2.65-2.69). The base case for the simulation study is given in Table 2.12.

## TABLE 2.12

## BASE CASE FOR SIMULATION OF SINGLE CONVERTER

| | |
|---|---|
| Inlet pressure | 140 atm |
| Outlet pressure | 140 atm |
| Feed temperature | 290°F |
| $H_2$ feed | 10,243 lb-mole/hr |
| $N_2$ feed | 3,414 lb-mole/hr |
| $NH_3$ feed | 330 lb-mole/hr |
| Ar feed | 727 lb-mole/hr |
| $CH_4$ feed | 1,817.5 lb-mole/hr |
| Fraction feed through exchanger | 0.58 |
| Fraction feed for first bed quench | 0.03 |
| Fraction feed for second bed quench | 0.12 |
| Fraction feed for third bed quench | 0.12 |
| Fraction feed for fourth bed quench | 0.15 |
| Outlet temperature of bed 1 | 897.9°F |
| Outlet temperature of bed 2 | 891.8°F |
| Outlet temperature of bed 3 | 880°F |
| Outlet temperature of bed 4 | 859.5°F |
| Mole fraction inerts in converter feed | 0.154 |
| $H_2/N_2$ ratio | 3.0 |
| Mole fraction ammonia in feed | 0.02 |
| Mole fraction ammonia in effluent | 0.1265 |

------

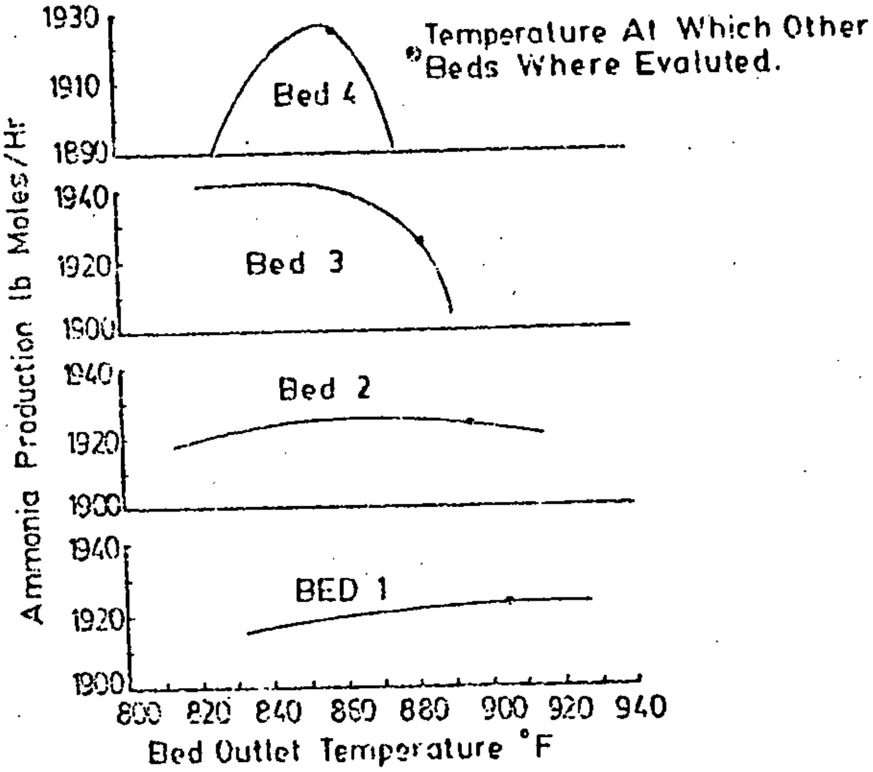

Figure 2.8 Ammonia production vs. bed outlet temperature.

Figure 2.8 shows the effect of temperature upon production in the four bed quench converter. The effect on the first two beds is very slight; the effect in the third bed is much if the temperature is too high. At high temperature the reaction rate is decreased and so conversion is less in the bed. This less conversion and additional quench reduces considerably the concentration of ammonia into the fourth bed. Therefore to avoid a substantial decrease in production, the third bed temperature should not be allowed to exceed by 20-30°F to that of the fourth bed.

The fourth bed temperature is of the greatest importance; this was also reported by Stephens (1975). A series of simulation was done for the said process variables and these effects can be related to the fourth bed temperature. By adjusting the quench flow a declining temperature profile was found for the fourth bed. This temperature was very sensitive to the fraction of feed through the exchanger. Simulation calculations were completed with the obtainment of maximum converter efficiency

Some of the more important results of the simulation study are as follows:

(i) For the same temperature, increase in pressure increases the ammonia outlet concentration as well as equilibrium concentrations. For the same pressure, both outlet concentration and equilibrium concentration decreases with the increase of feed temperature.

(ii) For the same temperature, ammonia outlet concentration as well as equilibrium concentration decreases with increase in inert content in the feed. For the same inert percentage, the effect of temperature is the same as (i).

(iii) Higher equilibrium concentration is obtainable at $H_2:N_2 = 3:1$ whereas 2.5:1 ratio gives higher converter efficiency.

(iv) The feed temperature has little effect upon the converter efficiency, although conversion is increased slightly at lower temperature.

(v) The ammonia content of feed slightly increases the effluent ammonia concentration with a net decrease in conversion.

(vi) Low space velocity gives higher ammonia outlet concentration approaching equilibrium value, with a decrease in production rate.

(vii) More active catalyst gives better ammonia percentage and therefore converter efficiency decreases with activity of the catalyst particles.

(viii) Simulation suggests a fourth bed temperature in the range 850°-870°F for maximum converter efficiency.

On the basis of the results obtained, the author proposed a control system to maintain/control the fourth bed temperature for the improvement of converter efficiency.

The Tennessee Valley Authority reactor (TVA reactor) is a particular design of a Haber-Bosch reactor. Slack, Allgood and Maune (1953, 1976) described the operating characteristics of a TVA reactor. They reported the process variables as the temperature of the feed, reactor pressure, ammonia and inert content of the feed gas, hydrogen and nitrogen in the feed.

Investigation results are as follows:

(i) the reactor stability decreases with the increase of space velocity; the reactor blows off and ammonia concentration decreases monotonically,

(ii) for maximum production of ammonia, an optimum value of feed temperature exists,

(iii) the temperature profile passes through a maximum, called the "hot spot" or "peak temperature",

(iv) both the optimum temperature and peak temperature vary with the process variables and catalyst activity,

(v) with less active catalysts, a higher value in average feed temperature is necessary for better ammonia production and to avoid instability.

Van Heerden (1953), Beutler and Roberts (1956) and Annable (1962) have derived one dimensional mathematical models to study the steady-state behaviour of Haber-Bosch type reactors. They derive the model equations allowing temperature and compositions variations in the logitudinal directions only. Their simulation results were supported by experimental results; however none of them investigated the effect of operating and design variables on the production, stability and temperature profiles in the reactor. Kjaer's (1963) model consists of three partial differential equations and are derived allowing for temperature variations in both axial and radial directions. The temperature and concentration profiles were computed for only one set of operating conditions. The agreement of these results with plant data was good.

Steady-state simulation of a TVA ammonia synthesis converter has been made by Baddour, Brian, Logeais and Emery (1965). A mathematical model for the reactor was formulated and the effects of operating and design variables on

(i) the optimum feed temperature,
(ii) the stability of the reactor and
(iii) the temperature profiles in the reactor

were investigated using the simulation model. The operating variables reported were; space velocity, ammonia and inert content of the feed and catalyst activity. The design variable was the heat conductance per unit volume of the reactor between the reacting gas and the gas in the cooling tube. The range of parameters are presented in Table 12.13.

## TABLE 2.13

Parameters and range of Variations

| Parameter | Lower Limit | Standard | Upper Limit |
|---|---|---|---|
| Space velocity, $V_o$ $(hr)^{-1}$ | 9000 | 13,800 | 18,000 |
| Ammonia in feed, $y_{NH_3}$ | 0.01 | 0.05 | 0.10 |
| Inert in feed, $y_{int}$ | 0.01 | 0.08 | 0.15 |
| Catalyst activity, f | 0.4 | 1.0 | 1.0 |
| Total heat conductance, U*S | 30,000 | 35,000 | 80,000 |

A one-dimensional mathematical model was developed for the TVA ammonia synthesis converter (Baddour et al., 1965). The assumption made were:

(i) no temperature and concentration gradient in the radial direction,

(ii) the pressure in the reactor is constant,

(iii) the temperature of the gas flowing through the catalyst is equal to the temperature of the catalyst particles.

(iv) no heat and mass diffusion in the longitudinal direction,

(v) the heat capacity of the gas is independent of temperature and the effect of pressure on enthalpy is negligible.

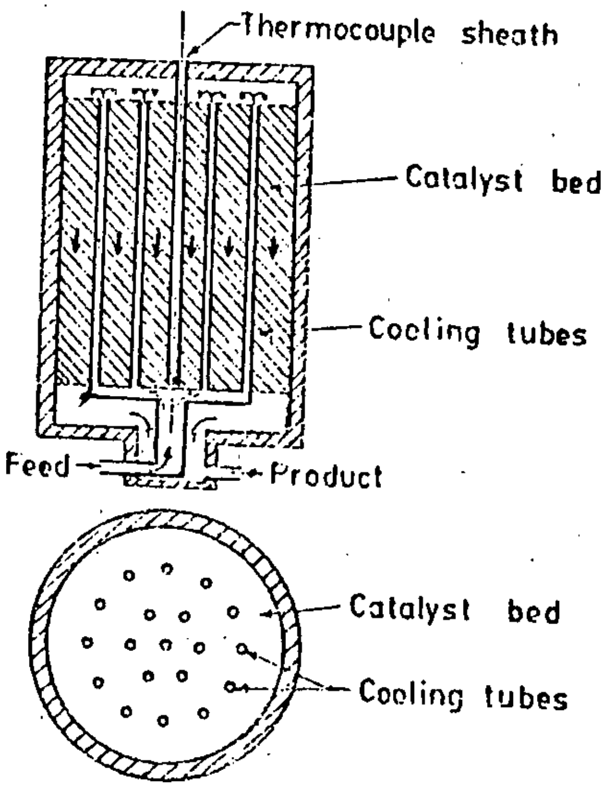

Figure 2.9 The countercurrent cooled tubular reactor.

The TVA reactor is shown in figure 2.9 and its idealized representation for mathematical model is shown in figure 2.10. The empty tube section represents the gas inside the cooling tubes and the catalyst section includes the catalyst particles and the gas flowing through them. The temperature T and $T_c$ vary longitudinally in both direction.

Temkin-Pyzhev equation with constants obtained from Sidorov's experimental results were used. The equation for reaction rate becomes a unique function of temperature and gas composition, as mass transfer and pore diffusion resistances were neglected.

A material balance around a differential slice of catalyst section and enthalpy balance in the empty tube section and in the catalyst section characterises the steady-state behaviour of the TVA reactor and comprises the mathematical model. Equation are presented in the dimensionless forms.

(a) Material balance:

$$\frac{dx}{d\alpha} = \left\{ \left( \frac{fA}{T_{top}^{*} V_0} \right) \left( \frac{1}{T_c} \right) \exp \left[ \left( -20{,}300 / T_{top}^{*} \right) \left( \frac{1}{T_c} \right) \right] \right.$$

$$\left. \left[ (K_p P)^2 A (B - x)^{1.5} (b - x) / x - \frac{Dx}{(B - x)^{1.5}} \right] \frac{(1+x)^2}{1+x^{*}} \right\} \qquad \text{---} \quad (2.70)$$

(b) Energy balance in the empty tube section:

$$dT/d\alpha = (US/F\,\Delta C)\;(\Delta C/\bar{C}_{po})\,(T_t - T_c) \qquad (2.71)$$

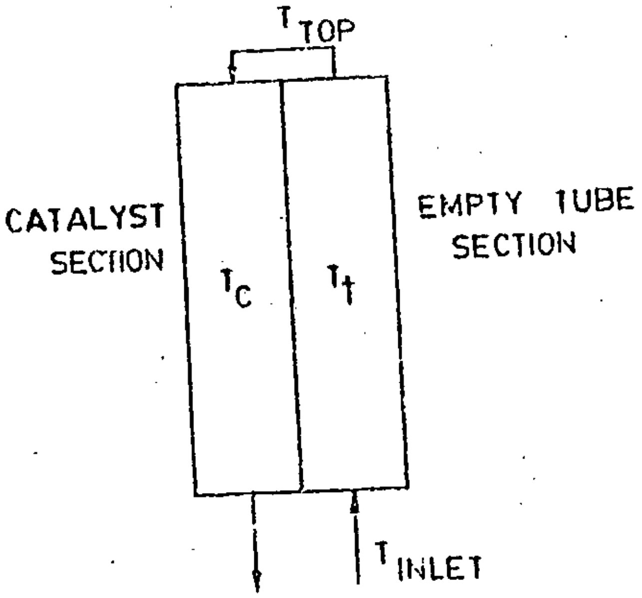

Figure 2.10 Lumped model of T.V.A. reactor.

(c) Energy balance in the catalyst section:

$$\left[1-\frac{\Delta C}{C_{P_0}}\left(\frac{x-x^*}{1+x}\right)\right]\frac{dT_t}{d\alpha}+\left(\frac{US}{F\Delta C}\right)\left(\frac{\Delta C}{C_{P_0}}\right)\left(T_c-T_t\right)$$

$$-\left[\frac{(-\Delta H_0)-T_b^*\Delta C}{T_{up}^*\, C_{P_0}}+\left(\frac{\Delta C}{C_{P_0}}\right)T_c\right]*\frac{1+x^*}{(1+x)^2}\frac{dx}{d\alpha}=0$$

---- (2.72)

where $y_{NH_3}$, $y_{H_2}$, $y_{N_2}$ = inlet mole fractions of $NH_3$, $H_2$, $N_2$ respectively

$f$ = catalyst activity factor

$P$ = pressure (assumed constant)

$K_p$ = equilibrium constant, $atm^{-1}$

$\alpha$ = length of the reactor

$$A = (1.5 - y_{H_2})\frac{0.5 - y_{N_2}}{(1 + y_{NH_3})^{2.5}}$$

$$B = (y_{H_2} + 1.5\, y_{NH_3})/(1.5 - y_{H_2})$$

$$b = (y_{N_2} + 0.5\, y_{NH_3})/(0.5 - y_{N_2})$$

$$D = (1 + y_{NH_3}) \,/\, (1.5 - y_{NH_3})^{1.5} \qquad (2.73)$$

In the above equations the temperature is normalized with respect to the temperature at the top of the reactor where the gas reverses its direction to enter the catalyst section.

The boundary conditions associated with the model are specified at the top of reactor by: at $\alpha = 0$, $T_c = 1$, $T_t = 1$, $x = x^*$. The system of ordinary differential equations was solved by using Runge-Kutta formulas, with increment sizes

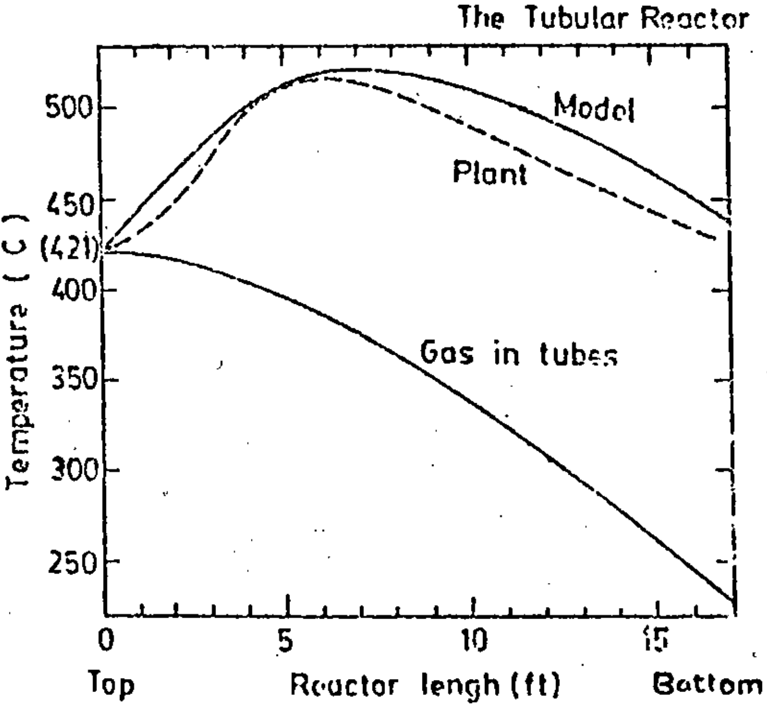

Figure 2.11 Comparison of solution of simulation model and actual ammonia converter temperature profile

$\Delta \alpha = 0.05$ for $0 < \alpha < 0.5$

$\Delta \alpha = 0.10$ for $0.5 < \alpha < 1.0$

The computed results were compared with plant data provided by Allgood (1953) obtained in a converter 17 ft. long with a catalyst volume of 144 ft³. The operating variables used in the model and in the plant are given below:

| Parameter | Actual Converter | Model |
|---|---|---|
| $H_2$ mole fraction in feed | 0.625 | 0.6375 |
| $N_2$ mole fraction in feed | 0.219 | 0.2125 |
| $NH_3$ mole fraction in feed | 0.052 | 0.050 |
| Inert mole fraction in feed | 0.079 | 0.080 |
| Space velocity($hr^{-1}$) | 13,800 | 13,800 |
| Pressure, atm | 286 | 300 |
| Catalyst volume, ft³ | 144 | 144 |

A value of heat transfer conductance, U*S, equal to 55,000 Btu/hr°F was found to give the best fit between the temperature profiles. And this is close to the value 57,300 obtained by calculations.

Typical temperature profiles are shown in figure 2.11 for both model data and plant data. Figure 2.12 shows the variation of production rate with top temperature for a fixed feed composition. With the standard space velocity of 13,800, it is clear that the optimum is about 425°C. By increasing the flowrate so that the space velocity is 18,000, a greater production can be

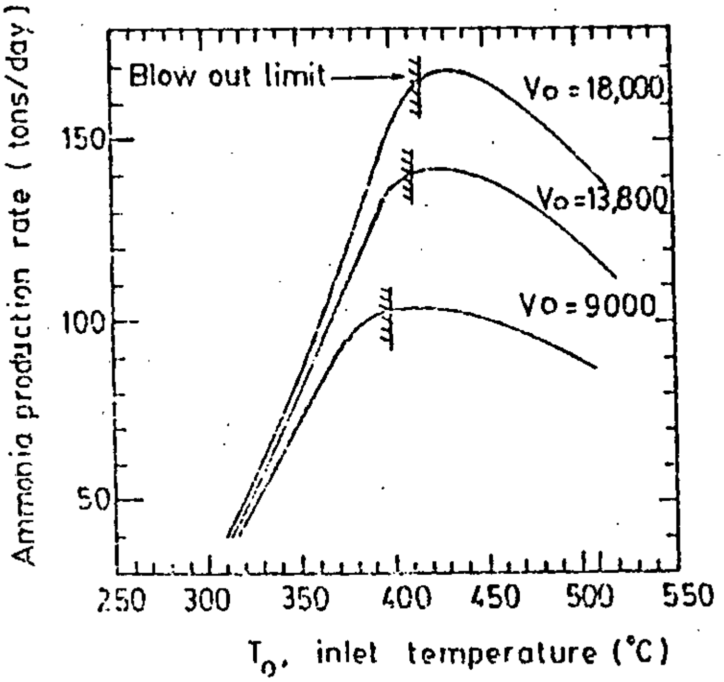

Figure 2.12 The variation of production with $T_O$ for several flow rates.

achieved with $T_{top}$ = 430°C; but it is somewhat more sensitive to a change in top temperature. A decrease in flowrate lowers the production and makes it less sensitive to variations in temperature.

An analogous result is found with the ammonia content of the feed. The production rate of the TVA reactor is quite sensitive to the change in ammonia mole fraction in the feed gas and much less sensitive to changes in the inert content of the feed gas. A decrease in catalyst activity decreases the production rate and requires the reactor to be operated at higher temperature. Furthermore, at low catalyst activity, the production rate is more sensitive to changes in top temperature. The Stanton number has been found to have a small effect on production and the range of Stanton number for maximum production is flat. Aris (1969) reported the effect of variables on production by tabulating the sensitivities. Sensitivity has been defined in the following fashion,

$$\sigma = \frac{\Delta P/P}{\Delta q/q} \qquad (2.74)$$

where P is the production for a parameter of value q and $\Delta$ P is the change in production due to a change in $\Delta q$ in q. From the calculation of Baddour about the base condition, the following sensitivities of the maximum production rate can be summarized:

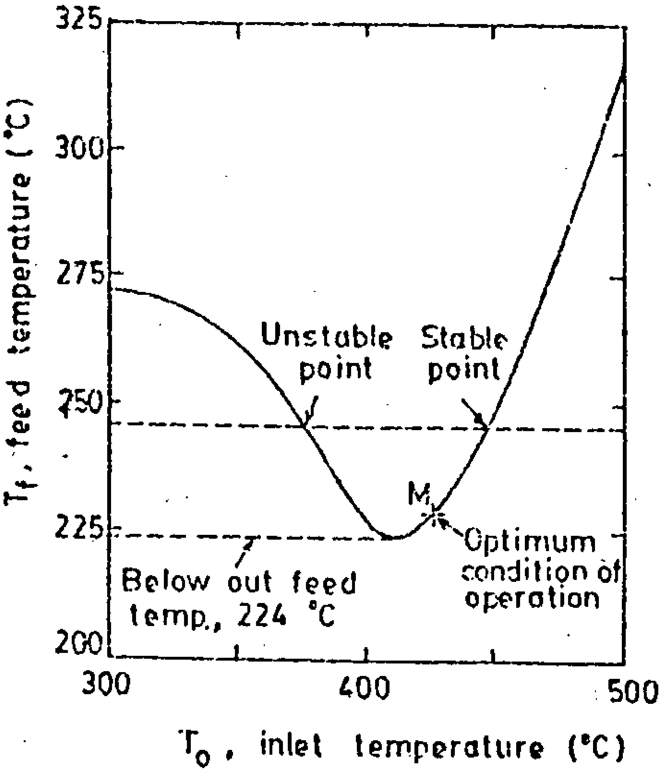

Figure 2.13 Variation of $T_f$ with $T_o$.

| Operating variables | Standard value | Sensitivity |
|---|---|---|
| Space velocity | 13,800 1/hr | 0.7 |
| Inlet $NH_3$ mole fraction | 0.05 | -0.30 |
| Inert mole fraction | 0.08 | -0.15 |
| Catalyst activity | 1.00 | 0.35 |

----

Baddour's calculation give important information on the stability of the reactor. If a value of $T_o$ is chosen and the value of feed temperature $T_f = T_o(L)$ is calculated then for this value of $T_f$, the value of $T_o$ will be chosen and the profile as calculated. If these calculations are made for several values of $T_o$, all others parameters being kept constant, then $T_f$ can be plotted against $T_o$, and for any prescribed $T_f$, the unknown $T_o$ can be read off. Figure 2.13 shows the results of Baddour's calculations on the standard case and it is at once evident that for $T_f$ between 224°C and 270°C there can be two values of $T_o$. The smaller of these is unstable because the slope of the curve is negative here and an increase in $T_f$ actually decreases $T_o$. The minimum feed temperature of 224°C is called the blow-out feed temperature for there is no intersection on the figure at all. Stable operation which is also profitable is to be found only on the part of the curve to the right of the minimum. The maximum production rate actually corresponds to the point M. The feed temperature below which the reaction will not sustain itself is obviously of great importance: the hatched line in figure 2.12 shows the variation of this for three different space velocities.

