AN ABSTRACT OF THE THESIS OF

Nichakorn Kraisuwansarn for the degree of <u>Master of Science</u>
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Title: <u>Simulation of a Membrane Reactor for Ammonia</u>
<u>Decomposition</u>

Abstract approved:

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(Dr. J Douglas Way)

The purpose of this research is to study the
feasibility of combining reaction and separation in a
membrane separation unit. The asymmetric ceramic membrane
reactor applied to the gas-phase catalytic decomposition
reaction of ammonia from an IGCC (Integrated Gasification
Combined Cycle Processes) gas mixture was simulated in the
temperature range of 810-1366 K and over the pressure range
of 18.248E5-35.482E5 Pa. The assumptions for the development
of the model equations were plug flow on both sides of the
membrane, negligible reverse reaction, and negligible heat
and mass transfer resistance in the catalyst. A mass balance
over a differential volume of the reactor gives eight
simultaneous ordinary differential equations for four gas
components. These equations were solved simultaneously as an
initial value problem using the DIVPAG subroutine(Gear's

method) from the IMSL Math Library. The conversion for ammonia decomposition was successfully increased beyond the value obtained in a plug flow reactor by removing the product from the reaction zone via Knudsen diffusion through reactor walls. The general behavior of the membrane reactor and the plug flow reactor are compared from the viewpoint of equilibrium conversion shift. Decreasing the pressure ratio and increasing the total flow rate of the sweep gas in the separation side contributed to the higher conversion shift. The optimum thickness of the ceramic membrane selective layer was found to be in the range of 3-9 μm. The fractional conversion of membrane reactor is always greater than plug flow reactor.

Simulation of a Membrane Reactor for

Ammonia Decomposition

by

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A area of membrane (m^2)

a_i activity of component i (Pa)

B_i second virial coefficient of component i

B_{ij} second cross coefficient of component i and j

B_m second virial coefficient of gas mixture

Da Damkohler number, $kL_o v_r P_t^{-0.5}/F_{Ao}$

D_k Knudsen diffusivity (cm^2/s)

$D_{k,eff}$ effective Knudsen diffusivity (cm^2/s)

E activation energy (J/mol)

F_i molar flow rate of component i in reaction side (mol/s)

F_{io} initial molar flow rate of component i in reaction side (mol/s)

f_i fugacity of component i (Pa)

k reaction rate constant ($mol/m^3.s.Pa^{-0.5}$)

k_o pre-exponential factor ($mol/m^3.s.Pa^{-0.5}$)

K equilibrium constant (Pa)

J permeation rate (mole/s)

L_o reactor length (m)

M_i molecular weight (g/mol)

p_i partial pressure of component i (Pa)

P_i permeability of component i (mol/m.s.Pa)

P_t total pressure on reaction side (Pa)

P_s total pressure on separation side (Pa)

P_r pressure ratio (P_s/P_r)

P_{ci} critical pressure of component i (bar)

s_m area of permeation/unit length of reactor (m^2/m)

Q_i molar flow rate of component i in separation side
        (mol/s)

Q_{io} initial molar flow rate of component i in separation
        side (mol/s)

r_A rate of reaction for ammonia decomposition
        (mol/m^3.s)

r_{gi} radius of gas molecule (cm)

r_p pore radius of membrane (cm)

R universal gas constant

S_m area of membrane per length of reactor (m^2/m)

t_m membrane thickness (m)

T temperature of the system (K)

T_{ri} reduce temperature of component i

T_{ci} critical temperature of component i (K)

v molar volume of gas (cm^3/mol)

v_r volume of reactor/unit length of reactor (m^3/m)

Y_i mole fraction of gas i

Z_m compressibility factor of component i

α_{ij} selectivity of component i over component j

ε porosity of membrane

τ tortuosity of membrane

γ_i fugacity coefficient of component i

β exponential constant in rate law

δ ratio of permeation rate to reaction rate,

$P_H S_m P_t^{1.5} / (t_m k v_r)$

Subscript

A   ammonia

N   nitrogen

H   hydrogen

I   inert (helium)

SIMULATION OF A MEMBRANE REACTOR FOR

AMMONIA DECOMPOSITION

1   INTRODUCTION

Because of thermodynamic limitations, a reversible reaction does not occur to completion if the reaction reaches equilibrium at any fixed conditions. If gas separation membranes are used, continuous and selective removal of products from the reaction mixtures and can be accomplished, the forward reaction will advance and will go to completion. In recent years, applications of combined reaction and separation processes has generated substantial interest. This system is known as a membrane reactor.

One of the many applications for the membrane reactor is removal of fuel-bound nitrogen from the Integrated Gasification Combined Cycle Processes(IGCC). The IGCC process is an advanced power generation system. The process consists of a gasifier to produce synthetic gas to fuel a gas turbine generator (Figure 1). Ammonia is one of the contaminants in the high temperature and high pressure IGCC gas streams. Removal of ammonia will reduce subsequent production of NO_x which are toxic and corrosive contaminants and are difficult to remove at atmospheric pressure. The concept of the membrane reactor was introduced to decompose the fuel-bound nitrogens and separate the reaction products simultaneously
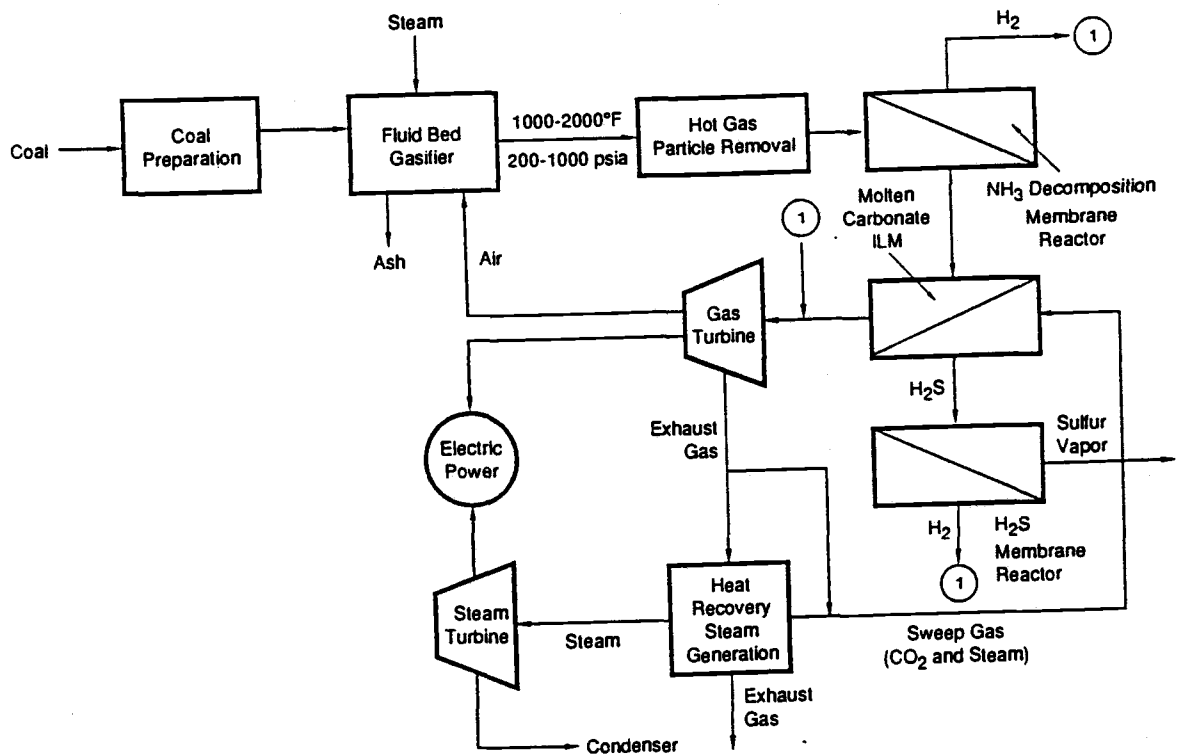
Figure 1. A flow diagram of a IGCC process including possible location for membrane reactor

at the condition of the gas streams. The high temperature gas separation process have a thermodynamic efficiency advantage over conventional gas separation processes such as chemical and physical absorption which operate at about ambient temperature (Barron, 1966). Integrating separation and reaction functions using the membrane reactor could be used to improve this power generation system.

Use of a membrane reactor may decrease the energy requirement and increase the product yield. The membrane reactor is more efficient because it can operate at existing temperature and pressure conditions while increasing the conversion or it can operate at lower temperature to maintain the same conversion as an equilibrium reactor. Also, the membrane reactor is a very cost-effective operation because it combines both reaction and separation in a single unit process.

2 SCOPE AND OBJECTIVE OF THE RESEARCH

The scope and objective of this research is to study the performance of high temperature, high pressure tubular ceramic membrane reactor. A gas phase reaction occurs by catalytic reaction in the tube side where the catalyst is located. All the component gases will preferentially diffuse through the selective layer at different speed and will continuously removed from the reactor. This research will develop predictive mathematical models and a simulation program for such a novel chemical reactor. This research will also include the studies of membrane reactor characteristics, the effect of operating parameters, physical properties, and the comparison of the membrane reactor with a conventional plug flow reactor.

3 BACKGROUND AND LITERATURE SURVEY

3.1 Membrane in Separation

The concepts of membrane, membrane separation and membrane reactor will be briefly reviewed below. In fact, membranes and membrane separation techniques have been used in an industrial processing for many years. In recent years, interest in the separation of gas mixtures using a membrane has dramatically increased.

A synthetic membrane can be defined as a semi-permeable barrier between two phases which differential transport can occur. Separation using membrane processes results from differences in the transport rates of chemical species through the membrane. Mass transport through a membrane is caused by diffusion of individual molecules or ions due to gradient in pressure, temperature or concentration. The permeation rate is determined by the driving force or forces acting on the individual component and by the surface chemistry of the pores.

The subject of membrane reactors has been arranged in many different classifications: (1) Classification by the nature of the membrane such as natural membrane or synthetic membrane: (2) Classification by structure of the membrane such as porous and nonporous membrane: (3) Classification by

application of the membrane such as gas-phase systems, gas-liquid systems: (4) Classification by application of the membrane such as diffusion membrane, or ion-exchange membrane. Four basic types of membrane modules are used: plate-and-frame, spiral-wound, tube-in-shell, and hollow fiber (Matson et al.1983)

A membrane can be organic or inorganic material, porous or nonporous membrane, symmetric or asymmetric membrane. The permeation of gases through the nonporous membrane occurs due to differences in their diffusivity and solubility in the membrane matrix. In a microporous membrane, the separation of gases depends on the ratio of the pore size to the mean free path of gas. An asymmetric membrane consists of either a microporous or a dense layer deposited on a porous support.

To perform fluid mixture separation by membranes, the most three important membrane properties are the following:

-Membrane productivity

-Membrane selectivity

-Membrane durability

The productivity, or membrane permeability is a measure of the quantity of a substance that permeates through the

membrane per unit area of the surface at a given time.

The selectivity is the basis for separating a fluid mixture. It means the ability to permeate one particular chemical species at a different speed than another chemical species. The selectivity is defined as the ratio of permeability of component i over component j.

The durability is a measure of the membrane's ability to maintain its selectivity and productivity for a period of time at a set of specific operating conditions. The factors that affect the membrane durability include temperature, pressure, membrane swelling and fouling.

A permselective membrane is a thin film or layer of material that can selectively pass one or more components of a mixture. It is possible to select inorganic membranes which can either serve as the catalyst or as a support for a catalyst while separating reactants from products.

Polymeric membranes normally carry a high selectivity in some application, but their efficiency may decrease with time due to chemical degradation, physical and thermal instability. Most of the polymeric membranes are limited to operation at low temperature (373 K) while most of the industrial chemical reactions are operated at high temperature (above 473 K). In contrast, inorganic membrane such as metals or ceramics can be used at very high temperature and high pressure. Inorganic membranes often

use different transport mechanisms than polymer membranes. The mechanisms commonly encountered for microporous membranes will be described in detail below. Since this thesis deals with a high temperature application, the discussion will focus on microporous inorganic membranes.

3.2 Membrane Reactor

A membrane is fixed into a vessel which separates the unit into two compartments (Figure 2). A feed stream of a fluid mixture is introduced to the reaction side, and as it flows through the reaction side, some components may permeate at different rate through the membrane to the permeation side. On the separation side, a vacuum or inert sweep gas is used to remove permeated gases. If the permeability of these components in the membrane are different, the higher permeability components will be concentrated on the permeation side of the membrane, giving partial separation or even high purity separation.

The membrane reactor was studied for use in a reversible reaction to shift the equilibrium since late 1960S. Michaels(1968) and Shah et al.(1970) reported that the selective removal of products from a reacting mixture could result in a favorable chemical equilibrium shift.

H2

Large pore support

A → A → B + H2 → B

Small pore top layer for selective for H2

H2
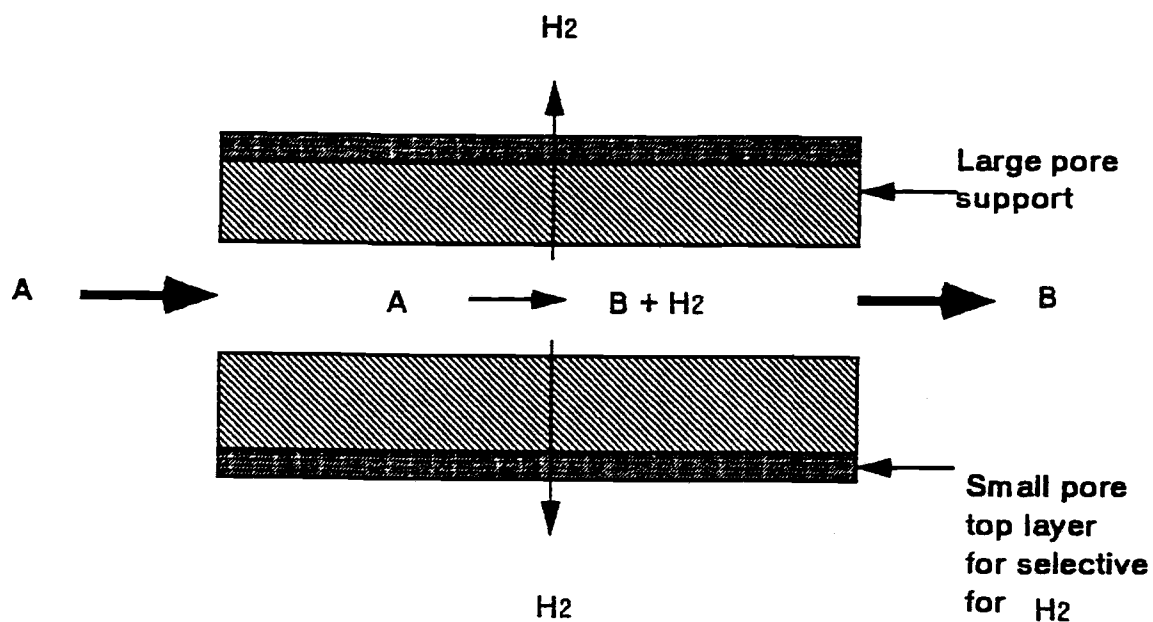
Example of a decomposition reaction

A ⇌ B + H2

Figure 2. Axial cross-section of tubular membrane
reactor

Raymont(1975) suggested a membrane reactor configuration to remove hydrogen continuously from a hydrogen sulfide decomposition reactor.

Kameyama et al.(1979) measured the hydrogen /hydrogen sulfide separation factor by using a Knudsen diffusion mechanism in a Vycor glass membrane (a mean pore size of 45 Å). The microporous silica membrane was selective for hydrogen sulfide at high pressure and selective for hydrogen at low pressure. The deviation from Knudsen diffusion behavior is the result of adsorption and surface diffusion of hydrogen sulfide at high pressure.

Kameyama et al.(1981) demonstrated the application of a membrane reactor with a microporous glass membrane adjacent to the reaction zone. The porous glass membrane reactor doubled the equilibrium conversion of hydrogen sulfide.

Itoh et al.(1984) studied the decomposition of hydrogen iodide showed that equilibrium shift is possible when hydrogen was separated using porous Vycor glass. He claimed that thin membrane and/or membrane with large surface area per unit volume will give high permeation flux.

Itoh et al.(1985) and Mohan and Govind (1986) reported experimental data, theoretical studies and computer simulation of cyclohexane dehydrogenation by using the porous glass membrane reactor. They showed that for given

rates of permeation and reaction, there is an optimum thickness of membrane which maximum conversion is obtained.

Itoh (1987) has reported that the reaction cannot occur to completion because the feed gases also permeate through the membrane. However, he claimed that almost complete conversion of cyclohexane can be achieved by using a membrane reactor equipped with a palladium hollow tube, which allows the permeation of hydrogen only. High conversion could be achieved by decreasing the feed flow rate or increasing the residence time.

The membrane processes have several advantages which make them attractive as a new separating tool. In many cases the membrane processes are faster, more economical and more efficient than conventional separation techniques. The separation can be performed at ambient operating conditions by using membrane reactors, therefore, temperature-sensitive fluids may be treated without the constituents being damaged or chemically changed.

3.3 Mechanism of Gas Transport in Microporous Membrane

In general, the mass transfer through a microporous membrane are occurs by several processes in series:

1. Gas diffusion through the boundary layer.

2. Gas sorption into the membrane.

3. Gas diffusion through the membrane.

4. Gas desorption out of the membrane.

5. Gas diffusion through the boundary layer.

The major mechanisms of gas transport through porous membrane materials are

-Molecular diffusion

-Knudsen diffusion

-Surface diffusion

-Capillary condensation

-Molecular sieving

The Knudsen number is defined as the ratio of the mean free path of the gas molecules to the pore radius. With a partial pressure difference and using a membrane with pores smaller than mean free path of the gas molecule, four separate mechanisms of transport can be shown (Figure 3). Because pore size is a qualitative guide. Figure 4 shows the broad range of pore size which each of the mechanisms is dominant.

If the pore is much smaller than the mean free path of the gas molecules (Knudsen number >10) , then Knudsen diffusion occurs. In particular, the theory applies to

(1) Knudsen diffusion

(2) Surface diffusion

(3) Capillary condensation
with liquid flow

(4) Molecular sieving
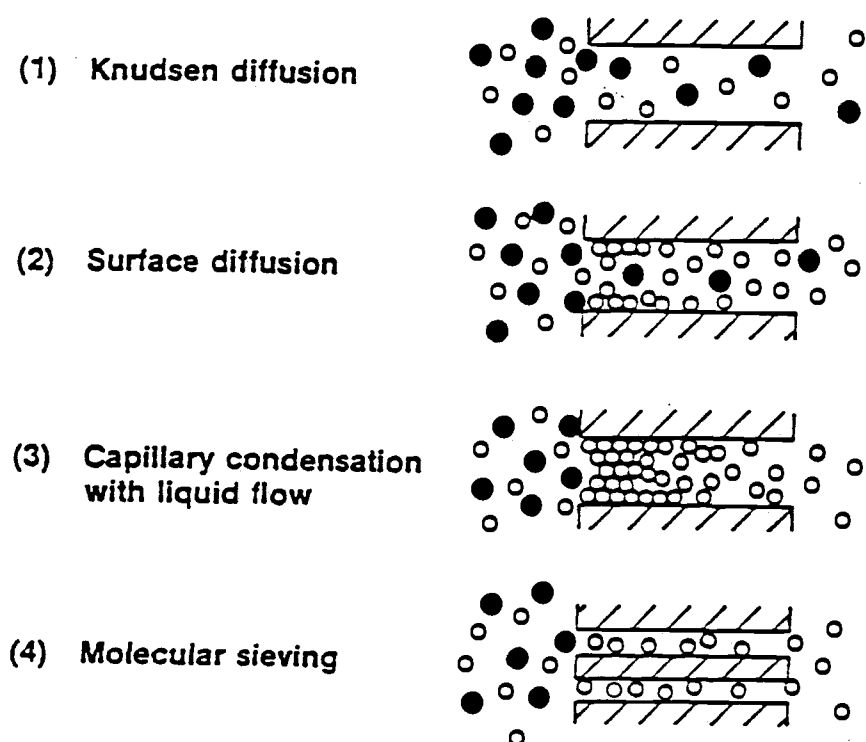
Figure 3. Mechanisms of mass transfer through
microporous membrane
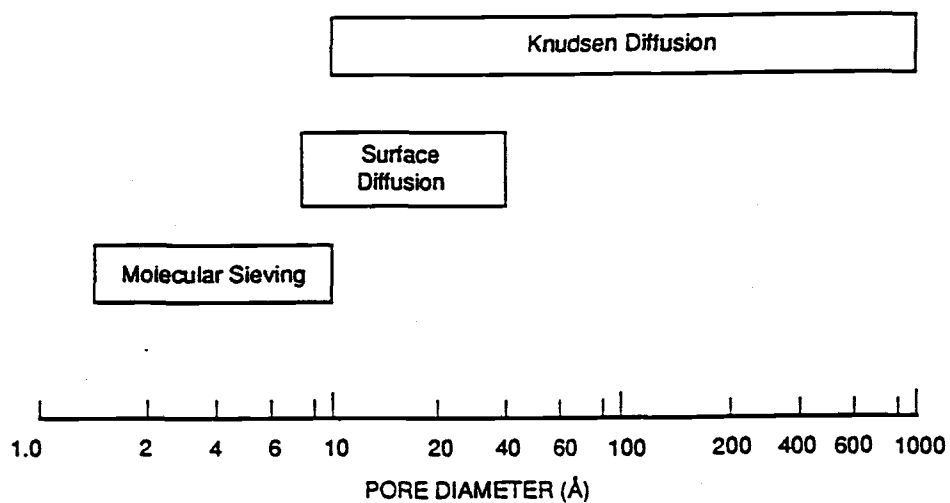
Figure 4. Approximate operative pore size ranges

for various mechanisms
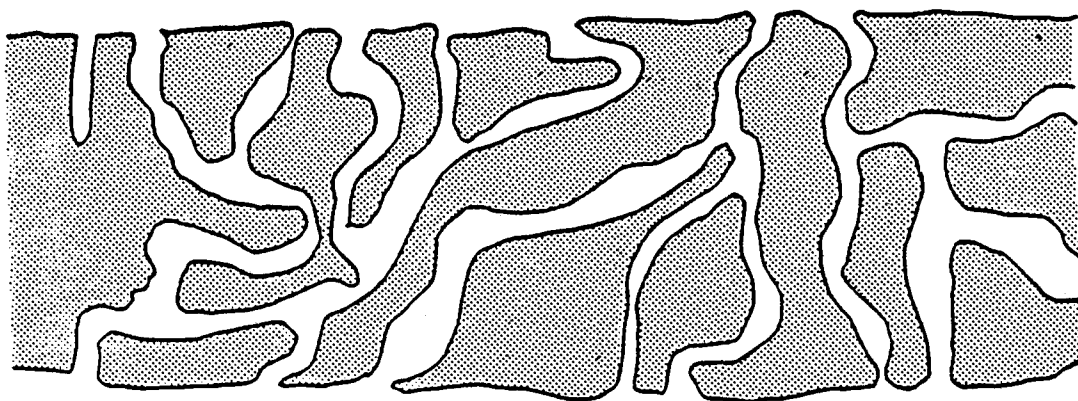
Figure 5. Cross-section of a microporous membrane

membranes with pore sizes that are so small (< 20 Å) that well-known mechanisms such as Knudsen diffusion are no longer valid.

Instead, surface diffusion and molecular sieving are the dominating transport mechanisms. These mechanisms are highly dependent on the internal surface and the physical character(size/shape) of the internal pore structure.

Diffusion in porous membrane may occur by one or more of five mechanisms. In this work and experimental work which will follow, we will be using commercial available ceramic filters with pore greater than 20 Å. Two possible mechanisms, Knudsen diffusion and/or Surface diffusion, could be involved. Because of the lack of diffusivity data for surface diffusion, we will assume that Knudsen diffusion is the only mechanism for diffusion. The transport of gases through a microporous composite membrane with separation layer 4 μm thick and supporting layer 2000 μm only Knudsen diffusion occurs in the separation layer(Keizer et al. 1988).

Knudsen diffusion: This is encountered in pores containing a gas if the mean free path of the gas molecules is large compared with the pore diameter. In this case, the molecules collide much more frequently with the pore walls than with each other. The molecules rebound from the wall in nearly random directions. The resistance to diffusion along

the pore is then due primarily to molecular collisions with
the wall rather than with each other. There is no chemical
information necessary to compute the flux, when all other
factors are equal, the ratio of the flow of species *i* to
that of species *j* is given by the inverse square root of
their molecular weight ratios or the ratio of the
permeabilities. The selectivity, α_{ij} , of the porous membrane
is given by

$$\alpha_{ij} = (\frac{Mj}{Mi})^{0.5} = \frac{\overline{P_i}}{\overline{P_j}} \tag{1}$$

There are several factors that complicate efforts to
analyze mass transfer within microporous membranes. They
include the factors that:

1) The pore geometry is very complex, and not subject
to realistic modeling in terms of a small number of
parameters (Figure 5).

2) Different molecular phenomena are responsible for
the mass transfer. Consequently, it is often useful to
characterize the mass transfer process in terms of an
"effective diffusivity".

If the porous walls are an array of cylinders parallel
to the diffusion path, the diffusion flux per unit total

cross section of the porous solid would be the fraction ε of the flux under similar conditions with no solid present. The length of the tortuous diffusion path in real pores is greater than the distance along a straight line in the mean direction of diffusion. Moreover, the channels through which diffusion occurs are irregular shape and varying cross section. Both of these factors cause the flux to be less than would be possible in a uniform pore of the same length and mean radius.

Thus, we may express a diffusion coefficient per unit cross section of the porous membrane, $D_{i,eff}$, as

$$D_{i,eff} = \frac{\varepsilon}{\tau} D_i \qquad (2)$$

ε is the porosity and τ is the tortuosity of the membrane which allows for both the varying direction of diffusion and varying pore cross section.

Molecules of gas may exist on the internal surface of the pore or in the gas phase of the pore. Transport on the surface is controlled by the surface diffusion, and transport through the gas phases is controlled by the Knudsen diffusion or molecular sieving mechanism. Gas separation can be achieved by Knudsen diffusion. A mathematical model describing the mechanism for Knudsen diffusion is listed as follows:

$$\frac{J}{A} = \frac{\epsilon}{\tau}\frac{D_k}{RT}\frac{\Delta P}{L} \tag{3}$$

$$D_k = \frac{2}{3}r_p\sqrt{\frac{8RT}{\pi M}} \tag{4}$$

where J : rate of permeation

P : a mean permeability coefficient

A : area of membrane

D_k : Knudsen equivalent diffusivity

r_p : pore radius

M : molecular weight

ΔP : pressure different

Permeation stands for a general phenomena of mass transmission through the membrane. The permeability is a measure of permeation through not only the membrane but also the boundary on either side of the membrane. The equation for permeation can be written:

$$\frac{J}{A} = \overline{P}\frac{\Delta P}{L} \tag{5}$$

This equation may be used independently of the actual permeation mechanism and the resistance of the boundary regions is included in the permeability. Thus, from equation 3 and equation 5 .

$$\overline{P} = \frac{\varepsilon}{\tau}\frac{D_k}{RT} \tag{6}$$

4   NON-IDEAL BEHAVIOR OF GASES

4.1   Compressibility Factor

The non-ideality of a gas is expressed by the compressibility factor Z:

$$Z = \frac{Pv}{RT} \qquad (7)$$

where P = absolute pressure

v = molar volume

R = universal gas constant

T = absolute temperature

For an ideal gas $Z = 1$ and for real gases, Z is not equal to 1.

4.2   Fugacity Coefficient

The activity, a_i, of a component is given by definition as

$$a_i = \frac{f_i}{f_i^*} \qquad (8)$$

where f_i^* as the fugacity of component i at an arbitrarily chosen standard state. We have chosen the standard state as pure component i at a pressure of 1 bar and a temperature

equal to the temperature of the system.

$$a_i = f_i = y_i f_i^\circ \qquad (9)$$

where f_i° is the pure component fugacity and for pure component

$$f_i^\circ = \gamma_i P \qquad (10)$$

Where γ_i is fugacity coefficient which measures how much component i deviates from ideal gas behavior. Fugacity is a corrected pressure and for a pure, ideal gas, the fugacity is equal to the pressure. For a component i in a mixture of ideal gases, the fugacity is equal to the partial pressure of that component. Substituting, we obtain

$$(11)$$
$$f_i = \gamma_i y_i P$$

There are many methods to calculate the fugacity coefficient. For this thesis, two methods are used to calculate the fugacity coefficient to correct for the effect of high pressure and the resulting non-ideality.

- The virial equation of state
- Empirical correlations of the gas phase fugacity coefficient

4.2.1 The Virial Equation of State

The virial equation is a power series in the reciprocal molar volume, $1/v$

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \ldots \tag{12}$$

where B is the second virial coefficient, and C is the third virial coefficient. Information is rarely available for the third and higher virial coefficients, so that the virial equation is often truncated to maintain only the second virial coefficient.

The virial equation for a mixture, truncated after the second term, is given by

$$Z_m = \frac{Pv}{RT} = 1 + \frac{B_m}{v} \tag{13}$$

where Z_m is the compressibility factor of a mixture, v is the molar volume of the mixture, and B_m is the second virial coefficient of the mixture. A mixture of n components, the second virial coefficient for a mixture, B_m, is given by

$$B_m = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j B_{ij} \tag{14}$$

where $B_{ij} (i \neq j)$ is the second virial cross coefficient and y_i,

y_j are the mole fractions of component i and component j. The subscript m stands for a mixture.

Pure component

<u>Non-polar gases</u>: The gases in this case for our system are He, H_2 and N_2. Three parameters, the critical temperature, the critical pressure ,and the acentric factor were used to correlate the second virial coefficient. The second virial coefficient was estimated by a modified Pitzer-Curl correlation (Tsonopoulos, 1974).

$$\frac{BP_c}{RT_c} = B^\circ + \omega B' \tag{15}$$

$$B^\circ = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \tag{16}$$

$$B' = 0.0637 + \frac{0.331}{Tr^2} - \frac{0.423}{Tr^3} - \frac{0.008}{Tr^8} \tag{17}$$

<u>Polar gases</u>: For polar gases, the modified Pitzer-Curl correlation is also used. For polar molecules , an additional term is used in the modified Pitzer-Curl correlation. For a polar compound, this effect is correlated by a non-zero dipole which expresses the effect of the

electrostatic forces between molecules. The gas in this case for our system is NH_3, a hydrogen bonding compound. Thus,

$$\frac{BP_c}{RT_c} = B^\circ + \omega B' + B''$$ (18)

$$B'' = -2.112*10^{-4}\mu_r - 3.8877*10^{-21}\mu_r^8$$

This expression is function of the reduced dipole moment.

$$\mu_r = \frac{10^5\mu_r^2 P_c}{T_c^2}$$ (20)

Mixture

The Pseudo-critical method is used to calculate the second cross virial coefficient, B_{ij}, with the following equation.

$$T_{c_m} = \sum_i \sum_j y_i y_j T_{c_{ij}}$$ (21)

$$T_{c_{ij}} = (T_{c_i} T_{c_j})^{\frac{1}{2}} (1 - k_{ij})$$ (22)

$$V_{c_{ij}} = [\frac{V_{c_i}^{\frac{1}{3}} + V_{c_j}^{\frac{1}{3}}}{2}]^3$$ (23)

$$Z_{c_{ij}} = \frac{Z_{c_i} + Z_{c_j}}{2} \tag{24}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \tag{25}$$

$$P_{c_{ij}} = \frac{Z_{c_{ij}} R T_{c_{ij}}}{V_{c_{ij}}} \tag{26}$$

Combining equations 15-26 gives the second virial cross coefficient for 2 gases.

The fugacity coefficient for any component i in a mixture of n components is

$$\ln\gamma_i = \frac{2}{V}\sum_{j=1}^{n} y_j B_{ij} - \ln Z_m \tag{27}$$

This is the one of the most useful equations in thermodynamics. It relates the fugacity of a component in the vapor phase to its pressure through the theoretically derived virial equation of state.