The sensitivities of the blow-out feed temperature to various parameters based on Baddour's calculations has been summarised by Aris as follows:

| Operating variables | Standard value | Sensitivity |
|---|---|---|
| Space velocity | 13,800 | 0.10 |
| Inlet $NH_3$ mole fraction | 0.05 | 0.028 |
| Inlet inert mole fraction | 0.08 | 0.015 |
| Catalyst activity | 1.00 | -0.09 |
| Heat transfer conductance or Stanton Number | 55,000 Btu/hr°F | 0.74 |

Another operating variable of importance is the peak temperature which is about 529°C. The sensitivity of the peak temperature as given below shows its relative insensitivity to different variables.

| Operating variables | Standard value | Sensitivity |
|---|---|---|
| Inlet $NH_3$ mole fraction | 0.05 | -0.04 |
| Inlet inert | 0.08 | -0.02 |
| Activity | 1.00 | -0.04 |
| Heat transfer conductance | 55,000 Btu/hr°F | +0.076 |

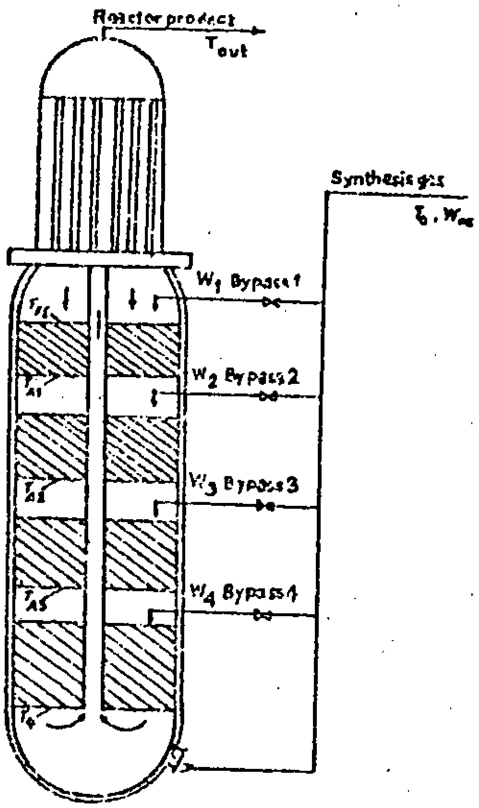

Figure 2.14 Reactor for ammonia synthesis.

Lutschutenkow et al. (1978) investigated the reactor sensitivity to changes in perturbation and control variables over a broad operating range. They also estimated and analysed the reactor properties and showed them as a basis for structural and parametric synthesis of the control system.

The reactor under consideration consists of a high pressure shell, the catalyst section consist of four packed beds and heat exchanger. The feed is divided into two streams before reaching the reactor. The larger stream is directed through slotted chambers to cool the high-pressure shell. It is then preheated in the heat exchanger; from which it enters the first catalyst bed. The second part of the feed stream is further separated by bypasses. It provides fresh feed gas and cooling of the synthesis gas between the catalyst beds and it establishes the temperature required for ammonia synthesis in the reactor. The reactor is shown in figure 2.14.

On the basis of the following assumptions the equation of mass, energy and momentum were written as the steady-state mathematical model of the fixed bed reactor:

1. Catalyst and feed gas can be considered as a quasi homogeneous phase.
2. The pressure gradient along the length of the reactor can be disregarded. This obviates the necessity for the momentum balance.
3. There is no gas mixing in the axial direction.

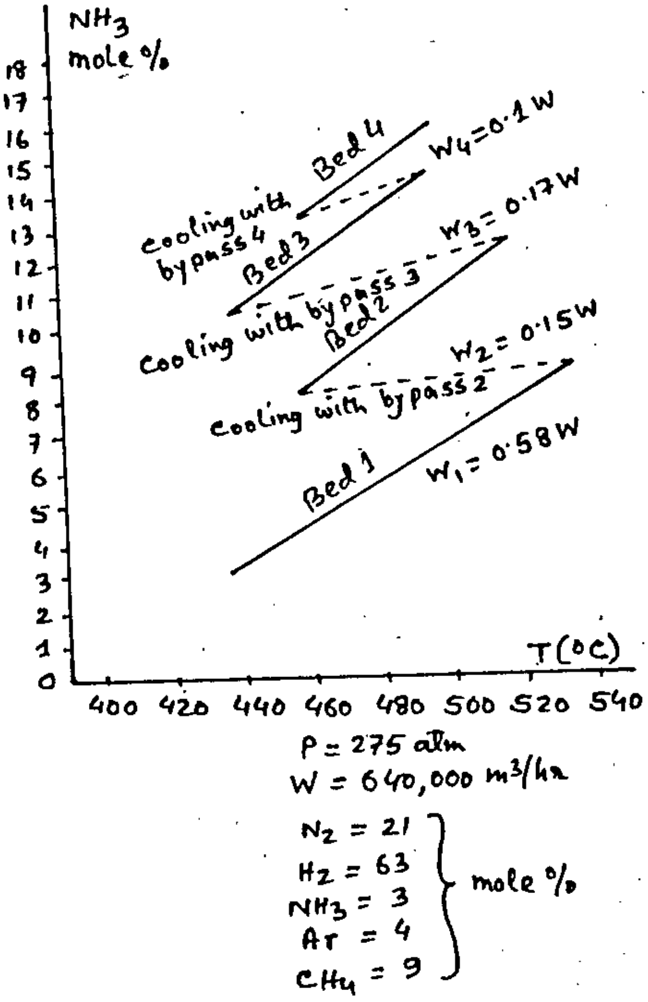

Figure 2.15 Reactor temperature and concentration profiles.

4. There is complete radial mixing.
5. There is no heat exchange in the axial direction.
6. Because the reactor model is well insulated, there is no heat loss.

The reactor model consists of a set of ordinary differential equations for the contact beds along with the necessary constraints, equation for the mixing of the gas streams and heat and mass balance equations for the heat exchanger.

The set of equations was solved on a computer and computed profiles for temperature and concentration in the reactor are shown in figure 2.15.

Investigation of the sensitivity of the operational behaviour of the four-stage reactor for ammonia synthesis produced the following results:

1. Productivity as function of control variables has a very pronounced extremal nature.

2. Maximum productivity is near the autothermy limit.

3. There is no way to control independently the exit temperature from the i-th bed with the i-1 th bed alone.

4. Productivity is extremal as a function of $H_2/N_2$ ratio and the bed exit temperature.

5. There is practically no influence on productivity by temperature variations at the reactor intake.

6. Both productivity and bed exit temperature have a monotonic curve with respect to the other disturbance variables.

7. Sudden changes occur in the operational behaviour of the reactor in the vicinity of the autothermy limit.

The above studies clearly reveal that simulation is a useful tool to obtain informations on the performance of an ammonia synthesis reactor.