4.2.2 Empirical Correlation of the Gas Phase Fugacity Coefficient

The literature expressions for the fugacity coefficients of ammonia, nitrogen, and hydrogen are as follows (Cooper, 1967: Newton, 1935):

$$\gamma_A = 0.1438996 + 0.2028538*10^{-2}T - 0.4487672*10^{-3}P \qquad (28)$$
$$-0.1142945*10^{-5}T^2 + 0.2761216*10^{-6}P^2$$

$$\gamma_N = 0.93431737 + 0.3101804*10^{-3}T + 0.295896*10^{-3}P \qquad (29)$$
$$-0.2707279*10^{-6}T^2 + 0.4775207*10^{-6}P^2$$

$$\gamma_H = \exp[e^{(-3.8402T^{0.125}+0.541)}P - e^{(-0.1263T^{0.5}-15.980)}P^2 \qquad (30)$$
$$+300[e^{(-0.011901T-5.941)}](e^{-P/300}-1)]$$

where A=NH$_3$, N=N$_2$, H=H$_2$

No expression was found for system of the fugacity coefficient of helium in the literature.

Both methods, the virial equation and the empirical correlations, were used to calculate fugacity coefficients for NH$_3$, N$_2$, and H$_2$ giving results which are not significantly different. Because the empirical equation for He was not found, the virial equation of state was used for calculating fugacity coefficients in this project.

5 AMMONIA DECOMPOSITION

5.1 Thermodynamic Equilibria

The chemical reaction equilibrium for the ammonia decomposition reaction is dependent on the temperature and partial pressure of the gases. For the ammonia decomposition:

$$NH_3 \rightleftharpoons 0.5 \; N_2 + 1.5 \; H_2$$
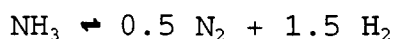
the equilibrium constant is

$$K = \frac{(a_N)^{0.5}(a_H)^{1.5}}{(a_A)} \tag{31}$$

Where a_N , a_H, and a_A are the activities of nitrogen, hydrogen, and ammonia, respectively. The value of equilibrium constant and equilibrium conversion is in the Appendix C. At the arbitrary standard state of 1 bar and temperature equal to the temperature of the system,

$$a_i = f_i = \gamma_i y_i P \tag{32}$$

The fugacity coefficient is a function of temperature, total pressure and composition of the gas phase.

As mentioned in Chapter 4, the fugacity was used to correct for non-ideal behavior. In a mixture of ideal gases the fugacity is equal to the partial pressure. In a real gas mixture the fugacity should be used instead of the partial

pressure. At low pressure, it is a reasonable to model a gas mixture as an ideal gas, but at moderate to high pressure the fugacity coefficient is often different from unity. The equilibrium constant can be expressed as

$$K = \frac{(\gamma_N y_N P_T)^{0.5} (\gamma_H y_H P_T)^{1.5}}{(\gamma_A y_A P_T)} \tag{33}$$

5.2   Kinetics

The following rate expression is used for the ammonia decomposition (Temkin and Pyzhev, 1940)

$$r_A = -k\left[\frac{(NH_3)^2}{(H_2)^3}\right]^{\beta} \tag{34}$$

and

$$k = k_o e^{\frac{-E}{RT}} \tag{35}$$

Where r_A = rate of ammonia decomposition

k = rate constant

k_o = pre-exponential factor

E = activation energy

β = constant

β may vary with catalyst composition. Temkin proposed that β = 0.5 on all iron catalysts. The results from experimental data correlation in the literature show little

significant difference when β varies from 0.5 to 0.7. Thus ,the value of $\beta = 0.5$ will be used for this work.

For a high pressure system, we use the fugacity to correct non-ideal behavior; thus,

$$r_A = -k \left[\frac{f_A^2}{f_H^3} \right]^{0.5} \tag{36}$$

or

$$r_A = -k \left[\frac{(\gamma_A y_A P_T)^2}{(\gamma_H y_H P_T)^3} \right]^{0.5} \tag{37}$$

6 MODEL DEVELOPMENT AND SIMULATION

The general material balance for the system may be written in the following way:

Input   –   Output   +   Generation

(mass enters   (mass leaves   (mass produced

the system)   the system)   within the system)

– Permeation   =   Accumulation

  (mass permeated   (mass build up

   from the system)   within system)

For steady state, the accumulation term is equal to zero. Using this general equation, a mass balance of each gaseous component along a dimensionless length the reactor is desired. Two reactor configurations are modeled: a plug flow reactor (PFR) with catalyst pellets packed inside and a tubular ceramic membrane reactor (MR) with catalyst pellets packed inside (Figure 6). For four gases in the system, the mass balance gives three and eight simultaneous ordinary differential equations as a model for the plug flow reactor and the membrane reactor, respectively

for a reaction of the form

$$a\ A \rightleftharpoons b\ N + c\ H$$
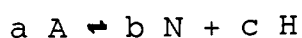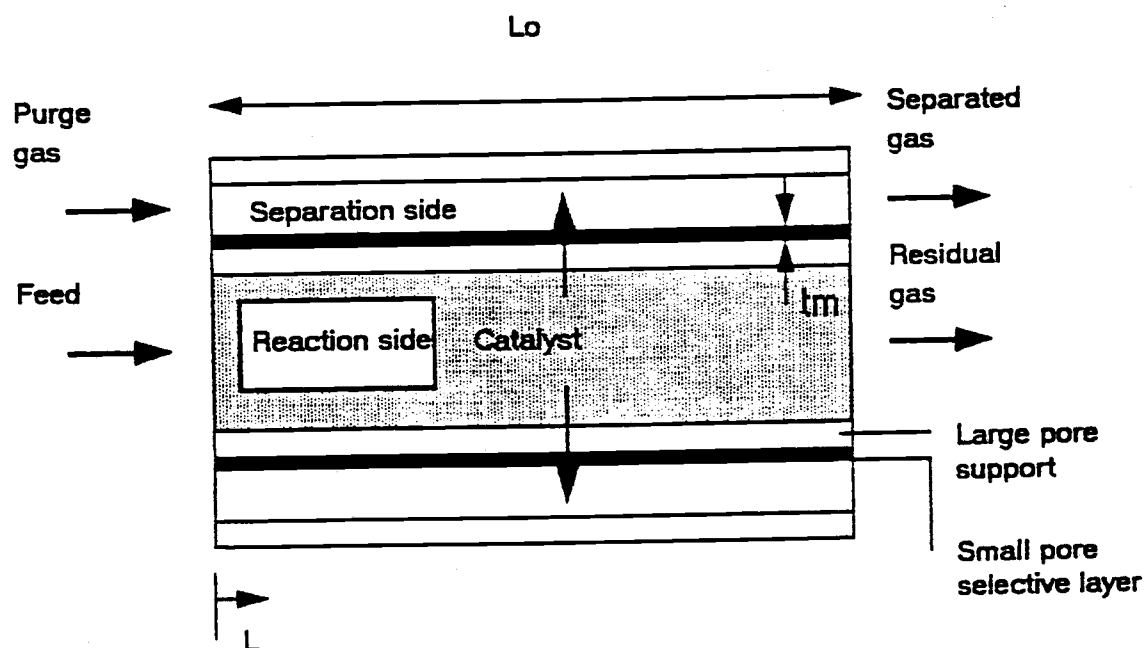
Figure 6.   Diagram of the membrane reactor

and using helium gas as a sweep gas(I). The material balance equations are developed below:

6.1 Model for Plug Flow Reactor (PFR)

There is no reaction of inert gas with the other gases in the system. The model for the plug flow reactor is:

$$\frac{d\frac{F_A}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} [ar_A] \tag{38}$$

$$\frac{d\frac{F_N}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} [-br_A] \tag{39}$$

$$\frac{d\frac{F_H}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} [-cr_A] \tag{40}$$

where A = NH$_3$, N = N$_2$, H = H$_2$, I = He

6.2 Model for Membrane Reactor (MR)

$$\frac{d\frac{F_A}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} [ar_A - \frac{2P_t}{R_1 t_m}\overline{P_A}(\frac{\frac{F_A}{F_{Ao}}}{\frac{F_T}{F_{Ao}}}\gamma_{At} - \frac{\frac{Q_A}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}}\gamma_{As}P_r)] \tag{41}$$

$$\frac{d\frac{F_N}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} \left[-br_A - \frac{2P_t}{R_1 t_m} \overline{P_N} \left(\frac{\frac{F_N}{F_{Ao}}}{\frac{F_T}{F_{Ao}}} \gamma_{Nt} - \frac{\frac{Q_N}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}} \gamma_{Ns} P_r \right) \right] \qquad (42)$$

$$\frac{d\frac{F_H}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} \left[-cr_A - \frac{2P_t}{R_1 t_m} \overline{P_H} \left(\frac{\frac{F_H}{F_{Ao}}}{\frac{F_T}{F_{Ao}}} \gamma_{Ht} - \frac{\frac{Q_H}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}} \gamma_{Hs} P_r \right) \right] \qquad (43)$$

$$\frac{d\frac{F_I}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} \left[- \frac{2P_t}{R_1 t_m} \overline{P_I} \left(\frac{\frac{F_I}{F_{Ao}}}{\frac{F_T}{F_{Ao}}} \gamma_{It} - \frac{\frac{Q_I}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}} \gamma_{Is} P_r \right) \right] \qquad (44)$$

$$\frac{d\frac{Q_A}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} \left[\frac{2P_t}{R_1 t_m} \overline{P_A} \left(\frac{\frac{F_A}{F_{Ao}}}{\frac{F_T}{F_{Ao}}} \gamma_{At} - \frac{\frac{Q_A}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}} \gamma_{As} P_r \right) \right] \qquad (45)$$

$$\frac{d\frac{Q_N}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} \left[\frac{2P_t}{R_1 t_m} \overline{P_N} \left(\frac{\frac{F_N}{F_{Ao}}}{\frac{F_T}{F_{Ao}}} \gamma_{Nt} - \frac{\frac{Q_N}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}} \gamma_{Ns} P_r \right) \right] \qquad (46)$$

$$\frac{d\frac{Q_H}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} \left[\frac{2P_t}{R_1 t_m} \overline{P_H} \left(\frac{\frac{F_H}{F_{Ao}}}{\frac{F_T}{F_{Ao}}} \gamma_{Ht} - \frac{\frac{Q_H}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}} \gamma_{Hs} P_r \right) \right] \qquad (47)$$

$$\frac{d\frac{Q_I}{F_{Ao}}}{d\frac{L}{L_o}} = \frac{V}{F_{Ao}} \left[\frac{2P_t}{R_1 t_m} \overline{P_I} \left(\frac{\frac{F_I}{F_{Ao}}}{\frac{F_T}{F_{Ao}}} \gamma_{It} - \frac{\frac{Q_I}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}} \gamma_{Is} P_r \right) \right] \qquad (48)$$

These differential equations are material balances over a differential length for the reactants and products on both side of the membrane.

If we nondimensionlize these differential equations, we obtain 2 dimensionless groups. The Damkohler number, **Da**, is a measure of the maximum forward reaction rate achieved in the given membrane reactor and the rate ratio, δ, is the maximum permeation rate of hydrogen to maximum reaction rate.

$$Da = \frac{kL_o v_r P_t^{-0.5}}{F_{Ao}} \tag{49}$$

$$\delta = \frac{\overline{P_H} s_m P_t^{1.5}}{t_m k v_r} \tag{50}$$

The dimensionless model equations for membrane reactor are

$$\frac{1}{Da} \frac{d\frac{F_A}{F_{Ao}}}{d\frac{L}{L_o}} = af_r - \delta\alpha_A \left(\frac{\frac{F_A}{F_{Ao}}}{\frac{F_T}{F_{Ao}}} \gamma_{At} - \frac{\frac{Q_A}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}} \gamma_{As} P_r \right) \tag{51}$$

$$\frac{1}{Da} \frac{d\frac{F_N}{F_{Ao}}}{d\frac{L}{L_o}} = -bf_r - \delta\alpha_N \left(\frac{\frac{F_N}{F_{Ao}}}{\frac{F_T}{F_{Ao}}} \gamma_{Nt} - \frac{\frac{Q_N}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}} \gamma_{Ns} P_r \right) \tag{52}$$

$$\frac{1}{Da}\frac{d\frac{F_H}{F_{Ao}}}{d\frac{L}{L_o}}=-cf_r-\delta\alpha_H\left(\frac{\frac{F_H}{F_{Ao}}}{\frac{F_T}{F_{Ao}}}\gamma_{Ht}-\frac{\frac{Q_H}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}}\gamma_{Hs}P_r\right) \tag{53}$$

$$\frac{1}{Da}\frac{d\frac{F_I}{F_{Ao}}}{d\frac{L}{L_o}}=-\delta\alpha_I\left(\frac{\frac{F_I}{F_{Ao}}}{\frac{F_T}{F_{Ao}}}\gamma_{It}-\frac{\frac{Q_I}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}}\gamma_{Is}P_r\right) \tag{54}$$

$$\frac{1}{Da}\frac{d\frac{Q_A}{F_{Ao}}}{d\frac{L}{L_o}}=+\delta\alpha_A\left(\frac{\frac{F_A}{F_{Ao}}}{\frac{F_T}{F_{Ao}}}\gamma_{At}-\frac{\frac{Q_A}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}}\gamma_{As}P_r\right) \tag{55}$$

$$\frac{1}{Da}\frac{d\frac{Q_N}{F_{Ao}}}{d\frac{L}{L_o}}=+\delta\alpha_N\left(\frac{\frac{F_N}{F_{Ao}}}{\frac{F_T}{F_{Ao}}}\gamma_{Nt}-\frac{\frac{Q_N}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}}\gamma_{Ns}P_r\right) \tag{56}$$

$$\frac{1}{Da}\frac{d\frac{Q_H}{F_{Ao}}}{d\frac{L}{L_o}}=+\delta\alpha_H\left(\frac{\frac{F_H}{F_{Ao}}}{\frac{F_T}{F_{Ao}}}\gamma_{Ht}-\frac{\frac{Q_H}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}}\gamma_{Hs}P_r\right) \tag{57}$$

$$\frac{1}{Da}\frac{d\frac{Q_I}{F_{Ao}}}{d\frac{L}{L_o}}=+\delta\alpha_I\left(\frac{\frac{F_I}{F_{Ao}}}{\frac{F_T}{F_{Ao}}}\gamma_{It}-\frac{\frac{Q_I}{F_{Ao}}}{\frac{Q_T}{F_{Ao}}}\gamma_{Is}P_r\right) \tag{58}$$

and

$$f_r = \left[\frac{(\gamma_A y_A)^2}{(\gamma_H y_H)^3} \right]^{0.5} \tag{59}$$

The membrane reactor models are derived subjected to the following assumptions.

-Plug flow operation on both sides of the membrane

-Reaction takes place only in the reaction zone

-Isothermal operation

-No axial or radial diffusion

-Negligible pressure drop on both sides of membrane

-Permeability for each gas in the gas mixture are the same as for pure gas.

-Negligible reverse reaction

-Negligible heat and mass transfer resistance in catalyst

These equation were solved simultaneously as an initial value problem using the commercial numerical integration software library IMSL. The jacobian matrix was supplied to the program.

The computation with kinetic data values showed that these systems produce a very stiff system because of the fast chemical reaction rate. The Gear's method numerical subroutine (DIVPAG) from the IMSL library was used to solve

with the problem and the steady state solution was obtained
when proper initial and parameter values were used.

The inlet conditions for the plug flow reactor at $L=0$
are

$$F_A = F_{Ao}$$

$$F_N = F_{No}$$

$$F_H = F_{Ho}$$

The inlet conditions for the membrane reactor at $L=0$
are

$$F_A = F_{Ao}$$

$$F_N = F_{No}$$

$$F_H = F_{Ho}$$

$$F_I = F_{Io}$$

$$Q_A = 0$$

$$Q_N = 0$$

$$Q_H = 0$$

$$Q_I = Q_{Io}$$

The membrane used is a microporous ceramic membrane
(microporous modified γ-Al_2O_3 membrane). It is an asymmetric
type of membrane, porosity of 0.52, tortuosity of 6.5,
separation layer thickness 5 μm(Keizer et al.,1988).

The average pore diameter in the separation layer is
about 40 Å. The inside tube diameter is 0.007 m, the outside
tube diameter is 0.01 m, the inside shell radius is 0.02 m,

and the reactor is a length of 0.0254 m.

The pre-exponential factor (2.514E7 gmol/(sec.g cat.atm$^{-0.5}$)) and activation energy (1.84E5 atm.cm^3/mol) are preliminary estimates from steady-state kinetic experiments conducted at Department of Chemical Engineering, Oregon State University for the alumina catalyst particles which were obtained from United Technologies, Inc., Louisville, KY (Product No. CS308).

$$k = k_o e^{\frac{-E}{RT}} \qquad (35)$$

These quantities agree with the data published in the master thesis of Nandy (Nandy, 1981). Feed composition and operating variables appropriate to IGCC conditions are the values used in this simulation (except other as specified). A typical IGCC gas composition is given in Table 1. All the other gases except ammonia, hydrogen, nitrogen were replaced by helium. The total flow rate of gas mixture to the reaction side is 3.718E-3 mol/s and the separation side flow rate is 7.436E-3 mol/s. The operating conditions of the system are in the temperature range of 810-1366 K and pressure range of 18.248E5-35.482E5 Pa.

Typical Gas Composition for IGCC Process

Gas Composition (Vol %)

N_2	48.0
O_2	<0.1
CO_2	5.0
CO	21.0
H_2	20.0
H_2O	1.0
CH_4	4.5
H_2S	0.5
NH_3	0.3

System Temperature Range: 810-1366 K

Table 1. Typical gas composition for the IGCC process

7 RESULTS AND DISCUSSION

In this chapter, the results from the numerical simulation program will be compared with the experimental results. In addition, the program will be used to simulate the decomposition of ammonia from the IGCC gas mixture stream. Also, the optimum thickness and fractional conversion at various temperature will be discussed. The parameters fractional conversion and fractional removal are used throughout this chapter. We define the fractional conversion as the ratio of total ammonia decomposing to the total ammonia feed and the fractional removal as the ratio of total ammonia removed by reaction and permeation (from reaction side to separation side) to total ammonia feed on the reaction side.

Fractional conversion $= \dfrac{NH_{3\ (reacted)}}{NH_{3\ (in)}}$

Fractional removal $= \dfrac{(NH_{3\ (reacted)} + NH_{3\ (permeated)})}{NH_{3\ (in)}}$

The abbreviation for PFR is stands for Plug Flow Reactor and MR is stands for Membrane Reactor. The conversion ratio is defined as the ratio of fractional conversion in membrane reactor to plug flow reactor.

Conversion ratio   = <u>Fractional conversion in MR</u>
                                  Fractional conversion in PFR

7.1 Comparison of the Results from the Simulation Program to Experimental Results for the Plug Flow Reactor

Experimental studies of catalytic ammonia decomposition on a Ni/Al_2O_3 catalyst conducted in the Department of Chemical Engineering, Oregon State University gave preliminary data for the pre-exponential factor and activation energy. Unfortunately, the membrane reactor is not ready to start experimentation, thus, we cannot compare the simulation program predictions with the experimental results for the membrane reactor. However, using the kinetic data with the simulation program, we have predicted the behavior of a plug flow reactor. The results of the comparison are shown in Table 2.

Table 2 gives the comparison between experimental data and results from simulation program at three different temperature levels, two different pressure values, various feed compositions and various feed flow rates. In the kinetic experiments, the fractional conversion of ammonia was kept low because this experiment was used to investigate kinetic parameters using the differential reactor method.

The results from simulation program are not much different from the experimental data especially at

| Temperature (K) | Pressure (Pa) | Experimental results | | | | | |
| | | Total flow in (mol/s) | Mole fraction | | Total flow out (mol/s) | Mole fraction | |
			NH3	H2		NH3	N2
673	18.248E5	4.4729E-4	0.005252	0.027450	4.4731E-4	0.005202	0.000025
		5.9305E-4	0.005252	0.027404	5.9308E-4	0.005210	0.000021
	35.482E5	6.1237E-4	0.005301	0.001828	6.1239E-4	0.005265	0.000023
		1.1905E-3	0.002727	0.005859	1.1906E-3	0.000265	0.000037
723	18.248E5	6.3503E-4	0.002559	0.055196	6.3506E-4	0.002500	0.000029
		1.2361E-3	0.002621	0.031818	1.2362E-3	0.002541	0.000040
	35.482E5	9.3251E-4	0.002609	0.036605	9.3255E-4	0.002562	0.000023
		1.2312E-3	0.002632	0.027972	1.2313E-3	0.002576	0.000028
773	18.248E5	6.4863E-4	0.002506	0.075010	6.4883E-4	0.002199	0.000153
		9.7096E-4	0.002506	0.074510	9.7116E-4	0.002298	0.000104
	35.482E5	6.3778E-4	0.002548	0.059272	6.3793E-4	0.002308	0.000120
		9.5498E-4	0.002548	0.059270	9.5513E-4	0.002382	0.000082

Table 2. Comparing with experimental data for plug flow

reactor

			Simulation results				
		Total flow out	Mole fraction				
H2	% Conversion	(mol/s)	NH3	N2	H2	% Conversion	% Error
0.027523	0.947	4.4731E-4	0.005201	0.000025	0.027524	0.966	**1.999**
0.027466	0.795	5.9307E-4	0.005214	0.000019	0.027460	0.720	**9.525**
0.018349	0.848	6.1239E-4	0.005253	0.000002	0.018353	0.906	**6.772**
0.005970	2.374	1.1906E-3	0.002658	0.000034	0.005957	2.516	**8.034**
0.055286	2.321	6.3507E-4	0.002498	0.000031	0.055286	2.393	**3.121**
0.031937	3.044	1.2362E-3	0.002547	0.000037	0.031927	2.816	**7.498**
0.036673	1.792	9.2356E-4	0.002553	0.000028	0.036685	2.136	**19.226**
0.002805	2.122	1.2313E-3	0.002569	0.000032	0.028065	2.387	**12.501**
0.075446	12.224	6.4880E-4	0.002236	0.000135	0.075393	10.750	**12.055**
0.075046	8.281	9.7114E-4	0.002321	0.000092	0.075014	7.365	**11.060**
0.059617	9.397	6.3795E-4	0.002272	0.000138	0.059669	10.807	**15.004**
0.059057	6.499	9.5516E-4	0.002360	0.000094	0.059541	7.361	**13.252**

Table 2. Comparing with experimental data for plug flow

reactor (continued)

temperature of 673 K. At other temperature levels greater than 673 K, the errors are much greater, and the % error in the fractional conversion ranges from 1.999 to 19.227, because the kinetic parameters are preliminary and estimated for testing the program. Only a few sets of data from the experiment were used to get these parameters and the fractional conversion in every experiment was kept low. The operating conditions (temperature and pressure) in the simulation that are different from the set of data used for preliminary kinetic data estimation would cause large errors in the fractional conversion.

The other potential source of error is the form of the rate expression used in the program. Results from experiment show that the rate law equation is not the same for all operating conditions, especially at high temperature, and at high pressure. It is difficult to determine exactly which rate expression is valid at a specific range of temperature or pressure. For purpose of preliminary simulation, the rate expression in equation 37 is used. The accuracy of results could be improved if the experiments provide the specific rate law equation corresponding to the specific range of operation.

7.2   Simulation of Ammonia Decomposition in the IGCC Processes Comparing the Plug Flow Reactor and Membrane Reactor

The simulation program can be used to compare the ammonia removal in the case of an ordinary plug flow reactor to a membrane reactor at typical IGCC conditions (921.89 K and 35.482E5 Pa). All the membrane configurations are the same as in section 7.1. Figure 7 shows the fractional conversion of ammonia versus dimensionless length of the reactor. It is clear that at the same conditions with negligible reverse reaction, the membrane reactor increased the fractional conversion over an ordinary plug flow reactor by nearly a factor of two (conversion ratio = 1.706). Higher fractional conversion in the membrane reactor resulted mostly from removing hydrogen from the reaction zone to the permeation zone by diffusion through the selective layer of the ceramic membrane. The rate of gas permeation through microporous membrane depends on the pore size, porosity, and the thickness of the membrane. We assumed that the permeation of the gas through the microporous membrane follows Knudsen theory. At constant temperature, the permeation rate is inversely proportional to the square root of the molecular weight.

Since hydrogen has the lowest molecular weight, it will
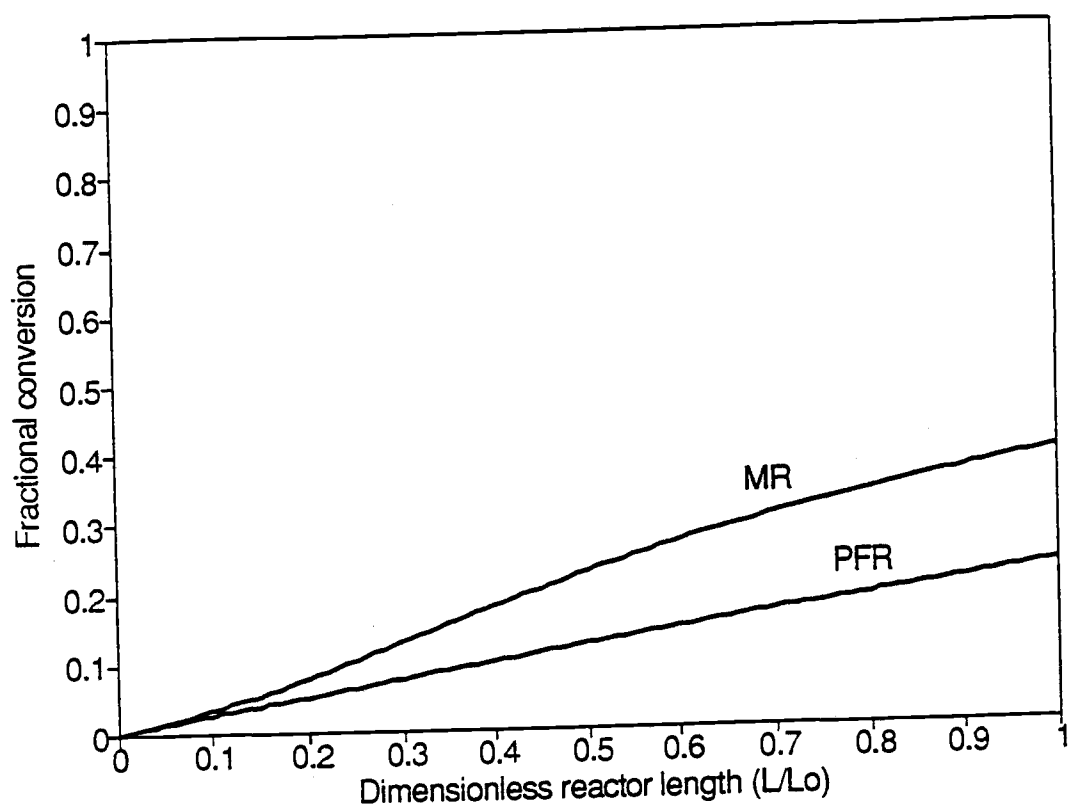
Figure 7. Fractional conversion and dimensionless reactor length comparing between PFR and MR

permeate through the membrane fastest. Fast removal of hydrogen from the reaction side will increase the driving force for the forward reaction, and results in higher fractional conversion.

Figure 8,9, and 10 show the concentration profiles of the four gases in the two types of reactors. The amount of ammonia fed to the reaction zone (NH_3 mole fraction = 0.003) is small compared with the other gases. From Figure 7 the fractional conversion of ammonia in the plug flow reactor is approximately 0.229 and little significant difference is seen in the mole fraction profile of each component. Such behavior is shown in Figure 8. The ammonia flow rate is 0.1115E-4 mol/s and is small compared with the total gas mixture flow rate of 0.372E-2 mol/s. At 0.229 fractional conversion, corresponding to 2.688E-6 mol/s of ammonia decomposition, this ammonia decomposition rate will generate 5.376E-6 mol/s of products. Both the ammonia reacted and the product generated are small compared with the mole fraction of nitrogen (0.48), hydrogen (0.20), and helium (0.317) in the feed. This is the reason why concentration profiles for plug flow reactor in Figure 8 do not show any changes. The concentration profile in small scale for each gas will be shown below. In contrast, in the membrane reactor not only does ammonia decompose to produce product gases but also each gas permeates through the membrane. Redistribution of
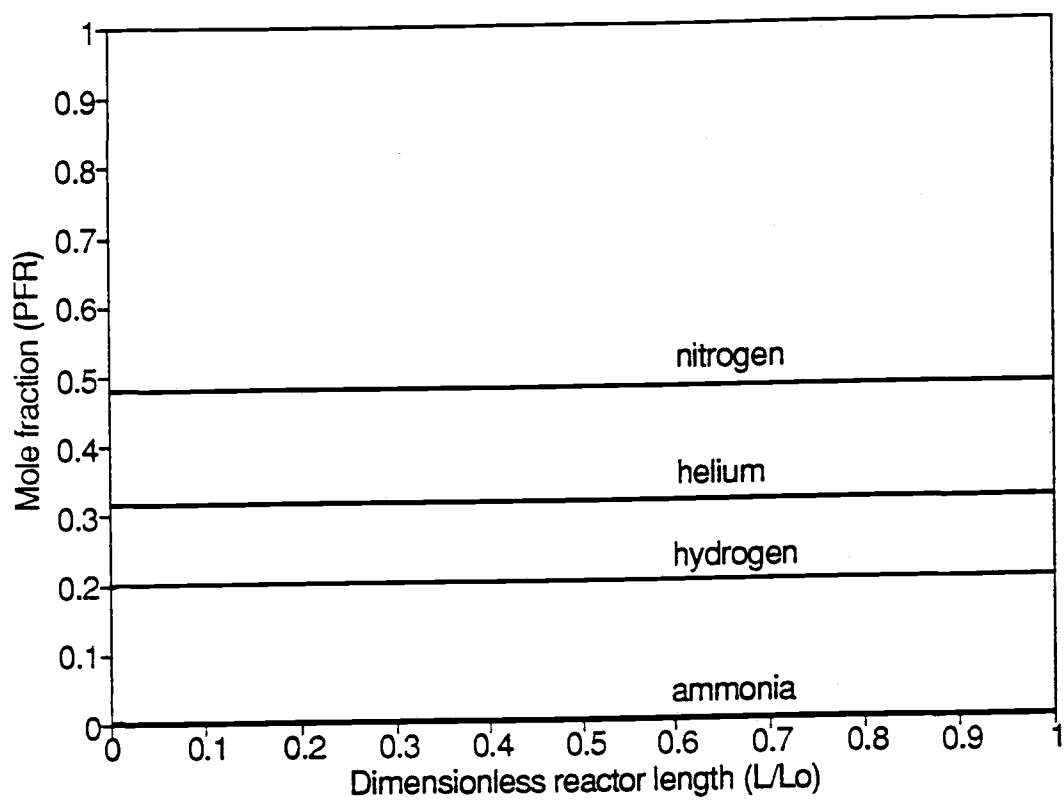
Figure 8. Concentration profiles in PFR
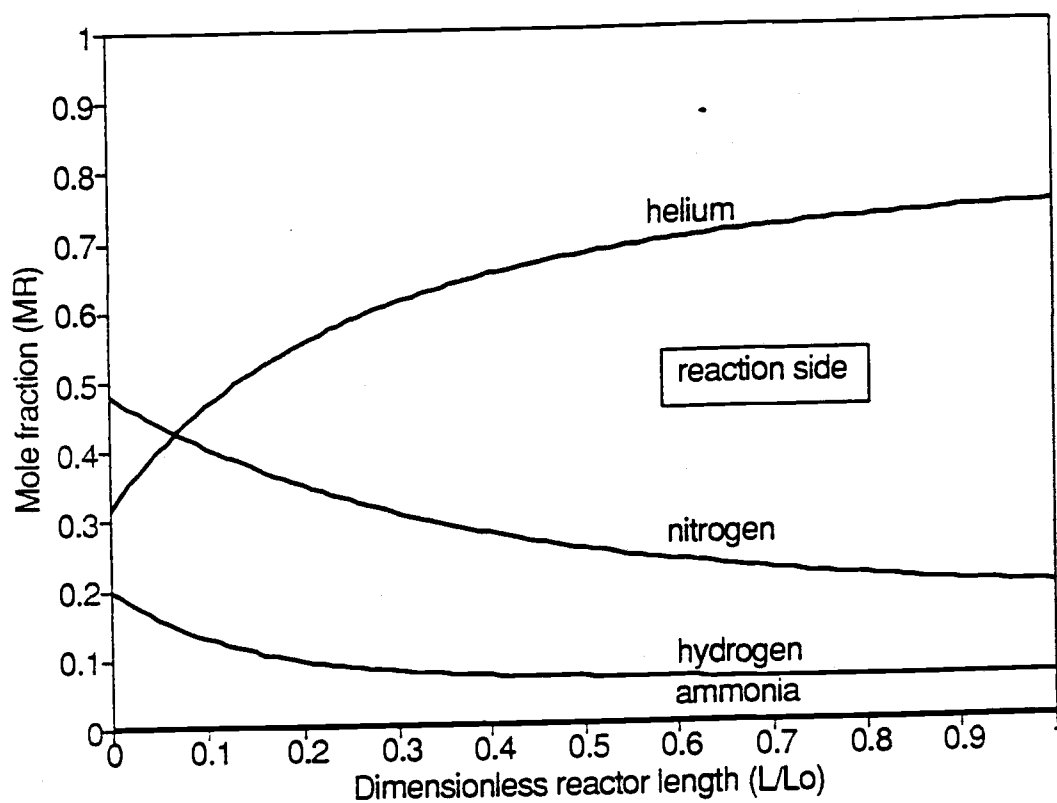
Figure 9. Concentration profiles in MR (reaction side)
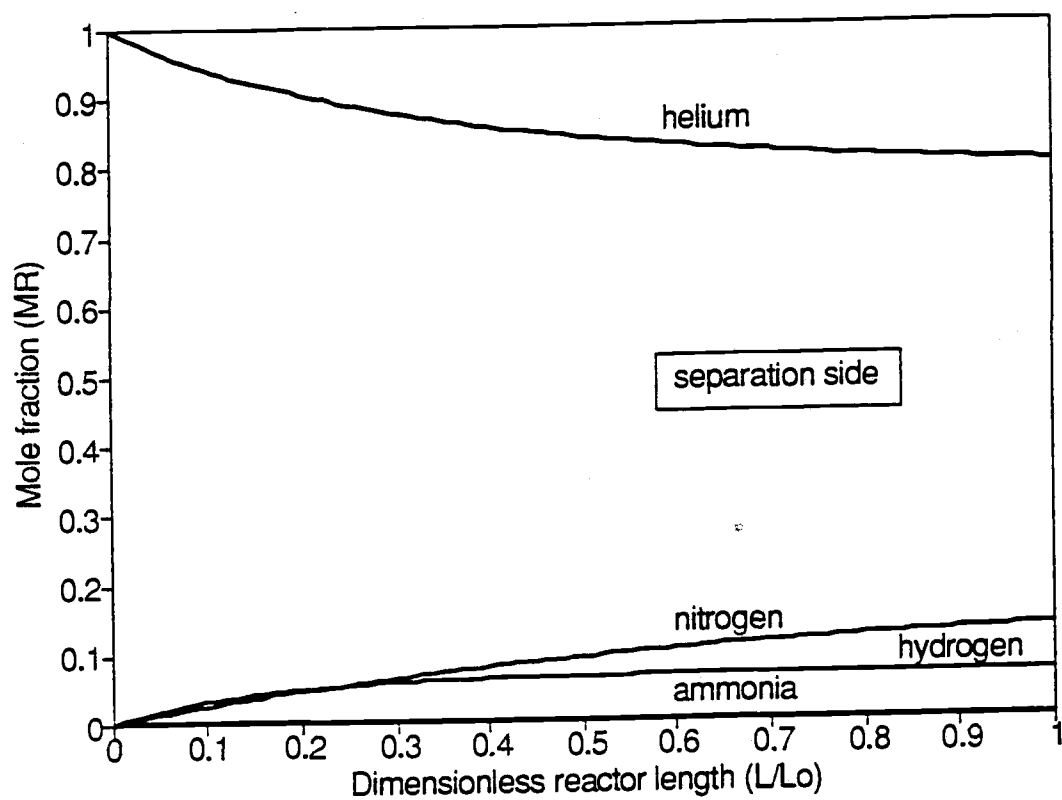
Figure 10. Concentration profiles in MR (separation side)

the mole fractions on the reaction side and the separation side of the membrane is shown in Figure 9 and Figure 10. Ammonia, nitrogen, and hydrogen mole fractions in the reaction side decrease due to permeation through the membrane to the separation side. On the other hand, the mole fraction of helium increases due to permeation from the separation side. In the permeation side, the mole fractions of all gases except helium increase due to permeation from the reaction side. The decrease in mole fraction of helium is caused by high partial pressure on separation side.