# APPENDIX III

```
C
C
C***  MAIN LINE PROGRAM FOR COMPLEX ALGORITHM OF BOX
C
C
C     IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION X(10,4),F(10),G(4),H(4),XC(4),DELTA(4)
      INTEGER GAMMA
C     COMMON/VAR/TEMPIN(47),TEMP2(47),TEMP3(47),PP(47),PROD(47),
C    .           TIM(47),KKK
C     COMMON/SUB/CPROD(47)
C     COMMON/HUB/LL
C     KKK=1
      OPEN(UNIT=90,FILE='IN',STATUS='OLD')
      OPEN(UNIT=21,FILE='IN1',STATUS='NEW')
      READ(90,1) N,M,K,ITMAX,IC,IPRINT
 1    FORMAT(6I5)
      READ(90,2) ALPHA,BETA,(DELTA(I),I=1,N),GAMMA
 2    FORMAT(6F10.5,I5)
      READ(90,3) (X(1,J),J=1,N)
 3    FORMAT(4G10.5)
C     READ(90,4)((R(II,JJ),JJ=1,N),II=2,K)
C4    FORMAT(2F10.4)
      CLOSE(90)
C     CALL READ
      WRITE(21,15)
 15    FORMAT(//,' ** CONSTRAINED OPTIMIZATION BY COMPLEX  PROCEDURE  OF
     .X ** ')
      WRITE(21,22)
 22   FORMAT(//,2X,'** PARAMETERS **')
      WRITE(21,25) N,M,K,ITMAX,IC,IPRINT,ALPHA,BETA,(DELTA(I),I=1,N)
     .,GAMMA
 25   FORMAT(//,'NO. OF EXPLICIT VARIABLES(N)=',I2,3X,
     .'TOTAL NUMBER OF CONSTRAINTS(M)=',I2,/,
     .'TOTAL NO. OF POINTS IN THE COMPLEX(K)=',I2,3X,
     .'MAX. NO. OF ITERATIONS(ITMAX)=',I5,/,
     .'NO. OF IMPLICIT VARIABLES(IC)=',I2,3X,
     .'PRINT CONTROL COUNTER(IPRINT)=',I2,/,
     .'REFLEXION PARAMETER(ALPHA)=',G10.4,/,
     .'CONVERGENCE PARAMETER(BETA)=',G10.4,/,
     .'EXPLICIT CONSTRAINT VIOLATION CORRECTION TERM(DELTA(I)=',
     .4(1X,G10.4),/,'CONVERGENCE PARAMETER(GAMMA)=',I5)
C     IF(IPRINT.EQ.1) THEN
C        WRITE(21,50)((J,I,R(J,I),I=1,N),J=2,K)
C     ENDIF
C50   FORMAT(/'**RANDOM NUMBERS**'/,(2(2X,'R(',I1,',',I1,') =',F6.4)))
 60   CALL CONSX(N,M,K,ITMAX,ALPHA,BETA,GAMMA,DELTA,X,R,F,
     .           IT,IEV2,G,H,XC,IPRINT)
C
      IF(IT.LE.ITMAX) THEN
         WRITE(21,70) ABS(F(IEV2))
 70      FORMAT(///,'FINAL VALUE OF THE FUNCTION=',1PE16.7)
```

```
         WRITE(21,80)(J,X(IEV2,J),J=1,N)
 80      FORMAT(///,´FINAL X VALUES **´/,(2X/,´ X(´,I1,´)=´,E12.7))
C        WRITE(21,420)
C        WRITE(21,520)(PROD(J),CPROD(J),J=1,47)
C420     FORMAT(12X,´PROD´,9X,´CPROD´)
C520     FORMAT(10X,G10.4,4X,G10.4)
C        WRITE(21,230) IT
C230     FORMAT(5X,´ITERATION NO.=´,I5)
      ELSE
         WRITE(21,90) ITMAX
 90      FORMAT(//,´THE MAXIMUM NO. OF ITERATION´,I3,2X,´HAS EXCEEDED´/
     .   ´PROGRAM TERMINATED´)
      ENDIF
C        NN=47
C        SD=0.0
C        DO 1000 I=1,NN
C1000     SD=SD+(PROD(I)-CPROD(I))**2
C        STD=SQRT(SD/(NN-1))
C        WRITE(21,620) STD
C620     FORMAT(5X,´STANDARD DEVIATION=´,G10.4)
 200  STOP
      END
      SUBROUTINE CONSX(N,M,K,ITMAX,ALPHA,BETA,GAMMA,DELTA,X,R,F,
     .                 IT,IEV2,G,H,XC,IPRINT)
C
C.....COORDINATES SPECIAL PURPOSE SUBROUTINE
C.....  VARIABLES:
C.....  IT= ITERATION INDEX
C.....  IEV1= INDEX OF POINT WITH MINIMUM FUNCTION VALUE
C.....  IEV2= INDEX OF POINT WITH MAXIMUM FUNCTION VALUE
C.....  I= POINT INDEX
C.....  KODE= CONTROL KEY USED TO DETERMINE IF IMPLICIT
C.....        CONSTRAINTS ARE PROVIDED
C.....  K1= DO LOOP LIMIT
C     IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      INTEGER GAMMA
      DIMENSION X(K,M),R(K,N),F(K),G(M),H(M),XC(N)
C     COMMON/VAR/TEMPIM(47),TEMP2(47),TEMP3(47),PP(47),PROD(47),
C    .           TIM(47),KKK
C     COMMON/SUB/CPROD(47)
C     COMMON/HUB/LL
      OPEN(UNIT=23,FILE=´OUT2´,STATUS=´NEW´)
      IT=1
      KODE=0
      IF(M.GT.N) THEN
         KODE=1
      ENDIF
      DO 10 II=2,K
      DO 10 J=1,N
         X(II,J)=0.0
 10   CONTINUE
```

```
C.....CALCULATE COMPLEX POINTS AND CHECK AGAINST CONSTRAINTS.
      IX=25591
      DO 30 II=2,K
      DO 20 J=1,N
         I=II
         CALL CONST(N,M,K,X,G,H,I)
 45      CALL RANDOM(IX,IY,YFL)
         IX=IY
         KX=YFL*10000
         IF(KX.GE.10000) CALL RANDOM(IX,IY,YFL)
         IF(KX.GE.10000) IX=IY
         IF(KX.GE.10000) KX=YFL*10000
         IF(KX.GE.10000) GOTO 45
         A=FLOAT(KX)/10000.0
         X(II,J)=G(J)+A*(H(J)-G(J))
C        X(II,J)=G(J)+R(II,J)*(H(J)-G(J))
 20   CONTINUE
      K1=II
      CALL CHECK(N,M,K,X,G,H,I,KODE,XC,DELTA,K1)
      IF(II.GT.2) GOTO 65
        IF(IPRINT.EQ.1) THEN
           WRITE(23,50)
 50        FORMAT(//,2X,' ** COORDINATES OF INITIAL COMPLEX ** ')
           IO=1
           WRITE(23,60)(IO,J,X(IO,J),J=1,N)
 60        FORMAT(/,4(2X,'X(',I2,',',I2,')=',1PE13.6))
        ENDIF
 65   IF(IPRINT.EQ.1) THEN
         WRITE(23,60)(II,J,X(II,J),J=1,N)
      ENDIF
 30   CONTINUE
      ITER=1
      K1=K
      DO 40 I=1,K
         CALL FUNC(N,M,K,X,F,I)
         ITER=ITER+1
         WRITE(23,*) F(I)
 40   CONTINUE
      KOUNT=1
      IA=0
C.....FIND POINT WITH LOWEST FUNCTION VALUE
      IF(IPRINT.EQ.1) THEN
         WRITE(23,80)(J,ABS(F(J)),J=1,K)
 80      FORMAT(' ** VALUES OF THE FUNCTION ** '/
         ,5(2X,'F(',I2,')=',1PE13.7))
      ENDIF
 85   IEV1=1
      DO 90 ICM=2,K
         IF(F(IEV1).GT.F(ICM)) THEN
            IEV1=ICM
         ENDIF
 90   CONTINUE
```

```
C.....FIND POINT WITH HIGHEST FUNCTION VALUE
      IEV2=1
      DO 100 ICM=2,K
         IF(F(IEV2).LE.F(ICM)) THEN
            IEV2=ICM
         ENDIF
 100  CONTINUE
C.....CHECK CONVERGENCE CRITERIA
      IF(F(IEV2).LT.(F(IEV1)+BETA)) THEN
         KOUNT=KOUNT+1
      ELSE
         KOUNT=1
         GOTO 150
      ENDIF
      IF(KOUNT.GE.GAMMA) THEN
         GOTO 500
      ENDIF
C.....REPLACE POINT WITH LOWEST FUNCTION VALUE
 150  CALL CENTR(N,M,K,IEV1,I,XC,X,K1)
      DO 110 JJ=1,N
         X(IEV1,JJ)=(1.0+ALPHA)*(XC(JJ))-ALPHA*(X(IEV1,JJ))
 110  CONTINUE
      I=IEV1
      ITER=ITER+1
      CALL CHECK(N,M,K,X,G,H,I,KODE,XC,DELTA,K1)
      CALL FUNC(N,M,K,X,F,I)
C.....REPLACE NEW POINT IF IT REPEATS AS LOWEST FUNCTION VALUE
 170  IEV2=1
      DO 120 ICM=2,K
         IF(F(IEV2).GT.F(ICM)) THEN
            IEV2=ICM
         ENDIF
 120  CONTINUE
      IF(IEV2.EQ.IEV1) THEN
         DO 130 JJ=1,N
            X(IEV1,JJ)=(X(IEV1,JJ)+XC(JJ))/2.0
 130     CONTINUE
         I=IEV1
         ITER=ITER+1
         CALL CHECK(N,M,K,X,G,H,I,KODE,XC,DELTA,K1)
         CALL FUNC(N,M,K,X,F,I)
         GOTO 170
      ENDIF
      IF(IPRINT.EQ.1) THEN
         WRITE(23,230) IT
 230     FORMAT(/,'ITERATION NO.=',I5)
         WRITE(23,250)(IEV1,JC,X(IEV1,JC),JC=1,N)
 250     FORMAT(/,2X,' COORDINATES OF CORRECTED POINT'/
     .   ,4(2X,'X(',I2,',',I2,')=',1PE13.6))
         WRITE(23,80) (I,ABS(F(I)),I=1,K)
         WRITE(23,260) (JC,XC(JC),JC=1,N)
 260     FORMAT(/,2X,' COORDINATES OF THE CENTROID'/
     .   ,4(2X,'X(',I2,',','C)=',1PE13.6))
      ENDIF
```

```
      IT=IT+1
      IF(IT.LE.ITMAX) THEN
         GOTO 85
      ENDIF
C500  LL=1
C     CALL FUNC(N,M,K,X,F,IEV2)
 500  RETURN
      END
      SUBROUTINE RANDOM(IX,IY,YFL)
C     IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      IY=IX*65539
      IF (IY) 5,15,15
 5    IY=IY+2147483647+1
 15   YFL=IY
      YFL=YFL*0.4656613E-9
      RETURN
      END
```

```
C
C***  SUBROUTINE CHECK
C
      SUBROUTINE CHECK(N,M,K,X,G,H,I,KODE,XC,DELTA,K1)
      DIMENSION X(K,M),G(M),H(M),XC(N),DELTA(N)
 10   KT=0
      CALL CONST(N,M,K,X,G,H,I)
C.....CHECK AGAINST EXPLICIT CONSTRAINTS
      DO 50 J=1,N
         IF(X(I,J).LT.G(J)) THEN
            X(I,J)=G(J)+DELTA(J)
         ELSE IF(X(I,J).GT.H(J)) THEN
                 X(I,J)=H(J)-DELTA(J)
         ENDIF
 50   CONTINUE
C.....CHECK AGAINST THE IMPLICIT CONSTRAINTS
      IF(KODE.EQ.0) GOTO 110
      NN=N+1
      DO 100 J=NN,M
         CALL CONST(N,M,K,X,G,H,I)
         IF(X(I,J)-G(J)) 80,70,70
 70      IF(H(J)-X(I,J)) 80,100,100
 80      IEV1=I
         KT=1
         CALL CENTR(N,M,K,IEV1,I,XC,X,K1)
         DO 90 JJ=1,N
            X(I,JJ)=(X(I,JJ)+XC(JJ))/2.0
 90      CONTINUE
 100  CONTINUE
      IF(KT.GT.0) THEN
         GOTO 10
      ENDIF
 110  RETURN
      END
C
C***  SUBROUTINE CENTR
C
      SUBROUTINE CENTR(N,M,K,IEV1,I,XC,X,K1)
      DIMENSION X(K,M),XC(N)
      DO 20 J=1,N
         XC(J)=0.0
         DO 10 IL=1,K1
            XC(J)=XC(J)+X(IL,J)
 10      CONTINUE
         RK=K1
         XC(J)=(XC(J)-X(IEV1,J))/(RK-1.0)
 20   CONTINUE
      RETURN
      END
```

```
C
C***  SUBROUTINE CONST
C
      SUBROUTINE CONST(N,M,K,X,G,H,I)
      DIMENSION X(K,M),G(M),H(M)
C
C     AMMONIA SYNTHESIS LOOP OPTIMIZATION
C
      G(1)=2.5
      H(1)=4.0
      G(2)=0.001
      H(2)=0.04
      G(3)=420.0
      H(3)=500.0
      G(4)=3.5
      H(4)=5.0
      RETURN
      END
C
C***  SUBROUTINE FUNC
C
      SUBROUTINE FUNC(N,M,K,X,F,I)
      DIMENSION X(K,M),F(K)
      COMMON/AL1/XNH3,PRODCT,SPNH3,TEMPIN,TEMPC,SEPTEM,SEPP,RECYLR,
     .           FPRGE,ALCATW,HBED(3),PRDROP(3),TMAX
      COMMON/GCOM4/RATIO,XINRF
      COMMON/CST5/TOTCST
      RATIO=X(I,1)
      XINRF=X(I,2)
      TEMPC=X(I,3)
      RECYLR=X(I,4)
      CALL AMONIA
      F(I)=-TOTCST/(1.0E06)
      RETURN
      END
```

```
C
C***   SUBROUTINE AMONIA
C
       SUBROUTINE AMONIA
C      PROGRAM FOR THE DESIGN & SIMULATION
C      OF AN AMMONIA SYNTHESIS REACTOR,BASED
C      ON INTERBED QUENCH REACTOR SYSTEM.
C      THIS CASE IS BASED ON THE FOLLOWING
C      KNOWN QUANTITIES:
C          1) PERCENT INERTS(CH4+ARGON) IN THE TOTAL MIXED FEED.
C          2) NUMBER OF BEDS IN THE REACTOR
C          3) INLET & OUTLET TEMP. OF EACH BED.
C          4) COLD SHOT TEMP.
C          5) AMMONIA PRODUCTION RATE
C          6) PRESSURE AT REACTOR INLET & AT SEPARATOR.
C      *********** VARIABLES ***************
C      XNH3=MOLE FRACTION OF AMMONIA IN THE CRUDE PRODUCT.
C      PRODCT=REQUIRED AMMONIA PRODUCTION RATE,KMOLE/S.
C      TEMPIN=FIRST BED INLET TEMPERATURE,K
C      TMAX=MAX. ALLOWABLE TEMP. IN THE BED,K
C      TEMPC=COLD SHOT TEMPERATURE,K
C      SEPTEM=SEPARATOR OPERATING TEMP.,K
C      SEPP=SEPARATOR OPERATING PRESSURE,KPA
C      RECYLR=RECYCLE RATIO
C      HBED(I)=HEIGHT OF BED I,M
C      PRDROP(I)=PRESSURE DROP IN BED I,KPA
C      DW=INTEGRATION STEP SIZE,KG
C      ALLCAT(I)=CATALYST IN BED I,KG
C      FRACF(I)=FRACTION OF MIXED FEED USED IN BED I
C               EITHER AS FEED OR AS COLD SHOT
C      T=INSTANTANEOUS GAS TEMP.,K
C      NBED=NUMBER OF BED
       DIMENSION EQCOST(15),YR(8),YRR(8),RF(8)
       INTEGER OPTN1,OPTN2,OPTN3,OPTN4
       COMMON/AL1/XNH3,PRODCT,SPNH3,TEMPIN,TEMPC,SEPTEM,SEPP,RECYLR,FPRGE
      .,ALCATW,HBED(3),PRDROP(3),TMAX
       COMMON/AL2/DW,ITMAX,ALLCAT(3),FRACF(5)
       COMMON/AL3/YN2R,YH2R,YNH3R,YCH4R,YARR,CONVCR
       COMMON/AL4/T,F(8),Y(8),AG(9),DIFNH3
       COMMON/AL13/QUSPC,FRACCL
       COMMON/AL14/GTOT,TOTALE,YY(8),YE(8)
       COMMON/AL16/CATCST,STMCS1,STMCS2,COLWCS,ELECST
       COMMON/CONVRT/FEEDGS,YN2F,YH2F,YNH3F,YCH4F,YARF
       COMMON/GCOM1/CATDEN,DIA,P,EP,DP
       COMMON/GCOM2/DZ,NBED
       COMMON/GCOM3/N
       COMMON/GCOM4/RATIO,XINRF
       COMMON/CST1/CSIND2,FLANG,COST
       COMMON/CST5/TOTCST
       COMMON/COM1/TPRDRP,FACTRM
       COMMON/COM2/FG(8),YG(8),TG
       COMMON/COM3/EFFCB,SATP,HEATLD
```

```
      COMMON/PV1/RADIV,HEGHT,NOTRA,HEADV
      COMMON/PV2/OPTN1,OPTN2,OPTN3,OPTN4
      COMMON/HX1/ALPHAS,ALPHAT,FOULS,FOULT,SPRESD,TPRESD,PREST
      COMMON/HX2/FS(8),FT(8)
      COMMON/HX3/IPTN11,IPTN12,IPTN13,IPTN14,IPTN15,IPTN16,NTPASS,NS,NT
      COMMON/HX4/AO,AI
      COMMON/HX5/TSIN,TSOUT,TTIN,TTOUT
      COMMON/HTV1/TL,HVT(8),CPL(8),SPVL(8),VISL(8)
      COMMON/HTV2/NC
      COMMON/HTV3/TCL(8),GPCL(8),AMWL(8)
      COMMON/PH1/TC(8),GPC(8),AMW(8),HV(8)
      COMMON/PH3/AVMW,PROCPG,VISGM
      COMMON/AR1/FL(5)
      COMMON/AR3/NN,NL
      COMMON/AR4/FPOWER,ULTPWF
      COMMON/CMP1/PIN,POUT,RLMT,TGIN,TGOUT,STEAMP
      COMMON/HTCOEF/HCANUL,HCCTB,HTCOV1,HTCOV2,FA1,FB1
      COMMON/DSC3/NSTAGE
      COMMON/DSC4/COSTRB,COSTCN,ULTSTM,ULTCOL
      CSIND1=569.0
      T2=TEMPC
      R1=RECYLR
      CALL INPUT
      TEMPC=T2
      RECYLR=R1
      PRES=P
      CALL PREL
      OPEN(UNIT=50,STATUS='NEW',FILE='OUT1')
      IW=50
      THBED=0.0
      DO 10 I=1,NBED
 10      THBED=THBED+HBED(I)
      DO 20 I=1,N
         YR(I)=Y(I)
 20      Y(I)=YE(I)
      CALL CONVER
      FACTRM=1.0
      HEGHT=THBED+QUSPC
      RADIV=DIA/2.0
      CALL PRESSV
      JEQ=1
      COST=COST*FLANG*CSIND2/CSIND1
C     COST OF AMMONIA CONVERTER
      EQCOST(JEQ)=COST
C     CALCULATION OF CATALYST COST;1.50 US $
C     PER TON OF AMMONIA PRODUCED
      WRITE(IW,500) JEQ,COST,CATCST,PRES,P
 500  FORMAT(/' *** AMMONIA CONVERTER *** '//
     .'EQUIPMENT NO.=',I2,/'INSTALLED COST OF THE REACTOR($)=',E12.3,
     ./'CATALYST COST($/TON AMMONIA)=',F10.3/'REACTOR INLET PRESSURE(KPA
     .)=',F12.3,/'REACTOR EXIT PRESSURE(KPA)=',F12.3)
```

```
C     CALCULATION FOR CONVERTER HEAT EXCHANGER(E1)
C          GAS-GAS HEAT EXCHANGER
      CALL HTEXX1
      PREST=P
      PRESS=PRES
      JEQ=JEQ+1
      TTIN=T
      TSIN=TEMPC
      NT=N
      NS=N
      DO 30 I=1,NT
         FS(I)=(FA1+FB1)*YY(I)
 30      FT(I)=TOTALE*YE(I)
      CALL HEATEX
      EQCOST(JEQ)=COST
      PREST=P-TPRESD
      PRESS=PRES-SPRESD
      P=PREST
      TOTALF=0.0
      DO 40 I=1,NS
 40      TOTALF=TOTALF+FS(I)
      WRITE(IW,1000) JEQ,COST,P,TTOUT,TOTALF,AO
 1000 FORMAT(/´ *** CONVERTER HEAT EXCHANGER *** ´//
     .´EQUIPMENT NO.=´,I2,/´COST OF HEAT EXCHANGER($)=´,E12.3,/
     .´EXIT PRESSURE(KPA)=´,F12.3,/´EXIT TUBE SIDE TEMP(K)=´,E10.3,/
     .´GAS USED IN THE SHELL SIDE(KMOLE/S)=´,F12.3/
     .´OUTSIDE AREA(M**2)=´,E10.3)
C     CALCULATION FOR THE WASTE HEAT BOILER(E2)
C      GAS-LIQUID WATER TO STEAM HEAT EXCHANGER
      JEQ=JEQ+1
      TT=TTOUT
      CALL HTEXX2
      TTIN=TT
C     SHELL SIDE IS WATER
      DO 55 I=1,NS
 55      FS(I)=0.0
      FS(2)=1.0
      CALL HEATEX
C     CALCULATE THE AMOUNT OF STEAM(3 BAR SAT.) THAT COULD BE RAISED
C     BY THE HEAT CONTENT OF THE GAS(FEED WATER 308 K)
      STMBFW=ABS(HEATLD)*3.1536E7*EFFCB/2163.0*STMCS2*CSIND2/CSIND1
      EQCOST(JEQ)=COST
      WRITE(IW,1200) JEQ,COST,FS(2),TTOUT,STMBFW,AO
 1200 FORMAT(/´ *** WASTE HEAT BOILER *** ´//
     .´EQUIPMENT NO.=´,I2,/´COST($)=´,E10.3,/´BOILER FEED WATER USED(KMO
     .L/S)=´,E10.4,/´EXIT TUBE SIDE TEMP(K)=´,E10.3,/
     .´VALUE OF STEAM THAT CAN BE MADE($/YEAR)=´,E10.4/
     .´OUTSIDE AREA(M**2)=´,E10.3)
      T1=TTOUT
```

```
      CALL HTEXX3
C     CALCULATION FOR PROCESS GAS HEAT EXCHANGER(E3)
C        GAS-GAS HEAT EXCHANGER
      TTIN=T1
      TSOUT=TEMPC
      TS1=TSIN
      JEQ=JEQ+1
C     SHELL SIDE FLOW CALCULATION
      YRR(1)=YN2R
      YRR(2)=YH2R
      YRR(3)=YNH3R
      YRR(4)=YCH4R
      YRR(5)=YARR
      YRR(6)=0.0
      YRR(7)=0.0
      YRR(8)=0.0
      DO 60 I=1,NS
         PF=FPRGE*RECYLR*FEEDGS*YRR(I)
         RF(I)=(1.-FPRGE)*RECYLR*FEEDGS*YRR(I)
 60      FS(I)=RF(I)-FA1*YRR(I)
      TOTLS=0.0
      DO 70 I=1,NS
 70      TOTLS=TOTLS+FS(I)
      CALL HEATEX
      EQCOST(JEQ)=COST
      PREST=P-TPRESD
      P=PREST
      WRITE(IW,1300) JEQ,COST,TTOUT,TOTLS,AO
 1300 FORMAT(/´ *** PROCESS GAS HEAT EXCHANGER *** ´//
     .´EQUIPMENT NO.=´,I2,/´COST($)=´,E10.4,/´EXIT TUBE SIDE TEMP(K)=´
     .E10.3,/´PROCESS GAS USED IN THE SHELL SIDE(KMOLE/S)=´,E10.4/
     .´OUTSIDE AREA(M**2)=´,E10.3)
      TT=TTOUT
      CALL HTEXX4
C     CALCULATION FOR WATER COOLER(E4)
C        GAS-LIQUID WATER HEAT EXCHANGER
      TTIN=TT
      JEQ=JEQ+1
C     SHELL SIDE IS WATER
      DO 90 I=1,NS
 90      FS(I)=0.0
      FS(2)=1.0
      CALL HEATEX
C     CALCULATIION OF COST OF COOLING WATER
      ULTCL1=FS(2)*AMWL(2)*3.1536E7/EFFCB*COLWCS*CSIND2/CSIND1
      EQCOST(JEQ)=COST
      PREST=P-TPRESD
      P=PREST
      WRITE(IW,1400) JEQ,COST,P,TTOUT,ULTCL1,AO
 1400 FORMAT(/´ *** WATER COOLER *** ´//´EQUIPMENT NO.=´,I2,/
     .´COST($)=´,E10.4,/´EXIT TUBE SIDE PRESSURE(KPA)=´,E10.4,/
     .´EXIT TUBE SIDE TEMP(K)=´,E10.3,/
     .´COOLING WATER COST($/YEAR)=´,E10.4/,´OUTSIDE AREA(M**2)=´,E10.3)
```

```
C     CALCULATION FOR COLD EXCHANGER(E5)
C        GAS-GAS HEAT EXCHANGER
      JEQ=JEQ+1
      TT=TTOUT
      CALL HTEXX5
C     CALCULATION OF SHELL SIDE FLOWRATE
      TTIN=TT
      TS=TSOUT
      DO 100 I=1,NS
 100     FS(I)=RECYLR*FEEDGS*YRR(I)
      CALL HEATEX
      EQCOST(JEQ)=COST
      WRITE(IW,1500) JEQ,COST,TTOUT,AO
 1500 FORMAT(/' *** COLD EXCHANGER *** '//'EQUIPMENT NO.=',I2,/
     .'COST($)=',E10.4,/'EXIT TUBE SIDE TEMP(K)=',E10.4/
     .'OUTSIDE AREA(M**2)=',E10.3)
C     CALCULATION FOR MAIN FEED GAS COMPRESSOR
      CALL COMP2
      JEQ=JEQ+1
      POUT=PREST
      F(1)=YN2F*FEEDGS
      F(2)=YH2F*FEEDGS
      F(3)=YNH3F*FEEDGS
      F(4)=YCH4F*FEEDGS
      F(5)=YARF*FEEDGS
      F(6)=0.0
      F(7)=0.0
      F(8)=0.0
      DO 130 I=1,N
 130     FG(I)=F(I)
      CALL COMPRS
      EQCOST(JEQ)=COST
      EMNCSF=0.04*COST
      ULTPCF=FPOWER*3.1536E7/STEAMP/0.8*STMCS1*CSIND2/CSIND1
      WRITE(IW,1800) JEQ,COST,FPOWER,NSTAGE,TGOUT,EMNCSF,ULTPCF
 1800 FORMAT(/' *** MAKEUP FEED COMPRESSOR *** '//
     .'EQUIPMENT NO.=',I2,/'COST($)=',E10.4,/
     .'TOTAL POWER REQUIREMENT(KW)=',E10.4,/'NO. OF COMPRESSION STAGE='
     .I2,/'EXIT TEMP. OF COMPRESSED GAS(K)=',F10.4,/
     .'COMPRESSOR MAINTAINENCE COST($/YEAR)=',E10.4,/
     .'STEAM COST FOR COMPRESSION($/YEAR)=',E10.4)
      II=1
      TOTG=0.0
      DO 131 I=1,N
 131     TOTG=TOTG+F(I)
      DO 132 I=1,N
 132     YG(I)=F(I)/TOTG
      TG=TGOUT
      CALL HEATTR
      PROCTG=PROCPG*(TG-298.0)
      DO 133 I=1,N
         FG(I)=FT(I)
 133     YG(I)=YE(I)
```

```
      TG=TTOUT
      CALL HEATTR
      PROCTT=PROCPG*(TG-298.0)
      TOTG=TOTG+TOTALE
      DO 134 I=1,N
         FG(I)=F(I)+TOTALE*YE(I)
 134     YG(I)=FG(I)/TOTG
 129  TG=TGOUT
      CALL HEATTR
      TTT=(PROCTG+PROCTT)/PROCPG+298.0
      IF(ABS(TTT-TG).LE.0.1.OR.II.GE.4) GOTO 135
      II=II+1
      TGOUT=TTT
      GOTO 129
C     CALCULATION FOR NH3 CHILLER(E6)
C        GAS-LIQUID NH3 CHILLER
C     CALCULATION FOR SHELL SIDE FLOWRATE(LIQUID NH3)
 135  JEQ=JEQ+1
      TT=TTT
      CALL HTEXX6
      TTIN=TT
      NS=2
      NT=N
      DO 111 I=1,NS
 111     FS(I)=0.0
      FS(1)=1.0
      DO 112 I=1,NT
 112     FT(I)=FT(I)+FEEDGS*YY(I)
      CALL HEATEX
      EQCOST(JEQ)=COST
      WRITE(IW,1550) JEQ,COST,TTOUT,ULTCOL,AO
 1550 FORMAT(/' *** NH3 CHILLER *** '//'EQUIPMENT NO.=',I2,/
     .'COST($)=',E10.4,/'EXIT TUBE SIDE TEMP(K)=',E10.4,/
     .'NH3 REFRIGERATION REQUIRED($/YEAR)=',E10.3/
     .'OUTSIDE AREA(M**2)=',E10.3)
C     CALCULATION FOR SEPARATOR
      FL(1)=PRODCT*XNH3
      FL(2)=(1.-XNH3)*PRODCT
      NL=2
      NN=N
      CALL SEPX
      JEQ=JEQ+1
      FT(3)=FT(3)-FL(1)
      P=SEPP
      T=TTOUT
      DO 110 I=1,N
 110     F(I)=FT(I)
      CALL SEPAR
      EQCOST(JEQ)=COST
      P=P-TPRDRP
      WRITE(IW,1600) JEQ,COST,P
 1600 FORMAT(/' *** AMMONIA SEPARATOR *** '//
     .'EQUIPMENT NO.=',I2,/'COST($)=',E10.4,/
     .'EXIT PRESSURE(KPA)=',E10.4)
```

```
C     CALCULATION FOR CIRCULATING COMPRESSOR
C     COMPRESSOR IS DRIVEN BY STEAM TURBINE USING
C     STEAM(3550 KPA,650K)
      CALL COMP1
      TGIN=TS
      PIN=SEPP
      POUT=PRES
C     CALCULATION OF FLOWRATE OF GASES
      DO 120 I=1,N
 120     FG(I)=RF(I)
      JEQ=JEQ+1
      CALL COMPRS
      EQCOST(JEQ)=COST
      EMNCSC=0.04*COST
      ULTPWC=FPOWER*3.1536E7/STEAMP/0.8*STMCS1*CSIND2/CSIND1
      WRITE(IW,1700) JEQ,COST,FPOWER,NSTAGE,TGOUT,EMNCSC,ULTPWC
 1700 FORMAT(/' *** CIRCULATING COMPRESSOR *** '//
     .'EQUIPMENT NO.=',I2,/'COST($)=',E10.4,/'TOTAL POWER REQUIREMENT(KW
     .)=',E10.4,/'NO. OF COMPRESSION STAGE=',I2,/
     .'EXIT TEMP. OF COMPRESSED GAS(K)=',F10.4,/
     .'COMPRESSOR MAINTAINENCE COST($/YEAR)=',E10.4,/
     .'STEAM COST FOR COMPRESSION($/YEAR)=',E10.4)
C     CALCULATION OF TOTAL COST OF ALL EQUIPMENTS.
      TOTCST=0.0
      DO 140 I=1,JEQ
 140     TOTCST=TOTCST+EQCOST(JEQ)
C     CALCULATION OF TOTAL COST OF ALL UTILITY USED.
      TULTCS=ULTCL1+ULTPWC+ULTPCF+ULTCOL
C     CALCULATION OF ANNUAL OPERATING COST($/YEAR)
C     ON THE BASIS OF 1000 TONS/DAY AMMONIA PRODUCTION.
C     FIXED COST ARE PROPORTIONED BY USING 6/10TH RULE;
C     UTILITY & OTHER COSTS ARE ADJUSTED PROPORTIONATELY.
      PRODCT=PRODCT*AMWL(1)*3600.*24.*365./1000.0
      TOTCST=0.2*TOTCST*(365000.0/PRODCT)**0.6+(EMNCSC+EMNCSF+TULTCS-
     .STMBFW)*(365000.0/PRODCT)+CATCST*365000.0
      WRITE(IW,1900)TOTCST,PRODCT
 1900 FORMAT(///' ** ANNUAL OPERATING COST($/YEAR)='//
     .2X,1PE14.6,//' ** ANNUAL PRODUCTION OF AMMONIA(MTON/YEAR)='//
     .2X,1PE14.5)
      RETURN
      END
```

```
C
C***   SUBROUTINE INPUT
C
       SUBROUTINE INPUT
C      SUBROUTINE TO INPUT THE NECESSARY DATA REQUIRED FOR SIMULATION AND
C      DESIGN OF AMMONIA SYNTHESIS LOOP.
       INTEGER OPTN1,OPTN2,OPTN3,OPTN4
       COMMON/AL1/XNH3,PRODCT,SPNH3,TEMPIN,TEMPC,SEPTEM,SEPP,RECYLR,
     .            FPRGE,ALCATW,HBED(3),PRDROP(3),TMAX
       COMMON/AL2/DW,ITMAX,ALLCAT(3),FRACF(5)
       COMMON/AL3/YN2R,YH2R,YNH3R,YCH4R,YARR,CONVCR
       COMMON/AL9/CVUPRL,CVLWRL,NFREQA,FRACMN,ICOUNF
       COMMON/AL13/QUSPC,FRACCL
       COMMON/AL16/CATCST,STMCS1,STMCS2,COLWCS,ELECST
       COMMON/CONVRT/FEEDGS,YN2F,YH2F,YNH3F,YCH4F,YARF
       COMMON/GCOM1/CATDEN,DIA,P,EP,DP
       COMMON/GCOM2/DZ,NBED
       COMMON/GCOM3/N
       COMMON/CST1/CSIND2,FLANG,COST
       COMMON/COM1/TPRDRP,FACTRM
       COMMON/COM3/EFFCB,SATP,HEATLD
       COMMON/HX1/ALPHAS,ALPHAT,FOULS,FOULT,SPRESD,TPRESD,PREST
       COMMON/HX3/IPTN11,IPTN12,IPTN13,IPTN14,IPTN15,IPTN16,NTPASS,NS,NT
       COMMON/HX5/TSIN,TSOUT,TTIN,TTOUT
       COMMON/CMP1/PIN,POUT,RLMT,TGIN,TGOUT,STEAMP
       COMMON/PV1/RADIV,HEGHT,NOTRA,HEADV
       COMMON/PV2/OPTN1,OPTN2,OPTN3,OPTN4
       COMMON/HTV2/NC
       OPEN(UNIT=10,STATUS='OLD',FILE='INPUT')
       READ(10,100)FEEDGS
       READ(10,150)YN2F,YH2F,YNH3F,YCH4F,YARF
       READ(10,200)YN2R,YH2R,YNH3R,YCH4R,YARR
       READ(10,250)XNH3,PRODCT,SPNH3
       READ(10,300)TEMPIN,TMAX,TEMPC,SEPTEM,SEPP
       READ(10,350)P,ITMAX
       READ(10,400)N,DW,NBED
       READ(10,450)CATDEN,DIA,EP,DP
       READ(10,500)RECYLR,FPRGE,CONVCR
       READ(10,550)(FRACF(I),I=1,5)
       READ(10,600)CVUPRL,CVLWRL,NFREQA,ICOUNF,FRACMN
       READ(10,650)(PRDROP(I),I=1,NBED)
       READ(10,700)(ALLCAT(I),I=1,NBED)
       CLOSE(UNIT=10,STATUS='KEEP')
  100  FORMAT(F10.4)
  150  FORMAT(5F10.4)
  200  FORMAT(5F10.4)
  250  FORMAT(3F10.4)
  300  FORMAT(5F10.4)
  350  FORMAT(F10.2,I10)
  400  FORMAT(I10,F10.4,I10)
  450  FORMAT(4F10.4)
  500  FORMAT(3F10.4)
  550  FORMAT(5F10.6)
  600  FORMAT(2F10.4,2I10,F10.4)
  650  FORMAT(3F10.3)
```

```
 700  FORMAT(3F10.1)
      RETURN
      ENTRY CONVER
C     DATA FOR AMMONIA CONVERTER
      OPEN(UNIT=11,STATUS='OLD',FILE='INPUT1')
      READ(11,750) OPTN1,OPTN2,OPTN3,OPTN4,FLANG,CSIND2,QUSPC,NOTRA
      READ(11,800) CATCST,STMCS1,STMCS2,COLWCS,ELECST,EFFCB
      CLOSE(UNIT=11,STATUS='KEEP')
 750  FORMAT(4I5,3F10.3,I2)
 800  FORMAT(6E10.4)
      RETURN
      ENTRY HTEXX1
C     DATA FOR CONVERTER HEAT EXCHANGER
C        GAS-GAS HEAT EXCHANGER
C     ------- DATA NEEDED --------
C     TSOUT=SHELL SIDE OUTLET TEMPERATURE(K)
C     TSIN= SHELL SIDE INLET  REMPERATURE(K)
C     TTIN=TUBE SIDE INLET TEMPERATURE(K)
C     TTOUT=TUBE SIDE OUTLET TEMPERATURE(K)
C     ALPHAS=SHELL SIDE HEAT TRANSFER COEFFICIENT
C            (KW/M**2/K)
C     ALPHAT=TUBE SIDE HEAT TRANSFER COEFFICIENT
C            (KW/M**2/K)
C     FOULS=SHELL SIDE FOULING RESISTANCE(M**2-K/KW)
C     FOULT=TUBE SIDE FOULING RESISTANCE(M**2-K/KW)
C     OPTIONS:IPTN11,IPTN12,IPTN13,IPTN14,IPTN15,IPTN16
      OPEN(UNIT=12,STATUS='OLD',FILE='INPUT2')
      READ(12,950) TSIN,TSOUT,TTIN,TTOUT,ALPHAS,ALPHAT,FOULS,FOULT
     .,FLANG,NTPASS,NS,NT,IPTN11,IPTN12,IPTN13,IPTN14,IPTN15,IPTN16
 950  FORMAT(6F10.3/,3F10.3/,9I5)
      CLOSE(UNIT=12,STATUS='KEEP')
      RETURN
      ENTRY HTEXX2
C     DATA FOR WASTE HEAT BOILER
C     GAS-LIQUID WATER TO STEAM HEAT EXCHANGER
C     ------- INPUT DATA -------
      OPEN(UNIT=13,STATUS='OLD',FILE='INPUT3')
      READ(13,1350) TSIN,TSOUT,TTIN,TTOUT,ALPHAS,ALPHAT,FOULS,FOULT,
     .FLANG,NTPASS,NS,NT,IPTN11,IPTN12,IPTN13,IPTN14,IPTN15,IPTN16
1350  FORMAT(6F10.3,/3F10.3,/9I5)
      CLOSE(UNIT=13,STATUS='KEEP')
      RETURN
      ENTRY HTEXX3
C     DATA FOR PROCESS GAS HEAT EXCHANGER
C      GAS-GAS HEAT EXCHANGER
C     -------- INPUT DATA ---------
      OPEN(UNIT=14,STATUS='OLD',FILE='INPUT4')
      READ(14,1450)TSIN,TSOUT,TTIN,TTOUT,ALPHAS,ALPHAT,FOULS,FOULT,
     .FLANG,NTPASS,NS,NT,IPTN11,IPTN12,IPTN13,IPTN14,IPTN15,IPTN16
1450  FORMAT(6F10.3,/3F10.3,/9I5)
      CLOSE(UNIT=14,STATUS='KEEP')
      RETURN
```

```
      ENTRY HTEXX4
C     DATA FOR WATER COOLER
C      GAS-LIQUID WATER HEAT EXCHANGER
C     ------- INPUT DATA -------
      OPEN(UNIT=15,STATUS='OLD',FILE='INPUT5')
      READ(15,1550)TSIN,TSOUT,TTIN,TTOUT,ALPHAS,ALPHAT,FOULS,FOULT,
     .FLANG,NTPASS,NS,NT,IPTN11,IPTN12,IPTN13,IPTN14,IPTN15,IPTN16
 1550 FORMAT(6F10.3,/3F10.3,/9I5)
      CLOSE(UNIT=15,STATUS='KEEP')
      RETURN
      ENTRY HTEXX5
C     DATA FOR COLD EXCHANGER
C      GAS-GAS HEAT EXCHANGER
C     ------- INPUT DATA -------
      OPEN(UNIT=16,STATUS='OLD',FILE='INPUT6')
      READ(16,1650)TSIN,TSOUT,TTIN,TTOUT,ALPHAS,ALPHAT,FOULS,FOULT,
     .FLANG,NTPASS,NS,NT,IPTN11,IPTN12,IPTN13,IPTN14,IPTN15,IPTN16
 1650 FORMAT(6F10.3,/3F10.3,/9I5)
      CLOSE(UNIT=16,STATUS='KEEP')
      RETURN
      ENTRY COMP2
C     DATA FOR MAIN FEED GAS COMPRESSOR
C     ------- INPUT DATA -------
      OPEN(UNIT=7,STATUS='OLD',FILE='INPUT10')
      READ(7,1250)TGIN,PIN,RLMT,FLANG,STEAMP
 1250 FORMAT(5F10.3)
      CLOSE(UNIT=7,STATUS='KEEP')
      RETURN
      ENTRY HTEXX6
C     DATA FOR NH3 CHILLER
C      GAS-LIQUID NH3 HEAT EXCHANGER
C     ------- INPUT DATA -------
      OPEN(UNIT=17,STATUS='OLD',FILE='INPUT7')
      READ(17,1660)TSIN,TSOUT,TTIN,TTOUT,ALPHAS,ALPHAT,FOULS,FOULT,
     .FLANG,NTPASS,NS,NT,IPTN11,IPTN12,IPTN13,IPTN14,IPTN15,IPTN16
 1660 FORMAT(6F10.3,/3F10.3,/9I5)
      CLOSE(UNIT=17,STATUS='KEEP')
      RETURN
      ENTRY SEPX
C     DATA FOR GAS-LIQUID SEPARATOR
C     ******* INPUT DATA ********
C     OPTN1,OPTN2,OPTN3,OPTN4
C     FACTRM=FACTOR FOR MATERIAL OF CONSTRUCTION
      OPEN(UNIT=18,STATUS='OLD',FILE='INPUT8')
      READ(18,1050)OPTN1,OPTN2,OPTN3,OPTN4,FACTRM,FLANG
 1050 FORMAT(4I5,2F10.3)
      CLOSE(UNIT=18,STATUS='KEEP')
      RETURN
```

```
      ENTRY COMP1
C     DATA FOR CIRCULATING COMPRESSOR
C     -------- INPUT DATA --------
C
      OPEN(UNIT=19,STATUS='OLD',FILE='INPUT9')
      READ(19,1150)TGIN,PIN,RLMT,FLANG,STEAMP
 1150 FORMAT(5F10.3)
      CLOSE(UNIT=19,STATUS='KEEP')
      RETURN
      END
```

```
C
C***  SUBROUTINE PREL
C
      SUBROUTINE PREL
C     SUBROUTINE TO DO PRELIMINARY CALCULATION FOR AMMONIA SYNTHESIS.
C     1=N2,2=H2,3=NH3,4=CH4,5=ARGON,6=H2O,7=CO,8=CO2
      COMMON/AL1/XNH3,PRODCT,SPNH3,TEMPIN,TEMPC,SEPTEM,SEPP,RECYLR,
                 FPRGE,ALCATW,HBED(3),PRDROP(3),TMAX
      COMMON/AL2/DW,ITMAX,ALLCAT(3),FRACF(5)
      COMMON/AL3/YN2R,YH2R,YNH3R,YCH4R,YARR,CONVCR
      COMMON/AL4/T,F(8),Y(8),AG(9),DIFNH3
      COMMON/AL6/RATE,PNUN,PNUH,PNUA
      COMMON/AL7/CLDST(3),CATWT(3)
      COMMON/AL9/CVUPRL,CVLWRL,NFREQA,FRACMN,ICOUNF
      COMMON/AL10/S(4,8),LK,ICOUNT
      COMMON/AL11/M
      COMMON/AL14/GTOT,TOTALE,YY(8),YE(8)
      COMMON/AL15/K
      COMMON/CONVRT/FEEDGS,YN2F,YH2F,YNH3F,YCH4F,YARF
      COMMON/GCOM1/CATDEN,DIA,P,EP,DP
      COMMON/GCOM2/DZ,NBED
      COMMON/GCOM3/N
      COMMON/GCOM4/RATIO,XINRF
      COMMON/PH1/TC(8),GPC(8),AMW(8),HV(8)
      COMMON/PH2/HG(8)
      COMMON/PH3/AVMW,PROCPG,VISGM
      COMMON/COM2/FG(8),YG(8),TG
      COMMON/HTCOEF/HCANUL,HCCTB,HTCOV1,HTCOV2,FA1,FB1
      DIMENSION FGS(8),RF(8),PF(8),FB(8),QUNCH(8)
C     CALCULATION OF AMMONIA & WATER CONCENTRATION IN THE PURGE
C     PNH3,PH2O,VAP. PRESSURE OF AMMONIA & WATER,KPA.
      OPEN(UNIT=20,STATUS='NEW',FORM='FORMATTED',FILE='OUTPUT')
C     OPEN(UNIT=30,STATUS='NEW',FORM='FORMATTED',FILE='OUT')
      PRINT *,'*** AMMONIA REACTOR CALCULATION STARTS ***'
      PNH3=(EXP(16.9481-2132.50/(SEPTEM-32.98)))*0.133
      PH2O=(EXP(18.3036-3816.44/(SEPTEM-46.13)))*0.133
      YCH4F=XINRF/2.0
      YARF=YCH4F
      YN2F=(1.0-XINRF)/(1.0+RATIO)
      YH2F=RATIO*YN2F
      YINR=YCH4R+YARR
      YINF=YCH4F+YARF
      ITER=1
      FN2=FEEDGS*YN2F
      FH2=FEEDGS*YH2F
      FNH3=FEEDGS*YNH3F
      FCH4=FEEDGS*YCH4F
      FAR=FEEDGS*YARF
      DO 5 I=1,3
 5       HBED(I)=ALLCAT(I)/(CATDEN*0.786*DIA**2)
```

```
      LK=0
      ICOUNT=0
      DW1=DW
      PINLT=P
 100  TOTCAT=0.0
      RECYCL=FEEDGS*RECYLR
      TOTALG=RECYCL
      YINTF=(FEEDGS*YINF+RECYCL*YINR)/TOTALG
      GTOT=TOTALG
      DW=DW1
      P=PINLT
C     CALCULATION OF MOLE FRACTION OF DIFFERENT GASES IN THE
C     MIXED FEED.
      RF(1)=RECYCL*YN2R
      RF(2)=RECYCL*YH2R
      RF(3)=RECYCL*YNH3R
      RF(4)=RECYCL*YCH4R
      RF(5)=RECYCL*YARR
      RF(6)=0.0
      RF(7)=0.0
      RF(8)=0.0
      F(1)=RF(1)
      F(2)=RF(2)
      F(3)=RF(3)
      F(4)=RF(4)
      F(5)=RF(5)
      F(6)=0.0
      F(7)=0.0
      F(8)=0.0
      DO 12 I=1,N
         Y(I)=F(I)/TOTALG
 12      YY(I)=Y(I)
      PRINT *,ITER
      T=TEMPIN
      T1=T
      K=1
      W=0.0
      GC=9.81
      R=8.314
      MM=0
C     CALCULATION STARTS FOR THE FIRST BED
      TOTLG=FRACF(1)*TOTALG
      FB1=FRACF(2)*TOTLG
      FA1=TOTALG-TOTLG
      QUENCH=TOTLG-FB1
      QUENC1=(TOTLG-FB1)*FRACF(3)
C     QUENCH=QUENCH-QUENC1
      FEED1=FB1+FA1+QUENC1
      TM=((FA1+FB1)*(T1-298.0)+QUENC1*(TEMPC-298.0))/(FEED1)+298.0
      DO 13 I=1,N
         FB(I)=(FA1+FB1)*Y(I)
 13      QUNCH(I)=QUENC1*Y(I)
```

```
      DO 14 I=1,N
         FG(I)=FB(I)
 14      YG(I)=Y(I)
      II=1
      TG=T1
      CALL HEATTR
      PROCPB=PROCPG*(TG-298.0)
      DO 15 I=1,N
         FG(I)=QUNCH(I)
 15      YG(I)=Y(I)
      TG=TEMPC
      CALL HEATTR
      PROCPC=PROCPG*(TG-298.0)
      DO 16 I=1,N
         FG(I)=FEED1*Y(I)
 16      YG(I)=Y(I)
      TG=TM
 11   CALL HEATTR
      T=(PROCPB+PROCPC)/PROCPG+298.0
      IF(ABS(T-TG).LE.0.1.OR.II.GE.4) GOTO 17
      II=II+1
      TG=T
      GOTO 11
 17   DO 20 I=1,N
 20      F(I)=FEED1*Y(I)
 200  PBEDIN=P
C     WRITE(30,1000) K
C     WRITE(30,1050) T,(Y(I),I=1,5)
      TG=T
      DO 25 I=1,N
         FG(I)=F(I)
 25      YG(I)=Y(I)
      CALL HEATTR
      G1=AVMW*FEED1/(0.786*DIA*DIA)
      TOTAM1=F(3)
      DEN1=P*AVMW/R/T
      REYNO=DP*G1/VISGM
      FK=1.75+150.0*(1.0-EP)/REYNO
      PRDROP(K)=HBED(K)*FK*G1*G1*(1.0-EP)/(EP*EP*EP)/(DP*DEN1)/1000.0
      P=P-PRDROP(K)/2.0
 220  CONTINUE
 250  CALL DIFEQN
      F(1)=F(1)-0.5*DIFNH3
      F(2)=F(2)-1.5*DIFNH3
      TOTALG=0.0
      DO 30 I=1,N
 30      TOTALG=TOTALG+F(I)
      DO 40 I=1,N
 40      Y(I)=F(I)/TOTALG
C     EQNH3=(Y(3)/(Y(1)**0.5*Y(2)**1.5)/P)*(PNUA/(PNUN**0.5*PNUH**1.5))
      W=W+DW
      TOTCAT=TOTCAT+DW
```

```
      IF(MM.EQ.1) GOTO 520
      IF(ABS(W-ALLCAT(K)).LE.0.01) GOTO 520
      IF(W.GT.ALLCAT(K)) GOTO 500
C     IF(ITER.EQ.1) WRITE(20,1200) T,(Y(I),I=1,5)
      GOTO 220
C     CALCULATION STARTS FOR SUBSEQUENT BEDS
 500  DO 50 I=1,N
 50      F(I)=AG(I+1)
      T=AG(1)
      TOTCAT=TOTCAT-DW
      W=W-DW
      DW=ALLCAT(K)-W
      MM=1
      GOTO 250
 520  CATWT(K)=W
C     WRITE(30,1100) K
C     WRITE(30,1150) T,(Y(I),I=1,5)
      W=0.0
      TOTAMP=F(3)-TOTAM1
      DW=DW1
      MM=0
      TG=T
      DO 60 I=1,N
         FG(I)=F(I)
 60      YG(I)=Y(I)
      CALL HEATTR
      P=PBEDIN-PRDROP(K)
      DEN2=P*AVMW/R/T
      DO 70 I=1,N
 70      FGS(I)=F(I)
      IF(K.GE.NBED) GOTO 600
      PRCPGI=PROCPG*(T-298.0)
      DO 80 I=1,N
 80      F(I)=YY(I)
      T=TEMPC
      TG=T
      DO 90 I=1,N
         FG(I)=F(I)
 90      YG(I)=Y(I)
      CALL HEATTR
      PRCPCI=PROCPG*(T-298.0)
      CLDST(K)=FRACF(K+3)*QUENCH
      TOTALG=TOTALG+CLDST(K)
      DO 95 I=1,N
         F(I)=FGS(I)+CLDST(K)*YY(I)
         Y(I)=F(I)/TOTALG
 95   CONTINUE
      T=TEMPIN
      TG=T
      DO 85 I=1,N
         FG(I)=F(I)
 85      YG(I)=Y(I)
```

```
      II=1
 86   CALL HEATTR
      T=(PRCPCI*CLDST(K)+PRCPGI)/PROCPG+298.0
      IF(ABS(T-TG).LE.0.1.OR.II.GE.4) GOTO 87
      II=II+1
      TG=T
      GOTO 86
 87   T1=T
      K=K+1
      GOTO 200
 600  TOTALE=TOTALG
      DO 75 I=1,N
 75      YE(I)=Y(I)
C     WRITE(20,2050)TOTALG,T,(F(I),I=1,5),(Y(I),I=1,5)
      TOTALG=TOTALE+FEEDGS
      F(1)=TOTALE*YE(1)+FEEDGS*YN2F
      F(2)=TOTALE*YE(2)+FEEDGS*YH2F
      F(3)=TOTALE*YE(3)+FEEDGS*YNH3F
      F(4)=TOTALE*YE(4)+FEEDGS*YCH4F
      F(5)=TOTALE*YE(5)+FEEDGS*YARF
      F(6)=0.0
      F(7)=0.0
      F(8)=0.0
C     CHECKING CONVERGENCE
      TOTLIQ=F(3)
      XNH3=F(3)/TOTLIQ
      TOTDG=TOTALG-F(3)
      YNH3R=PNH3*XNH3/SEPP
      TOTALG=TOTDG/(1.0-YNH3R)
      AMONIA=F(3)-YNH3R*TOTALG
      F(3)=YNH3R*TOTALG
      PRODCT=AMONIA
      XNH3=AMONIA/PRODCT
C     WRITE(20,2200)PRODCT,XNH3
      DO 110 I=1,N
 110     Y(I)=F(I)/TOTALG
C     WRITE(20,2060)TOTALG,(F(I),I=1,5),(Y(I),I=1,5)
      PURGE=TOTALG-RECYCL
      FPRGE=PURGE/FEEDGS
      DO 120 I=1,N
 120     PF(I)=PURGE*Y(I)
      DIFIN=(FCH4+FAR)-(PF(4)+PF(5))
C     WRITE(20,2070)PURGE,FPRGE,DIFIN,(PF(I),I=1,5)
C     CHECK THE TOTAL ABSOLUTE DIFFERENCE BETWEEN ASSUMED AND CALCULATED
C     AMOUNTS OF DIFFERENT COMPONENTS IN THE RECYCLE.
      DO 130 I=1,N
 130     F(I)=RECYCL*Y(I)
      TOTDIF=0.0
      DO 140 I=1,N
 140     TOTDIF=TOTDIF+ABS(RF(I)-F(I))
C     WRITE(20,1300)(RF(I),F(I),I=1,5)
C     WRITE(20,1400) TOTDIF
```

```
      IF(TOTDIF/RECYCL.LE.CONVCR) GOTO 900
      IF(LK.EQ.(NFREQA-1)) THEN
      DO 150 I=1,N
        S(1,I)=RF(I)
150     S(2,I)=F(I)
      IF(LK.EQ.NFREQA) THEN
      DO 160 I=1,N
         S(3,I)=RF(I)
 160     S(4,I)=F(I)
      CALL WEGSTN
      ENDIF
      LK=LK+1
      TOTALG=0.0
      DO 170 I=1,N
 170     TOTALG=TOTALG+F(I)
      DO 180 I=1,N
 180     Y(I)=F(I)/TOTALG
      ITER=ITER+1
      IF(ITER.GT.ITMAX) GOTO 980
      YINR=Y(4)+Y(5)
      YN2R=Y(1)
      YH2R=Y(2)
      YNH3R=Y(3)
      YCH4R=Y(4)
      YARR=Y(5)
C     WRITE(20,1250)FEED1,(CATWT(I),I=1,K),(CLDST(I),I=1,K-1),
C    .(PRDROP(I),I=1,K)
      GOTO 100
 980  WRITE(20,1700)
      RETURN
 900  WRITE(20,1500)
C *********************************************************************
 1000 FORMAT(35X,´START OF BED´,I3,/,35X,15(1H=))
 1050 FORMAT(2X,´BED ENTRANCE TEMP(K)=´,F10.3,/,2X,´MOLE FRAC. OF COMPON
     .ENTS N2,H2,NH3,CH4,AR...=´,5F10.4)
 1100 FORMAT(36X,´END OF BED´,I3,/,36X,13(1H=))
 1150 FORMAT(2X,´BED EXIT TEMP(K)=´,F10.3,/,2X,´MOLE FRAC. OF COMPONENTS
     . N2,H2,NH3,CH4,AR...=´,5F10.4)
 1200 FORMAT(2X,´INSTANTANEOUS BED TEMP(K)=´,F10.3,/,
     .´CORRESPONDING MOLE FRAC. OF N2,H2,NH3,CH4,AR...=´,5F10.4/)
 1250 FORMAT(´FEED USED IN FIRST BED(KMOL/SEC)=´,G12.4,/´WEIGHT OF CATAL
     .YST IN DIFFERENT BEDS(KG)=´/3F12.2,/´COLD SHOT(KMOL/SEC) IN DIFFER
     .ENT BEDS..´/2F12.4,/´PRESSURE DROP IN THE BEDS(KPA)..´/3F12.4)
 1300 FORMAT(/´ASSUMED AND ACTUAL MOLES OF COMPONENTS IN THE RECYCLE´/,(
     .2F12.4,´;´,2F12.4,´;´,2F12.4))
 1400 FORMAT(/´SUM OF ABS.DIFF.OF MOLES OF COMPONENT IN THE RECYCLE´,
    ..F10.4)
 1500 FORMAT(//´CONVERGENCE ACHIEVED´)
 1700 FORMAT(/´MAX.NO.OF ITERATION IS EXCEEDED´)
 2050 FORMAT(/´CONDITION AT THE EXIT OF THE REACTOR..´,/´TOTAL MOLES=´,
     .G12.4,´EXIT GAS TEMP(K)=´,G12.4/´N2,H2,NH3,CH4,AR...´,/´MOLES..´,
     .5G12.4/´MOLE FRAC. ´,5F10.6)
```

```
 2060 FORMAT(/'CONDITION AT THE RECYCLE BEFORE PURGE.',/,'TOTAL MOLES=',
     .G12.6/'N2,H2,NH3,CH4,AR.',/,'MOLES.',5G12.6/'MOLE FRAC.',5F10.6)
 2200 FORMAT(/'CRUDE AMMONIA PRODUCTION RATE(KMOL/SEC)=',F12.6/
     .'AMMONIA FRAC.IN PRODUCT=',F10.6)
 2070 FORMAT('PURGE=',F8.6,'PURGE AS A FRACTION OF FEED=',F8.6/'DIFFEREN
     .CE OF INERT IN FEED & PURGE=',F10.6/'DIFF. MOLES IN PURGE'/5F10.6)
 990  RETURN
      END
C
C***  SUBROUTINE DIFEQN
C
      SUBROUTINE DIFEQN
C     RUNGE-KUTTA-GILL METHOD IS USED TO SOLVE THE SET OF
C     DIFFERENTIAL EQUATIONS.
      COMMON/AL2/DW,ITMAX,ALLCAT(3),FRACF(5)
      COMMON/AL4/G(9),Y(8),AG(9),DIFNH3
      COMMON/AL5/DG(2)
      COMMON/AL11/MM
      COMMON/GCOM3/N
      DIMENSION AK1(5),AK2(5),AK3(5),AK4(5)
      DIFNH3=0.0
      M=N+1
      CALL FUNCT
      DO 5 I=1,M
 5       AG(I)=G(I)
      DO 12 I=1,2
 12      AK1(I)=DG(I)
 70   DO 20 I=1,2
         IF(I.NE.2)K=I
         IF(I.EQ.2)K=4
 20      G(K)=AG(K)+AK1(I)*DW/2.0
      DIFNH3=G(4)-AG(4)
      CALL FUNCT
      DO 30 I=1,2
         AK2(I)=DG(I)
         IF(I.NE.2)K=I
         IF(I.EQ.2)K=4
         G(K)=AG(K)+(-1.0/2.0+1.0/SQRT(2.0))*DW*AK1(I)+
     .   (1.0-1.0/SQRT(2.0))*DW*AK2(I)
 30   CONTINUE
      DIFNH3=G(4)-AG(4)
      CALL FUNCT
      DO 40 I=1,2
         AK3(I)=DG(I)
         IF(I.NE.2)K=I
         IF(I.EQ.2)K=4
         G(K)=AG(K)-1.0/SQRT(2.0)*DW*AK2(I)+(1.0+1.0/SQRT(2.))*DW*AK3(I)
 40   CONTINUE
      DIFNH3=G(4)-AG(4)
      CALL FUNCT
      DO 50 I=1,2
 50      AK4(I)=DG(I)
```

```
      DO 60 I=1,2
         DIFF=DW/6.0*(AK1(I)+2.0*(1.0-1.0/SQRT(2.0))*AK2(I)+2.0*(1.0+1.0
     .   /SQRT(2.0))*AK3(I)+AK4(I))
         IF(MM.EQ.1) GOTO 55
         IF(I.EQ.2) GOTO 55
         IF(ABS(DIFF).GT.5.0) GOTO 300
         IF(ABS(DIFF).LT.0.001)GOTO 400
 55      IF(I.NE.2)K=I
         IF(I.EQ.2)K=4
         G(K)=AG(K)+DIFF
 60   CONTINUE
      GOTO 500
 300  IF(DW.LE.200.) THEN
      DW=200.
      ELSE
      DW=DW/2.0
      ENDIF
      GOTO 70
 400  IF(DW.GE.2000.) THEN
      DW=2000.
      ELSE
      DW=2.0*DW
      ENDIF
      GOTO 70
 500  DIFNH3=G(4)-AG(4)
      DO 80 I=2,M
         IF(I.EQ.4) GOTO 80
         G(I)=AG(I)
 80   CONTINUE
      RETURN
      END
C
C***  SUBROUTINE FUNCT
C
      SUBROUTINE FUNCT
C     THIS SUBROUTINE CALCULATES THE FUNCTION VALUES F(Y,W) OF THE
C     DIFFERENTIAL EQUATIONS PRODUCED FROM MASS AND HEAT BALANCES
C     OF THE AMMONIA SYNTHESIS REACTOR.
C     THE FIRST DIFFERENTIAL EQUATION REPRESENTS THE CHANGE IN
C     GAS TEMPERATURE.
C     THE SECOND DIFFERENTIAL EQUATION REPRESENTS THE CHANGE IN
C     CONCENTRATION OF NH3.
C     N2=1,H2=2,NH3=3,CH4=4,ARGON=5,H2O=6,CO=7,CO2=8
      COMMON/AL1/XNH3,PRODCT,SPNH3,TEMPIN,TEMPC,SEPTEM,SEPP,RECYLR,FPRGE
     .,ALCATW,HBED(3),PRDROP(3),TMAX
      COMMON/AL2/DW,ITMAX,ALLCAT(3),FRACF(5)
      COMMON/AL4/T,F(8),Y(8),AG(9),DIFNH3
      COMMON/AL5/DT,DF3
      COMMON/GCOM1/CATDEN,DIA,P,EP,DP
      COMMON/GCOM3/N
      COMMON/AL6/RATE,PNUN,PNUH,PNUA
      COMMON/PH2/HG(8)
```

```
      COMMON/PH3/AVMW,PROCPG,VISGM
      COMMON/COM2/FG(8),YG(8),TG
      COMMON/HTCOEF/HCANUL,HCCTB,HTCOV1,HTCOV2,FA1,FB1
      COMMON/CONVRT/FEEDGS,YN2F,YH2F,YNH3F,YCH4F,YARF
      F(1)=F(1)-0.5*DIFNH3
      F(2)=F(2)-1.5*DIFNH3
      TOTALG=0.0
      DO 12 I=1,N
 12      TOTALG=TOTALG+F(I)
      DO 20 I=1,N
 20      Y(I)=F(I)/TOTALG
      CALL RATES
      TG=T
      DO 30 I=1,N
         FG(I)=F(I)
 30      YG(I)=Y(I)
      CALL HEATTR
      HR=HG(3)-0.5*HG(1)-1.5*HG(2)
      TOTHR=-(HR*RATE+(HTCOV1*3.1415*DIA*(T-303.)+HTCOV2*3.1415
     .*0.203*(T-700.))/(CATDEN*0.789*DIA*DIA))
C     DIFFERENTIAL EQUATIONS
      DT=TOTHR/PROCPG
      DF3=RATE
      RETURN
      END
C
C***  SUBROUTINE RATES
C
      SUBROUTINE RATES
C     IN THIS SUBROUTINE THE RATE OF AMMMONIA SYNTHESIS
C     IS CALCULATED.
C     REACTION:1/2*N2+3/2*H2=NH3
C     RATE:RATE OF REACTION(KMOL AMMONIA/KG-CAT/SEC)
      COMMON/AL1/XNH3,PRODCT,SPNH3,TEMPIN,TEMPC,SEPTEM,SEPP,RECYLR,
     .FPRGE,ALCATW,HBED(3),PRDROP(3),TMAX
      COMMON/AL2/DW,ITMAX,ALLCAT(3),FRACF(5)
      COMMON/AL4/T,F(8),Y(8),AG(9),DIFNH3
      COMMON/AL6/RATE,PNUN,PNUH,PNUA
      COMMON/GCOM1/CATDEN,DIA,P,EP,DP
      COMMON/GCOM3/N
      COMMON/AL15/K
      COMMON/PH2/HG(8)
      DIMENSION B(7)
      DATA B/-4.6757259,.02354872,4.687353,-3.463308E-5,-11.28031,
     .1.540881E-8,10.46627/
      R=1.987
      P=P/101.325
      PN2=P*Y(1)
      PH2=P*Y(2)
      PNH3=P*Y(3)
```

```
C     CALCULATION OF RATE OF AMMONIA SYNTHESIS REACTION
      GLK=-2.69112*ALOG(T)-1.271086E-04*T+4.257931E-07*T*T+4009.6848/T+
     .6.194839
      GK=EXP(GLK)
      PNU=EXP(-3.8402*T**0.125+0.541)*P-EXP(-0.1263*SQRT(T)-15.98)
     .*(P*P)+300.*(EXP(-0.011901*T-5.941))*(EXP(-P/300.)-1.0)
      PNUH=EXP(PNU)
      PNUN=0.93431737+0.3101804E-03*T+0.295896E-03*P-0.2707279E-06*T*T
     .+0.4775207E-06*P*P
      PNUA=0.1438996+0.2028538E-02*T-0.4487672E-03*P-0.1142945E-05*T*T