Comparison of the mole fraction profile of each gas for the plug flow reactor and the membrane reactor (reaction side) is shown on figures 11, 12, 13, and 14. For all the gases except helium, the mole fraction in the membrane reactor decreases more rapidly than in the plug flow reactor because of permeation. Conversely, the helium mole fraction increases because of opposite permeation.

Figure 15, 16, 17, and 18 show the comparison of the mole fraction profile for each gas component in the membrane reactor for both the reaction and separation side. Ammonia, nitrogen, and hydrogen mole fractions in the separation side increase along the length of the reactor. The mole fractions of ammonia and hydrogen in the separation side increase until they are slightly above the mole fraction on the reaction side. This occurs because the total flow rate of
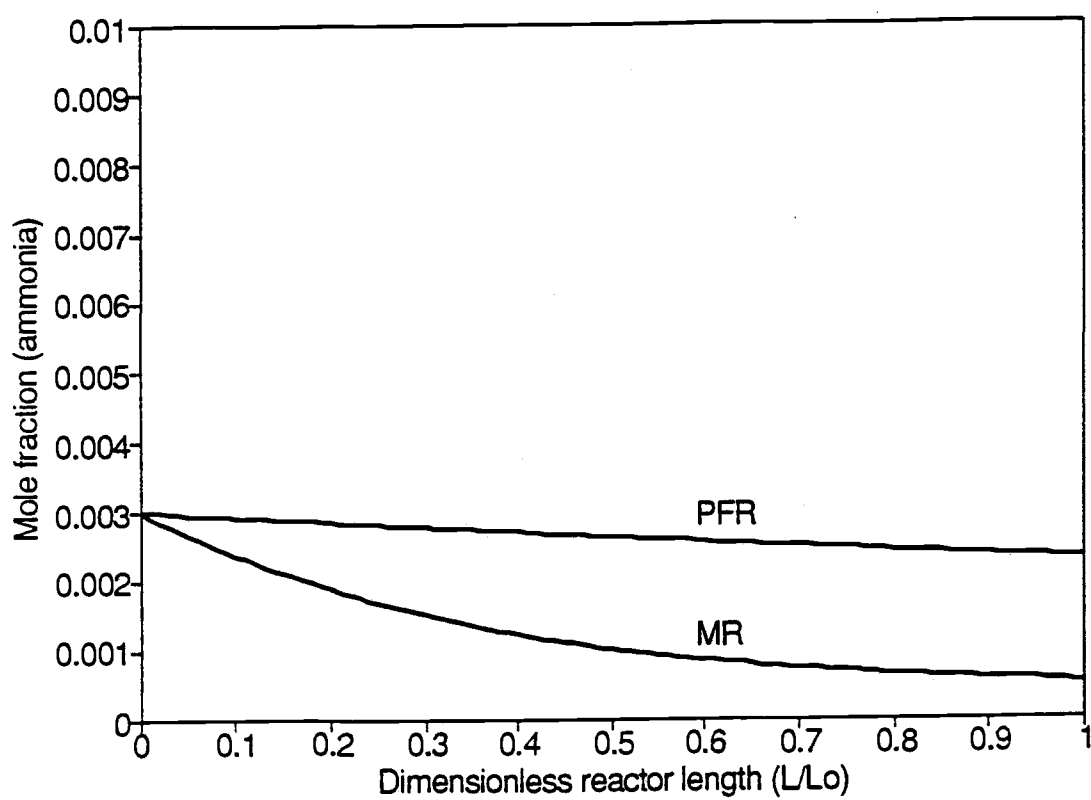
Figure 11. Concentration profiles of ammonia in PFR and MR
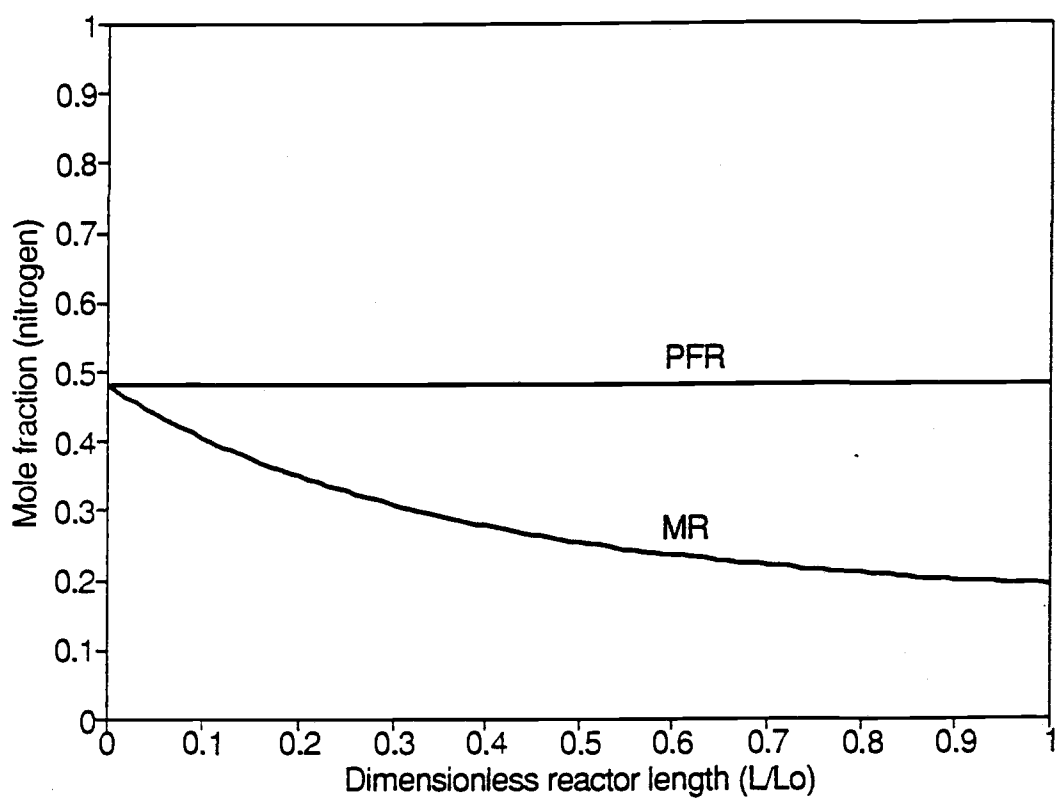
Figure 12. Concentration profiles of nitrogen in PFR and MR
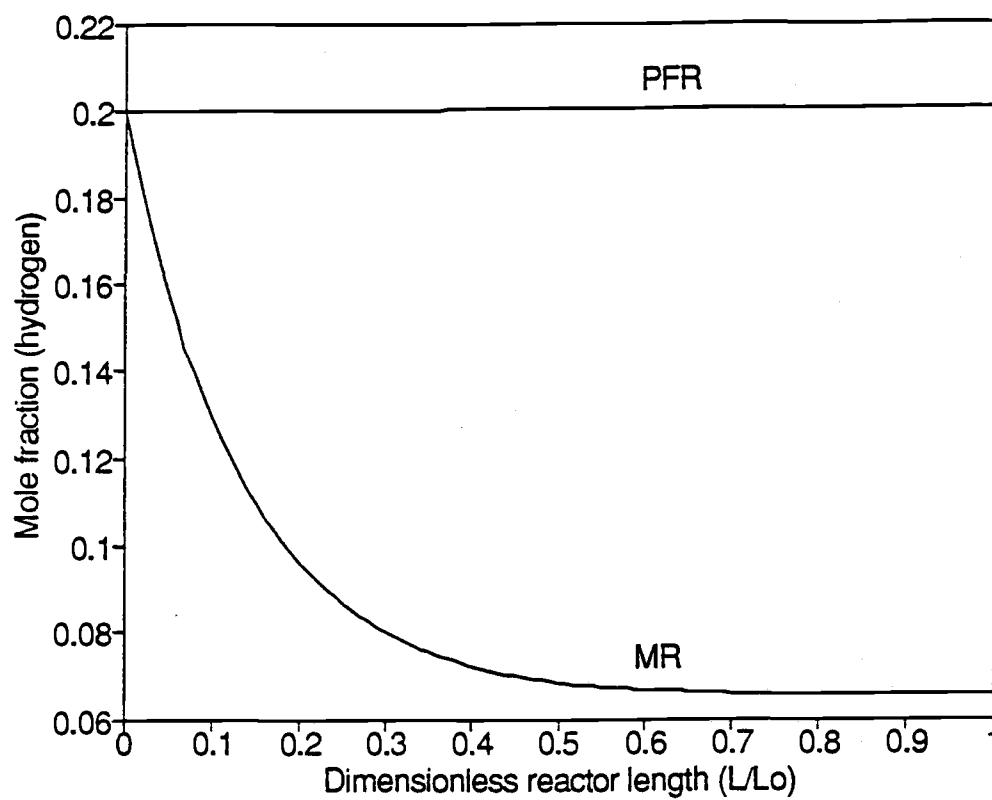
Figure 13. Concentration profiles of hydrogen in PFR and MR
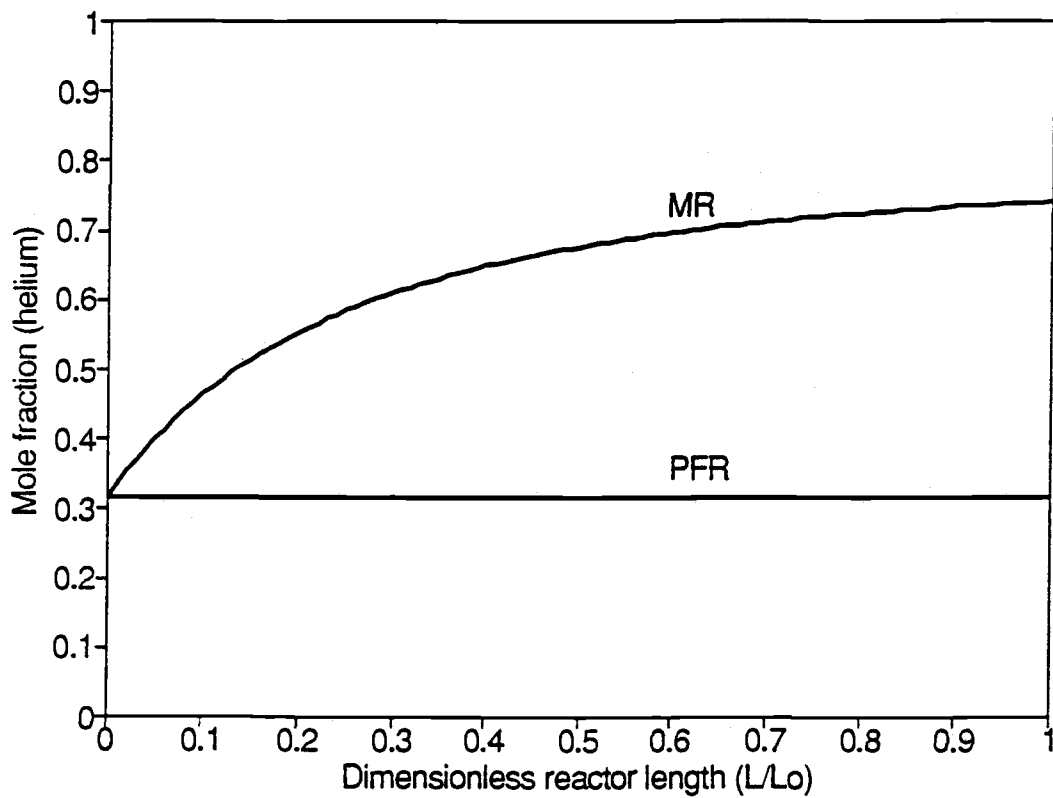
Figure 14. Concentration profiles of helium in PFR and MR
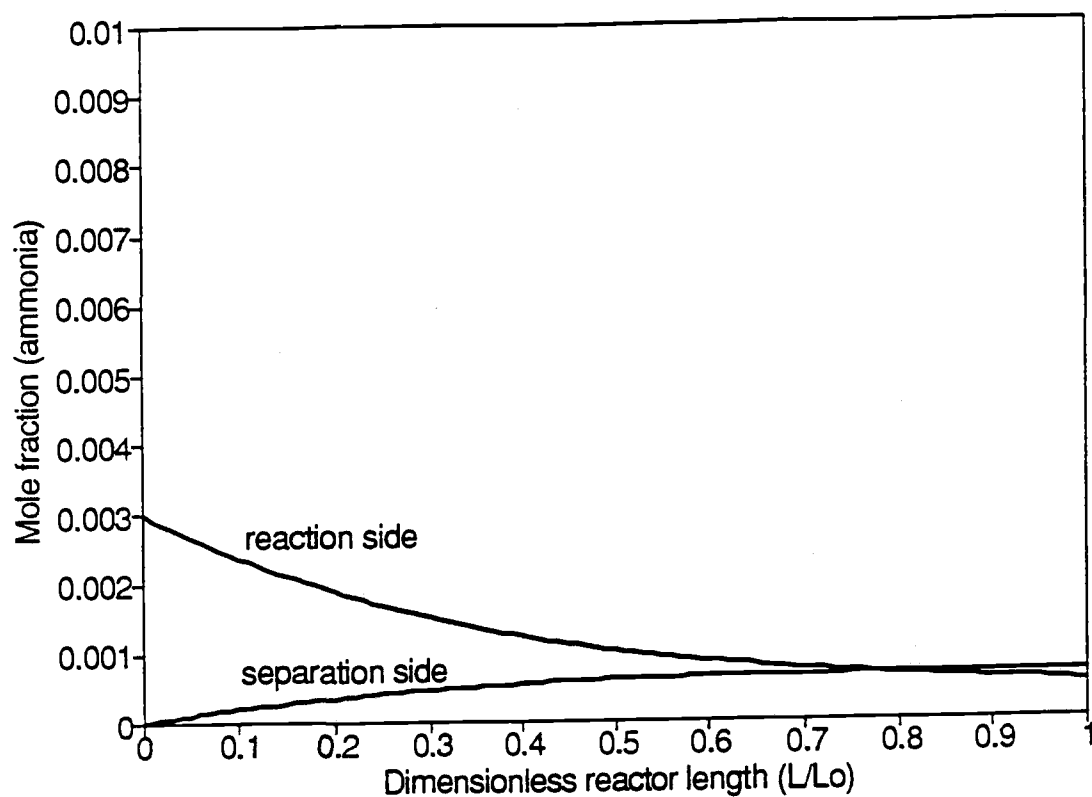
Figure 15. Concentration profiles of ammonia in MR both reaction side and permeation side
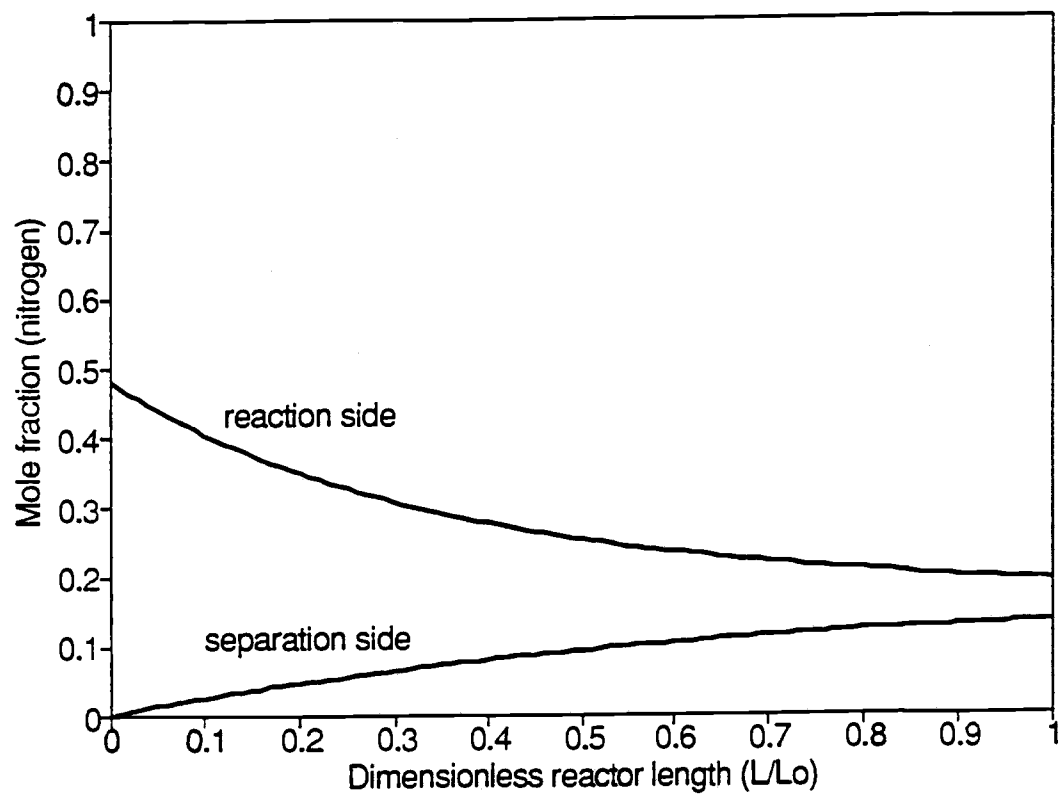
Figure 16. Concentration profiles of nitrogen in MR both reaction side and permeation side
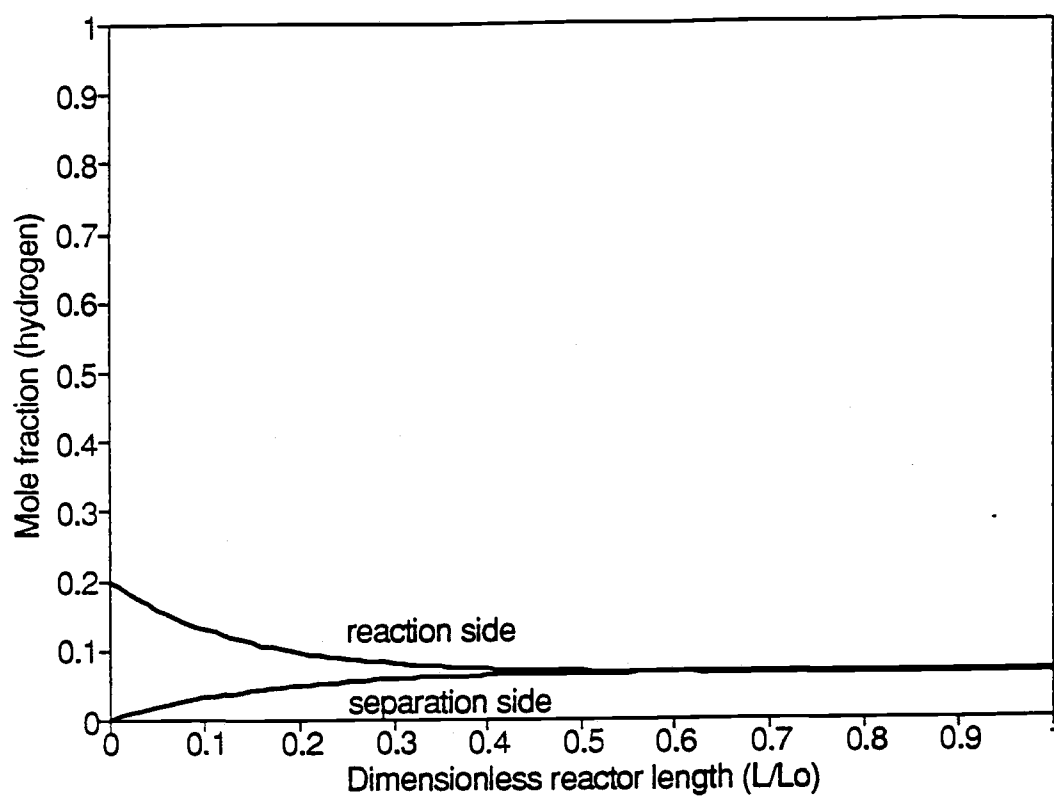
Figure 17. Concentration profiles of hydrogen in MR
both reaction side and permeation side
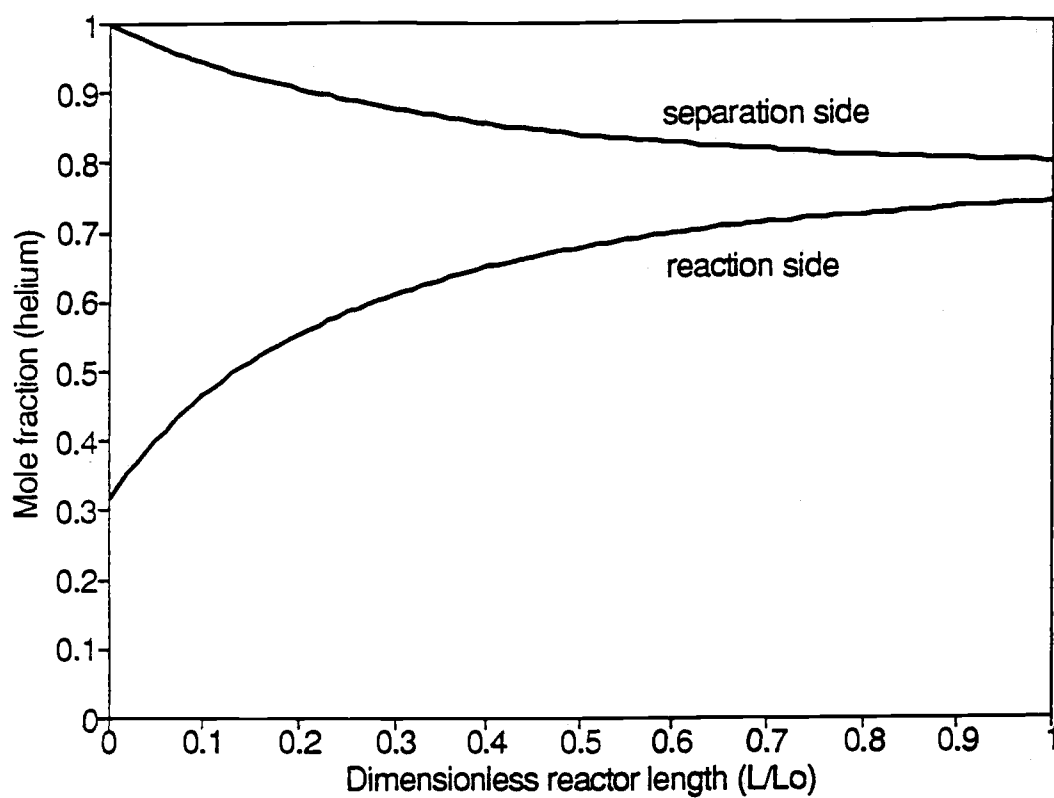
Figure 18. Concentration profiles of helium in MR both reaction side and permeation side

the gas mixture in both sides is high compared to the reactor length. The dynamic equilibrium between reaction and permeation is not established immediately in the reactor. A lag time is required before the dynamic equilibrium in partial pressure is reached. The decrease of the helium mole fraction in the separation side is caused by the high partial pressure (He mole fraction = 1) in the separation side. The partial pressure of all gases changed on both sides of reactor due to permeation until equilibrium occurs. Figure 19 shows the influence of the nitrogen mole fraction in the feed gas with negligible reverse reaction. Because there is no nitrogen term in the rate law, the fractional conversion at different mole fractions of nitrogen is nearly constant. In contrast, Figure 20 shows that the ammonia conversion is dependent on the hydrogen mole fraction in the feed gas stream. Twenty percent hydrogen in the feed gas will lower the conversion to nearly one half of the value when the gas feed contains ten percent hydrogen. If there is no hydrogen in feed, the conversion is always complete at temperatures above 820 K. If we include the reverse reaction in the rate expression, the fractional conversion of ammonia will decrease with increasing nitrogen and hydrogen feed mole fractions because of the equilibrium limitation. Please see Appendix D for a discussion of the effects of incorporating the reverse reaction in the rate expression.
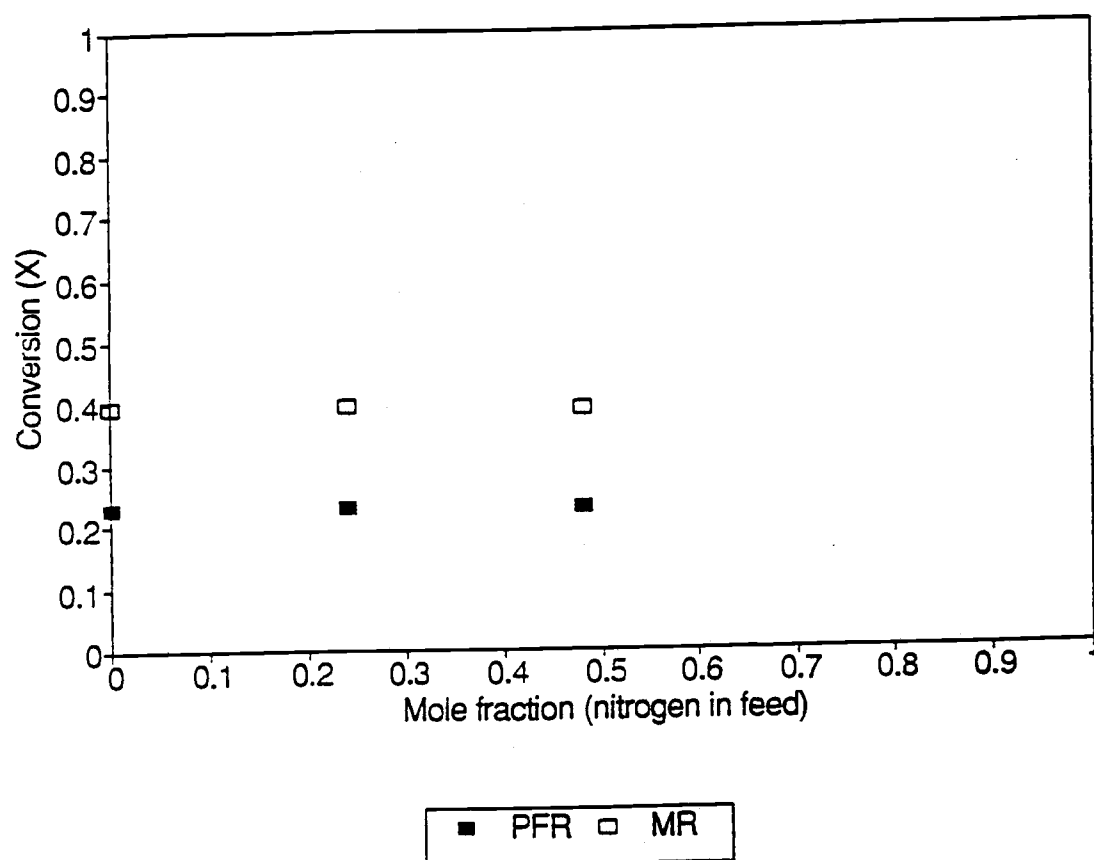
Figure 19. The effect of nitrogen on fractional conversion
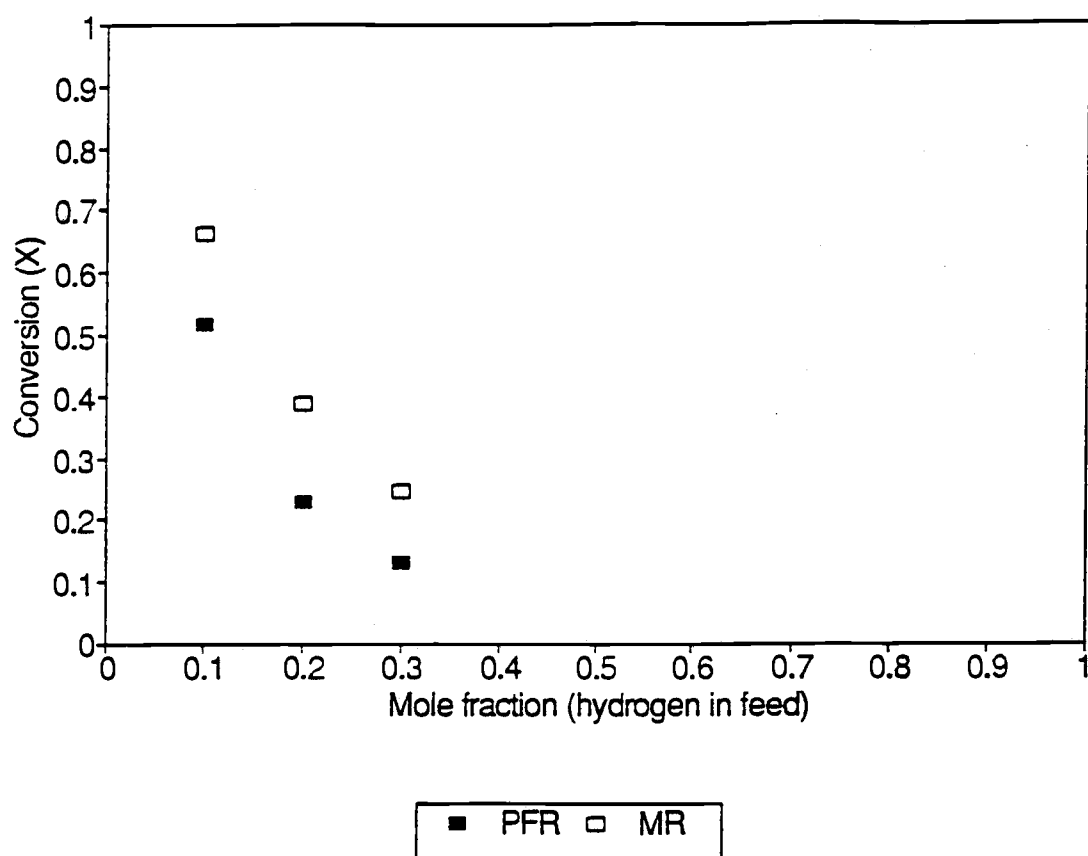
Figure 20. The effect of hydrogen on fractional conversion

7.3 The Optimum Parameters for Operation

The differential equations were presented in dimensionless form in equations 49 to 59. The rate ratio(δ), the ratio of the maximum permeation rate of hydrogen to maximum reaction rate, represents the effect of membrane thickness value.

$$\delta = \frac{\overline{P_H} S_m P_t^{1.5}}{t_m k v_r}$$ (50)

When all the parameters are constant except membrane thickness, the optimum thickness that gives the highest ammonia conversion could be found using Figure 21. At two different pressures, the optimum thickness is in the rate ratio range of 80-250, corresponding to 3-9 μm of separation layer thickness. For this work, the thickness of 5 μm was used because of an available commercial ceramic membrane product. This chosen value is in the range of the predicted optimum thickness. This optimum thickness will permeate the appropriate flux for reactants and products to produce highest ammonia conversion.