     .+0.2761216E-06*P*P
      X=F(3)/(F(3)+2.0*F(1))
C     EFFECTIVENESS FACTOR
      ETA=B(1)+B(2)*T+B(3)*X+B(4)*T*T+B(5)*X*X+B(6)*T*T*T+B(7)*X*X*X
      XX1=0.9017344E+00
      XX2=0.1415377E-05
      XX3=0.1499977E+02
      XX4=0.4216922E+01
      TIME=5.00
      RATE=1.0E15*ETA*EXP(-XX4*1.0E04/(R*T))*XX3*((1.0-XX2)+XX2*EXP(
     .     -XX1*TIME))*((GK*GK*P**1.5*(PNUN*Y(1)*((PNUH*Y(2))**1.5))
     .     /(PNUA*Y(3)))-1./(SQRT(P))*((PNUA*Y(3))/((PNUH
     .     *Y(2))**1.5)))*(0.87)/3600.0/CATDEN
      P=P*101.325
      RETURN
      END
C
C***  SUBROUTINE HEATTR
C
      SUBROUTINE HEATTR
C     SUBROUTINE TO CALCULATE THE CONVECTIVE AND OVERALL HEAT
C     TRANSFER COEFFICIENT.
C ********VARIABLES*********
C     CPG(I)=SPECIFIC HEAT OF COMPONENT I AT GAS
C            PHASE TEMPERATURE,KJ/KMOL/K
C     VIS(I)=VISCOSITY OF COMPONENT I,KG/M/S
      DIMENSION VIS(8),THC(8)
      COMMON/GCOM1/CATDEN,DIA,P,EP,DP
      COMMON/GCOM3/N
      COMMON/DD/HS(8),CPS(8),CPG(8),ES(8),EG(8)
      COMMON/PH1/TC(8),GPC(8),AMW(8),HV(8)
      COMMON/PH2/HG(8)
      COMMON/PH3/AVMW,PROCPG,VISGM
      COMMON/COM2/FG(8),YG(8),TG
      COMMON/HTCOEF/HCANUL,HCCTB,HTCOV1,HTCOV2,FA1,FB1
      AVMW=0.0
      ANUM1=0.0
      ANUM2=0.0
      DNOM1=0.0
      DNOM2=0.0
      HTCAM=0.0
```

```
      TOTALG=0.0
      DCT=0.203
      AREA=3.1415*DIA*DIA/4.0
      DO 12 I=1,N
         AVMW=AVMW+YG(I)*AMW(I)
 12      TOTALG=TOTALG+FG(I)
      PROCPG=0.0
      DO 20 M=1,N
         CALL VISCO(M,TG,VIS(M))
         CALL CPH(M,TG,CPG(M),EG(M),HG(M))
 20      PROCPG=PROCPG+FG(M)*CPG(M)
C     VISCOSITY OF THE GAS MIXTURE IS DETERMINED BY SOME
C     AVERAGING TECHNIQUE(PERRY,5TH,EDITION.P:3-249)
      DO 30 I=1,N
         ANUM1=ANUM1+YG(I)*VIS(I)*SQRT(AMW(I))
         DNOM1=DNOM1+YG(I)*SQRT(AMW(I))
 30      HTCAM=HTCAM+YG(I)*CPG(I)
      VISGM=ANUM1/DNOM1
C     THERMAL CONDUCTIVITY OF THE GASEOUS MIXTURE IS
C     DETERMINED BY SOME AVERAGING TECHNIQUE,
C     (PERRY,5TH EDITION.P:3-244)
      DO 40 M=1,N
         CALL CPH(M,TG,CPG(M),EG(M),HG(M))
         CALL THCON(M,TG,CPG(M),VIS(M),THC(M))
 40   CONTINUE
      DO 50 I=1,N
         ANUM2=ANUM2+YG(I)*THC(I)*AMW(I)**0.33
 50      DNOM2=DNOM2+YG(I)*AMW(I)**0.33
C     R IS THE UNIVERSAL GAS CONSTANT,KPA-M**3/KMOLE-K
      R=8.314
      THCONM=ANUM2/DNOM2
      TOTGMF=TOTALG*AVMW/AREA
      REYNO=TOTGMF*DP/VISGM
      PRNO=HTCAM*VISGM/AVMW/THCONM
C     CONVECTIVE HEAT TRANSFER COEFFICIENT INSIDE TOWER
      HCBED1=0.023*THCONM/DIA*(REYNO)**0.8*(PRNO)**0.33
      HCBED2=HCBED1*DIA/DCT
C     OVERALL HEAT TRANSFER COEFFICIENT
      CALL CNVTTR
      HTCOV1=HCBED1*HCANUL/(HCBED1+HCANUL)
      HTCOV2=HCBED2*HCCTB/(HCBED2+HCCTB)
      RETURN
      END
C
C***  SUBROUTINE CNVTTR
C
      SUBROUTINE CNVTTR
C     SUBROUTINE TO CALCULATE THE ANNULUS AND CENTRE TUBE
C     CONVECTIVE HEAT TRANSFER COEFFICIENT
      DIMENSION VIS(8),THC(8)
```

```
      COMMON/GCOM1/CATDEN,DIA,P,EP,DP
      COMMON/GCOM3/N
      COMMON/DD/HS(8),CPS(8),CPG(8),ES(8),EG(8)
      COMMON/PH1/TC(8),GPC(8),AMW(8),HV(8)
      COMMON/PH2/HG(8)
      COMMON/PH3/AVMW,PROCPG,VISGM
      COMMON/COM2/FG(8),YG(8),TG
      COMMON/HTCOEF/HCANUL,HCCTB,HTCOV1,HTCOV2,FA1,FB1
      TCNTB=700.0
      TANULS=303.0
      K=1
 111  AVMW=0.0
      ANUM1=0.0
      ANUM2=0.0
      DNOM1=0.0
      DNOM2=0.0
      HTCAM=0.0
      IF(K.EQ.1) TT=TANULS
      IF(K.EQ.2) TT=TCNTB
      DO 12 I=1,N
 12      AVMW=AVMW+YG(I)*AMW(I)
      DO 20 M=1,N
         CALL VISCO(M,TT,VIS(M))
 20      CALL CPH(M,TT,CPG(M),EG(M),HG(M))
C     VISCOSITY OF THE GAS MIXTURE IS DETERMINED
C     BY SOME AVERAGING TECHNIQUE
      DO 30 I=1,N
         ANUM1=ANUM1+YG(I)*VIS(I)*SQRT(AMW(I))
         DNOM1=DNOM1+YG(I)*SQRT(AMW(I))
 30      HTCAM=HTCAM+YG(I)*CPG(I)
      VISGM=ANUM1/DNOM1
C     THERMAL CONDUCTIVITY OF THE GASEOUS MIXTURE IS
C     DETERMINED BY SOME AVERAGING TECHNIQUE
      DO 40 M=1,N
         CALL CPH(M,TT,CPG(M),EG(M),HG(M))
         CALL THCON(M,TT,CPG(M),VIS(M),THC(M))
 40   CONTINUE
      DO 50 I=1,N
         ANUM2=ANUM2+YG(I)*THC(I)*AMW(I)**0.33
 50      DNOM2=DNOM2+YG(I)*AMW(I)**0.33
      THCONM=ANUM2/DNOM2
      PRNO=HTCAM*VISGM/AVMW/THCONM
      IF(K.EQ.2) GOTO 60
C     CONVECTIVE HEAT TRANSFER COEFFICIENT OF THE
C     GAS MIXTURE IN THE ANNULUS
      SHELL=2.032
      ANULUS=3.1415*(SHELL-DIA)**2/4.0
      GMF=FA1*AVMW/ANULUS
      REYNO=GMF*(SHELL-DIA)/VISGM
      HCANUL=0.023*THCONM/DIA*(REYNO)**0.8*(PRNO)**0.33
```

```
C     CONVECTIVE HEAT TRANSFER COEFFICIENT OF THE
C     GAS MIXTURE IN THE CENTRE TUBE
      K=K+1
      TOTCNG=FA1+FB1
      GO TO 111
 60   DCT=0.203
      CNTRTB=3.1415*DCT*DCT/4.0
      CTGMF=TOTCNG*AVMW/CNTRTB
      REYNO=CTGMF*DCT/VISGM
      HCCTB=0.023*THCONM/DCT*(REYNO)**0.8*(PRNO)**0.33
      RETURN
      END
```

```
C
C***  SUBROUTINE COMPRS
C
      SUBROUTINE COMPRS
C     PROGRAM TO DESIGN A COMPRESSOR
C ********* INPUT DATA ***********
C     INLET GAS TEMP.,TGIN(K),INLET PRESSURE,PIN(KPA)
C     OUTLET PRESSURE,POUT(KPA)
C     FLOW RATES OF GASES (F(I),I=1,N) (KMOLE/S)
C     ALLOWABLE COMPRESSION RATIO,RLMT
C     N2=1,H2=2,NH3=3,CH4=4,ARGON=5,H2O=6,CO=7,CO2=8
C     CSIND1=MARSHALL & SWIFT EQUIPMENT COST INDEX FOR YEAR,1980
C     CSIND2=MARSHALL & SWIFT EQUIPMENT COST INDEX FOR 4TH QR. OF 1984.
      DIMENSION CPG(8)
      COMMON/CMP1/PIN,POUT,RLMT,TGIN,TGOUT,STEAMP
      COMMON/COM2/FG(8),YG(8),TG
      COMMON/CST1/CSIND2,FLANG,COST
      COMMON/AR4/FPOWER,ULTPWR
      COMMON/GCOM3/N
      COMMON/DSC3/NSTAGE
      CSIND1=569.0
      TOTALG=0.0
      DO 10 I=1,N
 10      TOTALG=TOTALG+FG(I)
      DO 20 I=1,N
 20      YG(I)=FG(I)/TOTALG
C     FROM THE VALUE OF COMPRESSION RATIO(POUT/PIN),CALCULATE THE
C     NUMBER OF STAGES TO BE USED IN THE COMPRESSOR,BASED ON THE
C     ASUMPTION THAT THE COMPRESSION RATIOWILL BE LESS THAN OR EQUAL
C     TO ALLOWABLE LIMIT,RLMT.
      COMPR=POUT/PIN
      RLMT1=RLMT
      NSTAGE=1
 30   IF(COMPR.LT.RLMT1) GOTO 40
      NSTAGE=NSTAGE+1
      RLMT1=RLMT1*RLMT
      GOTO 30
C     CALCULATION OF APPROXIMATE OUTLET TEMPERATURE OF THE GAS.
C     GAS CONSTANT,R=8.314 KPA-M**3/KMOLE-K
C     VOLUME OF FEED,VOLF(M**3/S)
 40   VOLF=TOTALG*8.314*TGIN/PIN
      EFFC=0.645+0.025*ALOG10(2118.9*VOLF)
      TGAV=TGIN
C     GAS CONSTANT,R=1.987 KCAL/KMOLE-K
      TOTK=0.0
      DO 50 I=1,N
         CALL CPH(I,TGAV,CPG(I),EN,H2)
         AK=CPG(I)/(CPG(I)-8.314)
 50      TOTK=TOTK+AK*YG(I)
      AN=1.0/(1.0-((TOTK-1.0)/(TOTK*EFFC)))
      TGOUT=TGIN*(COMPR)**((AN-1.0)/(AN*NSTAGE))
      TGAV=(TGIN+TGOUT)/2.0
```

```
      ZS=1.0
      ZD=ZS
      TOTK=0.0
      DO 60 I=1,N
         CALL CPH(I,TGAV,CPG(I),EN,H2)
         AK=CPG(I)/(CPG(I)-8.314)
 60      TOTK=TOTK+AK*YG(I)
      AN=1.0/(1.0-((TOTK-1.0)/TOTK/EFFC))
C     POWER(KW)
      FPOWER=AN/(AN-1.)*(ZS+ZD)/2.0*8.314*NSTAGE*TGIN*((COMPR)**((AN-1.0
     +)/(AN*NSTAGE))-1.0)*TOTALG/EFFC
      TGOUT=TGIN*(COMPR)**((AN-1.)/(AN*NSTAGE))
C     COSTING.....
C     BASE PRICE FOR CENTRIFUGAL COMPRESSOR(JUNE,1970,US$,
C     BACKHURST,ETAL,1973)
      COST=FPOWER*2260.0*(FPOWER)**(-0.5)
C     IF THE PRESSURE IS MORE THAN 6893 KPA,INCREASE THE COST
      IF(POUT.LE.6893.0) GOTO 70
      COST=COST*(1.0+0.00064*(POUT)**0.68)
C     USE LANG FACTOR=2.5 TO GET THE TOTAL CAPITAL INVESTMENT
C     FOR COMPRESSORS(PETER & TIMMERHAUS,1979)
 70   COST=COST*FLANG
C     UPDATE THE COST AT THE PRESENT TIME USING COST INDEXES
      COST=COST*CSIND2/CSIND1
      RETURN
      END
C
C***  SUBROUTINE PRESSV
C
      SUBROUTINE PRESSV
C     PROGRAM TO DESIGN CYLINDRICAL & SPHERICAL PRESSURE VESSEL.
C     DESIGN PRESSURE IS OBTAINED BY ADDING 10% OF MAXIMUM OPERATING
C     PRESSURE WITH THE OPERATING PRESSURE.
C     DESIGN TEMP. IS TAKEN AS OPERATING TEMP. PLUS 28 DEG. K
C     CONSTRUCTION MATERIAL IS ASSUMED TO BE CARBON STEEL(SA-285,GR.C)
C     EFFICIENCY OF THE WELDING JOINT(EFFJ),FRACTION
C     ALLOWABLE STRESS VALUE FOR THE MATERIAL OF CONSTRUCTION
C     (STRESS),KPA.
C     CORROSION ALLOWANCE(CORRA),M
C     DENSITY OF THE MATERIAL(DENSS),KG/M**3
C     FOLLOWING DATA ARE NEEDED FOR THIS SUBROUTINE....
C     DESIGN PRESSURE(DESGP),RADIUS OF VESSEL(RADIV),LENGTH OF VESSEL
C     (FOR CYLINDRICAL VESSEL HEGHT),DESIGN TEMP.(DESGT),NUMBER OF TRAY
C     (NOTRA),CAPACITY OF THE HEAD PORTION OF THE VESSEL(HEADV),M**3
C     DIFFERENT OPTIONS:OPTN1 IS FOR SHAPE OF VESSEL.
C     OPTN2 IS FOR TYPE OF VESSEL HEAD.
C     OPTN3 IS FOR VESSEL INSTALLED POSITION.
C     OPTN4 IS FOR CHECKING WHETHER TRAY COST TO BE CALCULATED OR NOT.
C     COST FACTOR FOR THE MATERIAL OF CONSTRUCTION(FACTRM).
```

```
C     OPTN1=1,FOR CYLINDRICAL VESSEL
C          =2,FOR SPHERICAL VESSEL
C     OPTN2=1,FOR HEMISPHERICAL VESSEL HEAD
C          =2,FOR ELLIPSOIDAL VESSEL HEAD
C     OPTN3=1,FOR VERTICAL INSTALLED POSITION
C          =2,FOR HORIZONTALINSTALLED POSITION
C     OPTN4=1,FOR NOT CALCULATING THE COST OF TRAYS
C          =2,FOR CALCULATING THE COST OF TRAYS
      INTEGER OPTN1,OPTN2,OPTN3,OPTN4
      COMMON/PV1/RADIV,HEGHT,NOTRA,HEADV
      COMMON/PV2/OPTN1,OPTN2,OPTN3,OPTN4
      COMMON/CST1/CSIND2,FLANG,COST
      COMMON/COM1/TPRDRP,FACTRM
      COMMON/GCOM1/CATDEN,DIA,P,EP,DP
      CSIND1=569.0
      EFFJ=0.85
      STRESS=82776.78
      DESGP=1.1*P
      DENSS=7835.0
      DIAV=2.0*RADIV
      CORRA=0.004
C     CALCULATION OF WALL THICKNESS
      IF(OPTN1.EQ.2) GOTO 10
C     CALCULATION FOR CYLINDRICAL VESSEL
      WALLT=DESGP*RADIV/(STRESS*EFFJ-0.6*DESGP)+CORRA
      IF(WALLT.LE.(RADIV/2.0).OR.DESGP.LE.0.385*STRESS*EFFJ) GOTO 20
      WALLT=RADIV*SQRT((STRESS*EFFJ+DESGP)/(STRESS*EFFJ-DESGP))
     +-RADIV+CORRA
 20   WEGHTS=2.0*3.1415*RADIV*HEGHT*WALLT*DENSS
      GOTO 30
C     CALCULATION FOR SPHERICAL VESSEL
 10   WALLT=DESGP*RADIV/(2.0*STRESS*EFFJ-0.2*DESGP)+CORRA
      IF(WALLT.LE.0.356*RADIV.OR.DESGP.LE.0.665*STRESS*EFFJ) GOTO 40
      WALLT=RADIV*((2.0*EFFJ*STRESS+2.0*DESGP)/(2.0*STRESS*EFFJ-DESGP))
     .**0.333-RADIV+CORRA
 40   WEGHTS=4.0*3.1415*RADIV*WALLT*(RADIV+WALLT)*DENSS
      WEGHTH=0.0
      GOTO 70
C     CALCULATION FOR DETERMINING THE WEIGHT OF THE HEAD PORTION OF THE
C     CYLINDRICAL VESSEL.
C     TOP & BOTTOM OF THE VESSEL ARE ASSUMED TO BE OF SAME SHAPE.
 30   IF(OPTN2.EQ.1) GOTO 60
C     FOR ELLIPSOIDAL HEAD....
      AN=1.2
      IF(DIAV.GT.1.524.AND.DIAV.LE.2.0) AN=1.21
      IF(DIAV.GT.2.001.AND.DIAV.LE.2.69) AN=1.22
      IF(DIAV.GT.2.69) AN=1.23
      WEGHTH=2.0*3.1415*(AN*DIAV+WALLT)*(AN*DIAV+WALLT)*WALLT*DENSS/4.
      HEADV=3.1415*DIAV*DIAV*DIAV/24.0
      GOTO 70
```

```
C     FOR HEMISPHERICAL HEAD....
 60   WEGHTH=4.0*3.1415*RADIV*RADIV*WALLT*DENSS
      HEADV=3.1415*DIAV*DIAV*DIAV/12.0
 70   WEGHTT=WEGHTS+WEGHTH
C     TO ACCOUNT FOR EXTRA WEIGHT DUE TO NOZZLES,MANHOLES,ETC. THE TOTAL
C     WEIGHT IS INCREASED BY 15% FOR HORIZONTAL POSITION OR BY 20% FOR
C     VERTICAL POSITION.
      IF(OPTN3.EQ.1) GOTO 80
      WEGHTT=1.15*WEGHTT
      GOTO 85
 80   WEGHTT=1.2*WEGHTT
C     CALCULATION OF THE COST OF THE VESSEL(PETER & TIMMERHAUS,
C     P-574,1979)
C     FACTRM(COST FACTOR FOR THE MATERIAL OF CONSTRUCTION)
 85   TOTCST=110.2*(2.204*WEGHTT)**(-0.34)*WEGHTT
C     INSTALLED COST OF THE VESSEL
      COST=TOTCST
      IF(OPTN4.EQ.1) GOTO 90
      COSTTR=NOTRA*(-67.2+350.39*DIAV)/(1.0-0.146*DIAV)
      GOTO 95
 90   COSTTR=0.0
 95   COST=COST+COSTTR
      RETURN
      END
C
C***  SUBROUTINE SEPAR
C
      SUBROUTINE SEPAR
C     PROGRAM TO DETERMINE THE DIAMETER AND HEIGHT AND
C     HENCE THE COST OF GAS-LIQUID SEPARATOR
C     **********INPUT DATA**********
C     GASEOUS COMPONENT FLOWRATE,F(I),KMOLE/S
C     LIQUID COMPONENT FLOWRATE,FL(I),KMOLE/S
C     OPERATING TEMPERATURE,SEPTEM,K
C     OPERATING PRASSURE,P,KPA
C     SPECIFIC VOLUME OF LIQUID COMPONENT J,SPVOL(J),M**3/KG
C     CALCULATION OF MAXIMUM ALLOWABLE SUPERFICIAL GAS VELOCITY,
C     BASED ON THE EXPRESSION;V=K*SQRT((DENL-DENG)/DENG)
C     CALCULATION OF LIQUID DENSITY(KG/M**3)
C     CSIND1=MARSHALL & SWIFT EQUIPMENT COST INDEX FOR
C            PROCESS INDUSTRIES FOR THE YEAR 1979
C     CSIND2=MARSHALL & SWIFT EQUIPMENT COST INDEX FOR
C            PROCESS INDUSTRIES FOR 3RD QR. OF 1984
      DIMENSION XL(5)
      INTEGER OPTN1,OPTN2,OPTN3,OPTN4
      COMMON/AL4/TG,F(8),Y(8),AG(9),DIFNH3
      COMMON/AR1/FL(5)
      COMMON/AR3/NN,NL
      COMMON/PV1/RADIV,HEGHT,NOTRA,HEADV
```

```
      COMMON/PV2/OPTN1,OPTN2,OPTN3,OPTN4
      COMMON/CST1/CSIND2,FLANG,COST
      COMMON/COM1/TPRDRP,FACTRM
      COMMON/PH1/TC(8),GPC(8),AMW(8),HV(8)
      COMMON/HTV1/TL,HVT(8),CPL(8),SPVL(8),VISL(8)
      COMMON/GCOM1/CATDEN,DIA,P,EP,DP
      CSIND1=569.0
      N=NN
      TOTALL=0.0
      DO 10 J=1,NL
 10      TOTALL=TOTALL+FL(J)
      DO 20 J=1,NL
 20      XL(J)=FL(J)/TOTALL
      TL=TG
      CALL DENLIQ
      TSPVOL=0.0
      DO 30 J=1,NL
 30      TSPVOL=TSPVOL+XL(J)*SPVL(J)
      AVDENL=1.0/TSPVOL
C     CALCULATION OF GAS DENSITY(KG/M**3)
C     GAS CONSTANT,R=8.314 M**3-KPA/KMOLE-K
      R=8.314
      TOTALG=0.0
      DO 40 I=1,N
 40      TOTALG=TOTALG+F(I)
      AVMOLG=0.0
      DO 50 I=1,N
         Y(I)=F(I)/TOTALG
 50      AVMOLG=AVMOLG+Y(I)*AMW(I)
      AVDENG=AVMOLG*P/(R*TG)
C     CALCULATION OF ALLOWABLE VELOCITY,(M/S)
C     80% OF ALLOWABLE VELOCITY IS USED
      AK=0.11
      ALVEL=0.8*AK*((AVDENL-AVDENG)/AVDENG)**0.5
      DIASEP=SQRT((4.0*TOTALG*R*TG)/(P*3.1415*ALVEL))
      RADIV=DIASEP/2.0
C     CALCULATION OF HEIGHT OF THE SEPARATOR
      HEGHT=3.0*DIASEP
C     COST OF MIST ELIMINATOR IS ASSUMED TO FIVE TIMES
C     THAT OF SIEVE TRAY
      NOTRA=5
      CALL PRESSV
C     CALCULATE TOTAL CAPITAL INVESTMENT FROM EQUIPMENT COST
C     BY USING LANG FACTOR,FLANG(PETER & TIMMERHAUS,P-181,1979)
      COST=COST*FLANG
C     UPDATE THE COST BY USING THE COST INDEXES.
      COST=COST*CSIND2/CSIND1
C     PRESSURE DROP CALCULATION FOR WIRE MESH DEMISTER
C     PRESSURE (KPA)
C     IN CASE OF WETTED AND DRAINED CASE:
      TPRDRP=0.0115*(3.28*ALVEL)**1.71*0.0254
      RETURN
      END
```

```
C
C***  SUBROUTINE HEATEX
C
      SUBROUTINE HEATEX
C     PROGRAM FOR PRELIMINARY DESIGN OF A SHELL & TUBE
C     HEAT EXCHANGER.
C     THE FOLLOWING OPTIONS ARE USED:
C         IPTN11=1  FOR ORDINARY HEAT EXCHANGER
C               =2  FOR CONDENSER
C               =3  FOR REBOILER
C         IPTN12=1  WHEN HEAT LOAD IS TO BE CALCULATED
C                   FROM SHELL SIDE FLUID
C               =2  WHEN HEAT LOAD IS TO BE CALCULATED
C                   FROM TUBE SIDE FLUID
C         IPTN13=1  WHEN SHELL SIDE FLUID IS LIQUID
C               =2  WHEN SHELL SIDE FLUID IS GAS/VAPOR
C         IPTN14=1  WHEN TUBE SIDE FLUID IS LIQUID
C               =2  WHEN TUBE SIDE FLUID IS GAS/VAPOR
C         IPTN15=1  WHEN SHELL SIDE PRESSURE DROP IS TO BE
C                   CALCULATED
C               = OTHER THAN 1,SHELL SIDE PRESSURE DROP NEED
C                   NOT TO BE CALCULATED
C         IPTN16=1  WHEN TUBE SIDE PRESSURE DROP IS TO BE
C                   CALCULATED
C               = OTHER THAN 1,TUBE SIDE PRESSURE DROP NEED
C                   NOT TO BE CALCULATED
C     FOR SIMPLIFYING THE CALCULATIONS,THE FOLLOWING AVERAGE VALUES
C     ARE USED:
C     BAFFLE SPACING=0.6*SHELL ID
C     BAFFLE SEGMENTAL CUT FRACTION BS=0.25
C     *********** VARIABLES ***********
C     ALPHAT=TUBE SIDE HEAT TRANSFER COEFFICIENT
C            (KW/M**2-K)
C     ALPHAS=SHELL SIDE HEAT TRANSFER COEFFICIENT
C            (KW/M**2-K)
C     FOULT=TUBE SIDE FOULING COEFFICIENT
C           (M**2-K/KW)
C     FOULS=SHELL SIDE FOULING COEFFICIENT
C           (M**2-K/KW)
C     CSIND1=MARSHALL AND SWIFT EQUIPMENT COST INDEX FOR
C            THE PROCESS INDUSTRIES FOR 1979.
C     CSIND2=COST INDEX FOR 3RD.QRT. OF 1984.
C     FLANG=LANG FACTOR=3.5
C     SATP=SATURATED STEAM PRESSURE,KPA ABS.
      DIMENSION CPS(8),CPT(8),XS(8),XT(8),VIS(8)
      COMMON/HX1/ALPHAS,ALPHAT,FOULS,FOULT,SPRESD,TPRESD,PREST
      COMMON/HX2/FS(8),FT(8)
      COMMON/HX3/IPTN11,IPTN12,IPTN13,IPTN14,IPTN15,IPTN16,
     .NTPASS,NS,NT
      COMMON/HX4/AO,AI
      COMMON/HX5/TSIN,TSOUT,TTIN,TTOUT
      COMMON/HTV1/T,HVT(8),CPL(8),SPVL(8),VISL(8)
```

```
      COMMON/HTV2/NC
      COMMON/HTV3/TCL(8),GPCL(8),AMWL(8)
      COMMON/PH1/TC(8),GPC(8),AMW(8),HV(8)
      COMMON/CST1/CSIND2,FLANG,COST
      COMMON/GCOM1/CATDEN,DIA,P,EP,DP
      COMMON/AL16/CATCST,STMCS1,STMCS2,COLWCS,ELECST
      COMMON/COM3/EFFCB,SATP,HEATLD
      COMMON/DSC3/NSTAGE
      COMMON/DSC4/COSTRB,COSTCN,ULTSTM,ULTNH3
C
C     CALCULATION OF OVERALL HEAT TRANSFER COEFFICIENT
C     OVRHT(KW/M**2-K)
      CSIND1=569.0
      OVRHT=1.0/(1.0/ALPHAT+1.0/ALPHAS+FOULT+FOULS)
      TOD=0.02
      TID=TOD-0.0042
      IF(IPTN11.EQ.2) GOTO 499
      IF(IPTN11.EQ.3) GOTO 600
C     CALCULATION OF SHELL SIDE FLUID PROPERTIES
      TOTLS=0.0
      PROCPS=0.0
      AVMOLS=0.0
      VISCOS=0.0
      ANUM1=0.0
      DENOM=0.0
      TSPVL=0.0
      NC=NS
      DO 10 J=1,NS
 10      TOTLS=TOTLS+FS(J)
      DO 20 J=1,NS
 20      XS(J)=FS(J)/TOTLS
      IF(TSIN.EQ.0.0) THEN
         AVTS=TSOUT
         ELSE IF(TSOUT.EQ.0.0) THEN
         AVTS=TSIN
      ELSE
         AVTS=(TSIN+TSOUT)/2.0
      ENDIF
      T=AVTS
      IF(IPTN13.EQ.1) THEN
C     SHELL SIDE FLUID IS LIQUID
         CALL VISLIQ
         CALL CPLQ
          CALL DENLIQ
         DO 30 J=1,NS
            CPS(J)=CPL(J)
            AVMOLS=AVMOLS+XS(J)*AMWL(J)
            VISCOS=VISCOS+XS(J)*ALOG(VISL(J))
 30         TSPVL=TSPVL+XS(J)*SPVL(J)
         VISCOS=EXP(VISCOS)
         DENS=1.0/TSPVL
      ELSE
```

```
C      SHELL SIDE FLUID IS GAS/VAPOR
          DO 40 J=1,NS
             AVMOLS=AVMOLS+XS(J)*AMW(J)
             CALL CPH(J,AVTS,CPS(J),EN,H2)
 40          CALL VISCO(J,AVTS,VIS(J))
          DO 50 J=1,NS
             ANUM1=ANUM1+XS(J)*VIS(J)*SQRT(AMW(J))
 50          DENOM=DENOM+XS(J)*SQRT(AMW(J))
          VISCOS=ANUM1/DENOM
       ENDIF
       IF(ABS(TOTLS-1.).GT.1.0E-4) THEN
          DO 60 J=1,NS
 60          PROCPS=PROCPS+FS(J)*CPS(J)
       ELSE
          DO 70 J=1,NS
 70          PROCPS=PROCPS+XS(J)*CPS(J)
       ENDIF
C      CALCULATION OF TUBE SIDE FLUID PROPERTIES
 499   TOTLT=0.0
       PROCPT=0.0
       AVMOLT=0.0
       VISCOT=0.0
       ANUM1=0.0
       DENOM=0.0
       TSPVL=0.0
       NC=NT
       DO 80 J=1,NT
 80       TOTLT=TOTLT+FT(J)
       DO 90 J=1,NT
 90       XT(J)=FT(J)/TOTLT
       IF(TTIN.EQ.0.0) THEN
          AVTT=TTOUT
          ELSE IF(TTOUT.EQ.0.0) THEN
          AVTT=TTIN
       ELSE
          AVTT=(TTIN+TTOUT)/2.0
       ENDIF
       T=AVTT
       IF(IPTN14.EQ.1) THEN
C      TUBE SIDE FLUID IS LIQUID
          CALL VISLIQ
          CALL CPLQ
          CALL DENLIQ
          DO 100 J=1,NT
          CPT(J)=CPL(J)
          AVMOLT=AVMOLT+XT(J)*AMWL(J)
          VISCOT=VISCOT+XT(J)*ALOG(VISL(J))
 100      TSPVL=TSPVL+XT(J)*SPVL(J)
          VISCOT=EXP(VISCOT)
          DENT=1.0/TSPVL
       ELSE
```

```
C       TUBE SIDE FLUID IS GAS/VAPOR
           DO 110 J=1,NT
              AVMOLT=AVMOLT+XT(J)*AMW(J)
              CALL CPH(J,AVTT,CPT(J),EN,H2)
 110          CALL VISCO(J,AVTT,VIS(J))
           DO 120 J=1,NT
              ANUM1=ANUM1+XT(J)*VIS(J)*SQRT(AMW(J))
 120          DENOM=DENOM+XT(J)*SQRT(AMW(J))
           VISCOT=ANUM1/DENOM
        ENDIF
        IF(ABS(TOTLT-1.).GT.1.0E-4) THEN
           DO 130 J=1,NT
 130          PROCPT=PROCPT+FT(J)*CPT(J)
        ELSE
        DO 140 J=1,NT
 140       PROCPT=PROCPT+XT(J)*CPT(J)
        ENDIF
        IF(IPTN12.NE.1) GOTO 300
C       HEAT LOAD CALCULATION FROM SHELL SIDE FLUID
        HEATLD=PROCPS*(TSOUT-TSIN)
C       CALCULATE EITHER THE INLET OR OUTLET TEMPERATURE
C       OF THE TUBE SIDE FLUID IF THE FLOWRATE IS KNOWN
        IF(TTIN.EQ.0.0) THEN
        TTIN=TTOUT+HEATLD/PROCPT
        ELSE IF(TTOUT.EQ.0.0) THEN
        TTOUT=TTIN-HEATLD/PROCPT
        ELSE
C       IF BOTH INLET & OUTLET TUBE SIDE TEMPERATURE ARE KNOWN THEN
C       CALCULATE THE TUBE SIDE FLOW REQUIREMENT
        TOTLT=HEATLD/(PROCPT*(TTIN-TTOUT))
        DO 150 J=1,NT