Ideally, if we could design a membrane with a lower selectivity for ammonia over hydrogen, preventing loss of reactant, the conversion should improve. The results were shown in Table 3. When the selectivity of ammonia with respect to hydrogen decrease to 10 percent of the Knudsen

selectivity by keeping all the parameters constant as in section 7.2.2, the conversion ratio increases from 1.706 to 2.420. At the same permeation rate of hydrogen and ammonia, the conversion is still greater than the conventional plug flow reactor. Thus, for a membrane which is permeable to all gases, the maximum fractional conversion shift is limited by how much of the reactant is lost and how much of the product permeates. If we could increase the membrane selectivity toward the product and decrease the selectivity of reactant, the conversion will be further improved. This phenomena is shown by Itoh(1987). A palladium membrane reactor for cyclohexane dehydrogenation increased the conversion from 18.7 % in plug flow reactor to 99.7 % in membrane reactor at (temperature 483 K and pressure 1 atm) because the palladium membrane is permeable only to hydrogen.
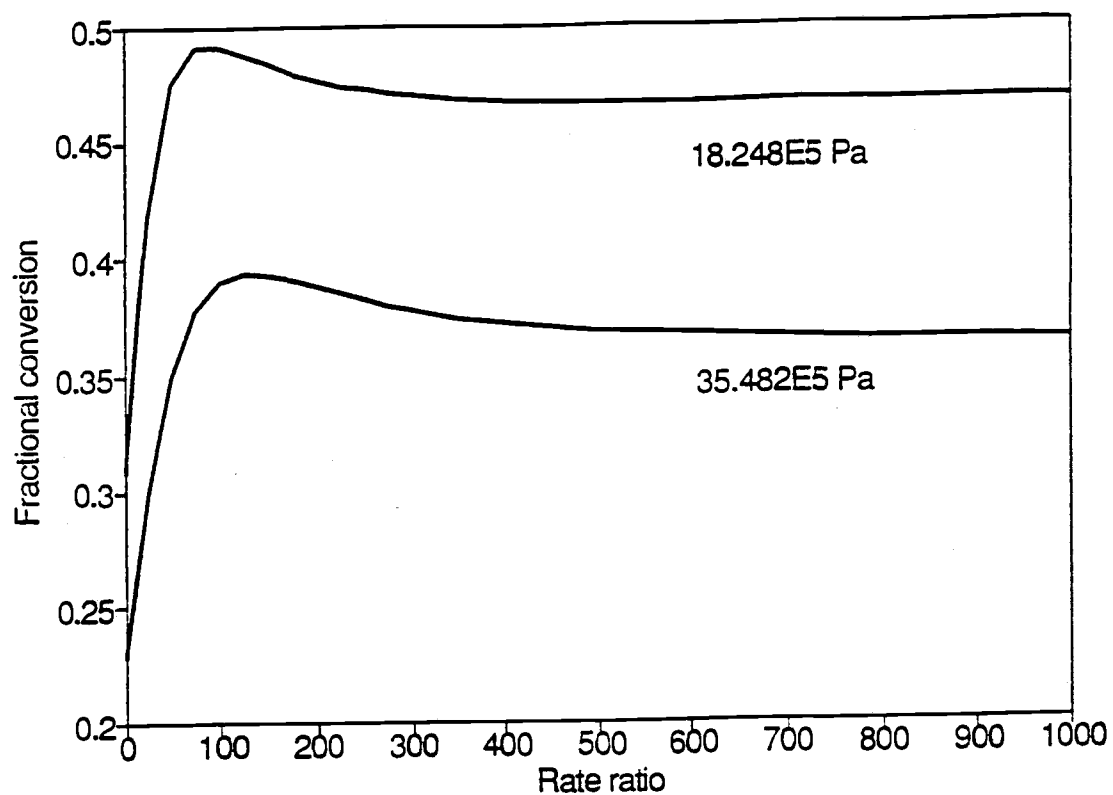
Figure 21. Fractional conversion and rate ratio in MR

Gas	Molecular Weight	Selectivity by Knudsen	Hypothetical Selectivity			
		$\alpha(i/H_2)$				
NH3	17.031	0.344	1	0.688	0.172	0.034
N2	28.013	0.268	0.268	0.268	0.268	0.268
H2	2.016	1	1	1	1	1
He	4.003	0.709	0.709	0.709	0.709	0.709
Conversion Ratio		1.706	1.404	1.474	1.993	2.420

(Fractional Conversion in PFR =0.229 with negligible reverse reaction)

Table 3. The effect of selectivity of ammonia on conversion

Pr	Conversion	Conversion Ratio
0.5	0.459	2.011
0.75	0.428	1.875
1.0	0.389	1.706

(Fractional Conversion in PFR =0.229 with negligible reverse
 reaction)

Table 4. The effect of pressure ratio on ammonia conversion

Total Flow in	Reaction Side (mol/s)	Separation Side (mol/s)	Separation Side Reaction Side	Conversion Ratio
	3.718E-3	1.859E-3	0.5	1.206
	3.718E-3	3.718E-3	1	1.392
	3.718E-3	7.436E-3	2	1.706
	3.718E-3	1.859E-2	5	2.169
	3.718E-3	3.718E-3	10	2.389
	3.718E-3	3.718E-1	100	2.486

(Fractional Conversion in PFR =0.229 with negligible reverse reaction)

Table 5. The effect of total flow in separation side on ammonia conversion

In addition, If one could decrease the total pressure in the separation zone, the conversion will improve. This is shown in Table 4. The pressure ratio is the ratio of the total pressure on the separation side to the total pressure on the reaction side. When the separation side pressure is half of the reaction side pressure, corresponding to a pressure ratio of 0.5, the conversion ratio increases from 1.706 to 2.011. This is because the partial pressure difference between the reaction zone and separation zone is the driving force for the separation. From equations 51-59, when the total pressure on separation side decreases, the partial pressure gradient between reaction side and separation side increases. As the partial pressure gradient increases, the permeation rate increases proportionally.

Table 5 shows the effect of the He sweep gas flow rate on the separation side on the ammonia conversion. Higher flow rates of sweep gas on the separation side will give a higher fractional conversion. Increasing the flow rate of the sweep gas to 10 times the flow rate on the reaction side , the conversion ratio increases from 1.392 to 2.389. On the separation side, all of permeating gas from the reaction side will be removed faster by using a higher flow rate of sweep gas. Thus, the partial pressure of gases on the separation side will decrease, causing a higher driving force and higher fractional conversion. Figure 22 show the
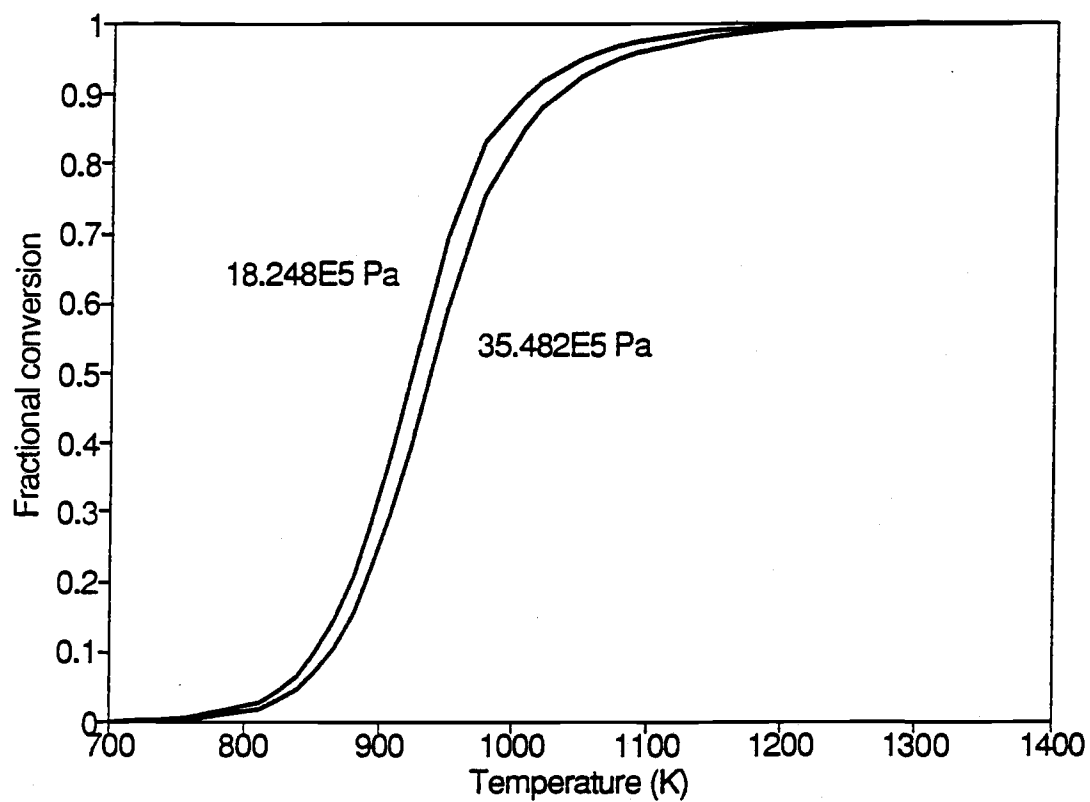
Figure 22. Fractional conversion and temperature

effect of a wide range of operating temperature at pressures of 18.248E5 Pa and 35.482E5 Pa for membrane reactor. At the same temperature, the ammonia conversion is inversely proprotional to the square root of pressure. Also, we can consider the fractional removal instead of the fractional conversion. The fractional removal is the ratio of the rate of ammonia decomposing in the reaction zone and permeating through the selective layer of the membrane to the rate of ammonia feed in reaction zone. The fractional removal in the membrane reactor is always greater than fractional conversion at all conditions (Figure 23).

The Damkohler number, Da, represents for the maximum forward reaction rate that can be achieved in the reactor and is proportional to the reactor volume.

$$Da = \frac{kL_o v_r P_t^{-0.5}}{F_{Ao}} \qquad (49)$$

Figure 24 and 25 show the relationship between fractional conversion and log(Da), which ranges from -2 to 4, corresponding to 700-1300 K. With higher temperature, a higher Da will give higher fractional conversion. These two graphs of fractional conversion and log(Da) at different pressure are nearly the same. The small different of fractional conversion is due to the non-ideality of the gases. If we assume ideal gas behavior for all gases, the fractional conversion graph for the membrane reactor at

various pressure and temperature would expected.
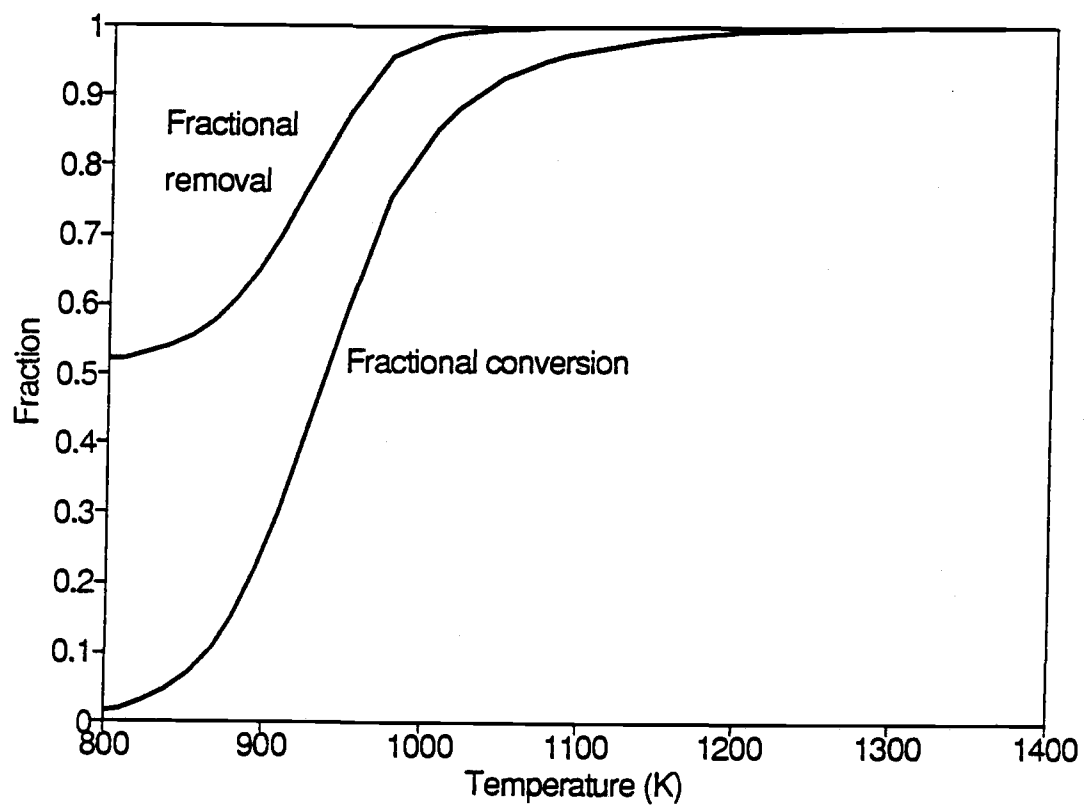
Figure 23   Fractional conversion and fractional removal at
35.482E5 Pa
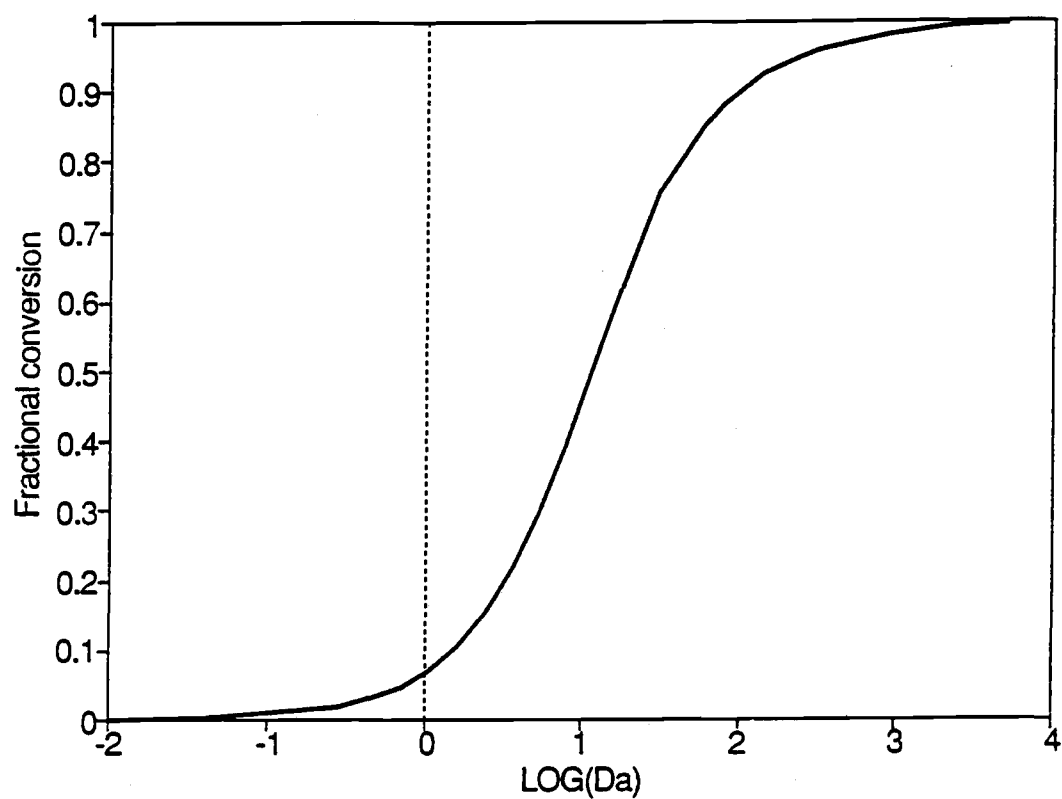
Figure 24. Fractional conversion and LOG(Da) at 18.248E5 Pa
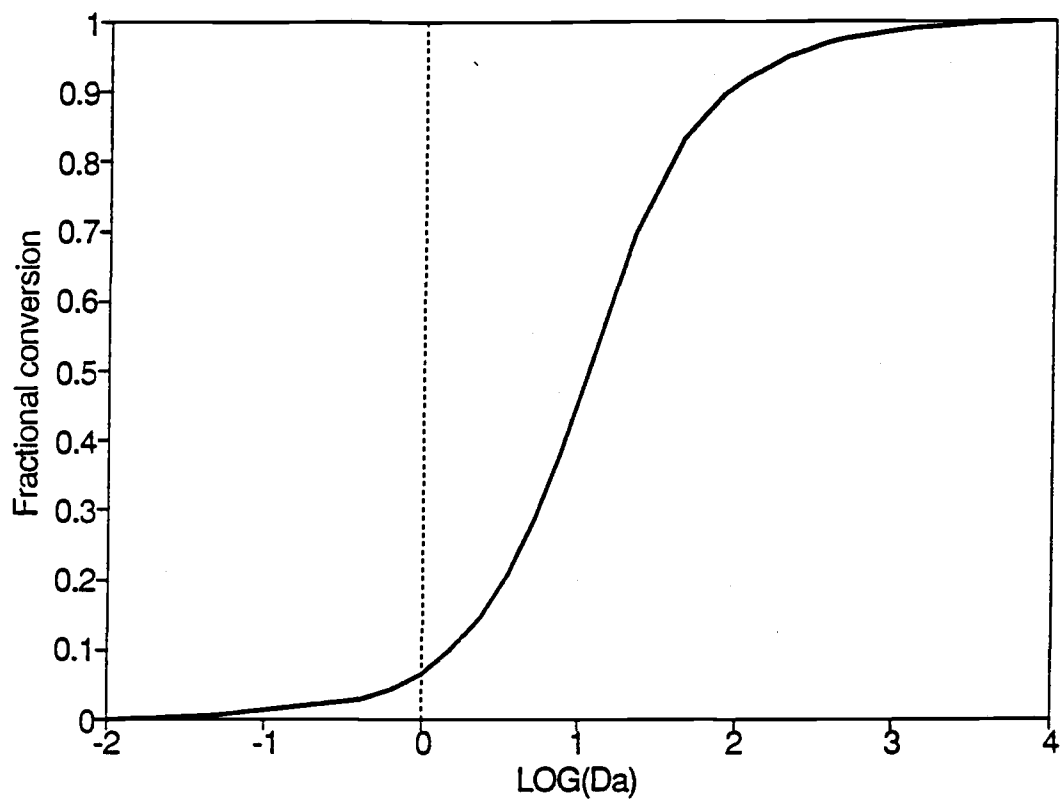
Figure 25. Fractional conversion and LOG(Da) at 35.482E5 Pa

8 CONCLUSIONS

The plug flow reactor model for ammonia decomposition using the Temkin and Pyzhev rate law expression has been shown to give good agreement between experimental and simulated results. Using the kinetic data from differential reactor experiments of ammonia decomposition, the feasibility of catalytic ammonia decomposition in membrane reactor has been successfully demonstrated. The general characteristics of membrane reactor are presented in term of fractional conversion shift and mole fraction profiles comparing with the plug flow reactor. The effects of product gases in the feed side are investigated. The optimum membrane thickness was found and the effect of operating parameters were studied. The following conclusions are drawn from this work.

1.   The extent of ammonia decomposition in the membrane reactor was successfully increased beyond the plug flow reactor by removing nitrogen and hydrogen from the reaction side.

2.   The optimum membrane thickness is in the range of 3-9 μm.

3.   For a fixed reactor length, fractional conversion and fractional removal of ammonia in the membrane reactor is

always better than the plug flow reactor at all
conditions.

4. The fractional conversion for ammonia decomposition
   in both the plug flow reactor and the membrane reactor
   depends on the mole fractions of hydrogen and nitrogen
   in feed gas because of the equilibrium limitation.

5. Additional equilibrium shift can be achieved by
   increasing the permeation of hydrogen and/or nitrogen
   and/or preventing the permeation of ammonia to the
   separation side (decreasing the selectivity of
   ammonia over hydrogen). Thus, a membrane with high
   selectivity [α (H_2/NH_3) >2.92] for products over
   reactants should be used.

6. Increasing temperature and/or decreasing total
   pressure will increase conversion in both reactors.

7. The effect of pressure in the system is small
   compared to the effect of temperature.

8. Decreasing the pressure ratio and/or increasing the
   sweep gas flow in the separation side will increase
   the conversion shift.

9. The general behavior of conversion and log (Da) could be
   found. There is a small difference in the fractional
   conversion due to gas phase non-ideality in the system.

10. At a fixed feed flow rate and other operating
    conditions, increasing the membrane reactor length will

increase the ammonia fractional conversion.

11. For a given reactor size and operating conditions, increasing the feed flow rate to the reaction zone will decrease ammonia conversion.

9   RECOMMENDATION

Some suggestions for further research in this area of membrane reactors for decomposition of ammonia are as follows:

1. The accuracy of membrane reactor is primarily depends on the rate expression, the kinetic parameters, and the permeability of the gases. For this work, the rate expression and kinetic parameters are a preliminary estimation. Further experiments will be necessary to investigate the mass transfer resistance effects in order to obtain a correct rate expression and the reaction rate constant for the catalytic decomposition of ammonia. In addition, the permeability of gases was assumed to occur by Knudsen diffusion. The other diffusion mechanisms are involved during the actual permeation process including surface diffusion and molecular sieving. Using an improved rate expression, more accurate kinetic parameters, and experimental permeability data improve the results of the simulation.

2. The equilibrium shift depends mostly on the permeation of product from the reaction side to the permeation side. If one could increase the permeation rate by increasing the area of permeation by using hollow fiber

type membrane and/or increasing the selectivity by using a membrane with higher selectivity for the product over the reactant, a larger conversion shift should be expected.

3. Thermal decomposition of ammonia occurs at temperatures above 923 K. Thus, above this temperature, there is an effect of thermal decomposition causing the error in the results for the simulation program.

4. Incorporating catalytic activity to the membrane material instead of using catalyst packed inside the reactor would be interesting to investigate.

BIBLIOGRAPHY

Antonson, C. R., R. J. Gardner, C. F. King, and D. Y. Ko, "Analysis of Gas Separation by Permeation in Hollow Fibers," Ind. Eng. Chem. Proc. Des. Dev., **16**, 473(1977).

Barron, R., Cryogenic Systems(Mc Graw-Hill, New York, 1966)

Blaisdell, C., and K. Kammermeyer,"Counter current and Cocurrent Gas Separation," Chem. Eng. Sci., **28**, 1249, (1983).

Carberry, J. J., Chemical and Catalytic Reaction Engineering, McGraw Hill, New York (1976).

Cooper, H. W.,"Fugacity for High Pressure and Temperature," Hydrocarbon Processing, **46**, 159, (1967).

Emmett, P.H.,"Fifty Years of Progress in the Study of the Catalysis Synthesis of Ammonia",The Physical Basis for Heterogeneous Catalysis., Edited by E. Drauglis and R. I. Jaffee., Plenum Press, New York, 2, (1975).

Egan, B. Z.,"Using Inorganic Membranes to Separate Gases: R & D Status Review,"ORNL/TM-11345, November, 1989.

Fukuda, K., M. Dokiya, T. Kameyama, and Y. Kotera,"Catalytic Decomposition of Hydrogen Sulphide,"Ind. Eng. Chem. Fund., **17**, 243 (1987).

Haraya, K., Y. Shindo, T. Hakuta, and H. Yoshitome,"Gas Separation By means of a Porous Membrane With Cocurrent and Countercurrent Flows," J. CHem. Eng. Jpn., **19**, 461, (1986).

Hill, C. G.,An Introduction to Chemical Engineering Kinetics and Reactor Design, John Wiley and Sons, New York, (1977)

Hougen, O. A., K. M. Watson, and R. A. Ragatz, Chemical Process Principles, Vol. II, John Wiley and Sons, New York, (1947).

Hwang, S. T., and K. Kammermeyer, <u>Membranes in Separations</u>, Wiley-Interscience, New York (1975).

<u>IMSL Math/Library</u> , 1.1 ed., IMSL, Houston, Texas, (1989).

Itoh, N., Y. Shindo, T. Hakuta, and Y. Yoshitome,"Enchanced Catalytic Decomposition of HI by Using a Microporous Membrane," <u>Int. J. Hydrogen Energy</u>, **9**, 834 (1984).

Itoh, N., Y. Shindo, K. Haraya, K. Obata, T. Hakuta, and H. Yoshitome, "Simulation of a Reaction Accompanied by Separation," <u>Int. Chem. Eng.</u>, **25**, 138 (1985).

Itoh, N., "A Membrane Reactor Using Palladium," <u>AIChE J</u>, **33**, 1576 (1987).

Itoh, N.,Shindo, Y., Haraya, K., Hakuta, T.,"A Membrane Reactor Using Porous Vycor Glass for Shifting Equilibrium of Cyclohexane Dehydrogenation," <u>J. Chem. Eng. Jpn.</u> , **21**, 399, (1988)

Kameyama, Y., Dokiya, M., Fukuda, K. and Kotera., "Diffusion Permeation of Hydrogen Sulfide Through a Microporous Vycor-Type Glass Membrane in the Separation System of Hydrogen and Hydrogen Sulfide", <u>Sep. Sci. Tech.</u>,**14**(10), 953, (1979)

Kameyama, T., M. Dokiya, M. Fujishige, and H. Yokokawa, "Possibility for Effective Production of Hydrogen from Hydrogen Sulphide by means of a Porous Vycor Glass Membrane," <u>Ind. Eng. Chem. Fund.</u>, **20**, 97 (1981).

Kameyama, T., M. Dokiya, M. Fujishige, H. Yokokawa, and K. Fukuda, "Production of Hydrogen from Hydrogen Sulphide by Means of Selective Diffusion Membranes," <u>Int. J. Hydrogen Energy</u>, **8**, 5 (1983).

Keizer, K., R. J. R. Uhlhorn, R. J. Van Vuren, and A. J. Burggraaf,"Gas Separation Mechanisms in Microporous Modified γ-Al2O3 Membranes,"<u>J. Memb. Sci.</u>, **39**, 285, (1988).

Krishnan, G. N., B. J. Wood, and A. Sanjurjo,"Study of Ammonia Removal in Coal Gasification Processes, Topical Report: Literature Review,"DOE Contract DE-AC21-86MC23087, May 1987.

Levenspiel, O., <u>Chemical Reaction Engineering</u>, 2nd ed., John Wiley and Sons, New York, (1972).

Michaels, A. S., "New Separation Technique for the CPI, "<u>Chem. Eng. Prog.</u>, 64(12), 31, (1968).

Mohan, K., and R. Govind, "Analysis of a Cocurrent Membrane Reactor," <u>AIChE J.</u>, **32**, 2083 (1986).

Mohan, K., and R. Govind, "Effect of Temperature on Equilibrium Shift in Reactors with a Permselective Wall," <u>Ind. Eng. Chem. Res.</u>, **27**, 2064, (1988a).

Mohan, K., and R. Govind, "Analysis of Equilibrium Shift in Isothermal Reactors with a Permselective Wall," <u>AIChE J.</u>, **34**, 1493, (1988b).

Mohan, K., and R. Govind, "Studies on a Membrane Reactor," <u>Sep. Sci. Technol.</u>, **23**, 1715, (1988).

Newton, R. H.,"Activity Coefficients of Gases,"<u>Ind. Eng. Chem.</u>, **27**, 302, (1935).

Nandy, S.," Observation on Catalytic of Ammonia at High Pressure", M.S. Thesis, Colorado State University, 1981

Ozaki, I, Taylor, H. S. ,and Boudart, M.,"Kinetics and Mechanism of the Ammonia Synthesis," <u>Proc. Roy. Soc. (London)</u>, **A258**, 47, (1960).

Raymont, M. E. D.,"Make Hydrogen from Hydrogen Sulfide,"<u>Hydroc. Process.</u>, **54**, 139 (1975).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, <u>The </u>

Properties of Gases and Liquids, 3rd ed., McGraw-Hill, New York, (1977).

Satterfield, C. N. ,Heterogeneous Catalysis in Practice, McGraw-Hill, Newyork, (1980).

Shah, Y.T, "A Note on Isothermal Permeable Wall Plug Flow Reactor," Chem. Eng. Sci., 25, 1947 (1970).

Shindo, Y. T., Hakuta, H Yoshitome, and H. Inoue,"Gas Diffusion in Microporous Media in Knudsen's Regime," J. Chem. Eng. Jpn., 16, 120, (1983).

Shinji, O., M. Misonou, and Y.Oneda,"The Dehydrogenation of Cyclohexane by the Use of a Porous-Glass Reactor,"Bull. Chem. Soc. Jpn., 55, 2760 (1982).

Smith, J. M. , and Van Ness, H. C.,Introduction to Chemical Engineering Thermodynamics, 3rd ed, McGraw-Hill, New York, (1975).

Sun, Y. M., Khang, S. J. ,"Catalytic Membrane for Simultaneous Chemical Reaction and Separation Applied to a Dehydrogenation Reaction," Ind. Eng. Chem. Res., 27, 1136, (1988).

Sun, Y. M., Khang, S. J. ,"A Catalytic Membrane Reactor: Its Performance in Comparison with Other Types of Reactors,"Ind. Eng. Chem. Res., 29, 232, (1990).

Temkin, M and Pyzhev, V., "Kinetics of the Synthesis of Ammonia on Promoted Iron Catalysts," Acta Physicochimica, U.R.S.S., 12(3), 327, (1940).

APPENDICES

APPENDIX A

Data Entry Procedure

Two programs of membrane reactor simulation were written, the first program for dimensional parameters and the second program for dimensionless parameters. Input data for both programs are made by a series of selections of options for the type of reactor, choices of permeability calculation (calculation by program or user supplied), ideal gas state or real gas state. These selections are made through the data by selecting the appropriate parameter number. The data input section is selected as a data file. The user must create the data file before using the program.

The user can select the type of reactor by setting all of the permeabilities all the gases equal to zero for a plug flow reactor and by giving all permeabilities of all gases for membrane reactor. In addition, the simulation program can calculate permeability data by setting all the permeabilities equal to 999. Further, the user can apply ideal or real gas equations to the system by setting the following parameters.