 150       FT(J)=TOTLT*XT(J)
        ENDIF
        GOTO 700
 300    CONTINUE
C       HEAT LOAD CALCULATION FROM TUBE SIDE SPECIFICATIONS
        HEATLD=PROCPT*(TTIN-TTOUT)
C       CALCULATE EITHER THE INLET OR OUTLET TEMPERATURE
C       OF THE SHELL SIDE FLUID IF THE FLOWRATE IS KNOWN
        IF(IPTN11.EQ.2) GOTO 511
        IF(TSIN.EQ.0.0) THEN
        TSIN=TSOUT-HEATLD/PROCPS
        ELSE IF(TSOUT.EQ.0.0) THEN
        TSOUT=TSIN+HEATLD/PROCPS
        ELSE
C       IF BOTH INLET & OUTLET SHELL SIDE TEMPERATURE ARE KNOWN
C       THEN CALCULATE SHELL SIDE FLOW REQUIREMENT
        TOTLS=HEATLD/(PROCPS*(TSOUT-TSIN))
        DO 160 J=1,NS
 160       FS(J)=TOTLS*XS(J)
        ENDIF
        GOTO 700
C500    CONTINUE
```

```
C      CALCULATION FOR CONDENSER.
C      ASSUMPTIONS:
C      1) VAPORS ARE IN THE SHELL SIDE.
C      2) COOLING MEDIUM IS WATER,IN THE TUBE SIDE
C      3) NO SUPERHEATED VAPOR AND SUBCOOLING OF THE
C         CONDENSED LIQUID.
C      4) MAXIMUM OUTLET COOLING WATER TEMPERATURE IS
C         ASSUMED TO BE ALWAYS BELOW 322 K
C         (ACCORDING TO BACKHURST & HARKER,P-80(1973)
C          SCALING TENDS TO INCREASE AT THIS PIONT)
C      CALCULATION OF HEAT LOAD
C      TOTLT=0.0
C      DO 170 J=1,NT
C170      TOTLT=TOTLT+FT(J)
C      DO 180 J=1,NT
C180      XT(J)=FT(J)/TOTLT
C      AVTT=(TTIN+TTOUT)/2.0
C      T=AVTT
C      CALCULATION OF AVERAGE LATENT HEAT OF CONDENSATION OR
C      VAPORISATION.
C      CALL HTVAP
C      THVT=0.0
C      DO 190 J=1,NS
C190      THVT=THVT+XS(J)*HVT(J)
C      HEATLD=TOTLS*THVT
C      CALCULATION OF COOLING WATER REQUIREMENT
C      AND ITS ANNUAL COST
 511   AVTS=TSIN
       T=AVTS
       NC=NS
       CALL CPLQ
C      CLWATR=ABS(HEATLD)/(CPL(2)*(TTOUT-TTIN))/EFFCB
C      ULTCOL=CLWATR*3.1536E7*COLWCS*CSIND2/CSIND1
       ALQNH3=ABS(HEATLD)/(CPL(1)*AVTS*EFFCB)
       ULTNH3=ALQNH3*AMWL(1)*3.1536E7*1.0E-3*CSIND2/CSIND1
       GOTO 700
 600   CONTINUE
C      CALCULATION FOR REBOILER
C      ASSUMPTIONS:
C      1) HEATING MEDIUM IS SATURATED STEAM IN THE TUBE SIDE.
C         CALCULATION OF AMOUNT OF STEAM REQUIREMENT.
C         CALCULATION OF SATURATED STEAM TEMPERATURE(K) AND
C         LATENT HEAT OF CONDENSATION(KJ/KG)
C         SATP,SATURATED STEAM ABSOLUTE PRESSURE(KPA)
C         (MAX. ALLOWABLE RANGE 1000 KPA)
       TOTLS=0.0
       DO 200 J=1,NS
 200      TOTLS=TOTLS+FS(J)
       DO 210 J=1,NS
 210      XS(J)=FS(J)/TOTLS
       AVTS=TSIN
       AVTT=(TTIN+TTOUT)/2.0
       T=AVTS
```

```
C     CALCULATION OF AVERAGE LATENT HEAT OF CONDENSATION OR
C     VAPORISATION.
      CALL HTVAP
      THVT=0.0
      DO 220 J=1,NS
 220     THVT=THVT+XS(J)*HVT(J)
      HEATLD=TOTLS*THVT
      SP=SATP/100.0
      SATT=349.74+26.634*SP-2.94406*SP**2+0.133348*SP**3
      DELHS=2353.569-93.024*SP+113.05*SP**2-0.551*SP**3
C     CALCULATION OF ANNUAL STEAM REQUIREMENT & ITS COST
      STEAMF=ABS(HEATLD)/DELHS/EFFCB
      ULTSTM=STEAMF*3.1536E7*STMCS2*CSIND2/CSIND1
      TSIN=SATT
      TSOUT=TSIN
C     CALCULATION OF LOGMEAN TEMPERATURE DIFFERENCE
 700  CONTINUE
      DELT1=ABS(TSIN-TTOUT)
      DELT2=ABS(TSOUT-TTIN)
      IF(IPTN11.EQ.2) GOTO 740
       ALMTD=ABS((DELT1-DELT2)/ALOG(DELT1/DELT2))
       FCOR=1.0
       IF(NTPASS.GT.1) THEN
         IF(TSIN.GT.TTIN) THEN
            TR=(TSIN-TSOUT)/(TTOUT-TTIN)
            TS=(TTOUT-TTIN)/(TSIN-TTIN)
         ELSE
            TR=(TTIN-TTOUT)/(TSOUT-TSIN)
            TS=(TSOUT-TSIN)/(TTIN-TSIN)
       ENDIF
C     CALCULATION FOR (1-2N) SHELL & TUBE LMTD CORRECTION FACTOR
      DELTA=(TR-1.)/ALOG((1.0-TS)/(1.0-TS*TR))
      SQ=SQRT(TR*TR+1.)
      ALOGIE=(2.0-TS*(1.0+TR-SQ))/(2.0-TS*(1.0+TR+SQ))
       IF(ALOGIE.LT.0.0) THEN
          FCOR=1.0
       ELSE
          FCOR=SQ/DELTA/ALOG(ALOGIE)
       ENDIF
      ENDIF
      AMTD=FCOR*ALMTD
      WRITE(6,*)'TR=',TR,'TS=',TS,'FCOR=',FCOR,'ALMTD=',ALMTD
      GOTO 745
 740  AMTD=ABS(TSIN-TTIN)
C     ESTIMATION OF HEAT TRANSFER AREA BASED ON OUTSIDE TUBE AREA
 745  AO=ABS(HEATLD)/(OVRHT*AMTD)
C     CALCULATION OF APPROXIMATE NO. OF TUBES,TUBE & SHELL
C     GEOMETRIES.
C     USING AN EFFECTIVE TUBE LENGTH OF 8.0 METRE AND AN AVERAGE
C     DCTL/LTA=0.15(FROM HEDH,P3.1.4-7);
C     DCTL=DS(INSIDE SHELL DIAMETER)-(LBB+DT);LBB=INSIDE SHELL
C     DIAMETER-TO-TUBE BUNDLE BY PASS CLEARANCE
C     TOD=OUTER DIA. OF THE TUBE
```

```
      TLEN=8.0
      TOD=0.02
C     WALL THICKNESS OF TUBE IS 0.0021 M
      TID=TOD-0.0042
      SPRESD=0.0
      TPRESD=0.0
      IF(IPTN15.NE.1.AND.IPTN16.NE.1) GOTO 900
 750  DCTL=0.15*TLEN
C     ASSUMING SPLIT RING & PACKED FLOATING HEAD.OD OF TUBE=0.02 M
      AVLLB=0.042
      DS=DCTL+(TOD+AVLLB)
      ALLB=0.025+0.017*DS
      DS=DCTL+(TOD+ALLB)
C     ASSUMING ALTP(TUBE PITCH) IS 1.33*TOD
C     THE 30 DEG. STAGGERED LAYOUT IS ASSUMED HERE.
C     C1=A TUBE FIELD LAYOUT CONSTANT BASED ON TUBE LAYOUT
C     CHARACTERISTIC ANGLE.FOR 30 DEG. C1=0.866,
C     FOR 45 & 90 DEGREES C1=1.0
C     CALCULATION FOR THE TOTAL NO. OF TUBES
      C1=0.866
      ALTP=1.33*TOD
      TOTNT=0.78*DCTL**2/(C1*(ALTP**2))
C     CORRECTION FACTOR FOR NO. OF PASSES.
C     (FROM HEDH,P 3.3.5-12)
      IF(NTPASS.EQ.1) PHIC=0.0
      IF(NTPASS.NE.1) PHIC=NTPASS*0.025
      TOTNT=(1.0-PHIC)*TOTNT
C     CALCULATION OF EFFECTIVE TUBE LENGTH
      TLEN=AO/(TOTNT*3.1415*TOD)
C     CHECK WHETHER TUBE LENGTH IS TOO SMALL OR TOO BIG;
C     ADJUST TUBE LENGTH BETWEEN 3.0 & 12.0 M
C     CALCULATION OF SHELL SIDE BAFFLE SPECIFICATION.
C     AVERAGE BAFFLE SPACING IS 3/5*DS(FROM HEDH,P 3.3.5-7)
      IF(TLEN.LT.2.4) TLEN=3.0
      IF(TLEN.GT.10.0) TLEN=12.0
      TOTNT=AO/(3.1415*TOD*TLEN)
      DCTL=SQRT(TOTNT*C1*ALTP**2/0.78)
      DS=DCTL+(TOD+AVLLB)
      ALLB=0.025+0.017*DS
      DS=DCTL+(TOD+ALLB)
      TOTNT=TOTNT*(1.0-PHIC)
      BAFS=3.0/5.0*DS
C     CALCULATION OF TOTAL LENGTH OF THE TUBE
C     CALCULATION OF TUBE SHEET THICKNESS
      ALTS=0.1*DS
      TTLEN=TLEN+2.0*ALTS
C     CHECK WHETHER TUBE SIDE PRESSURE DROP CALCULATION IS NEEDED.
      IF(IPTN16.NE.1) GOTO 800
C     CALCULATION OF TUBE SIDE PRESSURE DROP
C     CALCULATION OF TUBE SIDE VELOCITY.
```

```
      IF(IPTN14.EQ.2) THEN
      VELT=TOTLT*8.314*AVTT/PREST/(TOTNT/NTPASS*0.785*TID**2)
      DENT=PREST*AVMOLT/(8.314*AVTT)
      ELSE
      VELT=TOTLT*AVMOLT/DENT/(TOTNT/NTPASS*(0.785*TID**2))
      ENDIF
C     CALCULATION OF TUBE SIDE REYNOLDS NUMBER,TNRE
      TNRE=DENT*TID*VELT/VISCOT
C     CALCULATION OF TUBE SIDE FRICTION FACTOR
C     FOR(1000<TNRE<10**6)
      FRICF=0.05573/(TNRE**0.261)
      TPRESD=8.0*FRICF*(TLEN/TID)*DENT*VELT**2/2.0*NTPASS
C     ADDITION OF PRSSURE DROP DUE TO CHANGE IN DIRECTION
C     FOUR VELOCITY HEADS PER PASS
      VELH=4.0*VELT**2/(2.0*DENT)
      TPRESD=(TPRESD+NTPASS*4.0*VELH)/1000.0
  800 CONTINUE
C     CHECK WHETHER SHELL SIDE PRESSURE DROP IS NEEDED OR NOT
      IF(IPTN15.NE.1) GOTO 900
C     CALCULATION OF SHELL SIDE PRESSURE DROP
C     CALCULATION OF SHELL SIDE REYNOLDS NUMBER.
C     CALCULATION OF THE CROSS-SECTIONAL FLOW AREA,SM
C     AT THE SHELL CENTER LINE WITHIN ONE BAFFLE SPACING.
      IF(IPTN13.EQ.2) THEN
      DENS=P*AVMOLS/(8.314*AVTS)
      ENDIF
      DCTL=0.15*TLEN
      DS=DCTL+(TOD+AVLLB)
      ALLB=0.025+0.017*DS
      SM=BAFS*(ALLB+DCTL/ALTP*(ALTP-TOD))
      SNRE=TOD*(TOTLS*AVMOLS/SM)/VISCOS
C     CALCULATION OF AVERAGE WALL TEMPERATURE
      TWALL=AVTT+(AVTS-AVTT)/(1.0+ALPHAT/ALPHAS)
C     CALCULATION OF THE SHELL SIDE FRICTION FACTOR
      IF(SNRE.GE.1.0E04) THEN
      B1=0.372
      B2=-0.123
      ELSE IF(SNRE.LT.1.0E04.AND.SNRE.GE.1.0E03) THEN
      B1=0.486
      B2=-0.152
      ELSE IF(SNRE.LT.1.0E03.AND.SNRE.GE.1.0E02) THEN
      B1=4.57
      B2=-0.476
      ELSE IF(SNRE.LT.1.0E02.AND.SNRE.GE.10.) THEN
      B1=45.1
      B2=-0.973
      ENDIF
      B3=7.0
      B4=0.5
      B=B3/(1.0+0.14*(SNRE)**B4)
      FRICF=B1*(1.33/(ALTP/TOD))**B*(SNRE**B2)
```

```
C     CALCULATION OF TOTAL NO. OF TUBE CROSSES.
      ALPP=0.866*ALTP
      BC=0.25
      ANTCC=DS/ALPP*(1.0-2.0*BC)
      SPRESD=2.0*FRICF*ANTCC*(TOTLS*AVMOLS/SM)**2/DENS*1.0E-3
C     TO GET ACTUAL PRESSURE DROP INCREASE THE
C     SHELL SIDE PRESSURE DROP BY A FACTOR OF 5
C     (APPROXIMATELY TAKEN FROM HEDH,P 3.3.9-6)
      SPRESD=5.0*SPRESD
C     COST ESTIMATION
C     FLOATING HEAD EXCHANGER IS ASSUMED.
C     OPERATING PRESSURE=6892.85 KPA
C     PURCHASED COST IN $(JAN,1979)
 900  AI=AO*TID/TOD
      COST=1621.81*(AI)**0.582
C     CORRECTION FOR TUBE DIA.
      CORTD=(0.7397-0.1977*TOD*39.37)/(1.0-0.4598*TOD*39.37)
C     CORRECTION FOR TUBE LENGTH
      CORTL=(-0.2-0.275*3.28*TLEN)/(1.0-0.35*3.28*TLEN)
C     CORRECTION FOR OPERATING PRESSURE
      IF(P.LE.4300.0) THEN
      CORPR=(0.963659-0.000061*P)/(1.0-0.000128*P)
      ELSE
      CORPR=2.0
      ENDIF
      COST=COST*CORTD*CORTL*CORPR
C     CALCULATE THE TOTAL CAPITAL INVESTMENT & ALSO UPDATE IT.
      COST=COST*FLANG*CSIND2/CSIND1
      RETURN
      END
```

```
C
C***  SUBROUTINE CPH
C
      SUBROUTINE CPH(J,TEMP,CP,EN,H2)
C     This subroutine calculates the molar heat capacity and
C     enthalpy of gases at temperature TEMP
C     HFO = Heat of formation at 298 degres K.
C     Unit of enthalpy is kJ/kmole
C     Unit of Cp is kJ/kmole-K
C     T is in degree K;Cp = AB+BC*T+CC*T*T+DD*T**3
C     Unit of viscosity is kg/m-s
C     Unit of thermal conductivity is kJ/m-s-K
C     Unit of diffusivity(DIFF) is m**2/s
C     Components:1=N2,2=H2,3=NH3,4=CH4,5=ARGON,6=H2O,7=CO,8=CO2
C     ******* Variables *******
C     TC(I) = Critical temperature of component I,K
C     GPC(I) = Critical pressure of component I,kPa
C     AMW(I) = Molecular weight of component I,kg/kmole
C     HV(I) = Heating value of component I,kJ/kmole
C     HFO(I) = Standard heat of formation of component I,kcal/kmole
      COMMON/PH1/TC(8),GPC(8),AMW(8),HV(8)
      COMMON/GCOM1/CATDEN,DIA,P,EP,DP
      DIMENSION AB(8),BC(8),CC(8),DD(8),HFO(8),V(8)
      DATA AB,BC,CC,DD/7.44,6.483,6.524,4.598,4.969,7.701,7.373,4.728,
     .               -.324,.2215,.5692,1.245,.000767,.04595,-.307,1.754,
     .                .64,-.3298,.4078,.286,.001234,.2521,.6662,-1.338,
     .               -2.79,1.826,-2.83,-2.703,0.0,-.859,-3.037,4.097/
      DATA HFO/0.0,0.0,-10920.,-17889.,0.0,-57798.,-26416.,-94052./
      DATA V/17.9,7.07,14.9,24.4,16.1,12.7,18.9,26.9/
      A1=(TEMP-298.)
      A2=(TEMP*TEMP-298.*298.)/2.0
      A3=(TEMP*TEMP*TEMP-298.*298.*298.)/3.0
      A4=(TEMP*TEMP*TEMP*TEMP-298.*298.*298.*298.)/4.0
      CP=(AB(J)+BC(J)*TEMP*1.E-2+CC(J)*TEMP*TEMP*1.E-5+DD(J)
     .   *TEMP*TEMP*TEMP*1.E-9)*4.184
      EN=(AB(J)*A1+BC(J)*1.E-2*A2+CC(J)*1.E-5*A3+DD(J)*1.E-9*A4)*4.184
      H2=(HFO(J)+AB(J)*A1+BC(J)*1.E-2*A2+CC(J)*1.E-5*A3+DD(J)*1.E-9*A4)
     .   *4.184
      RETURN
C     Viscosity is determined by Reichenberg method
      ENTRY VISCO(J,TEMP,VISC)
      A=3.5*SQRT(AMW(J))*(GPC(J)/101.325)**.67/TC(J)**.17
      TR=TEMP/TC(J)
      VISC=A*TR/(1.+.36*TR*(TR-1.))**.17*(1.E-07)
      RETURN
C     Thermal conductivity of the gases is determined
C     by Eucken's method, Perry, 5th edtn,. p:3-243.
      ENTRY THCON(J,TEMP,SPH,VISC,THCO)
      THCO=(VISC*10.)/AMW(J)*(SPH/4.184+2.503)*4.184/10.
      RETURN
```

```
C     Diffusivity of the binary mixture is determined
C     by an optimized Gilliland type equation
C     Perry, 5th edtn., p:3-233
      ENTRY DFSVTY(K,J,TEMP,DIFF)
      DIFF=0.001*(TEMP*1.75)*SQRT(1./AMW(K)+1./AMW(J))/
     .(P/101.325*(V(K)**.333+V(J)**.333)**2)*(1.E-4)
      RETURN
      END
C
C***  BLOCK DATA
C
      BLOCK DATA
      COMMON/PH1/TC(8),GPC(8),AMW(8),HV(8)
      COMMON/HTV3/TCL(8),GPCL(8),AMWL(8)
      DATA TC/126.2,33.2,405.6,190.6,150.8,647.3,132.9,304.2/
      DATA GPC/3394.39,1296.96,11277.47,4600.16,4873.7,22048.32,3495.71,
     .         7376.46/
      DATA AMW/28.013,2.016,17.031,16.043,39.948,18.015,28.01,44.01/
      DATA TCL/405.6,647.3,6*0.0/
      DATA GPCL/11277.47,22048.32,6*0.0/
      DATA AMWL/17.031,18.015,6*0.0/
      END
C
C***  SUBROUTINE HTVAP
C
      SUBROUTINE HTVAP
C     This subroutine calculate either latent heat of vapourization
C     or condensation of pure vapour.
C     First latent heat is calculated at the normal boiling point
C     by the Reidel method, then it is updated using a correlation
C     HV2 = HV1*((1-TR2)/(1-TR1))**0.38
C     (Reid, Sherwood & Prausnitz, 1979)
C     The unit of HVT is kJ/kmole
C     1=NH3,2=H2O
C     R = Universal gas constant, kJ/kmole-K
C     TC = Critical temperature, K
C     GPC = Critical pressure, kPa
C     TB = Normal boiling temperature, K
      DIMENSION TB(8),ACWL(8),CPG(8),TRF(8),VR(8),VRRO(8),VRRT(8),
     .GAMMA(8),GAMMAR(8),TRC(8),TRRC(8),B(8),TO(8)
      COMMON/HTV1/T,HVT(8),CPL(8),SPVL(8),VISL(8)
      COMMON/HTV2/NC
      COMMON/HTV3/TCL(8),GPCL(8),AMWL(8)
      DATA ACWL/0.250,0.344,6*0.0/
      DATA TB/239.7,373.2,6*0.0/
      DATA TRF/273.2,293.0,6*0.0/
      DATA VR/1.565E-3,1.0E-3,6*0.0/
      R=8.314
      DO 10 J=1,NC
         HVB=1.093*R*TCL(J)*(TB(J)/TCL(J))*(ALOG(GPCL(J)/101.325)-1.00)
     .   /(0.93-TB(J)/TCL(J))
 10      HVT(J)=HVB*((1.0-T/TCL(J))/(1.0-TB(J)/TCL(J)))**0.38
      RETURN
```

```
      ENTRY CPLQ
C     This subroutine calculates the specific heat of pure liquid
C     The unit of CPL if kJ/kmole-K
C     1=NH3,2=H2O
C     Corresponding method is used
C     (Reid, Sherwood & Prausnitz, 1979)
C     R = Universal gas constant, 8.314 kJ/kmole-K
      R=8.314
      CALL CPH(3,T,CPG(1),EN,H2)
      CALL CPH(6,T,CPG(2),EN,H2)
      DO 20 J=1,NC
         TR=T/TCL(J)
 20      CPL(J)=CPG(J)+R*(0.5+2.2*ACWL(J))*(3.67+11.64*(1.0-TR)*(1.-TR)
     .   *(1.-TR)*(1.-TR)+0.634/(1.0-TR))
      RETURN
      ENTRY DENLIQ
C     Program to calculate specific volume of water and
C     ammonia by Gunn & Yamada method
C     1=NH3,2=H2O
      DO 30 I=1,2
         TRRC(I)=TRF(I)/TCL(I)
         TRC(I)=T/TCL(I)
      DO 40 J=1,2
         GAM=0.29607-0.09045*TRC(I)-0.04842*TRC(I)*TRC(I)
      IF(TRC(I).GE.0.8) GOTO 50
      VRO=0.33593-0.33953*TRC(I)+1.51941*TRC(I)*TRC(I)-2.02512
     .*TRC(I)*TRC(I)*TRC(I)+1.11422*TRC(I)*TRC(I)*TRC(I)*TRC(I)
      GOTO 55
 50   VRO=1.0+1.3*SQRT(1.0-TRC(I))*ALOG10(1.-TRC(I))-.50879
     .*(1.-TRC(I))-0.91534*(1.0-TRC(I))*(1.-TRC(I))
 55   IF(J.NE.1) GOTO 60
      GAMMA(I)=GAM
      VRRO(I)=VRO
      TRC(I)=TRRC(I)
 60   VRRT(I)=VRO
      GAMMAR(I)=GAM
 40   CONTINUE
      SPVL(I)=VR(I)*(VRRO(I)*(1.0-ACWL(I)*GAMMA(I)))/(VRRT(I)*
     .(1.0-ACWL(I)*GAMMAR(I)))
 30   CONTINUE
      RETURN
      ENTRY VISLIQ
C     This subroutine calculates viscosity of pure liquids.
C     Van Valzen, Cardazo & Langkemp´s method is used.
C     (Reid, Sherwood & Prausnitz, 1979)
C     The unit of ciscosity is kg/m-s
C     T = Temperature, K
C     1=NH3,2=H2O
      DATA B,TO/349.04,658.25,6*0.0,169.63,283.16,6*0.0/
      DO 70 I=1,NC
 70      VISL(I)=(10.0**(B(I)*(1.0/T-1.0/TO(I))))*1.0E-3
      RETURN
      END
```

```
C
C***  SUBROUTINE PRINT
C
      SUBROUTINE PRINT
C     The final results for Ammonia Synthesis loop are
C     printed in this subroutine
      COMMON IW,IR
      COMMON/AL1/XNH3,PRODCT,SPNH3,TEMPIN,TEMPC,SEPTEM,SEPP,RECYLR,FPRGE
     .,ALCATW,HBED(3),PRDROP(3),TMAX
      COMMON/AL2/DW,ITMAX,ALLCAT(3),FRACF(5)
      COMMON/AL4/T,F(8),Y(8),AG(9),DIFNH3
      COMMON/AL7/CLDST(3),CATWT(3)
      COMMON/AL14/GTOT,TOTALE,YY(8),YE(8)
      COMMON/CONVRT/FEEDGS,YN2F,YH2F,YNH3F,YCH4F,YARF
      COMMON/GCOM1/CATDEN,DIA,P,EP,DP
      COMMON/GCOM2/DZ,NBED
      COMMON/GCOM3/N
      OPEN(UNIT=20,STATUS='NEW',FILE='OUTPUT',FORM='FORMATTED')
C
      TOTALG=0.0
      DO 10 I=1,N
 10      TOTALG=TOTALG+F(I)
      DO 20 I=1,N
 20      Y(I)=F(I)/TOTALG
      WRITE(20,30)FEEDGS,YN2F,YH2F,YNH3F,YCH4F,YARF
      WRITE(20,40)TOTALE,(YE(I),I=1,5)
      WRITE(20,50)PRODCT
      WRITE(20,100)TOTALG,(Y(I),I=1,5)
      WRITE(20,200)T,(CLDST(I),I=1,NBED-1)
      WRITE(20,300)(CATWT(I),I=1,NBED)
      WRITE(20,400)(HBED(I),I=1,NBED)
 30   FORMAT(//'FRESH FEED USED(KMOL/S)=',F10.3,/,'MOLE FRAC. OF N2,H2,
     .NH3,CH4,AR...=',5F10.4)
 40   FORMAT('REACTOR EXIT GAS(KMOL/S)=',F10.3,/,'MOLE FRAC. OF N2,H2,
     .NH3,CH4,AR...=',5F10.4)
 50   FORMAT('AMMONIA PRODUCED(KMOL/S)=',F10.4)
 100  FORMAT('TOTAL RECYCLED GAS(KMOL/S)=',F10.3,/,'MOLE FRAC. OF COMP.
     .IN RECYCLE'/' N2,H2,NH3,CH4,ARGON...'/(5F12.5))
 200  FORMAT('EXIT TEMP. OF GAS(DEG K)=',F12.5,/
     .'COLD SHOT REQUIRED(KMOLE/S)=',(3F12.5))
 300  FORMAT('WEIGHT OF CATALYST IN DIFFERENT BEDS(KG)...=',(3F12.2))
 400  FORMAT('HEIGHT OF BEDS IN THE REACTOR(M)...='/(3F12.5))
      RETURN
      END

C
C***  SUBROUTINE WEGSTN
C
      SUBROUTINE WEGSTN
C     In this subroutine Wegestein's accelerating technique is used
C     for quick convergence.
C     Convergence forcing is used for each component whose ammount
C     is greater than a certain fraction in the recycle stream.
C     Accelerating method is used in an interval of a certain
C     no. of iterations.
C     CVUPRL=Upper limit of Q;CVLWRL=Lower limit of Q.
C     NFREQA=Interval of number of iterations at which
C            accelerating method is used.
```

```
C     FRACMN=Minimum fraction of component used in
C            Wegestein's application.
      COMMON IW,IR
      COMMON/AL2/DW,ITMAX,ALLCAT(3),FRACF(5)
      COMMON/AL4/T,F(8),Y(8),AG(9),DIFNH3
      COMMON/AL9/CVUPRL,CVLWRL,NFREQA,FRACMN,ICOUNF
      COMMON/AL10/S(4,8),LK,ICOUNT
      COMMON/GCOM3/N
      DIMENSION Q(8)
      TOTALG=0.0
      DO 10 I=1,N
 10      TOTALG=TOTALG+F(I)
      ICOUNT=ICOUNT+1
      DO 20 I=1,N
         IF(ICOUNT.GT.ICOUNF) THEN
         F(I)=(S(4,I)+S(3,I)+S(1,I))/3.0
         ICOUNT=0
         GOTO 20
         ENDIF
         IF(S(4,I)/TOTALG.LT.FRACMN) GOTO 200
         IF(ABS(S(3,I)-S(1,I)).LT.0.001) GOTO 200
         W=(S(4,I)-S(2,I))/(S(3,I)-S(1,I))
         Q(I)=-W/(1.0-W)
         IF(Q(I).GT.CVUPRL) Q(I)=CVUPRL
         IF(Q(I).LT.CVLWRL) Q(I)=CVLWRL
         GOTO 300
 200     Q(I)=0.0
 300     F(I)=Q(I)*S(3,I)+(1.-Q(I))*S(4,I)
 20   CONTINUE
C     WRITE(IW,1000)(Q(I),I=1,N)
      LK=0
 1000 FORMAT(' Q(I);VALUES...',8F10.4)
      RETURN
      END
```

```
*** DATA FOR AMMONIA REACTOR SIMULATION ***

1.391
0.2460    0.7401    0.0       0.0113    0.0026
0.1950    0.6311    0.0280    0.1057    0.0337
1.0       0.6262    1.0
700.00    794.11    463.0     268.0     28161.0
29848.8            30
         8500.0              3
2700.0    2.0       0.293     0.008
4.0       0.03      0.001
0.60      0.40      0.55      0.25       0.20
0.0       -30.0               3          2          0.001
5.0       10.0      35.0
16980.0   25470.0   39620.0

*** DATA FOR AMMONIA REACTOR ***

    1    1    1    15.6       811.2     2.73       7
0.1E01    4.210E-3  2.10E-3   2.640E-5  0.5E-01   0.75E00

*** DATA FOR CONVERTER HEAT EXCHANGER ***

463.0     700.0     0.0       0.0       0.75      0.8
0.05      0.05      3.5
    1    8    8    1    1    2    2    1    1

*** DATA FOR WASTE HEAT BOILER ***

306.0     318.0     0.0       513.0     6.0       0.75
0.2       0.05      3.5
    2    2    8    1    2    1    2    2    2

*** DATA FOR PROCESS GAS HEAT EXCHANGER ***

303.0     463.0     0.0       0.0       0.75      0.4
0.05      0.05      3.5
    2    8    8    1    1    2    2    1    1

*** DATA FOR WATER COOLER ***

306.0     318.0     0.0       312.0     6.0       0.75
0.2       0.05      3.5
    1    2    8    1    2    1    2    2    1

*** DATA FOR COLD EXCHANGER ***

265.0     293.0     0.0       0.0       0.75      0.8
0.05      0.05      3.5
    1    8    8    1    1    2    2    2    2
```

```
*** DATA FOR AMMONIA CHILLER ***

258.0      258.0      0.0        265.0      0.75       0.8
0.05       0.05       3.5
    1     2     8     2     2     1     2     2     2

*** DATA FOR AMMONIA SEPARATOR ***

    1     1     1     11.0        4.0

*** DATA FOR MAKEUP FEED COMPRESSOR ***


293.0      25200.0   4.0        2.5        534.48

*** DATA FOR RECYCLE GAS COMPRESSOR ***

296.0      24400.0   4.0        2.5        534.48
```

# APPENDIX IV

## Module for a centrifugal compressor

Some compressors perform closely to adiabatic conditions; many others deviate significantly from adiabatic conditions, and must be considered polytropic. In this work the compression cycle was assumed to be polytropic.

Compressor design here was based on the following steps:

(i) Calculation of the number of compression stages.

According to Peters and Timmerhaus (1979), multistage compression is necessary if the ratio of the delivery pressure and intake pressure exceeds approximately 5:1. For this work a ratio of 4:1 was chosen. We can thus easily calculate the number of compression stages necessary.

(ii) Calculation of outlet temperature.

Assuming equal division of work in each stage and intercooling in between stages are such that inlet temperature to each stage is identical to the initial temperature, the outlet temperature was calculated by the following expression:

$$T_d = T_s\,(r_c)^{(n-1)/(n*N_s)} \qquad \text{(IV-1)}$$

Where, $r_c = (P_o/P_i)$

$$\frac{n-1}{n} = \frac{k-1}{k}\left(\frac{1}{\eta_p}\right) \; ; \quad k = \frac{C_p}{C_v}$$

$\eta_p$ for centrifugal compressor having backward-curved impellers can be obtained by the following correlation,

$$\eta_p = 0.645 + 0.25\log_{10}(0.59\ V_F) \qquad \text{(IV-2)}$$

(iii)Calculation for power requirement:

The power required to compress the fluid was calculated using the following correlation:

$$\text{Power (kW)} = \frac{1}{\eta_p} \left(\frac{n}{n-1}\right)\left(\frac{Z_s+Z_d}{2}\right) * R * N_s * T_s(r_c^{n-1/(nN_s)} - 1) * F_g \qquad \text{(IV-3)}$$

where, $R = 8.314$ kJ kmole$^{-1}$ K$^{-1}$

(iv) Calculation of total cost of the compressor:

Compressor cost was calculated using, (Backhurst et al., 1973)

$$\text{Base price (\$/kW)} = 2260.0 \text{ kW}^{-0.5} \qquad \text{(IV-4)}$$

Cost was increased for pressure more than 6893 kPa.

% increase in price = $0.064\ P^{0.68}$

Where, P = highest operating pressure, kPa.

## Module for a gas liquid separator

Gas liquid separator was designed on the basis of following steps:

(i) Gaseous and liquid flow, operating pressure and temperature were passed to the separator subroutine as input data.

(ii) Maximum allowable superficial gas velocity was calculated using, (Peters and Timmerhaus, 1979)

$$V_g = K_v \frac{\rho_l - \rho_g}{\rho_g} \qquad \text{(IV-5)}$$

The necessary diameter of the separator was calculated using allowable operating gas velocity (70% of the maximum velocity) and volumetric gas flow rate.

$$D_{sp} = \frac{4\ G_{gf}}{\pi\ V_g} \qquad \text{(IV-6)}$$

(iv) Height of the separator was calculated assuming height is equal to three times of diameter.

$$H_{sp} = 3\ D_{sp} \qquad (IV-7)$$

(v) The pressure drop in the wire mesh demister was calculated using the following correlation for wetted and drained demister (Perry, et al., 1984).

$$P_{dr} = 0.0115\ (3.28\ V_{sg})^{1.771} * 0.0254\ \text{kPa} \qquad (IV-8)$$

(vii)The cost of the separator was calculated similarly like a pressure vessel; and also that of wire mesh demister assuming its cost was around four to five times that of sieve tray.

## Module for a pressure vessel

Assumptions:

(1) Design pressure is 10% more than the maximum operating pressure (Backhurst, et al., 1973).

(2) For vessels operating between 245 K and 615 K, the design temperature was taken as the maximum temperature plus 28 K (Backhurst, et al., 1973).

(3) Construction material was assumed to be carbon steel (SA - 285, Gr. C).

(4) Corrosion allowance was taken as 0.004 m.

Pressure vessel was designed on the basis of the following steps:-

(i) The following data were passed to the pressure vessel subroutine:

Shape of the vessel (Cylindrical or Spherical), shape of the head in case of cylindrical vessel (Elliptical or Hemispherical), maximum operating temperature and pressure, diameter and height of the vessel, allowable stress value of the material concerned, efimum operating temperature and pressure, diameter and height of the vessel, allowable stress value of the material concerned, efficiency of the welding joint, corrosion allowance, no. of trays and types (if used), density of the material concerned.

(ii) Wall thickness, $W_t$ (Peters and Timmerhaus, 1980) was calculated using,

For cylindrical shells:

$$W_t = \frac{P * R_i}{S * E - 0.6 P} + C_c \quad \text{for } W_t < 0.5 R_i \text{ or } P < 0.385 S * E \qquad \text{(IV-9)}$$

$$= R_i \frac{S * E + P}{S * E - P} - R_i + C_c \quad \text{for } W_t > 0.5 R_i \text{ or } P > 0.385 S * E \qquad \text{(IV-10)}$$

For spherical vessels:

$$W_t = \frac{P * R_i}{2 S * E - 0.2 P} + C_c \quad \text{for } W_t < 0.356 R_i \text{ or } P < 0.665 S * E \qquad \text{(IV-11)}$$

$$= \frac{2 S * E + 2 P}{2 S * E - P} - R_i + C_c \quad \text{for } W_t > 0.5 R_i \text{ or } P > .385 S * E \qquad \text{(IV-12)}$$

(iii)The weight of the cylindrical shell or that of the spherical vessel was calculated using,

For cylindrical shell:

$$W_{tv} = 2\pi R_i H_t W_t \rho_{mt} \qquad \text{(IV-13)}$$

For spherical vessels:

$$W_{tv} = 4\pi R_i W_t (R_i + W_t) \rho_{mt} \qquad \text{(IV-14)}$$

(iv) The weight of the head portion in case of a cylindrical vessel was calculated using,

For Ellipsoidal head:

$$W_{th} = \frac{\rho_{mt} [\pi(nD_o + W_t)^2 W_t]}{4} ; \qquad \text{(IV-15)}$$

$n = 1.20$ for $D_o < 1.524$

$n = 1.21$ for $1.525 < D_o < 2$

$n = 1.22$ for $2 < D_o < 2.69$

$$n = 1.23 \text{ for } D_a > 2.7$$

For Hemispherical head:

$$W_{th} = \rho_{mt} ( 2\pi L_a^2 W_t) \qquad \text{(IV-16)}$$

(v) The total weight of the vessel was increased by 15% for horizontal position or by 20% for vertical position to take into account of extra weight due to nozzles, manholes and skirts or saddles.