DREAL = 0 for using ideal gas law

DREAL = 1 for real gas using empirical correlation of gas phase fugacity coefficient

DREAL = 2 for real gas using virial equation of state

The name of the input data file for the first program

is NH3.DAT ,and for the second program is NH3DAMK.DAT and the data is read from the file by the program. If the file does not exist an error message is presented to the user. If there is an uncorrected data field in the data file, an error message is also present to user after running the program. Thus user must be sure to create the data file with the correct data fields.

The data saved in the data file are listed as follow:
File name NH3.DAT

Design Parameters

    -radius of the inner reaction side (DR1, m)

    -radius of the outer reaction side (DR2, m)

    -radius of the inner permeation side (DR3, m)

    -reactor length (DRLO, m)

    -void fraction of the membrane (DVOIDF)

    -geometric factor of the membrane (DGEOF)

    -pore radius of the membrane (DPORERAD, cm)

    -effective thickness of the membrane (DTHICK,m)

Operating Variables

    -temperature of the system (PTOT, K)

    -pressure of the reactor (DPSIG, psig)

    -pressure ratio (DPR)

    -state of calculation (DREAL)

-total flow input of reaction side (DSCCMIT, sccm)

-total flow output of permeation side (DSCCMIS, sccm)

-mole fraction input both reaction and permeation side
 (DMOLSFRAC(I))

Physical Constants

-coefficient of reaction rate's law (A,N,H)

-pre-exponential factor (DRKO, mol/m^3.s.Pa$^{-0.5}$)

-activation energy (DE, J/mol)

-permeability of each component (DPi, mol/m.s.Pa)

-critical temperature of each component (DTC(I), K)

-critical pressure of each component (DPC(I), bar)

-critical volume of each component (DVC(I), cm^3/mol)

-critical compressibility of each component (DZC(I))

-acentric factor of each component (DW(I))

-reduced dipole moment of each component (DMUR(I),
 debye)

-molecular weight of each component (DMW(I), g/mol)

-gas molecule radius (Di, cm)

-interaction parameter (DK(I,J))

```
0.0035      0.005       0.01        0.0254
0.52        6.5         20.D-8      0.000005
921.8889    500.        1.0         2.0

5000.            10000.0

0.003
0.48
0.20
0.317

0
0
0
1.

2.0           1.0            3.0
0.5           6.1363D15      186409.571989
1.450D-8      1.899D-8       1.4135D-8         1.2755D-8
999           0.0            0.0               0.0

405.5   113.5   72.5    0.244    0.250    1.47    17.031
126.2   33.9    89.8    0.290    0.039    0.0     28.013
33.2    13      65.1    0.306   -0.218    0.0      2.016
5.19    2.27    57.4    0.302   -0.365    0.0      4.003

0.0      0.25    -0.45    0.0
0.25     0.0      0.0     0.16
-0.45    0.0      0.0     0.0
0.0      0.16     0.0     0.0
```

```
DR1(m.)      DR2(m.)      DR3(m.)              DRLO(m.)
DVOID        DGEOF        DPORERAD(cm.)        DTHICK(m.)
DTEMP(K)     DPSIG(psig)  DPR                  DREAL(0,1,2)
DSCCMIT(sccm)     DSCCMIS(sccm)

DMOLSFRAC(j)

A    N     H
DBETA          DRKO(mol/(m^3.s.Pa^-0.5)      DE(J/mol)
DA   DN    DH    DI(cm.)
DPA  DPN   DPH   DPI(mol/m.s.Pa)

DTC(i)   DPC(i)   DVC(i)   DZC(i)   DW(i)   DMU(i)   DMW(i)

DK(i,1)  DK(i,2)  DK(i,3)  DK(I,4)
   i= NH3,N2,H2,He
```

File name NH3DAMK.DAT

Design Parameters

-Damkohler number (DAMKOLE)

-rate ratio (DRATERAT)

-void fraction of the membrane (DVOIDF)

-geometric factor of the membrane (DGEOF)

-pore radius of the membrane (DPORERAD, cm)

-reactor length (DRLO, m)

Operating Variables

-temperature of the system (PTOT, K)

-pressure of the reactor (DPSIG, psig)

-pressure ratio (DPR)

-state of calculation (DREAL)

-total flow input of reaction side (DSCCMIT, sccm)

-total flow output of permeation side (DSCCMIS, sccm)

-mole fraction input both reaction and permeation side

(DMOLSFRAC(I))

Physical Constants

-coefficient of reaction rate's law (A,N,H)

-pre-exponential factor (DRKO, $mol/m^3.s.Pa^{-0.5}$)

-activation energy (DE, J/mol)

-permeability of each component (DPi, mol/m.s.Pa)

-critical temperature of each component (DTC(I), K)

-critical pressure of each component (DPC(I), bar)

-critical volume of each component (DVC(I), cm^3/mol)

-critical compressibility of each component (DZC(I))

-acentric factor of each component (DW(I))

-reduced dipole moment of each component (DMUR(I), debye)

-molecular weight of each component (DMW(I), g/mol)

-gas molecule radius (Di, cm)

-interaction parameter (DK(I,J))

```
7.8188      182.8928
0.52         6.5           20.D-8
921.8889     500.0        1.0          2.0
5000.0              10000.0

0.003
0.48
0.20
0.317

0
0
0
1.

2.0            1.0           3.0
0.5            6.1363D15    186409.571989
1.450D-8       1.899D-8      1.4135D-8        1.2755D-8
999            0.0           0.0              0.0

405.5    113.5    72.5    0.244    0.250    1.47    17.031
126.2    33.9     89.8    0.290    0.039    0.0     28.013
33.2     13       65.1    0.306   -0.218    0.0      2.016
5.19     2.27     57.4    0.302   -0.365    0.0      4.003

0.0       0.25     -0.45     0.0
0.25      0.0       0.0      0.16
-0.45     0.0       0.0       0.0
0.0       0.16      0.0       0.0

0.0254
```

```
DAMKOLE         RATERAT
DVOID           DGEOF         DPORERAD(cm.)
DTEMP(K)        DPSIG(PSIG)   DPR           DREAL(0,1,2)
DSCCMIT(sccm)   DSCCMIS(sccm)

DMOLSFRAC(j)

A       N       H
DBETA            DRKO(mol/m^3.s.Pa^-0.5)    DE(J/mol)
DA      DN      DH      DI(cm.)
DPA     DPN     DPH     DPI(mol/m.s.Pa)

DTC(i)  DPC(i)  DVC(i)  DZC(i)  DW(i)  DMU(i) DMW(i)

DK(i,1) DK(i,2) DK(i,3) DK(i,4)
 i= NH3, N2, H2, He

DRLO(m.)
```

APPENDIX B

Output of Program

In the output phase, after program calculated successfully, the screen menu will show and ask for user choices whether the data will be presented on the screen or on the computer file or both choices. If user selects the choice for the computer file, the program will generate file NH3.RES for the first program and NH3DAMK.RES for the second program in the diskette drive A. Both choices present the results in the same format as follows:

File name NH3.RES and NH3DAMK.RES

-The conversion and mole fraction or flow rate of each component both reaction side and permeation side at every dimensionless length

-Temperature and pressure of both sides

-The total flow rate input and output both sides

-Damkohler number and rate ratio (for NH3.RES)

-Radius of reactor and separation layer (for NH3DAMK.RES)

********* RESULTS OF CALCULATION *********

MOLE FRACTION		REACTION ZONE			PERMEATION ZONE		
L/Lo	CONV	NH3	N2	H2	NH3	N2	H2
.00	.000000	.003000	.480000	.200000	.000000	.000000	.000000
.10	.032801	.002363	.404514	.129596	.000198	.025150	.032030
.20	.077477	.001878	.349276	.096261	.000349	.046526	.049096
.30	.128355	.001507	.308259	.080171	.000463	.064733	.058285
.40	.179050	.001226	.277276	.072355	.000545	.080223	.063224
.50	.225688	.001016	.253505	.068602	.000602	.093362	.065839
.60	.267044	.000860	.235024	.066876	.000639	.104468	.067178
.70	.303367	.000744	.220502	.066162	.000660	.113823	.067821
.80	.335424	.000656	.208991	.065949	.000671	.121674	.068089
.90	.364037	.000590	.199802	.065976	.000672	.128244	.068162
1.00	.389913	.000539	.192426	.066108	.000668	.133728	.068139

MOLE/S		REACTION ZONE			PERMEATION ZONE		
L/Lo	CONV	NH3	N2	H2	NH3	N2	H2
.00	.000000	.112E-04	.178E-02	.744E-03	.000E+00	.000E+00	.000E+00
.10	.032801	.937E-05	.160E-02	.514E-03	.142E-05	.181E-03	.230E-03
.20	.077477	.785E-05	.146E-02	.403E-03	.244E-05	.324E-03	.342E-03
.30	.128355	.658E-05	.135E-02	.350E-03	.314E-05	.440E-03	.396E-03
.40	.179050	.554E-05	.125E-02	.327E-03	.362E-05	.532E-03	.420E-03
.50	.225688	.472E-05	.118E-02	.319E-03	.392E-05	.608E-03	.429E-03
.60	.267044	.409E-05	.112E-02	.318E-03	.409E-05	.669E-03	.430E-03
.70	.303367	.360E-05	.107E-02	.320E-03	.417E-05	.719E-03	.428E-03
.80	.335424	.322E-05	.103E-02	.324E-03	.419E-05	.760E-03	.425E-03
.90	.364037	.293E-05	.993E-03	.328E-03	.416E-05	.793E-03	.422E-03
1.00	.389913	.270E-05	.966E-03	.332E-03	.410E-05	.821E-03	.418E-03

SCCM		REACTION ZONE			PERMEATION ZONE		
L/Lo	CONV	NH3	N2	H2	NH3	N2	H2
.00	.000000	15.000	2400.000	1000.000	.000	.000	.000
.10	.032801	12.598	2157.094	691.077	1.910	243.152	309.661
.20	.077477	10.562	1964.298	541.362	3.276	436.283	460.381
.30	.128355	8.843	1809.915	470.717	4.227	591.048	532.171
.40	.179050	7.451	1685.418	439.805	4.863	715.925	564.223
.50	.225688	6.349	1584.490	428.787	5.266	817.203	576.291
.60	.267044	5.496	1502.357	427.492	5.499	899.646	578.516
.70	.303367	4.840	1435.337	430.676	5.609	966.939	576.150
.80	.335424	4.336	1380.543	435.646	5.632	1021.973	571.901
.90	.364037	3.945	1335.681	441.051	5.595	1067.049	567.139
1.00	.389913	3.637	1298.916	446.244	5.514	1104.009	562.529

TEMP(K),PRESS(in),PRESS(out) (Psig)= 921.89 500.00 500.00
Total SCCM and MOL/S input for Tube and Shell =
   5000.00000 10000.00000 .37181E-02 .74363E-02
Total SCCM and MOL/S output for Tube and Shell =
   6750.19628 8255.65241 .50196E-02 .61391E-02
Da = 7.8189 RATE RATIO = 182.8928
Stop - Program terminated.

********* RESULTS OF CALCULATION *********

MOLE FRACTION		REACTION ZONE			PERMEATION ZONE		
L/Lo	CONV	NH3	N2	H2	NH3	N2	H2
.00	.000000	.003000	.480000	.200000	.000000	.000000	.000000
.10	.032801	.002363	.404514	.129596	.000198	.025150	.032030
.20	.077477	.001878	.349276	.096261	.000349	.046526	.049096
.30	.128355	.001507	.308259	.080171	.000463	.064733	.058285
.40	.179050	.001226	.277276	.072355	.000545	.080223	.063224
.50	.225688	.001016	.253505	.068602	.000602	.093362	.065839
.60	.267044	.000860	.235024	.066876	.000639	.104468	.067178
.70	.303367	.000744	.220502	.066162	.000660	.113823	.067821
.80	.335424	.000656	.208991	.065949	.000671	.121674	.068089
.90	.364037	.000590	.199802	.065976	.000672	.128244	.068162
1.00	.389913	.000539	.192426	.066108	.000668	.133728	.068139

MOLE/S		REACTION ZONE			PERMEATION ZONE		
L/Lo	CONV	NH3	N2	H2	NH3	N2	H2
.00	.000000	.112E-04	.178E-02	.744E-03	.000E+00	.000E+00	.000E+00
.10	.032801	.937E-05	.160E-02	.514E-03	.142E-05	.181E-03	.230E-03
.20	.077477	.785E-05	.146E-02	.403E-03	.244E-05	.324E-03	.342E-03
.30	.128355	.658E-05	.135E-02	.350E-03	.314E-05	.440E-03	.396E-03
.40	.179050	.554E-05	.125E-02	.327E-03	.362E-05	.532E-03	.420E-03
.50	.225688	.472E-05	.118E-02	.319E-03	.392E-05	.608E-03	.429E-03
.60	.267044	.409E-05	.112E-02	.318E-03	.409E-05	.669E-03	.430E-03
.70	.303367	.360E-05	.107E-02	.320E-03	.417E-05	.719E-03	.428E-03
.80	.335424	.322E-05	.103E-02	.324E-03	.419E-05	.760E-03	.425E-03
.90	.364037	.293E-05	.993E-03	.328E-03	.416E-05	.793E-03	.422E-03
1.00	.389913	.270E-05	.966E-03	.332E-03	.410E-05	.821E-03	.418E-03

SCCM		REACTION ZONE			PERMEATION ZONE		
L/Lo	CONV	NH3	N2	H2	NH3	N2	H2
.00	.000000	15.000	2400.000	1000.000	.000	.000	.000
.10	.032801	12.598	2157.094	691.077	1.910	243.152	309.661
.20	.077477	10.562	1964.298	541.362	3.276	436.283	460.381
.30	.128355	8.848	1809.915	470.717	4.227	591.048	532.171
.40	.179050	7.451	1685.418	439.805	4.863	715.925	564.223
.50	.225688	6.349	1584.490	428.787	5.266	817.203	576.291
.60	.267044	5.496	1502.357	427.492	5.499	899.646	578.516
.70	.303367	4.840	1435.337	430.676	5.609	966.939	576.150
.80	.335424	4.336	1380.543	435.646	5.632	1021.973	571.901
.90	.364037	3.945	1335.681	441.051	5.595	1067.049	567.139
1.00	.389913	3.637	1298.916	446.244	5.514	1104.009	562.529

TEMP(K),PRESS(in),PRESS(out) (Psig)=   921.89   500.00   500.00
Total SCCM and MOL/S input for Tube   and   Shell =
    5000.00000   10000.00000   .37181E-02   .74363E-02
Total SCCM and MOL/S output for Tube   and   Shell =
    6750.19628   8255.65241   .50196E-02   .61391E-02
R (m.) = .00350000 THICK (m.) =   .00000500
Stop - Program terminated.

APPENDIX C

Computer Program

```
      PROGRAM MR
C
C         This program solves for a decompositon of ammonia
C         in the conventional plug flow reactor or the membrane
C         reactor.
C
C              NH3 = 0.5 N2 + 1.5 H2
C
C              r = -k*(pA^A / pH^H)^BETA
C
C         Ammonia converts to nitrogen and hydrogen in the
C         reaction zone, using He as a dilution gas in the tube side
C         and as a sweep gas in the shell side.
C
C         Because high pressure operation give nonidelity to the
C         mixture gas, the fugacity coefficient was introduced instead
C         of partial pressure.
C
C         For the membrane reactor, while the reaction go on, each
C         component will permeate through the membrane, increasing
C         the conversion above equilibrium value.(No permeation for
C         plug flow reactor.)
C
C         Model equations are the system of eight ordinary
C         differential equations with initial value problem.
C
C         Eight simultaneous equations was solved using IMSL math
C         libraries. The results of this program are mole fraction of
C         each component and conversion in every dimensionless length.
C
C         --------------------------------
C         Defining variables and parameters
C         --------------------------------
C
C         **** Membrane configuration.****
C
C         DR1 = Inner radius-inner tube (m.)
C         DR2 = Outer radius-inner tube (m.)
C         DR3 = Outer radius-outer tube (m.)
C            DRLO   = Total length of reactor (m.)
C            DVOIDF = void fraction of membrane
C            DGEOF  = geometric factor of membrane
C            DPORERAD = Mean pore diameter (cm.)
C            DPj    = Permeability of component(j) (mol/(m.s.Pa))
C                     where j = A, N, H,I
C                     (A=ammonia, N=nitrogen, H=hydrogen, I=inert)
C
C         **** Kinetis and thermodynamics parameters.****
C
C         DTEMP = Temperature of the reactor (K)
C         DPTOT = Pressure of the reactor (Pa)
C         DPR   = Pressure ratio (Pt/Ps)
C
C            DRKO  = Pre-exponential factor (mol/(m^3.s.Pa^-0.5))
C            DRX   = Reaction rate constant (mol/(m^3.s.Pa^-0.5))
C            DE    = Activation energy (J/mol)
C            DBETA = Constant for the reaction rate law
C            DREAL = Parameter setting for ideal or real gas
C
```

```
C      DDKNH3  = Knudsen diffusivity for NH3  (m^2/S.)
C      DDKN2   = Knudsen diffusivity for N2   (m^2/S.)
C      DDKH2   = Knudsen diffusivity for H2   (m^2/S.)
C      DDKI    = Knudsen diffusivity for He   (m^2/S.)
C      DDNH3EFF = Effective Knudsen diffusivity for NH3  (m^2/S.)
C      DDN2EFF  = Effective Knudsen diffusivity for N2   (m^2/S.)
C      DDH2EFF  = Effective Knudsen diffusivity for H2   (m^2/S.)
C      DDIEFF   = Effective Knudsen diffusivity for He   (m^2/S.)
C
C            DFAT = Fugacity coefficient for NH3 in tube
C            DFNT = Fugacity coefficient for N2  in tube
C            DFHT = Fugacity coefficient for H2  in tube
C            DFIT = Fugacity coefficient for He  in tube
C            DFAS = Fugacity coefficient for NH3 in shell
C            DFNS = Fugacity coefficient for N2  in shell
C            DFHS = Fugacity coefficient for H2  in shell
C            DFIS = Fugacity coefficient for N2  in shell
C
C      **** IMSL parameters.****
C
C      PARAM(1) = HINT  = Initial value of step size.
C      PARAM(4) = MXSTEP= Maximum number of step.
C      PARAM(10)= INORM = Error estimate method.
C      PARAM(12)= IMETH = Numerical method.
C      PARAM(13)= MITER = Type of iteration.
C      PARAM(14)= MTYPE = Matrix type of jacobian.
C      PARAM(19)= IATYPE= Matrix type for A.
C            NEQ = Number of equation.
C            X   = Dimensionless length.
C            XEND= Value of X where solution is desired.
C            TOL = Error tolerance.
C      Y(NEQ) = Dimensionless molar flow rate of each component
C      Inner tube, Y(1)  for NH3
C                  Y(2)  for N2
C                  Y(3)  for H2
C                  Y(4)  for Inert gas(He)
C      Outer tube, Y(5)  for NH3
C                  Y(6)  for N2
C                  Y(7)  for H2
C                  Y(8)  for Inert gas(He)
C      YPRIME(NEQ)......dY(NEQ)/dX
C      DYPDY(j,k) ......Jacobian element
C
C      **** OUTPUT PARAMETERS. ****
C      DLENGTH  = Dimensionless length
C      DCONVER  = Conversion of reaction
C      DFTOT    = Dimensionless total molar flowrate in tube
C      DQTOT    = Dimensionless total molar flowrate in shell
C      DAIN     = Dimensionless molar flowrate of NH3 in tube
C      DNIN     = Dimensionless molar flowrate of N2  in tube
C      DHIN     = Dimensionless molar flowrate of H2  in tube
C      DIIN     = Dimensionless molar flowrate of He  in tube
C      DAOUT    = Dimensionless molar flowrate of NH3 in shell
C      DNOUT    = Dimensionless molar flowrate of N2  in shell
C      DHOUT    = Dimensionless molar flowrate of H2  in shell
C      DIOUT    = Dimensionless molar flowrate of He  in shell
C
C
C      ****** MAIN PROGRAM ******************************
C
C
```

```
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION DRKO,DE,DTEMP,DPTOT,DFAO,DEQ
     *               ,DR1,DR2,DR3,DRLO,DPA,DPN,DPH,DPI,DPR
      DOUBLE PRECISION X,Y,A,PARAM,HINIT,XEND,TOL
      DOUBLE PRECISION DCONV,DFAIN
      DOUBLE PRECISION DLENGTH,DCONVER,DFTOT,DQTOT,
     *               DAIN,DNIN,DHIN,DIIN,DAOUT,DNOUT,DHOUT,DIOUT
      DOUBLE PRECISION DMOLSFEED
      DOUBLE PRECISION DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
      INTEGER NEQ,NPARAM,MXSTEP,INORM,IMETH,MITER,MTYPE,
     *        IATYPE,IDO,IEND,ISET,I,II
      COMMON/SET1/DRKO,DE,DTEMP,DPTOT,DFAO,DEQ
     *           ,DR1,DR2,DR3,DRLO,DPA,DPN,DPH,DPI,DPR
      COMMON/FUGA/DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
      COMMON/FEED/Y
      COMMON/REAL/DREAL
      DIMENSION A(8,8),PARAM(50),Y(8)
      DIMENSION DLENGTH(101),DCONVER(101),DFTOT(101),DQTOT(101),
     *          DAIN(101)   ,DNIN(101)   ,DHIN(101)  ,DIIN(101),
     *          DAOUT(101)  ,DNOUT(101)  ,DHOUT(101) ,DIOUT(101)
      DIMENSION DMOLSFEED(8)
      EXTERNAL FCN,FCNJ,DIVPAG,SSET,UMACH
C     ***** READ DATA FROM NH3.DAT FILE ********************
C
C
      OPEN(UNIT=1,FILE='A:NH3.DAT',STATUS='OLD')
      CALL AREAD(DRKO,DE,DTEMP,DPTOT,DR1,DR2,DR3,DRLO,
     *           DPA,DPN,DPH,DPI,DPR,DMOLSFEED)
      DCONV=0.0
      X=0.0
      Y(1)  = DMOLSFEED(1)/DMOLSFEED(1)
      Y(2)  = DMOLSFEED(2)/DMOLSFEED(1)
      Y(3)  = DMOLSFEED(3)/DMOLSFEED(1)
      Y(4)  = DMOLSFEED(4)/DMOLSFEED(1)
      Y(5)  = DMOLSFEED(5)/DMOLSFEED(1)
      Y(6)  = DMOLSFEED(6)/DMOLSFEED(1)
      Y(7)  = DMOLSFEED(7)/DMOLSFEED(1)
      Y(8)  = DMOLSFEED(8)/DMOLSFEED(1)
            DFAIN=Y(1)
            DFAO=DMOLSFEED(1)
      CLOSE(1)
C
C     ***** SET INITIAL VALUE OF THE SYSTEM FOR OUTPUT *****
C
      ISET=1
      DCONVER(ISET)=DCONV
      DLENGTH(ISET)=X
      DFTOT(ISET)  =(Y(1)+Y(2)+Y(3)+Y(4))
      DQTOT(ISET)  =(Y(5)+Y(6)+Y(7)+Y(8))
      DAIN(ISET)    =Y(1)
      DNIN(ISET)    =Y(2)
      DHIN(ISET)    =Y(3)
      DIIN(ISET)    =Y(4)
      DAOUT(ISET)   =Y(5)
      DNOUT(ISET)   =Y(6)
      DHOUT(ISET)   =Y(7)
      DIOUT(ISET)   =Y(8)
C
C     -------------------------------------------------------
C
C     ***** CALL PERMEABILITY SUBROUTINE *********************
C
```

```
C
        IF(DPA.EQ.999.) THEN
        CALL PERM(DTEMP,DPA,DPN,DPH,DPI)
        GOTO 50
        ENDIF
C       ***** CALL FUGACITY SUBROUTINE *************************
C
  50 CALL FUGACITY(DFAT,DFNT,DFHT,DFIT,
     *             DFAS,DFNS,DFHS,DFIS,DTEMP,DPTOT,DPR,DREAL)
C
C       ***** SET IMSL PARAMETERS **************************
C
            NPARAM=50
            NEQ=8
            HINIT=1.0D-8
            MXSTEP=10000
            INORM=2
            IMETH=2
            MITER=1
            MTYPE=0
            IATYPE=0
       CALL SSET(50,0.0,PARAM,1)
          PARAM(1)=HINIT
          PARAM(4)=MXSTEP
          PARAM(10)=INORM
          PARAM(12)=IMETH
          PARAM(13)=MITER
          PARAM(14)=MTYPE
          PARAM(19)=IATYPE
           IDO=1
           TOL=1.0D-6
C
C       ---------------------------------------------------------
C
C
C       ***** CALL GEARS METHOD *****************************
C
        DO 10 IEND=1,100
           XEND=FLOAT(IEND)/100.
           IDO=1
           CALL DIVPAG(IDO,NEQ,FCN,FCNJ,A,X,XEND,TOL,PARAM,Y) .
           CALL FUGACITY(DFAT,DFNT,DFHT,DFIT,
     *                  DFAS,DFNS,DFHS,DFIS,
     *                  DTEMP,DPTOT,DPR,DREAL)
C
C       ***** DISPLAY RESULTS *****************************
C
            DCONV=1.-Y(1)/DFAIN-Y(5)/DFAIN
C    STORING RESULT
                I=IEND+1
                DLENGTH(I)=X
                DCONVER(I)=DCONV
                DFTOT(I)   =(Y(1)+Y(2)+Y(3)+Y(4))
                DQTOT(I)   =(Y(5)+Y(6)+Y(7)+Y(8))
                DAIN(I)    =Y(1)
                DNIN(I)    =Y(2)
                DHIN(I)    =Y(3)
                DIIN(I)    =Y(4)
                DAOUT(I)   =Y(5)
                DNOUT(I)   =Y(6)
                DHOUT(I)   =Y(7)
```

```fortran
                DIOUT(I)  =Y(8)
C
C
          IDO=3
          CALL DIVPAG(IDO,NEQ,FCN,FCNJ,A,X,XEND,TOL,PARAM,Y)
   10 CONTINUE
C
C     ***** OUTPUT PRINTING ******************************
C
C
      CALL WRITE(DLENGTH,DCONVER,DFTOT,DQTOT
     *          ,DAIN,DNIN,DHIN,DIIN,DAOUT,DNOUT,DHOUT,DIOUT,DFAO
     *          ,DTEMP,DPTOT,DPR)


      STOP
      END
C
C     ------------------------------------------------------------
C
C
C     This subroutine provide differential equation to IMSL.
C
      SUBROUTINE FCN (NEQ,X,Y,YPRIME)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION DRKO,DE,DTEMP,DPTOT,DFAO,DEQ
     *                ,DR1,DR2,DR3,DRLO,DPA,DPN,DPH,DPI,DPR
      DOUBLE PRECISION YPRIME,Y,X,DVTFAO,DRX,DRRATE
      DOUBLE PRECISION DBETA,DTHICK,A,N,H,DA,DN,DH,DI
      DOUBLE PRECISION DFAT,DFNT,DFHT,DFIT,
     *                DFAS,DFNS,DFHS,DFIS
      DOUBLE PRECISION DAMKOLE,DRATERAT
      INTEGER NEQ
      COMMON/SET1/DRKO,DE,DTEMP,DPTOT,DFAO,DEQ,
     *           DR1,DR2,DR3,DRLO,DPA,DPN,DPH,DPI,DPR
      COMMON/BET/DBETA,A,N,H,DA,DN,DH,DI
      COMMON/FUGA/DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
      COMMON/THICK/DTHICK
      COMMON/REAL/DREAL
      COMMON/DAMKO/DAMKOLE,DRATERAT
      DIMENSION Y(8),YPRIME(8)
          DRX=DRKO*DEXP(-DE/8.314/DTEMP)
          DAMKOLE=DRX*DRLO*3.14159265*(DR1**2)/DPTOT**0.5/DFAO
          DRATERAT=DPH*2.*3.141592654*DR1*DPTOT**1.5/(DTHICK*DRX*
     *             3.141592654*DR1**2)
          DVTFAO=3.141592654*(DR1)**2.*(DRLO)/DFAO
          DRRATE=-DRX *((DPTOT*DFAT*Y(1)/(Y(1)+Y(2)+Y(3)+Y(4)))**A/
     *                  (DPTOT*DFHT*Y(3)/(Y(1)+Y(2)+Y(3)+Y(4)))**H
     *                 )**DBETA
       YPRIME(1)=     ( 1.*    DRRATE- 2./DR1*DPA/(DTHICK)*DPTOT*
     *                         ( Y(1)/(Y(1)+Y(2)+Y(3)+Y(4))*DFAT
     *                          -Y(5)/(Y(5)+Y(6)+Y(7)+Y(8))*DFAS
     *                     *DPR         )
     *                 )
     *                    *DVTFAO
       YPRIME(2)=     (- 0.5*DRRATE-2./DR1*DPN/(DTHICK)*DPTOT*
     *                         ( Y(2)/(Y(1)+Y(2)+Y(3)+Y(4))*DFNT
     *                          -Y(6)/(Y(5)+Y(6)+Y(7)+Y(8))*DFNS
     *                     *DPR         )
     *                 )
     *                     *DVTFAO
```

```
      YPRIME(3)=      (- 1.5*DRRATE-2./DR1*DPH/(DTHICK)*DPTOT*
     *                          ( Y(3)/(Y(1)+Y(2)+Y(3)+Y(4))*DFHT
     *                          -Y(7)/(Y(5)+Y(6)+Y(7)+Y(8))*DFHS
     *                *DPR      )
     *                )
     *                  *DVTFAO
      YPRIME(4)=      (              -2./DR1*DPI/(DTHICK)*DPTOT*
     *                          ( Y(4)/(Y(1)+Y(2)+Y(3)+Y(4))*DFIT
     *                          -Y(8)/(Y(5)+Y(6)+Y(7)+Y(8))*DFIS
     *                *DPR      )
     *                )
     *                  *DVTFAO
      YPRIME(5)=      (               2./DR1*DPA/(DTHICK)*DPTOT*
     *                          ( Y(1)/(Y(1)+Y(2)+Y(3)+Y(4))*DFAT
     *                          -Y(5)/(Y(5)+Y(6)+Y(7)+Y(8))*DFAS
     *                 *DPR     )
     *                )
     *                  *DVTFAO
      YPRIME(6)=      (               2./DR1*DPN/(DTHICK)*DPTOT*
     *                          ( Y(2)/(Y(1)+Y(2)+Y(3)+Y(4))*DFNT
     *                          -Y(6)/(Y(5)+Y(6)+Y(7)+Y(8))*DFNS
     *                *DPR      )
     *                )
     *                  *DVTFAO
      YPRIME(7)=      (               2./DR1*DPH/(DTHICK)*DPTOT*
     *                          ( Y(3)/(Y(1)+Y(2)+Y(3)+Y(4))*DFHT
     *                          -Y(7)/(Y(5)+Y(6)+Y(7)+Y(8))*DFHS
     *                *DPR      )
     *                )
     *                  *DVTFAO
      YPRIME(8)=      (               2./DR1*DPI/(DTHICK)*DPTOT*
     *                          ( Y(4)/(Y(1)+Y(2)+Y(3)+Y(4))*DFIT
     *                          -Y(8)/(Y(5)+Y(6)+Y(7)+Y(8))*DFIS
     *                *DPR      )
     *                )
     *                  *DVTFAO
      RETURN
      END
C
C
C
C
C      ------------------------------------------------------------
C
C      This subroutine provide jacobian matrix to IMSL.
C
      SUBROUTINE FCNJ(NEQ,X,Y,DYPDY)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION DRKO,DE,DTEMP,DPTOT,DFAO,DEQ
     *                ,DR1,DR2,DR3,DRLO,DPA,DPN,DPH,DPI,DPR
      DOUBLE PRECISION DRX,DPPAT,DPPHT,DRDfA,DRDfN,DRDfH,DRDfI
      DOUBLE PRECISION DFT,DQT
      DOUBLE PRECISION Y,X,DYPDY
      DOUBLE PRECISION B,C,DCOEF1,DCOEF2,DVTFAO,DBETA,DTHICK
      DOUBLE PRECISION A,N,H,DA,DN,DH,DI
      DOUBLE PRECISION DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
      COMMON/SET1/DRKO,DE,DTEMP,DPTOT,DFAO,DEQ,
     *            DR1,DR2,DR3,DRLO,DPA,DPN,DPH,DPI,DPR
      COMMON/BET/DBETA,A,N,H,DA,DN,DH,DI
```

```
      COMMON/FUGA/DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
      COMMON/THICK/DTHICK
      DIMENSION Y(8),DYPDY(8,8)
C
      DVTFAO=3.141592654*(DR1)**2*(DRLO)/DFAO
      DRX=DRKO*DEXP(-DE/8.314/DTEMP)
      DPPAT=DPTOT*DFAT*Y(1)/(Y(1)+Y(2)+Y(3)+Y(4))
      DPPHT=DPTOT*DFHT*Y(3)/(Y(1)+Y(2)+Y(3)+Y(4))
      DCOEF1=DRX*DBETA*(DPPAT**A/DPPHT**H)**(DBETA-1.0)
      DCOEF2=2.0*DPTOT/DR1/DTHICK
      DFT=Y(1)+Y(2)+Y(3)+Y(4)
      DQT=Y(5)+Y(6)+Y(7)+Y(8)
      DRDfA = DCOEF1*( DPPHT**H*A*(DPPAT**(A-1))*DPTOT*DFAT*
     *                  (DFT-Y(1)) /DFT**2-
     *                 DPPAT**A*H*(DPPHT**(H-1))*DPTOT*DFHT*
     *                  (0.0-Y(3)) /DFT**2
     *                 )/DPPHT**(2*H)
      DRDfN = DCOEF1*( DPPHT**H*A*(DPPAT**(A-1))*DPTOT*DFAT*
     *                  (0.0-Y(1)) /DFT**2-
     *                 DPPAT**A*H*(DPPHT**(H-1))*DPTOT*DFHT*
     *                  (0.0-Y(3)) /DFT**2
     *                 )/DPPHT**(2*H)
      DRDfH = DCOEF1*( DPPHT**H*A*(DPPAT**(A-1))*DPTOT*DFAT*
     *                  (0.0-Y(1)) /DFT**2-
     *                 DPPAT**A*H*(DPPHT**(H-1))*DPTOT*DFHT*
     *                  (DFT-Y(3)) /DFT**2
     *                 )/DPPHT**(2*H)
      DRDfI = DCOEF1*( DPPHT**H*A*(DPPAT**(A-1))*DPTOT*DFAT*
     *                  (0.0-Y(1)) /DFT**2-
     *                 DPPAT**A*H*(DPPHT**(H-1))*DPTOT*DFHT*
     *                  (0.0-Y(3)) /DFT**2
     *                 )/DPPHT**(2*H)
C
      DYPDY(1,1)=DVTFAO*(1.*DRDfA - DCOEF2*DPA*(DFAT*
     *                              (DFT-Y(1)) /DFT**2
     *                                          )            )
      DYPDY(1,2)=DVTFAO*(1.*DRDfN - DCOEF2*DPA*(DFAT*
     *                              (0.0-Y(1)) /DFT**2
     *                                          )            )
      DYPDY(1,3)=DVTFAO*(1.*DRDfH - DCOEF2*DPA*(DFAT*
     *                              (0.0-Y(1)) /DFT**2
     *                                          )            )
      DYPDY(1,4)=DVTFAO*(1.*DRDfI - DCOEF2*DPA*(DFAT*
     *                              (0.0-Y(1)) /DFT**2
     *                                          )            )
      DYPDY(1,5)=DVTFAO*(0.0       - DCOEF2*DPA*(-DFAS*DPR*
     *                              (DQT-Y(5)) /DQT**2
     *                                          )            )
      DYPDY(1,6)=DVTFAO*(0.0       - DCOEF2*DPA*(-DFAS*DPR*
     *                              (0.0-Y(5)) /DQT**2
     *                                          )            )
      DYPDY(1,7)=DVTFAO*(0.0       - DCOEF2*DPA*(-DFAS*DPR*
     *                              (0.0-Y(5)) /DQT**2
     *                                          )            )
```

```
      DYPDY(1,8)=DVTFAO*(0.0        - DCOEF2*DPA*(-DFAS*DPR*
     *                              (0.0-Y(5))  /DQT**2
     *                                                )            )

C
      DYPDY(2,1)=DVTFAO*(-0.5*DRDfA -DCOEF2*DPN*(DFNT*
     *                              (0.0-Y(2))  /DFT**2
     *                                                )            )
      DYPDY(2,2)=DVTFAO*(-0.5*DRDfN -DCOEF2*DPN*(DFNT*
     *                              (DFT-Y(2))  /DFT**2
     *                                                )            )
      DYPDY(2,3)=DVTFAO*(-0.5*DRDfH -DCOEF2*DPN*(DFNT*
     *                              (0.0-Y(2))  /DFT**2
     *                                                )            )
      DYPDY(2,4)=DVTFAO*(-0.5*DRDfI -DCOEF2*DPN*(DFNT*
     *                              (0.0-Y(2))  /DFT**2
     *                                                )            )
      DYPDY(2,5)=DVTFAO*(0.0        -DCOEF2*DPN*(-DFNS*DPR*
     *                              (0.0-Y(6))  /DQT**2
     *                                                )            )
      DYPDY(2,6)=DVTFAO*(0.0        -DCOEF2*DPN*(-DFNS*DPR*
     *                              (DQT-Y(6))  /DQT**2
     *                                                )            )
      DYPDY(2,7)=DVTFAO*(0.0        -DCOEF2*DPN*(-DFNS*DPR*
     *                              (0.0-Y(6))  /DQT**2
     *                                                )            )
      DYPDY(2,8)=DVTFAO*(0.0        -DCOEF2*DPN*(-DFNS*DPR*
     *                              (0.0-Y(6))  /DQT**2
     *                                                )            )

C
      DYPDY(3,1)=DVTFAO*(-1.5*DRDfA -DCOEF2*DPH*(DFHT*
     *                              (0.0-Y(3))  /DFT**2
     *                                                )            )
      DYPDY(3,2)=DVTFAO*(-1.5*DRDfN -DCOEF2*DPH*(DFHT*
     *                              (0.0-Y(3))  /DFT**2
     *                                                )            )
      DYPDY(3,3)=DVTFAO*(-1.5*DRDfH -DCOEF2*DPH*(DFHT*
     *                              (DFT-Y(3))  /DFT**2
     *                                                )            )
      DYPDY(3,4)=DVTFAO*(-1.5*DRDfI -DCOEF2*DPH*(DFHT*
     *                              (0.0-Y(3))  /DFT**2
     *                                                )            )
      DYPDY(3,5)=DVTFAO*(0.0        -DCOEF2*DPH*(-DFHS*DPR*
     *                              (0.0-Y(7))  /DQT**2
     *                                                )            )
      DYPDY(3,6)=DVTFAO*(0.0        -DCOEF2*DPH*(-DFHS*DPR*
     *                              (0.0-Y(7))  /DQT**2
     *                                                )            )
      DYPDY(3,7)=DVTFAO*(0.0        -DCOEF2*DPH*(-DFHS*DPR*
     *                              (DQT-Y(7))  /DQT**2
     *                                                )            )
      DYPDY(3,8)=DVTFAO*(0.0        -DCOEF2*DPH*(-DFHS*DPR*
     *                              (0.0-Y(7))  /DQT**2
     *                                                )            )
```

```
c
      DYPDY(4,1)=DVTFAO*(0.0          -DCOEF2*DPI*(DFIT*
     *                                (0.0-Y(4)) /DFT**2
     *                                           )          )
      DYPDY(4,2)=DVTFAO*(0.0          -DCOEF2*DPI*(DFIT*
     *                                (0.0-Y(4)) /DFT**2
     *                                           )          )
      DYPDY(4,3)=DVTFAO*(0.0          -DCOEF2*DPI*(DFIT*
     *                                (0.0-Y(4)) /DFT**2
     *                                           )          )
      DYPDY(4,4)=DVTFAO*(0.0          -DCOEF2*DPI*(DFIT*
     *                                (DFT-Y(4)) /DFT**2
     *                                           )          )
      DYPDY(4,5)=DVTFAO*(0.0          -DCOEF2*DPI*(-DFIS*DPR*
     *                                (0.0-Y(8)) /DQT**2
     *                                           )          )
      DYPDY(4,6)=DVTFAO*(0.0          -DCOEF2*DPI*(-DFIS*DPR*
     *                                (0.0-Y(8)) /DQT**2
     *                                           )          )
      DYPDY(4,7)=DVTFAO*(0.0          -DCOEF2*DPI*(-DFIS*DPR*
     *                                (0.0-Y(8)) /DQT**2
     *                                           )          )
      DYPDY(4,8)=DVTFAO*(0.0          -DCOEF2*DPI*(-DFIS*DPR*
     *                                (DQT-Y(8)) /DQT**2
     *                                           )          )
c
      DYPDY(5,1)=DVTFAO*(0.0          +DCOEF2*DPA*(DFAT*
     *                                (DFT-Y(1)) /DFT**2
     *                                           )          )
      DYPDY(5,2)=DVTFAO*(0.0          +DCOEF2*DPA*(DFAT*
     *                                (0.0-Y(1)) /DFT**2
     *                                           )          )
      DYPDY(5,3)=DVTFAO*(0.0          +DCOEF2*DPA*(DFAT*
     *                                (0.0-Y(1)) /DFT**2
     *                                           )          )
      DYPDY(5,4)=DVTFAO*(0.0          +DCOEF2*DPA*(DFAT*
     *                                (0.0-Y(1)) /DFT**2
     *                                           )          )
      DYPDY(5,5)=DVTFAO*(0.0          +DCOEF2*DPA*(-DFAS*DPR*
     *                                (DQT-Y(5)) /DQT**2
     *                                           )          )
      DYPDY(5,6)=DVTFAO*(0.0          +DCOEF2*DPA*(-DFAS*DPR*
     *                                (0.0-Y(5)) /DQT**2
     *                                           )          )
      DYPDY(5,7)=DVTFAO*(0.0          +DCOEF2*DPA*(-DFAS*DPR*
     *                                (0.0-Y(5)) /DQT**2
     *                                           )          )
      DYPDY(5,8)=DVTFAO*(0.0          +DCOEF2*DPA*(-DFAS*DPR*
     *                                (0.0-Y(5)) /DQT**2
     *                                           )          )
c
      DYPDY(6,1)=DVTFAO*(0.0          +DCOEF2*DPN*(DFNT*
     *                                (0.0-Y(2)) /DFT**2
     *                                           )          )
      DYPDY(6,2)=DVTFAO*(0.0          +DCOEF2*DPN*(DFNT*
     *                                (DFT-Y(2)) /DFT**2
     *                                           )          )
      DYPDY(6,3)=DVTFAO*(0.0          +DCOEF2*DPN*(DFNT*
     *                                (0.0-Y(2)) /DFT**2
     *                                           )          )
```

```
      DYPDY(6,4)=DVTFAO*(0.0        +DCOEF2*DPN*(DFNT*
     *                               (0.0-Y(2)) /DFT**2
     *                                            )         )
      DYPDY(6,5)=DVTFAO*(0.0        +DCOEF2*DPN*(-DFNS*DPR*
     *                               (0.0-Y(6)) /DQT**2
     *                                            )         )
      DYPDY(6,6)=DVTFAO*(0.0        +DCOEF2*DPN*(-DFNS*DPR*
     *                               (DQT-Y(6)) /DQT**2
     *                                            )         )
      DYPDY(6,7)=DVTFAO*(0.0        +DCOEF2*DPN*(-DFNS*DPR*
     *                               (0.0-Y(6)) /DQT**2
     *                                            )         )
      DYPDY(6,8)=DVTFAO*(0.0        +DCOEF2*DPN*(-DFNS*DPR*
     *                               (0.0-Y(6)) /DQT**2
     *                                            )         )
C
      DYPDY(7,1)=DVTFAO*(0.0        +DCOEF2*DPH*(DFHT*
     *                               (0.0-Y(3)) /DFT**2
     *                                            )         )
      DYPDY(7,2)=DVTFAO*(0.0        +DCOEF2*DPH*(DFHT*
     *                               (0.0-Y(3)) /DFT**2
     *                                            )         )
      DYPDY(7,3)=DVTFAO*(0.0        +DCOEF2*DPH*(DFHT*
     *                               (DFT-Y(3)) /DFT**2
     *                                            )         )
      DYPDY(7,4)=DVTFAO*(0.0        +DCOEF2*DPH*(DFHT*
     *                               (0.0-Y(3)) /DFT**2
     *                                            )         )
      DYPDY(7,5)=DVTFAO*(0.0        +DCOEF2*DPH*(-DFHS*DPR*
     *                               (0.0-Y(7)) /DQT**2
     *                                            )         )
      DYPDY(7,6)=DVTFAO*(0.0        +DCOEF2*DPH*(-DFHS*DPR*
     *                               (0.0-Y(7)) /DQT**2
     *                                            )         )
      DYPDY(7,7)=DVTFAO*(0.0        +DCOEF2*DPH*(-DFHS*DPR*
     *                               (DQT-Y(7)) /DQT**2
     *                                            )         )
      DYPDY(7,8)=DVTFAO*(0.0        +DCOEF2*DPH*(-DFHS*DPR*
     *                               (0.0-Y(7)) /DQT**2
     *                                            )         )
C
      DYPDY(8,1)=DVTFAO*(0.0        +DCOEF2*DPI*(DFIT*
     *                               (0.0-Y(4)) /DFT**2
     *                                            )         )
      DYPDY(8,2)=DVTFAO*(0.0        +DCOEF2*DPI*(DFIT*
     *                               (0.0-Y(4)) /DFT**2
     *                                            )         )
      DYPDY(8,3)=DVTFAO*(0.0        +DCOEF2*DPI*(DFIT*
     *                               (0.0-Y(4)) /DFT**2
     *                                            )         )
      DYPDY(8,4)=DVTFAO*(0.0        +DCOEF2*DPI*(DFIT*
     *                               (DFT-Y(4)) /DFT**2
     *                                            )         )
      DYPDY(8,5)=DVTFAO*(0.0        +DCOEF2*DPI*(-DFIS*DPR*
     *                               (0.0-Y(8)) /DQT**2
     *                                            )         )
      DYPDY(8,6)=DVTFAO*(0.0        +DCOEF2*DPI*(-DFIS*DPR*
     *                               (0.0-Y(8)) /DQT**2
     *                                            )         )
      DYPDY(8,7)=DVTFAO*(0.0        +DCOEF2*DPI*(-DFIS*DPR*
```

```
      *                                    (0.0-Y(8))  /DQT**2
      *                                              )              )
       DYPDY(8,8)=DVTFAO*(0.0         +DCOEF2*DPI*(-DFIS*DPR*
      *                                  (DQT-Y(8))  /DQT**2
      *                                            )              )
       RETURN
       END
C
C
C
C
C
C      ------------------------------------------------------------
C
C      This subroutine provide input data to the program.
C
       SUBROUTINE AREAD(DRKO,DE,DTEMP,DPTOT,DR1,DR2,DR3,DRLO,
      *                 DPA,DPN,DPH,DPI,DPR,DMOLSFEED)
       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
       DOUBLE PRECISION DRKO,DE,DEQ,DR1,DR2,DR3,DRLO
      *                 ,DPA,DPN,DPH,DPI,DMOLSFEED,DMOLSFRAC
       DOUBLE PRECISION DVOIDF,DGEOF,DPORERAD
       DOUBLE PRECISION DBETA,A,N,H,DA,DN,DH,DI,DTHICK,DREACVOI
       DOUBLE PRECISION DTEMP,DPTOT,DPR,DREAL,DPSIG
       DOUBLE PRECISION DTC,DPC,DVC,DZC,DW,DMUR,DMW,DK
       DOUBLE PRECISION DFEEDIT,DFEEDIS,DSCCMIT,DSCCMIS
       INTEGER I
       COMMON/VOIDGEO/DVOIDF,DGEOF,DPORERAD
       COMMON/BET/DBETA,A,N,H,DA,DN,DH,DI
       COMMON/CRIT/DTC,DPC,DVC,DZC,DW,DMUR,DMW
       COMMON/INTERAC/DK
       COMMON/THICK/DTHICK
       COMMON/REAL/DREAL
       COMMON/SCCM/DFEEDIT,DFEEDIS,DSCCMIT,DSCCMIS
       DIMENSION DMOLSFEED(8),DMOLSFRAC(8)
       DIMENSION DTC(4),DPC(4),DVC(4),DZC(4),DW(4),DMUR(4),DMW(4),
      *          DK(4,4)
C
       READ(1,*) DR1,DR2,DR3,DRLO
       READ(1,*) DVOIDF,DGEOF,DPORERAD,DTHICK
       READ(1,*) DTEMP,DPSIG,DPR,DREAL
       READ(1,*) DSCCMIT,DSCCMIS
       DO 90 I=1,8
       READ(1,*) DMOLSFRAC(I)
    90 CONTINUE
       READ(1,*) A,N,H
       READ(1,*) DBETA,DRKO,DE
       READ(1,*) DA,DN,DH,DI
```

```fortran
      READ(1,*) DPA,DPN,DPH,DPI
      DO 30 I=1,4
      READ(1,*)DTC(I),DPC(I),DVC(I),DZC(I),DW(I),DMUR(I),DMW(I)
   80 CONTINUE
      DO 70 I=1,4
      READ(1,*)DK(I,1),DK(I,2),DK(I,3),DK(I,4)