(vi) Cost of the vessel (in US $, Jan, 1979, Peters and Timmerhaus, 1980) was calculated using,

$$C_{tv} = 110.2 ( 2.204 W_{tt})^{-0.34} W_{tt} \qquad \text{(IV-17)}$$

(vii)The cost was updated using factors for material of construction.

(viii)Installed cost of the vessel was calculated from the purchasing cost using Lang factors.

Lang factor = 3 for horizontally installed vessels.

Lang factor = 4 for vertically installed vessels.

(ix) Installed cost of trays (Peters anfd Timmerhaus, 1980) was calculated using,

$$C_{tr} = N_{tr} \frac{(-67.2 + 350.39 D_i)}{( 1.0 - 0.146 D_i)} \qquad \text{(IV-18)}$$

(x) The total cost of both vessel and trays were updated using cost indexes.

## Module for a Shell and Tube Heat Exchanger

This preliminary design algorithm of a shell and tube heat exchanger assumes:-

1. The overall heat transfer coefficient U, the flow rate and specific heat of the two streams are constant throughout the heat exchanger.
2. For pure countercurrent flow or cocurrent flow, the temperature of either fluid is uniform over any cross section of its path.
3. For a baffled shell and tube exchanger, the heat transferred in each baffle compartment is small compared to the overall heat load i.e. the no. of baffles is large (usually more than 5).
4. Isothermal boiling or condensation occurs uniformly over the whole length of the exchanger.
5. There is equal heat transfer in each tube or shell pass.
6. Heat losses to the surrounding are negligible.

Steps for heat exchanger design

(i) The overall heat transfer coefficient U, was calculated using, (individual heat transfer coefficients were obtained from Bell, 1983)

$$\frac{1}{U} = \frac{1}{h_t} + \frac{1}{h_s} + R_t + R_s \qquad (IV-19)$$

(ii) The heat duty Q, was calculated using,

$$Q = M_s C_{p.s} ( T_{s.i} - T_{s.o} ) \text{ or}$$
$$= M_t C_{p.t} ( T_{t.o} - T_{t.i} ) \qquad (IV-20)$$

or for condensing vapours, $Q = M \Delta h$

(iii)The log mean temperature difference, $\Delta T_{lm}$ and the correction factor for $\Delta T_{lm}$ if there are more than one tube or shell pass were calculated. For true countercurrent or cocurrent flow the rate equation for heat transfer is,

$$Q = U\,A\,\Delta T_{lm} \qquad \text{(IV-21)}$$

For multipass shell and tube heat exchangers the above equation is modified to,

$$Q = U\,A\,F\,\Delta T_{lm} \qquad \text{(IV-22)}$$

The correction factor F is a function of two dimensionless factors R and P defined as

$$R = \frac{(T_{s,i} - T_{s,o})}{(T_{t,o} - T_{t,i})} \quad ; \quad P = \frac{(T_{t,o} - T_{t,i})}{(T_{s,i} - T_{t,i})}$$

The values of F were obtained from Bell, (1983).

(iv) The heat transfer area (based on outside tube surface area) was estimated using,

$$A_o = \frac{Q}{U_o\,\Delta T_{lm}\,F} \qquad \text{(IV-23)}$$

(v) Approximate tube and shell geometries were estimated using,

--- calculation of no. of tubes (using $D_{to} = 0.02$ m, and $L_t = 8$ m)

$$N_{tt} = \frac{A_o}{\pi D_{t,o}\,L_t} \qquad \text{(IV-24)}$$

--- calculation of inside shell diameter, $D_{s,i}$ (using $L_{tp} = 1.35\,D_{to}$, $L_{bb} = 0.042$ m)

The following relationships were used:

$$N_{tt} = \frac{0.78}{C_1\,L_{tp}^2} * D_{ctl}^2 \qquad \text{(IV-25)}$$

$D_{s,i} = D_{ctl} + L_{bb} + D_t$

Where, $L_{bb}$ varies with types of heat exchanger head and shell outside diameter; for split ring and packed floating head, it can be expressed by a straight line,

$$L_{bb} = 0.025 + 0.017\ D_{s.i}$$

$C_1 = 0.866$ for 30 deg. tube layout characteristic angle.
$= 1.0$ for 45 and 90 deg. tube layout angle.

(vi) The correction factor, $\psi_c$ for the reduction in no. of tubes due to tube pass partitions was calculated using the following correlations:-

$$\begin{aligned} &\text{for } D_{ctl} = 2.0\text{ m};\ \Psi_c = 0.014 + 0.0115\ (N_{tp} - 2)\\ &\text{for } D_{ctl} = 1.5\text{ m};\ \Psi_c = 0.018 + 0.0160\ (N_{tp} - 2)\\ &\text{for } D_{ctl} = 1.0\text{ m};\ \psi_c = 0.025 + 0.0230\ (N_{tp} - 2)\\ &\text{for } D_{ctl} = 0.8\text{ m};\ \Psi_c = 0.033 + 0.0280\ (N_{tp} - 2) \end{aligned} \qquad \text{(IV-26)}$$

so,

actual $N_{tt}$ = previously calculated $N_{tt}\ (1 - \Psi_c)$

(vii)Effective tube length was calculated using,

$$L_{tt} = \frac{A_o}{\pi D_{t.o} N_{tt}} \qquad \text{(IV-27)}$$

(viii)The tube length was adjusted within 3 m and 12 m and consequently other shell and tube specifications.

(ix) The shell side pressure was calculated using,

(a) Average baffle spacing was calculated using,
$L_{bc} = 0.6\ D_{s,i}$

(b) Shell side cross-sectional flow area, $S_m$

was calculated using,

$$S_m = L_{bc}\left[L_{bb} + \frac{D_{ct1}}{L_{tp}} * (L_{tp} - D_{t.o})\right] \qquad \text{(IV-28)}$$

(c) Shell side Reynolds no., $N_{Re.s}$ was calculated using,

$$N_{Re.s} = \frac{D_{t.o}m_s}{\mu_s}$$

where, $m_s = (M_s/S_m)$

(d) Shell side fluid friction factor, $f_s$ was calculated in accordance to $N_{Re.s}$.

(e) Number of crosses by shell side fluid, $T_{cc}$ (using segmental baffle cut fraction, $B_c = 0.25$) was calculated using,

$$T_{cc} = \frac{D_{s.o}\ (\ 1 - 2\ B_c\ )}{L_{pp}} \qquad \text{(IV-29)}$$

Shell side pressure drop was calculated using,

$$\Delta P_s = \frac{2 * 10^{-3} f_s\ T_{cc}\ m^2}{\varphi_s} \qquad \text{(IV-30)}$$

(x) Tube side pressure drop was calculated using,

(a) Tube side velocity, $V_t$ was calculated using,

$$V_t = \frac{M_t}{0.786\ D_{t.i}^2\ \varphi_t\ (N_{tt}/N_{tp})} \qquad \text{(IV-31)}$$

(b) Tube side Reynolds no., $N_{Re.t}$ was calculated using,

$$N_{Re.t} = \frac{V_t\ \varphi_t\ D_{t.i}}{\mu_t} \qquad \text{(IV-32)}$$

(c) Tube side friction factor, $f_t$ was calculated using,

For $10^2 < N_{Re.t} < 10^6$,

$$f_t = \frac{0.05573}{N_{Re,t}^{0.261}} \qquad \text{(IV-33)}$$

Tube side frictional pressure drop, $\Delta P_t$ was calculated using,

$$\Delta P_t = \frac{4\ f_t\ L_t \rho_t V_t^2}{D_{t,i}} \qquad \text{(IV-34)}$$

Pressure drop due to change in direction (four velocity head for each pass) was added to the tube side pressure drop using,

$$\Delta P_t = \Delta P_t + \frac{4\ N_{tp}\ V_t^2}{2\ \rho_t} \qquad \text{(IV-35)}$$

(xi) Purchasing cost of the heat exchanger was calculated assuming a floating head heat exchanger using total heat transfer area based on tube inner diameter (Peters and Timmerhaus, 1980).

$$C_{EX} = 1621.81\ A_i^{0.582} \qquad \text{(IV-36)}$$

Correction factors for different tube lengths, operating pressure, tube diameter, material of construction was applied to the cost.

## NOMENCLATURE

Compressor:

| | |
|---|---|
| $C_v$, $C_p$ | Sp. heat of gas at constant volume and pressure respectively, kJ/(kmole-K) |
| $F_g$ | molal flow of gas, kmole/s |
| $k$ | gas specific heats ratio |
| $n$ | equivalent to k |
| $N_s$ | no. of compression stages |
| $r_c$ | compression ratio |
| $R$ | universal gas constant, kJ/(kmole-s) |
| $T_d$ | outlet temperature, K |
| $T_s$ | inlet temperature, K |
| $V_F$ | volumetric flow rate of gas, $m^3/s$ |

Greek letters:

| | |
|---|---|
| $\eta_p$ | compressor cycle polytropic efficiency |
| $\eta_F$ | overall efficiency of the compressor |

Gas liquid Separator:

| | |
|---|---|
| $V_g$ | maximum allowable gas velocity, m/s |
| $V'_{ag}$ | operating gas velocity, m/s |
| $K_v$ | constant |
| $D_{sp}$ | inside diameter of the separator vessel, m |
| $G_{gf}$ | mass flow rate of gas in the separator, kg/s |
| $H_{sp}$ | height of the separator, m |
| $P_{sr}$ | operating pressure of the separator, kPa |

Greek letters:

| | |
|---|---|
| $\rho_g$, $\rho_l$ | gas and liquid density, kg/m$^3$ |
| $\Delta P_{sr}$ | preesure drop of fluid in the separator, kPa |

Pressure vessel:

| | |
|---|---|
| $C_c$ | corrosion allowance, m |
| $C_{tv}$ | total cost of the vessel, \$ |
| $C_{tr}$ | installed cost of trays, \$ |
| $D_a$ | major axis of the ellipsoidal head, m |
| $D_i$ | inside diameter of the vessel, m |
| E | welded joint efficiency (fraction) |
| $H_t$ | height of the vessel, m |
| $L_a$ | inside radius of the hemispherical head, m |
| n | parameter constant |
| P | design pressure, kg/m$^2$ |
| $R_i$ | inside radius of the vessel, m |
| S | allowable working stress of the pressure vessel material, kg/m$^2$ |
| $W_t$ | wall thickness, m |
| $W_{th}$ | weight of the head portion, kg |
| $W_{tt}$ | total weight of the installed vessel, kg |

Greek letters:

| | |
|---|---|
| $\rho_{mt}$ | density of the vessel material, kg/m$^3$ |

Heat exchanger:

| | |
|---|---|
| A | heat transfer surface area, m$^2$ |
| $A_o$ | heat transfer surface area based on outside tube |

| | |
|---|---|
| | area, $m^2$ |
| $A_i$ | heat transfer surface area based on inside tube area, $m^2$ |
| $B_c$ | fraction of baffle cut |
| $C_1$ | constant |
| $C_{p.s}$ | sp. heat of fluid in the shell side, kJ/(kmole-K) |
| $C_{p.t}$ | sp. heat of fluid in the tube side, kJ/(kmole-K) |
| $D_{t.o}$ | outside tube diameter, m |
| $D_{s.i}$ | inside shell diameter, m |
| $D_{t.i}$ | tube inside diameter, m |
| F | dimensionless log mean temperature difference correction factor |
| $f_s$, $f_t$ | shell and tube side friction factors respectively |
| $h_s$, $h_t$ | shell and tube side heat transfer coefficients respectively, kW/($m^2$-K) |
| $L_{bb}$ | inside shell diameter to tube bundle by pass clearance, m |
| $L_{bc}$ | baffle spacing, m |
| $L_t$ | tube length, m |
| $L_{tp}$ | tube pitch, m |
| $M_s$, $M_t$ | molal flow in the shell and tube side, kmole/s |
| $N_{Re.s}$ | shell side Reynolds number |
| $N_{Re.t}$ | tube side Reynolds number |
| $N_{cc}$ | no. of crosses made by shell side fluid |
| $N_{tt}$ | total number of tubes in the heat exchanger |
| P | dimensionless factor |
| Q | total heat load of the heat exchanger, kW |
| R | dimensionless factor |
| $R_s$, $R_t$ | shell and tube side fouling resistances, $m^2$-K/kW |

| | |
|---|---|
| $S_m$ | shell side cross-sectional flow area, $m^2$ |
| $T_{s,i}$ | shell side fluid inlet temperature, K |
| $T_{t,i}$ | tube side fluid inlet temperature, K |
| $T_{s,o}$ | shell side fluid outlet temperature, K |
| $T_{t,i}$ | tube side fluid outlet temperature, K |
| U | overall heat transfer coefficient, $kW/(m^2-K)$ |
| $U_o$ | overall heat transfer coefficient based on outside tube surface area, $kW/(m^2-K)$ |
| $V_t$ | tube side fluid velocity, m/s |

Greek letters:

| | |
|---|---|
| $\Delta h$ | latent heat change, kJ/kmole |
| $\Delta T_{lm}$ | log mean temperature difference, K |
| $\Delta P_s$, $\Delta P_t$ | shell and tube side pressure drop, kPa |
| $\delta$ | a correlating variable |
| $\eta$ | a correlating variable |
| $\psi_c$ | a correlating variable |
| $\mu_t$ | tube side fluid viscosity, kg/(m-s) |
| $\rho_t$ | tube side fluid density, $kg/m^3$ |

## PROGRAM CALLING SEQUENCE

MAIN program calls the following subprogram:

CONSX

Subroutine CONSX calls the following subprograms:

CHECK, FUNC, CENTR, and CONST

Subroutine FUNC calls the following subprogram:

AMONIA

Subroutine AMONIA calls the following subprograms:

INPUT, PREL, PRINT, PRESSV, COMPRS, SEPAR, and HEATEX

Subroutine PREL calls the following subprograms:

DIFEQN, HEATTR, and WEGSTN

Subroutine DIFEQN calls the following subprogram:

FUNCT

Subroutine FUNCT calls the following subprograms:

RATES and HEATTR

Subroutine HEATTR calls the following subprograms:

CNVTTR and CPH

Subroutine HEATEX calls the following subprograms:

CPH and HTVAP

Subroutine SEPAR calls the following subprograms:

HTVAP and PRESSV

Subroutine COMPRS calls the following subprogram:

CPH

## APPENDIX V

(a):Plant data for parametric estimation (average values)

| Temperature (°K) | Pressure (atm) | Ammonia production (kg/hr) | Time (year) |
|---|---|---|---|
| 743.5 | 272.89 | 34967.92 | 0.0 |
| 743.0 | 274.84 | 34321.67 | 0.0417 |
| 742.5 | 273.85 | 34026.85 | 0.0444 |
| 742.0 | 273.85 | 33937.50 | 0.0861 |
| 745.0 | 275.5 | 33713.33 | 0.0889 |
| 744.5 | 279.77 | 33685.83 | 0.1361 |
| 743.5 | 277.7 | 35270.00 | 0.1667 |
| 743.0 | 273.5 | 34372.08 | 0.2056 |
| 749.5 | 287.00 | 33684.17 | 0.2556 |
| 752.0 | 288.50 | 34803.75 | 0.2833 |
| 750.5 | 272.86 | 32819.58 | 0.3333 |
| 760.5 | 267.93 | 35043.75 | 0.4611 |
| 750.0 | 287.67 | 33826.67 | 0.5056 |
| 765.5 | 258.06 | 31452.50 | 0.6194 |
| 768.5 | 264.97 | 31469.58 | 0.7056 |
| 755.5 | 248.19 | 28640.00 | 0.7972 |
| 767.0 | 259.05 | 30502.50 | 0.8806 |
| 763.5 | 242.27 | 28415.00 | 0.9500 |
| 763.0 | 243.26 | 27778.33 | 1.0167 |
| 764.5 | 248.19 | 28875.00 | 1.0639 |
| 765.5 | 259.05 | 31463.00 | 1.1417 |
| 770.5 | 301.48 | 29685.83 | 1.2694 |
| 769.5 | 297.57 | 31626.25 | 1.3139 |

(a):Plant data for parametric estimation (average values) (continued)

| Temperature (°K) | Pressure (atm) | Ammonia production (kg/hr) | Time (year) |
|---|---|---|---|
| 762.5 | 263.50 | 35010.42 | 1.5194 |
| 753.0 | 268.54 | 35481.67 | 1.5889 |
| 753.5 | 263.60 | 36642.92 | 1.6472 |
| 750.5 | 266.59 | 37383.33 | 1.6750 |
| 750.5 | 267.90 | 36051.67 | 1.7167 |
| 751.5 | 269.00 | 38879.17 | 1.7583 |
| 758.0 | 299.48 | 38896.25 | 1.8056 |
| 760.5 | 301.99 | 39640.83 | 1.8444 |
| 762.0 | 294.58 | 38774.17 | 2.0611 |
| 756.0 | 295.56 | 39411.25 | 2.0917 |
| 753.0 | 288.50 | 34112.08 | 2.3639 |
| 756.5 | 283.50 | 34372.50 | 2.3972 |
| 760.0 | 289.59 | 38395.42 | 2.4361 |
| 763.5 | 290.50 | 38747.08 | 2.4778 |
| 762.0 | 294.56 | 38737.50 | 2.5194 |
| 762.0 | 294.62 | 38986.67 | 2.5639 |
| 758.0 | 296.50 | 38764.58 | 2.5917 |
| 761.0 | 296.50 | 37502.50 | 2.6472 |
| 759.5 | 289.16 | 38925.42 | 2.6750 |
| 755.0 | 286.10 | 37994.58 | 2.7222 |
| 762.0 | 285.50 | 36069.17 | 2.8500 |
| 764.0 | 297.58 | 38632.92 | 2.8944 |
| 763.5 | 300.42 | 37992.92 | 3.0917 |
| 764.0 | 300.42 | 36604.58 | 3.1472 |

(b):Plant data for parametric estimation (average values)

| Molar flow(kmol/hr) | | | Mole fraction(mole/mole) | | |
|---|---|---|---|---|---|
| $N_2$ | $H_2$ | $NH_3$ | $N_2$ | $H_2$ | $NH_3$ |
| 4974.21 | 9278.62 | 1505.68 | 0.2754 | 0.5138 | 0.0834 |
| 3733.44 | 9935.05 | 1506.35 | 0.2138 | 0.5689 | 0.0863 |
| 3511.36 | 9765.03 | 1467.21 | 0.2064 | 0.5740 | 0.0863 |
| 3768.55 | 9656.37 | 1450.44 | 0.2195 | 0.5625 | 0.0845 |
| 3395.94 | 9980.70 | 1436.17 | 0.2013 | 0.5918 | 0.0852 |
| 3611.62 | 9937.19 | 1450.74 | 0.2066 | 0.5684 | 0.0830 |
| 3438.76 | 10181.44 | 1497.24 | 0.1972 | 0.5839 | 0.0859 |
| 3553.53 | 9991.94 | 1480.11 | 0.2035 | 0.5722 | 0.0848 |
| 3828.48 | 10052.58 | 1477.16 | 0.2152 | 0.5651 | 0.0830 |
| 3700.50 | 9884.27 | 1483.56 | 0.2110 | 0.5635 | 0.0846 |
| 3294.83 | 8847.31 | 1434.96 | 0.2076 | 0.5574 | 0.0904 |
| 3233.64 | 9361.47 | 1559.20 | 0.1942 | 0.5622 | 0.0936 |
| 3346.64 | 8977.60 | 1675.58 | 0.1973 | 0.5291 | 0.0988 |
| 3132.19 | 9101.94 | 1362.86 | 0.2040 | 0.5928 | 0.0888 |
| 3008.10 | 8872.64 | 1324.59 | 0.1992 | 0.5874 | 0.0877 |
| 3305.22 | 9403.11 | 1286.15 | 0.2070 | 0.5890 | 0.0806 |
| 2711.08 | 8314.72 | 1330.48 | 0.1922 | 0.5895 | 0.0943 |
| 2167.06 | 7625.65 | 1205.15 | 0.1731 | 0.6090 | 0.0965 |
| 2922.31 | 7556.51 | 1197.31 | 0.2193 | 0.5671 | 0.0899 |
| 2781.96 | 7727.19 | 1245.96 | 0.2080 | 0.5777 | 0.0932 |
| 2721.78 | 8142.88 | 1312.69 | 0.1939 | 0.5801 | 0.0935 |
| 3174.14 | 9112.67 | 1359.16 | 0.1976 | 0.5674 | 0.0846 |
| 3365.78 | 9452.22 | 1351.79 | 0.2103 | 0.5906 | 0.0845 |
| 3467.97 | 9473.61 | 1486.74 | 0.2061 | 0.5630 | 0.0883 |

(b):Plant data for parametric estimation (average values)
(continued)

| Molar flow(kmol/hr) | | | Mole fraction(mole/mole) | | |
|---|---|---|---|---|---|
| $N_2$ | $H_2$ | $NH_3$ | $N_2$ | $H_2$ | $NH_3$ |
| 3136.16 | 9376.90 | 1533.02 | 0.1900 | 0.5681 | 0.0929 |
| 3318.86 | 9666.59 | 1629.90 | 0.1908 | 0.5557 | 0.0937 |
| 2493.91 | 10027.99 | 1633.19 | 0.1488 | 0.5984 | 0.0975 |
| 2918.79 | 9592.12 | 1567.31 | 0.1738 | 0.5710 | 0.0933 |
| 3521.54 | 10702.69 | 1721.74 | 0.1864 | 0.5666 | 0.0911 |
| 4421.80 | 10623.52 | 1761.58 | 0.2232 | 0.5361 | 0.0889 |
| 3746.94 | 10273.77 | 1799.20 | 0.2004 | 0.5496 | 0.0962 |
| 3544.04 | 9814.37 | 1677.87 | 0.2006 | 0.5556 | 0.0950 |
| 3940.56 | 9568.94 | 1730.89 | 0.2162 | 0.5249 | 0.0949 |
| 4165.71 | 9977.70 | 1544.53 | 0.2265 | 0.5425 | 0.0840 |
| 3604.87 | 10633.30 | 1524.77 | 0.1973 | 0.5820 | 0.0834 |
| 3278.48 | 10743.73 | 1678.90 | 0.1765 | 0.5784 | 0.0904 |
| 3799.63 | 10564.43 | 1717.87 | 0.2009 | 0.5586 | 0.0908 |
| 3931.54 | 10072.56 | 1728.35 | 0.2118 | 0.5425 | 0.0931 |
| 3650.06 | 10357.13 | 1715.97 | 0.1966 | 0.5578 | 0.0924 |
| 4343.67 | 9849.26 | 1768.41 | 0.2301 | 0.5219 | 0.0937 |
| 3757.13 | 10212.41 | 1682.86 | 0.2032 | 0.5524 | 0.0910 |
| 4140.59 | 10298.42 | 1732.03 | 0.2159 | 0.5370 | 0.0903 |
| 6170.47 | 8892.42 | 1701.60 | 0.3110 | 0.4482 | 0.0858 |
| 3074.34 | 10466.40 | 1498.62 | 0.1782 | 0.6066 | 0.0868 |
| 4610.04 | 9999.84 | 1711.72 | 0.2365 | 0.5130 | 0.0878 |
| 3290.27 | 10594.24 | 1697.25 | 0.1800 | 0.5796 | 0.0928 |
| 4394.10 | 10559.11 | 1684.22 | 0.2269 | 0.5452 | 0.0870 |