   70 CONTINUE
C
C     ***CHANGE UNIT***
      DPTOT=DPSIG/1.40915902D-4
C     CHANGE SCCM TO MOL/S BASIS
C
      DFEEDIT=DSCCMIT*1.01325/273.15/83.14/60.0
      DFEEDIS=DSCCMIS*1.01325/273.15/83.14/60.0
      DO 60 I=1,4
      DMOLSFEED(I)=DMOLSFRAC(I)*DFEEDIT
   60 CONTINUE
      DO 50 I=5,8
      DMOLSFEED(I)=DMOLSFRAC(I)*DFEEDIS
   50 CONTINUE
C     ******************
      WRITE(*,*)
      WRITE(*,1000)
 1000 FORMAT( ' ********** CALCULATING  WAIT! **********')
      RETURN
      END
C
C
C     ------------------------------------------------------------
C
C     This subroutine give output result to printer and/or monitor.
C
      SUBROUTINE WRITE(DLENGTH,DCONVER,DFTOT,DQTOT
     *          ,DAIN,DNIN,DHIN,DIIN,DAOUT,DNOUT,DHOUT,DIOUT,DFAO
     *          ,DTEMP,DPTOT,DPR)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION DLENGTH,DCONVER,DFTOT,DQTOT,
     *     DAIN,DNIN,DHIN,DIIN,DAOUT,DNOUT,DHOUT,DIOUT
      DOUBLE PRECISION DFAO
      DOUBLE PRECISION DFEEDIT,DFEEDIS,DSCCMIT,DSCCMIS
      DOUBLE PRECISION DFEEDOT,DFEEDOS,DSCCMOT,DSCCMOS
      DOUBLE PRECISION DTEMP,DPTOT,DPR
      DOUBLE PRECISION DAMKOLE,DRATERAT
      REAL OUTPUT
      INTEGER I,II
      COMMON/DAMKO/DAMKOLE,DRATERAT
      COMMON/SCCM/DFEEDIT,DFEEDIS,DSCCMIT,DSCCMIS
      DIMENSION DLENGTH(101),DCONVER(101),DFTOT(101),DQTOT(101),
     *          DAIN(101)   ,DNIN(101)   ,DHIN(101)  ,DIIN(101),
     *          DAOUT(101)  ,DNOUT(101)  ,DHOUT(101) ,DIOUT(101)
      DFEEDOT=(DAIN(101)+DNIN(101)+DHIN(101)+DIIN(101))*DFAO
      DFEEDOS=(DAOUT(101)+DNOUT(101)+DHOUT(101)+DIOUT(101))*DFAO
      DSCCMOT=DFEEDOT*273.15*83.14*60.0/1.01325
      DSCCMOS=DFEEDOS*273.15*83.14*60.0/1.01325
      WRITE(*,*)
      WRITE(*,800)
      WRITE(*,*)
   50 WRITE(*,*)
      WRITE(*,900)
      WRITE(*,1000)
```

```
      READ(*,*) OUTPUT
      IF (OUTPUT.EQ.1.0) THEN
          GOTO 10
                          ELSE
                    IF (OUTPUT.EQ.0.0) THEN
                        GOTO 40
                                    ELSE
                              IF (OUTPUT.EQ.2.0) THEN
                                  GOTO 40
                                                ELSE
                                  GOTO 50
                                                ENDIF
                                    ENDIF
                          ENDIF
   40 WRITE(*,*)
      WRITE(*,100)
      WRITE(*,*)
      WRITE(*,250)
      WRITE(*,350)
      WRITE(*,*)
         DO 25 I=1,101,10
      WRITE(*,450) DLENGTH(I),DCONVER(I),
     *             DAIN(I)/DFTOT(I) ,DNIN(I)/DFTOT(I) ,DHIN(I)/DFTOT(I),
     *             DAOUT(I)/DQTOT(I),DNOUT(I)/DQTOT(I),DHOUT(I)/DQTOT(I)
   25    CONTINUE
      READ(*,*) II
c
      WRITE(*,*)
      WRITE(*,360)
      WRITE(*,350)
      WRITE(*,*)
         DO 26 I=1,101,10
      WRITE(*,460) DLENGTH(I),DCONVER(I),
     *             DAIN(I)*DFAO ,DNIN(I)*DFAO ,DHIN(I)*DFAO,
     *             DAOUT(I)*DFAO,DNOUT(I)*DFAO,DHOUT(I)*DFAO
   26 CONTINUE
      READ(*,*) II
c
      WRITE(*,*)
      WRITE(*,355)
      WRITE(*,350)
      WRITE(*,*)
         DO 27 I=1,101,10
      WRITE(*,465) DLENGTH(I),DCONVER(I),
     *             DAIN(I)*DFAO*273.15*83.14*60./1.01325,
     *             DNIN(I)*DFAO*273.15*83.14*60./1.01325,
     *             DHIN(I)*DFAO*273.15*83.14*60./1.01325,
     *             DAOUT(I)*DFAO*273.15*83.14*60./1.01325,
     *             DNOUT(I)*DFAO*273.15*83.14*60./1.01325,
     *             DHOUT(I)*DFAO*273.15*83.14*60./1.01325
   27    CONTINUE
      WRITE(*,*)
      WRITE(*,440)DTEMP,DPTOT*1.40915902D-4,DPTOT*DPR*1.40915902D-4
      WRITE(*,480) DSCCMIT,DSCCMIS,DFEEDIT,DFEEDIS
      WRITE(*,470) DSCCMOT,DSCCMOS,DFEEDOT,DFEEDOS
      WRITE(*,510) DAMKOLE,DRATERAT
      IF (OUTPUT.EQ.2.0) THEN
          GOTO 10
                          ELSE
```

```
          GOTO 60
                           ENDIF
C
    10 OPEN(UNIT=2,FILE='A:NH3.RES',STATUS='NEW')
       WRITE(2,*)
       WRITE(2,100)
       WRITE(2,*)
       WRITE(2,*)
       WRITE(2,200)
       WRITE(2,300)
       WRITE(2,*)
          DO 20 I=1,101
       WRITE(2,400) DLENGTH(I),DCONVER(I),
     *              DAIN(I)/DFTOT(I)  ,DNIN(I)/DFTOT(I)  ,DHIN(I)/DFTOT(I),
     *              DIIN(I)/DFTOT(I),
     *              DAOUT(I)/DQTOT(I),DNOUT(I)/DQTOT(I),DHOUT(I)/DQTOT(I)
     *             ,DIOUT(I)/DQTOT(I)
    20    CONTINUE
       WRITE(2,*)
       WRITE(2,*)
       WRITE(2,500)
       WRITE(2,300)
       WRITE(2,*)
          DO 30 I=1,101
       WRITE(2,600) DLENGTH(I),DCONVER(I),
     *              DAIN(I)*DFAO  ,DNIN(I)*DFAO  ,DHIN(I)*DFAO
     *             ,DIIN(I)*DFAO,
     *              DAOUT(I)*DFAO,DNOUT(I)*DFAO,DHOUT(I)*DFAO
     *             ,DIOUT(I)*DFAO
    30    CONTINUE
       WRITE(2,*)
       WRITE(2,*)
       WRITE(2,550)
       WRITE(2,300)
       WRITE(2,*)
          DO 35 I=1,101
       WRITE(2,650) DLENGTH(I),DCONVER(I),
     *              DAIN(I)*DFAO*273.15*83.14*60./1.01325,
     *              DNIN(I)*DFAO*273.15*83.14*60./1.01325,
     *              DHIN(I)*DFAO*273.15*83.14*60./1.01325,
     *              DIIN(I)*DFAO*273.15*83.14*60./1.01325,
     *              DAOUT(I)*DFAO*273.15*83.14*60./1.01325,
     *              DNOUT(I)*DFAO*273.15*83.14*60./1.01325,
     *              DHOUT(I)*DFAO*273.15*83.14*60./1.01325,
     *              DIOUT(I)*DFAO*273.15*83.14*60./1.01325
    35 CONTINUE
       WRITE(2,*)
       WRITE(2,440)DTEMP,DPTOT*1.40915902D-4,DPTOT*DPR*1.40915902D-4
       WRITE(2,480) DSCCMIT,DSCCMIS,DFEEDIT,DFEEDIS
       WRITE(2,470) DSCCMOT,DSCCMOS,DFEEDOT,DFEEDOS
       WRITE(2,510) DAMKOLE,DRATERAT
       CLOSE(2)
   100 FORMAT('           ******** RESULTS OF CALCULATION ********')
   200 FORMAT(' MOLE FRACTION                 REACTION ZONE
     *          PERMEATION ZONE')
   300 FORMAT('   L/Lo       CONV        NH3        N2         H2      INE
     *RT        NH3        N2        H2      INERT')
   400 FORMAT(2X,F4.2,4X,F8.6,3X,4(F10.6),2X,4(F10.6))
   500 FORMAT(' MOLE/S                        REACTION ZONE
     *          PERMEATION ZONE')
```

```
550 FORMAT(' SCCM                    REACTION ZONE
   *          PERMEATION ZONE')
555 FORMAT(' PRESS <0> TO CONTINUE')
510 FORMAT(' Da = ',F12.4,' RATE RATIO = ',F12.4)
600 FORMAT(2X,F4.2,4X,F8.6,3X,4(E10.4),2X,4(E10.4))
650 FORMAT(2X,F4.2,4X,F8.6,3X,4(F10.3),2X,4(E10.3))
250 FORMAT(' MOLE FRACTION           REACTION ZONE          PERME
   *ATION ZONE')
360 FORMAT(' MOLE/S                  REACTION ZONE          PERME
   *ATION ZONE')
355 FORMAT(' SCCM                    REACTION ZONE          PERME
   *ATION ZONE')
350 FORMAT('    L/Lo    CONV      NH3      N2      550 FORMAT(' SCCM
   *          PERMEATION ZONE')
555 FORMAT(' PRESS <0> TO CONTINUE')
510 FORMAT(' Da = ',F12.4,' RATE RATIO = ',F12.4)
600 FORMAT(2X,F4.2,4X,F8.6,3X,4(E10.4),2X,4(E10.4))
650 FORMAT(2X,F4.2,4X,F8.6,3X,4(F10.3),2X,4(E10.3))
250 FORMAT(' MOLE FRACTION           REACTION ZONE          PERME
   *ATION ZONE')
360 FORMAT(' MOLE/S                  REACTION ZONE          PERME
   *ATION ZONE')
355 FORMAT(' SCCM                    REACTION ZONE          PERME
   *ATION ZONE')
350 FORMAT('    L/Lo    CONV      NH3      N2      H2      NH3
   *  N2      H2')
440 FORMAT(' TEMP(K),PRESS(in),PRESS(out) (Psig)= ',3(F8.2))
450 FORMAT(2X,F4.2,2X,F8.6,2X,3(F9.6),1X,3(F9.6))
460 FORMAT(2X,F4.2,2X,F8.6,2X,3(E9.3),1X,3(E9.3))
465 FORMAT(2X,F4.2,2X,F8.6,2X,3(F9.3),1X,3(F9.3))
470 FORMAT(2X,'Total SCCM  and  MOL/S output for Tube    and    Shell
   *='/2X,F13.5,1X,F13.5,3X,E13.5,1X,E13.5)
480 FORMAT(2X,'Total SCCM  and  MOL/S  input for Tube    and    Shell
   *='/2X,F13.5,1X,F13.5,3X,E13.5,1X,E13.5)
800 FORMAT(' **** THE CALCULATION IS NOW COMPLETED ****')
900 FORMAT(' DO YOU WANT THE RESULTS ON MONITOR OR COMPUTER FILE.')
1000 FORMAT(' PRESS <0> FOR MONITOR OR <1> FOR COMPUTER FILE OR <2> FOR
   * BOTH DEVICES ')
 60 RETURN
    END
C
C
C
C     -------------------------------------------------------------
C
C     This subroutine calculate for permeability.
C
      SUBROUTINE PERM(DTEMP,DPA,DPN,DPH,DPI)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION DDKNH3,DDKN2,DDKH2,DDKI,DRT
     *            ,DDNH3EFF,DDN2EFF,DDH2EFF,DDIEFF
      DOUBLE PRECISION DTEMP,DPA,DPN,DPH,DPI
      DOUBLE PRECISION DVOIDF,DGEOF,DPORERAD
      DOUBLE PRECISION DBETA,A,N,H,DA,DN,DH,DI
      DOUBLE PRECISION DTC,DPC,DVC,DZC,DW,DMUR,DMW
      COMMON/VOIDGEO/DVOIDF,DGEOF,DPORERAD
      COMMON/CRIT/DTC,DPC,DVC,DZC,DW,DMUR,DMW
      COMMON/BET/DBETA,A,N,H,DA,DN,DH,DI
      DIMENSION DTC(4),DPC(4),DVC(4),DZC(4),DW(4),DMUR(4),DMW(4)
C     *** CALCULATION OF Dk ***
      DDKNH3= 9.7E3*(DPORERAD-DA)*(DTEMP/DMW(1))**0.5/100.**2
```

```
        DDKN2 = 9.7E3*(DPORERAD-DN)*(DTEMP/DMW(2))**0.5/100.**2
        DDKH2 = 9.7E3*(DPORERAD-DH)*(DTEMP/DMW(3))**0.5/100.**2
        DDKI  = 9.7E3*(DPORERAD-DI)*(DTEMP/DMW(4))**0.5/100.**2
        DRT=8.314*DTEMP
C
C    *** CALCULATION OF Dk(eff) INCLUDE POROSITY AND GEO FACTOR)
        DDNH3EFF =DDKNH3*DVOIDF/DGEOF
        DDN2EFF  =DDKN2 *DVOIDF/DGEOF
        DDH2EFF  =DDKH2 *DVOIDF/DGEOF
        DDIEFF   =DDKI  *DVOIDF/DGEOF
C
C    *** CALCULATION OF PERMEABILITY (MOL/M/S/Pa)
        DPA = DDNH3EFF /DRT
        DPN = DDN2EFF  /DRT
        DPH = DDH2EFF  /DRT
        DPI = DDIEFF   /DRT
      RETURN
      END
C
C
C    -----------------------------------------------------------
C
C    This subroutine calculate fugacity coefficient.
C
      SUBROUTINE FUGACITY(DFAT,DFNT,DFHT,DFIT,
     *               DFAS,DFNS,DFHS,DFIS,DTEMP,DPTOT,DPR,DREAL)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION DFAT,DFNT,DFHT,DFIT,
     *               DFAS,DFNS,DFHS,DFIS
      DOUBLE PRECISION DTEMP,DPTOT,DPT,DPR,DREAL
      IF (DREAL.EQ.0.0)THEN
           DFAT= 1.0
           DFNT= 1.0
           DFHT= 1.0
           DFIT= 1.0
           DFAS= 1.0
           DFNS= 1.0
           DFHS= 1.0
           DFIS= 1.0
           GOTO 100
                     ELSE
                        IF(DREAL.EQ.1.0)THEN
      DPT=DPTOT/1.013E5
      DFAT=0.1438996+0.2028538D-2*DTEMP-0.4487672D-3*DPT
     *      -0.1142945D-5*DTEMP**2+0.2761216D-6*DPT**2
      DFNT=0.93431737+0.3101804D-3*DTEMP+0.295896D-3*DPT
     *      -0.2707279D-6*DTEMP**2+0.4775207D-6*DPT**2
      DFHT=DEXP(DEXP(-3.8402*DTEMP**0.125+0.541)*DPT
     *      -DEXP(-0.1263*DTEMP**0.5-15.980)*DPT**2
     *      +300*DEXP(-0.011901*DTEMP-5.941)*(DEXP(-DPT/300)
     *                                      -1))
     *
      DFIT=1.0
      DFAS=0.1438996+0.2028538D-2*DTEMP-0.4487672D-3*DPT*DPR
     *      -0.1142945D-5*DTEMP**2+0.2761216D-6*(DPT*DPR)**2
      DFNS=0.93431737+0.3101804D-3*DTEMP+0.295896D-3*DPT*DPR
     *      -0.2707279D-6*DTEMP**2+0.4775207D-6*(DPT*DPR)**2
      DFHS=DEXP(DEXP(-3.8402*DTEMP**0.125+0.541)*DPT*DPR
     *      -DEXP(-0.1263*DTEMP**0.5-15.980)*(DPT*DPR)**2
     *      +300*DEXP(-0.011901*DTEMP-5.941)*(DEXP(-DPT*DPR/300)
     *                                      -1))
     *
```

```
          DFIS=1.0
                                          GOTO 100
                                          ELSE
                                          IF (DREAL.EQ.2.0)THEN
                                          CALL VIRIAL(DFAT,DFNT,DFHT,DFIT,
        *                                             DFAS,DFNS,DFHS,DFIS,
        *                                             DTEMP,DPTOT,DPR)
                                                      ELSE
                                          WRITE(*,120)
                                          STOP
                                                      ENDIF
                              ENDIF
                    ENDIF
   100 RETURN
   120 FORMAT(' ERROR IN STATE OF CALCULATION !  PROGRAM STOP!')
       END
C
C
C      -----------------------------------------------------------------
C
C      This subroutine calculate fugacity coefficient by virial eqution.
C
       SUBROUTINE VIRIAL(DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS,
        *                 DTEMP,DPTOT,DPR)
       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
       INTEGER I,J
       DOUBLE PRECISION DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
       DOUBLE PRECISION V,DPR,DTEMP,DPTOT
       DOUBLE PRECISION Y,Z
       DOUBLE PRECISION DFO ,DF1 ,DF2 ,D2COEF,
        *                 DFOM,DF1M,DF2M,D2COEFM,
        *                 DTC,DPC,DVC,DZC,DW,DMUR,DMW,DK,
        *                 DTR,FRAC,DPRESS,DZMIX,D2MIX,
        *                 DTCM,DVCM,DZCM,DWM,DPCM,DTRM
       DIMENSION DFO(4),DF1(4),DF2(4),D2COEF(4),
        *           DFOM(4,4),DF1M(4,4),DF2M(4,4),D2COEFM(4,4),
        *           DTC(4),DPC(4),DVC(4),DZC(4),DW(4),DMUR(4),DMW(4),
        *           DTR(4),FRAC(8),DK(4,4),
        *           DTCM(4,4),DVCM(4,4),DZCM(4,4),DWM(4,4),DPCM(4,4),
        *           DTRM(4,4)
       DIMENSION Y(8)
       COMMON/CRIT/DTC,DPC,DVC,DZC,DW,DMUR,DMW
       COMMON/FEED/Y
       COMMON/INTERAC/DK
C
       DO 30 I=1,4
       DTR(I)=DTEMP/DTC(I)
       DFO(I)=0.1445-0.330/DTR(I)-0.1385/DTR(I)**2
        *      -0.0121/DTR(I)**3-0.000607/DTR(I)**8
       DF1(I)=0.0637+0.331/DTR(I)**2-0.423/DTR(I)**3-0.008/DTR(I)**8
       DF2(I)=(-2.112D-4*DMUR(I)-3.877D-21*DMUR(I)**8)/DTR(I)**6
       D2COEF(I)=(DFO(I)+DW(I)*DF1(I)+DF2(I))*83.1439*DTC(I)/DPC(I)
       Z=1.+D2COEF(I)*(DPTOT/1.0D5)/(83.14*DTEMP)
    30 CONTINUE
C
       DO 10 I=1,4
           DO 20 J=1,4
       DTCM(I,J)=(DTC(I)*DTC(J))**0.5*(1-DK(I,J))
       DVCM(I,J)=((DVC(I)**(0.33333)+DVC(J)**(0.33333))/2.0)**3
       DZCM(I,J)=(DZC(I)+DZC(J))/2.0
```

```
      DWM(I,J)=(DW(I)+DW(J))/2.0
      DPCM(I,J)=(DZCM(I,J)*83.1439*DTCM(I,J))/DVCM(I,J)
      DTRM(I,J)=DTEMP/DTCM(I,J)
   20       CONTINUE
   10 CONTINUE
C
      DO 40 I=1,4
            DO 50 J=1,4
      DFOM(I,J)=0.1445-0.330/DTRM(I,J)-0.1385/DTRM(I,J)**2
     *          -0.0121/DTRM(I,J)**3-0.000607/DTRM(I,J)**8
      DF1M(I,J)=0.0637+0.331/DTRM(I,J)**2-0.423/DTRM(I,J)**3
     *          -0.008/DTRM(I,J)**8
      DF2M(I,J)=(-2.112D-4*DMUR(I)-3.877D-21*DMUR(I)**8)/
     *          DTRM(I,J)**6
      D2COEFM(I,J)=(DFOM(I,J)+DWM(I,J)*DF1M(I,J)+DF2M(I,J))
     *             *83.1439*DTCM(I,J)/DPCM(I,J)
   50       CONTINUE
   40 CONTINUE
C
C
      FRAC(1)=Y(1)/(Y(1)+Y(2)+Y(3)+Y(4))
      FRAC(2)=Y(2)/(Y(1)+Y(2)+Y(3)+Y(4))
      FRAC(3)=Y(3)/(Y(1)+Y(2)+Y(3)+Y(4))
      FRAC(4)=Y(4)/(Y(1)+Y(2)+Y(3)+Y(4))
      D2MIX  =FRAC(1)**2*D2COEF(1)+
     *        FRAC(2)**2*D2COEF(2)+
     *        FRAC(3)**2*D2COEF(3)+
     *        FRAC(4)**2*D2COEF(4)+
     *        2.0*FRAC(1)*FRAC(2)*D2COEFM(1,2)+
     *        2.0*FRAC(1)*FRAC(3)*D2COEFM(1,3)+
     *        2.0*FRAC(1)*FRAC(4)*D2COEFM(1,4)+
     *        2.0*FRAC(2)*FRAC(3)*D2COEFM(2,3)+
     *        2.0*FRAC(2)*FRAC(4)*D2COEFM(2,4)+
     *        2.0*FRAC(3)*FRAC(4)*D2COEFM(3,4)
      DPRESS=DPTOT/1.0E5
      V=83.1439*DTEMP/DPRESS
      DZMIX=1.0+D2MIX/V
      DFAT=DEXP(2.0/V*(FRAC(4)*D2COEFM(1,4)+FRAC(3)*D2COEFM(1,3)+
     *                 FRAC(2)*D2COEFM(1,2)+FRAC(1)*D2COEFM(1,1))
     *                 -DLOG(DZMIX))
      DFNT=DEXP(2.0/V*(FRAC(4)*D2COEFM(2,4)+FRAC(3)*D2COEFM(2,3)+
     *                 FRAC(2)*D2COEFM(2,2)+FRAC(1)*D2COEFM(2,1))
     *                 -DLOG(DZMIX))
      DFHT=DEXP(2.0/V*(FRAC(4)*D2COEFM(3,4)+FRAC(3)*D2COEFM(3,3)+
     *                 FRAC(2)*D2COEFM(3,2)+FRAC(1)*D2COEFM(3,1))
     *                 -DLOG(DZMIX))
      DFIT=DEXP(2.0/V*(FRAC(4)*D2COEFM(4,4)+FRAC(3)*D2COEFM(4,3)+
     *                 FRAC(2)*D2COEFM(4,2)+FRAC(1)*D2COEFM(4,1))
     *                 -DLOG(DZMIX))
C
      DPRESS=DPTOT/1.0E5*DPR
      FRAC(5)=Y(5)/(Y(5)+Y(6)+Y(7)+Y(8))
      FRAC(6)=Y(6)/(Y(5)+Y(6)+Y(7)+Y(8))
      FRAC(7)=Y(7)/(Y(5)+Y(6)+Y(7)+Y(8))
      FRAC(8)=Y(8)/(Y(5)+Y(6)+Y(7)+Y(8))
      D2MIX  =FRAC(5)**2*D2COEF(1)+
     *        FRAC(6)**2*D2COEF(2)+
     *        FRAC(7)**2*D2COEF(3)+
     *        FRAC(8)**2*D2COEF(4)+
     *        2.0*FRAC(5)*FRAC(6)*D2COEFM(1,2)+
```

```
*          2.0*FRAC(5)*FRAC(7)*D2COEFM(1,3)+
*          2.0*FRAC(5)*FRAC(8)*D2COEFM(1,4)+
*          2.0*FRAC(6)*FRAC(7)*D2COEFM(2,3)+
*          2.0*FRAC(6)*FRAC(8)*D2COEFM(2,4)+
*          2.0*FRAC(7)*FRAC(8)*D2COEFM(3,4)
 V=83.1439*DTEMP/DPRESS
 DZMIX=1.0+D2MIX/V
 DFAS=DEXP(2.0/V*(FRAC(8)*D2COEFM(1,4)+FRAC(7)*D2COEFM(1,3)+
*                 FRAC(6)*D2COEFM(1,2)+FRAC(5)*D2COEFM(1,1))
*                -DLOG(DZMIX))
 DFNS=DEXP(2.0/V*(FRAC(8)*D2COEFM(2,4)+FRAC(7)*D2COEFM(2,3)+
*                 FRAC(6)*D2COEFM(2,2)+FRAC(5)*D2COEFM(2,1))
*          *      2.0*FRAC(5)*FRAC(7)*D2COEFM(1,3)+
*          2.0*FRAC(5)*FRAC(8)*D2COEFM(1,4)+
*          2.0*FRAC(6)*FRAC(7)*D2COEFM(2,3)+
*          2.0*FRAC(6)*FRAC(8)*D2COEFM(2,4)+
*          2.0*FRAC(7)*FRAC(8)*D2COEFM(3,4)
 V=83.1439*DTEMP/DPRESS
 DZMIX=1.0+D2MIX/V
 DFAS=DEXP(2.0/V*(FRAC(8)*D2COEFM(1,4)+FRAC(7)*D2COEFM(1,3)+
*                 FRAC(6)*D2COEFM(1,2)+FRAC(5)*D2COEFM(1,1))
*                -DLOG(DZMIX))
 DFNS=DEXP(2.0/V*(FRAC(8)*D2COEFM(2,4)+FRAC(7)*D2COEFM(2,3)+
*                 FRAC(6)*D2COEFM(2,2)+FRAC(5)*D2COEFM(2,1))
*                -DLOG(DZMIX))
 DFHS=DEXP(2.0/V*(FRAC(8)*D2COEFM(3,4)+FRAC(7)*D2COEFM(3,3)+
*                 FRAC(6)*D2COEFM(3,2)+FRAC(5)*D2COEFM(3,1))
*                -DLOG(DZMIX))
 DFIS=DEXP(2.0/V*(FRAC(8)*D2COEFM(4,4)+FRAC(7)*D2COEFM(4,3)+
*                 FRAC(6)*D2COEFM(4,2)+FRAC(5)*D2COEFM(4,1))
*                -DLOG(DZMIX))
 RETURN
 END
```

```
      PROGRAM MRDAMK
C
C         This program solves for a decompositon of ammonia
C         in the conventional plug flow reactor or the membrane
C         reactor.
C
C              NH3 = 0.5 N2 + 1.5 H2
C
C              r = -k*(pA^A / pH^H)^DBETA
C
C         Ammonia Converts to nitrogen and hydrogen in the
C         reaction zone, using He as a dilution gas in the tube side
C         and as a sweep gas in the shell side.
C
C         Because high pressure operation give nonidelity to the
C         mixture gas, the fugacity coefficient was introduced instead
C         of partial pressure.
C
C         For the membrane reactor, while the reaction go on, each
C         component will permeate through the membrane, increasing
C         the conversion above equilibrium value.(No permeation for
C         plug flow reactor.)
C
C         Model equations given the system of eight ordinary
C         differential equations with initial value problem.
C         All the parameters are in dimensionless form.
C
C         Eight simultaneous equations was solved using IMSL math
C         libraries. The results of this program are mole fraction of
C         each component and conversion in every dimensionless length.
C
C         ----------------------------------
C         Defining variables and parameters
C         ----------------------------------
C
C         **** Membrane configuration.****
C
C             DVOIDF = void fraction of membrane
C             DGEOF  = geometic factor of membrane
C             DPORERAD = Mean pore diameter (cm.)
C             DPj    = Permeability of component(j) (mol/m.s.Pa)
C                      where j = A, N, H,I
C                      (A=ammonia, N=nitrogen, H=hydrogen, I=inert)
C
C         **** Kinetis and thermodynamics parameters.****
C
C         DTEMP = Temperature of the reactor (K)
C         DPTOT = Pressure of the reactor (Pa)
C         DPR   = Pressure ratio (Pt/Ps)
C             DBETA = Constant for the reaction rate law
C             DREAL = Parameter setting for ideal or real gas
C
C             DFAT = Fugacity coefficient for NH3 in tube
C             DFNT = Fugacity coefficient for N2  in tube
C             DFHT = Fugacity coefficient for H2  in tube
C             DFIT = Fugacity coefficient for He  in tube
C             DFAS = Fugacity coefficient for NH3 in shell
C             DFNS = Fugacity coefficient for N2  in shell
C             DFHS = Fugacity coefficient for H2  in shell
C
```

```
C              DFIS  = Fugacity coefficient for N2  in shell
C
C
C        **** IMSL parameters.****
C
C        PARAM(1) = HINT  = Initial value of step size.
C        PARAM(4) = MXSTEP= Maximum number of step.
C        PARAM(10)= INORM = Error estimate method.
C        PARAM(12)= IMETH = Numerical method.
C        PARAM(13)= MITER = Type of iteration.
C        PARAM(14)= MTYPE = Matrix type of jacobian.
C        PARAM(19)= IATYPE= Matrix type for A.
C              NEQ = Number of equation.
C              X   = Dimensionless length.
C              XEND= Value of X where solution is desired.
C              TOL = Error tolerance.
C        Y(NEQ) = Dimensionless molar flow rate of each component
C        Inner tube, Y(1) for NH3
C                    Y(2) for N2
C                    Y(3) for H2
C                    Y(4) for Inert gas(Ar)
C        Outer tube, Y(5) for NH3
C                    Y(6) for N2
C                    Y(7) for H2
C                    Y(8) for Inert gas(Ar)
C        YPRIME(NEQ)......dY(NEQ)/dX
C        DYPDY(j,k) ......Jacobian element
C
C        **** OUTPUT PARAMETERS. ****
C        DLENGTH = Dimensionless length
C        DCONVER = Conversion of reaction
C        DFTOT   = Dimensionless total molar flowrate in tube
C        DQTOT   = Dimensionless total molar flowrate in shell
C        DAIN    = Dimensionless molar flowrate of NH3 in tube
C        DNIN    = Dimensionless molar flowrate of N2  in tube
C        DHIN    = Dimensionless molar flowrate of H2  in tube
C        DIIN    = Dimensionless molar flowrate of He  in tube
C        DAOUT   = Dimensionless molar flowrate of NH3 in shell
C        DNOUT   = Dimensionless molar flowrate of N2  in shell
C        DHOUT   = Dimensionless molar flowrate of H2  in shell
C        DIOUT   = Dimensionless molar flowrate of He  in shell
C
C
C        ****** MAIN PROGRAM *****************************
C
        IMPLICIT DOUBLE PRECISION(A-H,O-Z)
        DOUBLE PRECISION DTEMP,DPTOT,DFAO
     *              ,DRLO,DPA,DPN,DPH,DPI,DPR,DAMKOLE,DRATERAT
        DOUBLE PRECISION X,Y,A,PARAM,HINIT,XEND,TOL
        DOUBLE PRECISION DCONV,DFAIN
        DOUBLE PRECISION DLENGTH,DCONVER,DFTOT,DQTOT,
     *              DAIN,DNIN,DHIN,DIIN,DAOUT,DNOUT,DHOUT,DIOUT
        DOUBLE PRECISION DMOLSFEED
        DOUBLE PRECISION DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
        INTEGER NEQ,NPARAM,MXSTEP,INORM,IMETH,MITER,MTYPE,
     *        IATYPE,IDO,IEND,ISET,I,II
        COMMON/SET1/DTEMP,DPTOT,DFAO
     *              ,DRLO,DPA,DPN,DPH,DPI,DPR,DAMKOLE,DRATERAT
        COMMON/FUGA/DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
        COMMON/FEED/Y
        COMMON/REAL/DREAL
```

```
      DIMENSION A(8,8),PARAM(50),Y(8)
      DIMENSION DLENGTH(101),DCONVER(101),DFTOT(101),DQTOT(101),
     *          DAIN(101)    ,DNIN(101)   ,DHIN(101) ,DIIN(101),
     *          DAOUT(101)   ,DNOUT(101)  ,DHOUT(101),DIOUT(101)
      DIMENSION DMOLSFEED(8)
      EXTERNAL FCN,FCNJ,DIVPAG,SSET,UMACH
C     ***** READ DATA FROM NH3DAMK.DAT FILE *********************
C
      OPEN(UNIT=1,FILE='A:NH3DAMK.DAT',STATUS='OLD')
      CALL AREAD(DTEMP,DPTOT,DRLO,
     *           DPA,DPN,DPH,DPI,DPR,DMOLSFEED,DAMKOLE,DRATERAT)
      CLOSE(1)
      DCONV=0.0
      X=0.0
      Y(1) = DMOLSFEED(1)/DMOLSFEED(1)
      Y(2) = DMOLSFEED(2)/DMOLSFEED(1)
      Y(3) = DMOLSFEED(3)/DMOLSFEED(1)
      Y(4) = DMOLSFEED(4)/DMOLSFEED(1)
      Y(5) = DMOLSFEED(5)/DMOLSFEED(1)
      Y(6) = DMOLSFEED(6)/DMOLSFEED(1)
      Y(7) = DMOLSFEED(7)/DMOLSFEED(1)
      Y(8) = DMOLSFEED(8)/DMOLSFEED(1)
         DFAIN=Y(1)
         DFAO=DMOLSFEED(1)
C
C     ***** SET INITIAL VALUE OF THE SYSTEM FOR OUTPUT *****
C
      ISET=1
      DCONVER(ISET)=DCONV
      DLENGTH(ISET)=X
      DFTOT(ISET)  =(Y(1)+Y(2)+Y(3)+Y(4))
      DQTOT(ISET)  =(Y(5)+Y(6)+Y(7)+Y(8))
      DAIN(ISET)   =Y(1)
      DNIN(ISET)   =Y(2)
      DHIN(ISET)   =Y(3)
      DIIN(ISET)   =Y(4)
      DAOUT(ISET)  =Y(5)
      DNOUT(ISET)  =Y(6)
      DHOUT(ISET)  =Y(7)
      DIOUT(ISET)  =Y(8)
C
C     -----------------------------------------------------------
C
C
C     ***** CALL PERMEABILITY SUBROUTINE *****************
C
      IF(DPA.EQ.999.) THEN
      CALL PERM(DTEMP,DPA,DPN,DPH,DPI)
      GOTO 50
      ENDIF
C     ***** CALL FUGACITY SUBROUTINE ********************
C
   50 CALL FUGACITY(DFAT,DFNT,DFHT,DFIT,
     *              DFAS,DFNS,DFHS,DFIS,DTEMP,DPTOT,DPR,DREAL)
C
C     ***** SET IMSL PARAMETERS ************************
C
      NPARAM=50
      NEQ=8
      HINIT=1.0D-8
      MXSTEP=10000
```

```
        INORM=2
        IMETH=2
        MITER=1
        MTYPE=0
        IATYPE=0
   CALL SSET(50,0.0,PARAM,1)
     PARAM(1)=HINIT
     PARAM(4)=MXSTEP
     PARAM(10)=INORM
     PARAM(12)=IMETH
     PARAM(13)=MITER
     PARAM(14)=MTYPE
     PARAM(19)=IATYPE
      IDO=1
      TOL=1.0D-6
C
C     -------------------------------------------------------
C
C     ***** CALL GEARS METHOD ****************************
C
   DO 10 IEND=1,100
       XEND=FLOAT(IEND)/100.
       IDO=1
       CALL DIVPAG(IDO,NEQ,FCN,FCNJ,A,X,XEND,TOL,PARAM,Y)
       CALL FUGACITY(DFAT,DFNT,DFHT,DFIT,
     *               DFAS,DFNS,DFHS,DFIS,
     *               DTEMP,DPTOT,DPR,DREAL)
C
C     ***** DISPLAY RESULTS ****************************
C
       DCONV=1.-Y(1)/DFAIN-Y(5)/DFAIN
C     STORING RESULT
           I=IEND+1
           DLENGTH(I)=X
           DCONVER(I)=DCONV
           DFTOT(I)  =(Y(1)+Y(2)+Y(3)+Y(4))
           DQTOT(I)  =(Y(5)+Y(6)+Y(7)+Y(8))
           DAIN(I)   =Y(1)
           DNIN(I)   =Y(2)
           DHIN(I)   =Y(3)
           DIIN(I)   =Y(4)
           DAOUT(I)  =Y(5)
           DNOUT(I)  =Y(6)
           DHOUT(I)  =Y(7)
           DIOUT(I)  =Y(8)
C
C
       IDO=3
       CALL DIVPAG(IDO,NEQ,FCN,FCNJ,A,X,XEND,TOL,PARAM,Y)
 10 CONTINUE
C
C     ***** OUTPUT PRINTING ****************************
C
   CALL WRITE(DLENGTH,DCONVER,DFTOT,DQTOT
     *        ,DAIN,DNIN,DHIN,DIIN,DAOUT,DNOUT,DHOUT,DIOUT,DFAO
     *        ,DTEMP,DPTOT,DPR)

   STOP
   END
C
```

```
C
C
C     ---------------------------------------------------------------
C
C     This subroutine provide differential equation to IMSL.
C
      SUBROUTINE FCN (NEQ,X,Y,YPRIME)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION DTEMP,DPTOT,DFAO,DRLO
     *               ,DPA,DPN,DPH,DPI,DPR,DAMKOLE,DRATERAT
      DOUBLE PRECISION YPRIME,Y,X,DRRATE
      DOUBLE PRECISION DBETA,A,N,H,DA,DN,DH,DI
      DOUBLE PRECISION DFAT,DFNT,DFHT,DFIT,
     *               DFAS,DFNS,DFHS,DFIS
      DOUBLE PRECISION DR1,DTHICK,DRKO,DE
      INTEGER NEQ
      COMMON/SET1/DTEMP,DPTOT,DFAO,
     *           DRLO,DPA,DPN,DPH,DPI,DPR,DAMKOLE,DRATERAT
      COMMON/BET/DBETA,A,N,H,DA,DN,DH,DI
      COMMON/FUGA/DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
      COMMON/REAL/DREAL
      COMMON/RTHICK/DR1,DTHICK,DRKO,DE
      DIMENSION Y(8),YPRIME(8)
          DR1= (DAMKOLE*DFAO/(DRKO*DEXP(-DE/8.314/DTEMP)*DRLO*
     *          DPTOT**(-0.5)*3.14159264))**0.5
          DTHICK=DPH*2.*3.14159264*DR1*DPTOT**1.5/(DRATERAT*(
     *          DRKO*DEXP(-DE/8.314/DTEMP))*3.14159265*DR1**2)
          DRRATE=-((DFAT*Y(1)/(Y(1)+Y(2)+Y(3)+Y(4)))**A/
     *          (DFHT*Y(3)/(Y(1)+Y(2)+Y(3)+Y(4)))**H
     *          )**DBETA
      YPRIME(1)=   ( 1.*    DRRATE- DPA/DPH*DRATERAT*
     *                      ( Y(1)/(Y(1)+Y(2)+Y(3)+Y(4))*DFAT
     *                      -Y(5)/(Y(5)+Y(6)+Y(7)+Y(8))*DFAS
     *                *DPR       )
     *                )
     *                *DAMKOLE
      YPRIME(2)=   (- 0.5*DRRATE-DPN/DPH*DRATERAT*
     *                      ( Y(2)/(Y(1)+Y(2)+Y(3)+Y(4))*DFNT
     *                      -Y(6)/(Y(5)+Y(6)+Y(7)+Y(8))*DFNS
     *                *DPR       )
     *                 )
     *                *DAMKOLE
      YPRIME(3)=   (- 1.5*DRRATE-DPH/DPH*DRATERAT*
     *                      ( Y(3)/(Y(1)+Y(2)+Y(3)+Y(4))*DFHT
     *                      -Y(7)/(Y(5)+Y(6)+Y(7)+Y(8))*DFHS
     *                *DPR       )
     *                )
     *                *DAMKOLE
      YPRIME(4)=   (              -DPI/DPH*DRATERAT*
     *                      ( Y(4)/(Y(1)+Y(2)+Y(3)+Y(4))*DFIT
     *                      -Y(8)/(Y(5)+Y(6)+Y(7)+Y(8))*DFIS
     *                *DPR       )
     *                )
     *                *DAMKOLE
      YPRIME(5)=   (              DPA/DPH*DRATERAT*
     *                      ( Y(1)/(Y(1)+Y(2)+Y(3)+Y(4))*DFAT
     *                      -Y(5)/(Y(5)+Y(6)+Y(7)+Y(8))*DFAS
     *                *DPR   )
     *                )
     *                *DAMKOLE
      YPRIME(6)=   (              DPN/DPH*DRATERAT*
```

```
*                                  ( Y(2)/(Y(1)+Y(2)+Y(3)+Y(4))*DFNT
*                                   -Y(6)/(Y(5)+Y(6)+Y(7)+Y(8))*DFNS
*                    *DPR     )
*                   )
*                    *DAMKOLE
 YPRIME(7)=          (             DPH/DPH*DRATERAT*
*                     ( Y(3)/(Y(1)+Y(2)+Y(3)+Y(4))*DFHT
*                      -Y(7)/(Y(5)+Y(6)+Y(7)+Y(8))*DFHS
*                    *DPR     )
*                   )
*                    *DAMKOLE
 YPRIME(8)=          (             DPI/DPH*DRATERAT*
*                     ( Y(4)/(Y(1)+Y(2)+Y(3)+Y(4))*DFIT
*                      -Y(8)/(Y(5)+Y(6)+Y(7)+Y(8))*DFIS
*                    *DPR     )
*                   )
*                    *DAMKOLE
  RETURN
  END
C
C
C
C       -------------------------------------------------------------
C
C       This subroutine provide jacobian matrix to IMSL.
C
  SUBROUTINE FCNJ(NEQ,X,Y,DYPDY)
  IMPLICIT DOUBLE PRECISION(A-H,O-Z)
  DOUBLE PRECISION DTEMP,DPTOT,DFAO,DRLO
 *               ,DPA,DPN,DPH,DPI,DPR,DAMKOLE,DRATERAT
  DOUBLE PRECISION DPPAT,DPPHT,DRDfA,DRDfN,DRDfH,DRDfI
  DOUBLE PRECISION DFT,DQT
  DOUBLE PRECISION Y,X,DYPDY
  DOUBLE PRECISION B,C,DCOEF1,DCOEF2
  DOUBLE PRECISION DBETA,A,N,H,DA,DN,DH,DI
  DOUBLE PRECISION DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
  DOUBLE PRECISION DR1,DTHICK,DRKO,DE
  INTEGER NEQ
  COMMON/SET1/DTEMP,DPTOT,DFAO,
 *            DRLO,DPA,DPN,DPH,DPI,DPR,DAMKOLE,DRATERAT
  COMMON/BET/DBETA,A,N,H,DA,DN,DH,DI
  COMMON/FUGA/DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
  COMMON/RTHICK/DR1,DTHICK,DRKO,DE
  DIMENSION Y(8),DYPDY(8,8)
C
  DPPAT=DFAT*Y(1)/(Y(1)+Y(2)+Y(3)+Y(4))
  DPPHT=DFHT*Y(3)/(Y(1)+Y(2)+Y(3)+Y(4))
  DCOEF1=DBETA*(DPPAT**A/DPPHT**H)**(DBETA-1.0)
  DCOEF2=DRATERAT
  DFT=Y(1)+Y(2)+Y(3)+Y(4)
  DQT=Y(5)+Y(6)+Y(7)+Y(8)
  DRDfA = DCOEF1*( DPPHT**H*A*(DPPAT**(A-1))*DFAT*
 *                  (DFT-Y(1)) /DFT**2-
 *                 DPPAT**A*H*(DPPHT**(H-1))*DFHT*
 *                  (0.0-Y(3)) /DFT**2
 *               )/DPPHT**(2*H)
  DRDfN = DCOEF1*( DPPHT**H*A*(DPPAT**(A-1))*DFAT*
 *                  (0.0-Y(1)) /DFT**2-
 *                 DPPAT**A*H*(DPPHT**(H-1))*DFHT*
 *                  (0.0-Y(3)) /DFT**2
 *               )/DPPHT**(2*H)
```

```
  DRDfH = DCOEF1*( DPPHT**H*A*(DPPAT**(A-1))*DFAT*
 *                      (0.0-Y(1)) /DFT**2-
 *                 DPPAT**A*H*(DPPHT**(H-1))*DFHT*
 *                      (DFT-Y(3)) /DFT**2
 *                 )/DPPHT**(2*H)
  DRDfI = DCOEF1*( DPPHT**H*A*(DPPAT**(A-1))*DFAT*
 *                      (0.0-Y(1)) /DFT**2-
 *                 DPPAT**A*H*(DPPHT**(H-1))*DFHT*
 *                      (0.0-Y(3)) /DFT**2
 *                 )/DPPHT**(2*H)
C
  DYPDY(1,1)=DAMKOLE*(1.*DRDfA - DCOEF2*DPA/DPH*(DFAT*
 *                      (DFT-Y(1)) /DFT**2           )
 *
  DYPDY(1,2)=DAMKOLE*(1.*DRDfN - DCOEF2*DPA/DPH*(DFAT*
 *                      (0.0-Y(1)) /DFT**2           )
 *
  DYPDY(1,3)=DAMKOLE*(1.*DRDfH - DCOEF2*DPA/DPH*(DFAT*
 *                      (0.0-Y(1)) /DFT**2           )
 *
  DYPDY(1,4)=DAMKOLE*(1.*DRDfI - DCOEF2*DPA/DPH*(DFAT*
 *                      (0.0-Y(1)) /DFT**2           )
 *
  DYPDY(1,5)=DAMKOLE*(0.0          - DCOEF2*DPA/DPH*(-DFAS*DPR*
 *                      (DQT-Y(5)) /DQT**2           )
 *
  DYPDY(1,6)=DAMKOLE*(0.0          - DCOEF2*DPA/DPH*(-DFAS*DPR*
 *                      (0.0-Y(5)) /DQT**2           )
 *
  DYPDY(1,7)=DAMKOLE*(0.0          - DCOEF2*DPA/DPH*(-DFAS*DPR*
 *                      (0.0-Y(5)) /DQT**2           )
 *
  DYPDY(1,8)=DAMKOLE*(0.0          - DCOEF2*DPA/DPH*(-DFAS*DPR*
 *                      (0.0-Y(5)) /DQT**2           )
 *
C
  DYPDY(2,1)=DAMKOLE*(-0.5*DRDfA -DCOEF2*DPN/DPH*(DFNT*
 *                      (0.0-Y(2)) /DFT**2           )
 *
  DYPDY(2,2)=DAMKOLE*(-0.5*DRDfN -DCOEF2*DPN/DPH*(DFNT*
 *                      (DFT-Y(2)) /DFT**2           )
 *
  DYPDY(2,3)=DAMKOLE*(-0.5*DRDfH -DCOEF2*DPN/DPH*(DFNT*
 *                      (0.0-Y(2)) /DFT**2           )
 *
  DYPDY(2,4)=DAMKOLE*(-0.5*DRDfI -DCOEF2*DPN/DPH*(DFNT*
 *                      (0.0-Y(2)) /DFT**2           )
 *
  DYPDY(2,5)=DAMKOLE*(0.0         -DCOEF2*DPN/DPH*(-DFNS*DPR*
 *                      (0.0-Y(6)) /DQT**2           )
 *
  DYPDY(2,6)=DAMKOLE*(0.0         -DCOEF2*DPN/DPH*(-DFNS*DPR*
 *                      (DQT-Y(6)) /DQT**2           )
 *
  DYPDY(2,7)=DAMKOLE*(0.0         -DCOEF2*DPN/DPH*(-DFNS*DPR*
 *                      (0.0-Y(6)) /DQT**2           )
 *
  DYPDY(2,8)=DAMKOLE*(0.0         -DCOEF2*DPN/DPH*(-DFNS*DPR*
 *                      (0.0-Y(6)) /DQT**2           )
 *
```

```
C
      DYPDY(3,1)=DAMKOLE*(-1.5*DRDfA -DCOEF2*DPH/DPH*(DFHT*
     *                           (0.0-Y(3)) /DFT**2
     *                                                )          )
      DYPDY(3,2)=DAMKOLE*(-1.5*DRDfN -DCOEF2*DPH/DPH*(DFHT*
     *                           (0.0-Y(3)) /DFT**2
     *                                                )          )
      DYPDY(3,3)=DAMKOLE*(-1.5*DRDfH -DCOEF2*DPH/DPH*(DFHT*
     *                           (DFT-Y(3)) /DFT**2
     *                                                )          )
      DYPDY(3,4)=DAMKOLE*(-1.5*DRDfI -DCOEF2*DPH/DPH*(DFHT*
     *                           (0.0-Y(3)) /DFT**2
     *                                                )          )
      DYPDY(3,5)=DAMKOLE*(0.0         -DCOEF2*DPH/DPH*(-DFHS*DPR*
     *                           (0.0-Y(7)) /DQT**2
     *                                                )          )
      DYPDY(3,6)=DAMKOLE*(0.0         -DCOEF2*DPH/DPH*(-DFHS*DPR*
     *                           (0.0-Y(7)) /DQT**2
     *                                                )          )
      DYPDY(3,7)=DAMKOLE*(0.0         -DCOEF2*DPH/DPH*(-DFHS*DPR*
     *                           (DQT-Y(7)) /DQT**2
     *                                                )          )
      DYPDY(3,8)=DAMKOLE*(0.0         -DCOEF2*DPH/DPH*(-DFHS*DPR*
     *                           (0.0-Y(7)) /DQT**2
     *                                                )          )
C
      DYPDY(4,1)=DAMKOLE*(0.0         -DCOEF2*DPI/DPH*(DFIT*
     *                           (0.0-Y(4)) /DFT**2
     *                                                )          )
      DYPDY(4,2)=DAMKOLE*(0.0         -DCOEF2*DPI/DPH*(DFIT*
     *                           (0.0-Y(4)) /DFT**2
     *                                                )          )
      DYPDY(4,3)=DAMKOLE*(0.0         -DCOEF2*DPI/DPH*(DFIT*
     *                           (0.0-Y(4)) /DFT**2
     *                                                )          )
      DYPDY(4,4)=DAMKOLE*(0.0         -DCOEF2*DPI/DPH*(DFIT*
     *                           (DFT-Y(4)) /DFT**2
     *                                                )          )
      DYPDY(4,5)=DAMKOLE*(0.0         -DCOEF2*DPI/DPH*(-DFIS*DPR*
     *                           (0.0-Y(8)) /DQT**2
     *                                                )          )
      DYPDY(4,6)=DAMKOLE*(0.0         -DCOEF2*DPI/DPH*(-DFIS*DPR*
     *                           (0.0-Y(8)) /DQT**2
     *                                                )          )
      DYPDY(4,7)=DAMKOLE*(0.0         -DCOEF2*DPI/DPH*(-DFIS*DPR*
     *                           (0.0-Y(8)) /DQT**2
     *                                                )          )
      DYPDY(4,8)=DAMKOLE*(0.0         -DCOEF2*DPI/DPH*(-DFIS*DPR*
     *                           (DQT-Y(8)) /DQT**2
     *                                                )          )
C
      DYPDY(5,1)=DAMKOLE*(0.0         +DCOEF2*DPA/DPH*(DFAT*
     *                           (DFT-Y(1)) /DFT**2
     *                                                )          )
      DYPDY(5,2)=DAMKOLE*(0.0         +DCOEF2*DPA/DPH*(DFAT*
     *                           (0.0-Y(1)) /DFT**2
     *                                                )          )
      DYPDY(5,3)=DAMKOLE*(0.0         +DCOEF2*DPA/DPH*(DFAT*
     *                           (0.0-Y(1)) /DFT**2
     *                                                )          )
```

```
      DYPDY(5,4)=DAMKOLE*(0.0          +DCOEF2*DPA/DPH*(DFAT*
                                        (0.0-Y(1)) /DFT**2
     *                                                      )
     *
      DYPDY(5,5)=DAMKOLE*(0.0          +DCOEF2*DPA/DPH*(-DFAS*DPR*
                                        (DQT-Y(5)) /DQT**2
     *                                               )        )
     *
      DYPDY(5,6)=DAMKOLE*(0.0          +DCOEF2*DPA/DPH*(-DFAS*DPR*
                                        (0.0-Y(5)) /DQT**2
     *                                               )        )
     *
      DYPDY(5,7)=DAMKOLE*(0.0          +DCOEF2*DPA/DPH*(-DFAS*DPR*
                                        (0.0-Y(5)) /DQT**2
     *                                               )        )
     *
      DYPDY(5,8)=DAMKOLE*(0.0          +DCOEF2*DPA/DPH*(-DFAS*DPR*
                                        (0.0-Y(5)) /DQT**2
     *                                               )        )
     *
C
      DYPDY(6,1)=DAMKOLE*(0.0          +DCOEF2*DPN/DPH*(DFNT*
                                        (0.0-Y(2)) /DFT**2
     *                                               )        )
     *
      DYPDY(6,2)=DAMKOLE*(0.0          +DCOEF2*DPN/DPH*(DFNT*
                                        (DFT-Y(2)) /DFT**2
     *                                               )        )
     *
      DYPDY(6,3)=DAMKOLE*(0.0          +DCOEF2*DPN/DPH*(DFNT*
                                        (0.0-Y(2)) /DFT**2
     *                                               )        )
     *
      DYPDY(6,4)=DAMKOLE*(0.0          +DCOEF2*DPN/DPH*(DFNT*
                                        (0.0-Y(2)) /DFT**2
     *                                               )        )
     *
      DYPDY(6,5)=DAMKOLE*(0.0          +DCOEF2*DPN/DPH*(-DFNS*DPR*
                                        (0.0-Y(6)) /DQT**2
     *                                               )        )
     *
      DYPDY(6,6)=DAMKOLE*(0.0          +DCOEF2*DPN/DPH*(-DFNS*DPR*
                                        (DQT-Y(6)) /DQT**2
     *                                               )        )
     *
      DYPDY(6,7)=DAMKOLE*(0.0          +DCOEF2*DPN/DPH*(-DFNS*DPR*
                                        (0.0-Y(6)) /DQT**2
     *                                               )        )
     *
      DYPDY(6,8)=DAMKOLE*(0.0          +DCOEF2*DPN/DPH*(-DFNS*DPR*
                                        (0.0-Y(6)) /DQT**2
     *                                               )        )
     *
C
      DYPDY(7,1)=DAMKOLE*(0.0          +DCOEF2*DPH/DPH*(DFHT*
                                        (0.0-Y(3)) /DFT**2
     *                                               )        )
     *
      DYPDY(7,2)=DAMKOLE*(0.0          +DCOEF2*DPH/DPH*(DFHT*
                                        (0.0-Y(3)) /DFT**2
     *                                               )        )
     *
      DYPDY(7,3)=DAMKOLE*(0.0          +DCOEF2*DPH/DPH*(DFHT*
                                        (DFT-Y(3)) /DFT**2
     *                                               )        )
     *
```

```
      DYPDY(7,4)=DAMKOLE*(0.0          +DCOEF2*DPH/DPH*(DFHT*
     *                                 (0.0-Y(3)) /DFT**2
     *                                            )              )
      DYPDY(7,5)=DAMKOLE*(0.0          +DCOEF2*DPH/DPH*(-DFHS*DPR*
     *                                 (0.0-Y(7)) /DQT**2
     *                                            )              )
      DYPDY(7,6)=DAMKOLE*(0.0          +DCOEF2*DPH/DPH*(-DFHS*DPR*
     *                                 (0.0-Y(7)) /DQT**2
     *                                            )              )
      DYPDY(7,7)=DAMKOLE*(0.0          +DCOEF2*DPH/DPH*(-DFHS*DPR*
     *                                 (DQT-Y(7)) /DQT**2
     *                                            )              )
      DYPDY(7,8)=DAMKOLE*(0.0          +DCOEF2*DPH/DPH*(-DFHS*DPR*
     *                                 (0.0-Y(7)) /DQT**2
     *                                            )              )
C
      DYPDY(8,1)=DAMKOLE*(0.0          +DCOEF2*DPI/DPH*(DFIT*
     *                                 (0.0-Y(4)) /DFT**2
     *                                            )              )
      DYPDY(8,2)=DAMKOLE*(0.0          +DCOEF2*DPI/DPH*(DFIT*
     *                                 (0.0-Y(4)) /DFT**2
     *                                            )              )
      DYPDY(8,3)=DAMKOLE*(0.0          +DCOEF2*DPI/DPH*(DFIT*
     *                                 (0.0-Y(4)) /DFT**2
     *                                            )              )
      DYPDY(8,4)=DAMKOLE*(0.0          +DCOEF2*DPI/DPH*(DFIT*
     *                                 (DFT-Y(4)) /DFT**2
     *                                            )              )
      DYPDY(8,5)=DAMKOLE*(0.0          +DCOEF2*DPI/DPH*(-DFIS*DPR*
     *                                 (0.0-Y(8)) /DQT**2
     *                                            )              )
      DYPDY(8,6)=DAMKOLE*(0.0          +DCOEF2*DPI/DPH*(-DFIS*DPR*
     *                                 (0.0-Y(8)) /DQT**2
     *                                            )              )
      DYPDY(8,7)=DAMKOLE*(0.0          +DCOEF2*DPI/DPH*(-DFIS*DPR*
     *                                 (0.0-Y(8)) /DQT**2
     *                                            )              )
      DYPDY(8,8)=DAMKOLE*(0.0          +DCOEF2*DPI/DPH*(-DFIS*DPR*
     *                                 (DQT-Y(8)) /DQT**2
     *                                            )              )
      RETURN
      END
C
C
C
C
C     --------------------------------------------------------------
C
C     This subroutine provide input data to the program.
C
      SUBROUTINE AREAD(DTEMP,DPTOT,DRLO,
     *                 DPA,DPN,DPH,DPI,DPR,DMOLSFEED,DAMKOLE,DRATERAT)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION DRLO,DPA,DPN,DPH,DPI,DMOLSFEED,DMOLSFRAC
      DOUBLE PRECISION DAMKOLE,DRATERAT
      DOUBLE PRECISION DVOIDF,DGEOF,DPORERAD
      DOUBLE PRECISION DBETA,A,N,H,DA,DN,DH,DI
      DOUBLE PRECISION DTEMP,DPTOT,DPR,DREAL,DPSIG
      DOUBLE PRECISION DTC,DPC,DVC,DZC,DW,DMUR,DMW,DK
      DOUBLE PRECISION DFEEDIT,DFEEDIS,DSCCMIT,DSCCMIS
      DOUBLE PRECISION DR1,DTHICK,DRKO,DE
      INTEGER I
```

```
      COMMON/VOIDGEO/DVOIDF,DGEOF,DPORERAD
      COMMON/BET/DBETA,A,N,H,DA,DN,DH,DI
      COMMON/CRIT/DTC,DPC,DVC,DZC,DW,DMUR,DMW
      COMMON/INTERAC/DK
      COMMON/REAL/DREAL
      COMMON/SCCM/DFEEDIT,DFEEDIS,DSCCMIT,DSCCMIS
      COMMON/RTHICK/DR1,DTHICK,DRKO,DE
      DIMENSION DMOLSFEED(8),DMOLSFRAC(8)
      DIMENSION DTC(4),DPC(4),DVC(4),DZC(4),DW(4),DMUR(4),DMW(4),
     *          DK(4,4)
      READ(1,*)  DAMKOLE,DRATERAT
      READ(1,*)  DVOIDF,DGEOF,DPORERAD
      READ(1,*)  DTEMP,DPSIG,DPR,DREAL
      READ(1,*)  DSCCMIT,DSCCMIS
      DO 90 I=1,8
      READ(1,*)  DMOLSFRAC(I)
   90 CONTINUE
      READ(1,*)  A,N,H
      READ(1,*)  DBETA,DRKO,DE
      READ(1,*)  DA,DN,DH,DI
      READ(1,*)  DPA,DPN,DPH,DPI
      DO 30 I=1,4
      READ(1,*)  DTC(I),DPC(I),DVC(I),DZC(I),DW(I),DMUR(I),DMW(I)
   80 CONTINUE
      DO 70 I=1,4
      READ(1,*)  DK(I,1),DK(I,2),DK(I,3),DK(I,4)
   70 CONTINUE
      READ(1,*)  DRLO
C     ***CHANGE UNIT***
      DPTOT=DPSIG/1.40915902D-4
C     CHANGE SCCM TO MOL/S BASIS
C
      DFEEDIT=DSCCMIT*1.01325/273.15/83.14/60.0
      DFEEDIS=DSCCMIS*1.01325/273.15/83.14/60.0
      DO 60 I=1,4
      DMOLSFEED(I)=DMOLSFRAC(I)*DFEEDIT
   60 CONTINUE
      DO 50 I=5,8
      DMOLSFEED(I)=DMOLSFRAC(I)*DFEEDIS
   50 CONTINUE
C     *****************
      WRITE(*,*)
      WRITE(*,1000)
 1000 FORMAT(' ******* CALCULATING WAIT ********')
      RETURN
      END
C
C
C     ------------------------------------------------------------
C
C
C     This subroutine give output result to printer and/or monitor.
C
      SUBROUTINE WRITE(DLENGTH,DCONVER,DFTOT,DQTOT
     *            ,DAIN,DNIN,DHIN,DIIN,DAOUT,DNOUT,DHOUT,DIOUT,DFAO
     *            ,DTEMP,DPTOT,DPR)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION DLENGTH,DCONVER,DFTOT,DQTOT,
     *      DAIN,DNIN,DHIN,DIIN,DAOUT,DNOUT,DHOUT,DIOUT
      DOUBLE PRECISION DFAO,DR1,DTHICK,DRKO,DE
      DOUBLE PRECISION DFEEDIT,DFEEDIS,DSCCMIT,DSCCMIS
```

```
      DOUBLE PRECISION DFEEDOT,DFEEDOS,DSCCMOT,DSCCMOS
      DOUBLE PRECISION DTEMP,DPTOT,DPR
      REAL OUTPUT
      INTEGER I,II
      COMMON/SCCM/DFEEDIT,DFEEDIS,DSCCMIT,DSCCMIS
      COMMON/RTHICK/DR1,DTHICK,DRKO,DE
      DIMENSION DLENGTH(101),DCONVER(101),DFTOT(101),DQTOT(101),
     *          DAIN(101)    ,DNIN(101)   ,DHIN(101)  ,DIIN(101),
     *          DAOUT(101)   ,DNOUT(101)  ,DHOUT(101) ,DIOUT(101)
      DFEEDOT=(DAIN(101)+DNIN(101)+DHIN(101)+DIIN(101))*DFAO
      DFEEDOS=(DAOUT(101)+DNOUT(101)+DHOUT(101)+DIOUT(101))*DFAO
      DSCCMOT=DFEEDOT*273.15*83.14*60.0/1.01325
      DSCCMOS=DFEEDOS*273.15*83.14*60.0/1.01325
      WRITE(*,*)
      WRITE(*,800)
      WRITE(*,*)
   50 WRITE(*,*)
      WRITE(*,900)
      WRITE(*,1000)
      READ(*,*) OUTPUT
      IF (OUTPUT.EQ.1.0) THEN
          GOTO 10
                         ELSE
                      IF (OUTPUT.EQ.0.0) THEN
                         GOTO 40
                                      ELSE
                                   IF (OUTPUT.EQ.2.0) THEN
                                      GOTO 40
                                                    ELSE
                                      GOTO 50
                                                    ENDIF
                                   ENDIF
                      ENDIF
   40 WRITE(*,*)
      WRITE(*,100)
      WRITE(*,*)
      WRITE(*,*)
      WRITE(*,250)
      WRITE(*,350)
      WRITE(*,*)
        DO 25 I=1,101,10
      WRITE(*,450) DLENGTH(I),DCONVER(I),
     *           DAIN(I)/DFTOT(I) ,DNIN(I)/DFTOT(I) ,DHIN(I)/DFTOT(I),
     *           DAOUT(I)/DQTOT(I),DNOUT(I)/DQTOT(I),DHOUT(I)/DQTOT(I)
   25    CONTINUE
      WRITE(*,555)
      READ(*,*) II
C
      WRITE(*,*)
      WRITE(*,360)
      WRITE(*,350)
      WRITE(*,*)
        DO 26 I=1,101,10
      WRITE(*,460) DLENGTH(I),DCONVER(I),
     *           DAIN(I)*DFAO  ,DNIN(I)*DFAO ,DHIN(I)*DFAO,
     *           DAOUT(I)*DFAO,DNOUT(I)*DFAO,DHOUT(I)*DFAO
   26 CONTINUE
      WRITE(*,555)
      READ(*,*) II
C
```

```
      WRITE(*,*)
      WRITE(*,355)
      WRITE(*,350)
      WRITE(*,*)
         DO 27 I=1,101,10
      WRITE(*,465) DLENGTH(I),DCONVER(I),
     *              DAIN(I)*DFAO*273.15*83.14*60./1.01325,
     *              DNIN(I)*DFAO*273.15*83.14*60./1.01325,
     *              DHIN(I)*DFAO*273.15*83.14*60./1.01325,
     *              DAOUT(I)*DFAO*273.15*83.14*60./1.01325,
     *              DNOUT(I)*DFAO*273.15*83.14*60./1.01325,
     *              DHOUT(I)*DFAO*273.15*83.14*60./1.01325
  27     CONTINUE
      WRITE(*,*)
      WRITE(*,440)DTEMP,DPTOT*1.40915902D-4,DPTOT*DPR*1.40915902D-4
      WRITE(*,480) DSCCMIT,DSCCMIS,DFEEDIT,DFEEDIS
      WRITE(*,470) DSCCMOT,DSCCMOS,DFEEDOT,DFEEDOS
      WRITE(*,510) DR1,DTHICK
      IF (OUTPUT.EQ.2.0) THEN
         GOTO 10
                        ELSE
         GOTO 60
                        ENDIF
C
   10 OPEN(UNIT=2,FILE='A:NH3DAMK.RES',STATUS='NEW')
      WRITE(2,*)
      WRITE(2,100)
      WRITE(2,*)
      WRITE(2,*)
      WRITE(2,200)
      WRITE(2,300)
      WRITE(2,*)
        DO 20 I=1,101
      WRITE(2,400) DLENGTH(I),DCONVER(I),
     *              DAIN(I)/DFTOT(I)  ,DNIN(I)/DFTOT(I)  ,DHIN(I)/DFTOT(I),
     *              DIIN(I)/DFTOT(I),
     *              DAOUT(I)/DQTOT(I),DNOUT(I)/DQTOT(I),DHOUT(I)/DQTOT(I)
     *              ,DIOUT(I)/DQTOT(I)
  20     CONTINUE
      WRITE(2,*)
      WRITE(2,*)
      WRITE(2,500)
      WRITE(2,300)
      WRITE(2,*)
        DO 30 I=1,101
      WRITE(2,600) DLENGTH(I),DCONVER(I),
     *              DAIN(I)*DFAO  ,DNIN(I)*DFAO  ,DHIN(I)*DFAO
     *              ,DIIN(I)*DFAO,
     *              DAOUT(I)*DFAO,DNOUT(I)*DFAO,DHOUT(I)*DFAO
     *              ,DIOUT(I)*DFAO
  30     CONTINUE
      WRITE(2,*)
      WRITE(2,*)
      WRITE(2,550)
      WRITE(2,300)
      WRITE(2,*)
        DO 35 I=1,101
      WRITE(2,650) DLENGTH(I),DCONVER(I),
     *              DAIN(I)*DFAO*273.15*83.14*60./1.01325,
     *              DNIN(I)*DFAO*273.15*83.14*60./1.01325,
```

```
    *                  DHIN(I)*DFAO*273.15*83.14*60./1.01325,
    *                  DIIN(I)*DFAO*273.15*83.14*60./1.01325,
    *                  DAOUT(I)*DFAO*273.15*83.14*60./1.01325,
    *                  DNOUT(I)*DFAO*273.15*83.14*60./1.01325,
    *                  DHOUT(I)*DFAO*273.15*83.14*60./1.01325,
    *                  DIOUT(I)*DFAO*273.15*83.14*60./1.01325
 35 CONTINUE
    WRITE(2,*)
    WRITE(2,440)DTEMP,DPTOT*1.40915902D-4,DPTOT*DPR*1.40915902D-4
    WRITE(2,480) DSCCMIT,DSCCMIS,DFEEDIT,DFEEDIS
    WRITE(2,470) DSCCMOT,DSCCMOS,DFEEDOT,DFEEDOS
    WRITE(2,510) DR1,DTHICK
    CLOSE(2)
100 FORMAT('           ********* RESULTS OF CALCULATION *********')
200 FORMAT(' MOLE FRACTION              REACTION ZONE
    *           PERMEATION ZONE')
300 FORMAT('   L/Lo     CONV       NH3        N2           H2      INE
    *RT         NH3        N2         H2       INERT')
400 FORMAT(2X,F4.2,4X,F8.6,3X,4(F10.6),2X,4(F10.6))
500 FORMAT(' MOLE/S                     REACTION ZONE
    *           PERMEATION ZONE')
550 FORMAT(' SCCM                       REACTION ZONE
    *           PERMEATION ZONE')
600 FORMAT(2X,F4.2,4X,F8.6,3X,4(E10.4),2X,4(E10.4))
650 FORMAT(2X,F4.2,4X,F8.6,3X,4(F10.3),2X,4(E10.3))
250 FORMAT(' MOLE FRACTION              REACTION ZONE                 PERME
    *ATION ZONE')
360 FORMAT(' MOLE/S                     REACTION ZONE                 PERME
    *ATION ZONE')
355 FORMAT(' SCCM                       REACTION ZONE                 PERME
    *ATION ZONE')
350 FORMAT('   L/Lo    CONV       NH3        N2          H2         NH3
    *  N2        H2')
440 FORMAT(' TEMP(K),PRESS(in),PRESS(out) (Psig)= ',3(F8.2))
450 FORMAT(2X,F4.2,2X,F8.6,2X,3(F9.6),1X,3(F9.6))
460 FORMAT(2X,F4.2,2X,F8.6,2X,3(E9.3),1X,3(E9.3))
465 FORMAT(2X,F4.2,2X,F8.6,2X,3(F9.3),1X,3(F9.3))
470 FORMAT(2X,'Total SCCM  and  MOL/S output for Tube      and    Shell
    *='/2X,F13.5,1X,F13.5,3X,E13.5,1X,E13.5)
480 FORMAT(2X,'Total SCCM  and  MOL/S  input for Tube      and    Shell
    *='/2X,F13.5,1X,F13.5,3X,E13.5,1X,E13.5)
800 FORMAT(' **** THE CALCULATION IS NOW COMPLETED ****')
900 FORMAT(' DO YOU WANT THE RESULTS ON MONITOR OR COMPUTER FILE.')
1000 FORMAT(' PRESS <0> FOR MONITOR OR <1> FOR COMPUTER FILE OR <2> FOR
    * BOTH DEVICES ')
 60 RETURN
    END
C
C
C
C     ------------------------------------------------------------
C
C     This subroutine calculate for permeability.
C
    SUBROUTINE PERM(DTEMP,DPA,DPN,DPH,DPI)
    IMPLICIT DOUBLE PRECISION(A-H,O-Z)
    DOUBLE PRECISION DDKNH3,DDKN2,DDKH2,DDKI,DRT
    *                 ,DDNH3EFF,DDN2EFF,DDH2EFF,DDIEFF
    DOUBLE PRECISION DTEMP,DPA,DPN,DPH,DPI
    DOUBLE PRECISION DVOIDF,DGEOF,DPORERAD
    DOUBLE PRECISION DBETA,A,N,H,DA,DN,DH,DI
```

```
      DOUBLE PRECISION DTC,DPC,DVC,DZC,DW,DMUR,DMW
      COMMON/VOIDGEO/DVOIDF,DGEOF,DPORERAD
      COMMON/CRIT/DTC,DPC,DVC,DZC,DW,DMUR,DMW
      COMMON/BET/DBETA,A,N,H,DA,DN,DH,DI
      DIMENSION DTC(4),DPC(4),DVC(4),DZC(4),DW(4),DMUR(4),DMW(4)
C     *** CALCULATION OF Dk ***
      DDKNH3= 9.7E3*(DPORERAD-DA)*(DTEMP/DMW(1))**0.5/100.**2
      DDKN2 = 9.7E3*(DPORERAD-DN)*(DTEMP/DMW(2))**0.5/100.**2
      DDKH2 = 9.7E3*(DPORERAD-DH)*(DTEMP/DMW(3))**0.5/100.**2
      DDKI  = 9.7E3*(DPORERAD-DI)*(DTEMP/DMW(4))**0.5/100.**2
      DRT=8.314*DTEMP
C
C     *** CALCULATION OF Dk(eff) INCLUDE POROSITY AND GEO FACTOR)
      DDNH3EFF =DDKNH3*DVOIDF/DGEOF
      DDN2EFF  =DDKN2 *DVOIDF/DGEOF
      DDH2EFF  =DDKH2 *DVOIDF/DGEOF
      DDIEFF   =DDKI  *DVOIDF/DGEOF
C
C     *** CALCULATION OF PERMEABILITY (MOL/M/S/Pa)
      DPA = DDNH3EFF /DRT
      DPN = DDN2EFF  /DRT
      DPH = DDH2EFF  /DRT
      DPI = DDIEFF   /DRT
      RETURN
      END
C
C
C     ------------------------------------------------------------
C
C
C     This subroutine calculate fugacity coefficient.
C
C
      SUBROUTINE FUGACITY(DFAT,DFNT,DFHT,DFIT,
     *                  DFAS,DFNS,DFHS,DFIS,DTEMP,DPTOT,DPR,DREAL)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION DFAT,DFNT,DFHT,DFIT,
     *                  DFAS,DFNS,DFHS,DFIS
      DOUBLE PRECISION DTEMP,DPTOT,DPT,DPR,DREAL
      IF (DREAL.EQ.0.0)THEN
          DFAT= 1.0
          DFNT= 1.0
          DFHT= 1.0
          DFIT= 1.0
          DFAS= 1.0
          DFNS= 1.0
          DFHS= 1.0
          DFIS= 1.0
          GOTO 100
                        ELSE
                        IF(DREAL.EQ.1.0)THEN
      DPT=DPTOT/1.013E5
      DFAT=0.1438996+0.2028538D-2*DTEMP-0.4487672D-3*DPT
     *      -0.1142945D-5*DTEMP**2+0.2761216D-6*DPT**2
      DFNT=0.93431737+0.3101804D-3*DTEMP+0.295896D-3*DPT
     *      -0.2707279D-6*DTEMP**2+0.4775207D-6*DPT**2
      DFHT=DEXP(DEXP(-3.8402*DTEMP**0.125+0.541)*DPT
     *      -DEXP(-0.1263*DTEMP**0.5-15.980)*DPT**2
     *      +300*DEXP(-0.011901*DTEMP-5.941)*(DEXP(-DPT/300)
     *                                             -1))
     *
      DFIT=1.0
      DFAS=0.1438996+0.2028538D-2*DTEMP-0.4487672D-3*DPT*DPR
```

```
      *      -0.1142945D-5*DTEMP**2+0.2761216D-6*(DPT*DPR)**2
       DFNS=0.93431737+0.3101804D-3*DTEMP+0.295896D-3*DPT*DPR
      *      -0.2707279D-6*DTEMP**2+0.4775207D-6*(DPT*DPR)**2
       DFHS=DEXP(DEXP(-3.8402*DTEMP**0.125+0.541)*DPT*DPR
      *      -DEXP(-0.1263*DTEMP**0.5-15.980)*(DPT*DPR)**2
      *      +300*DEXP(-0.011901*DTEMP-5.941)*(DEXP(-DPT*DPR/300)
      *                                      -1))
       DFIS=1.0
                                    GOTO 100
                                    ELSE
                                    IF (DREAL.EQ.2.0)THEN
                                    CALL VIRIAL(DFAT,DFNT,DFHT,DFIT,
      *                                  DFAS,DFNS,DFHS,DFIS,
      *                                  DTEMP,DPTOT,DPR)
                                        ELSE
                                    GOTO 100
                                        ENDIF
                      ENDIF
              ENDIF
  100 RETURN
      END
C
C
C
C      -----------------------------------------------------------
C
C      This subroutine calculate fugacity coefficient by virial eqution.
C
       SUBROUTINE VIRIAL(DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS,
      *                  DTEMP,DPTOT,DPR)
       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
       INTEGER I,J
       DOUBLE PRECISION DFAT,DFNT,DFHT,DFIT,DFAS,DFNS,DFHS,DFIS
       DOUBLE PRECISION V,DPR,DTEMP,DPTOT
       DOUBLE PRECISION Y
       DOUBLE PRECISION DFO ,DF1 ,DF2 ,D2COEF,
      *                 DFOM,DF1M,DF2M,D2COEFM,
      *                 DTC,DPC,DVC,DZC,DW,DMUR,DMW,DK,
      *                 DTR,FRAC,DPRESS,DZMIX,D2MIX,
      *                 DTCM,DVCM,DZCM,DWM,DPCM,DTRM
       DIMENSION DFO(4),DF1(4),DF2(4),D2COEF(4),
      *          DFOM(4,4),DF1M(4,4),DF2M(4,4),D2COEFM(4,4),
      *          DTC(4),DPC(4),DVC(4),DZC(4),DW(4),DMUR(4),DMW(4),
      *          DTR(4),FRAC(8),DK(4,4),
      *          DTCM(4,4),DVCM(4,4),DZCM(4,4),DWM(4,4),DPCM(4,4),
      *          DTRM(4,4)
       DIMENSION Y(8)
       COMMON/CRIT/DTC,DPC,DVC,DZC,DW,DMUR,DMW
       COMMON/FEED/Y
       COMMON/INTERAC/DK
C
       DO 30 I=1,4
       DTR(I)=DTEMP/DTC(I)
       DFO(I)=0.1445-0.330/DTR(I)-0.1385/DTR(I)**2
      *       -0.0121/DTR(I)**3-0.000607/DTR(I)**8
       DF1(I)=0.0637+0.331/DTR(I)**2-0.423/DTR(I)**3-0.008/DTR(I)**8
       DF2(I)=(-2.112D-4*DMUR(I)-3.877D-21*DMUR(I)**8)/DTR(I)**6
       D2COEF(I)=(DFO(I)+DW(I)*DF1(I)+DF2(I))*83.1439*DTC(I)/DPC(I)
       Z=1.+D2COEF(I)*(DPTOT/1.0D5)/(83.14*DTEMP)
   30 CONTINUE
C
```

```
      DO 10 I=1,4
          DO 20 J=1,4
      DTCM(I,J)=(DTC(I)*DTC(J))**0.5*(1-DK(I,J))
      DVCM(I,J)=((DVC(I)**(0.33333)+DVC(J)**(0.33333))/2.0)**3
      DZCM(I,J)=(DZC(I)+DZC(J))/2.0
      DWM(I,J)=(DW(I)+DW(J))/2.0
      DPCM(I,J)=(DZCM(I,J)*83.1439*DTCM(I,J))/DVCM(I,J)
      DTRM(I,J)=DTEMP/DTCM(I,J)
   20       CONTINUE
   10 CONTINUE
C
      DO 40 I=1,4
          DO 50 J=1,4
      DFOM(I,J)=0.1445-0.330/DTRM(I,J)-0.1385/DTRM(I,J)**2
     *          -0.0121/DTRM(I,J)**3-0.000607/DTRM(I,J)**8
      DF1M(I,J)=0.0637+0.331/DTRM(I,J)**2-0.423/DTRM(I,J)**3
     *          -0.008/DTRM(I,J)**8
      DF2M(I,J)=(-2.112D-4*DMUR(I)-3.877D-21*DMUR(I)**8)/
     *          DTRM(I,J)**6
      D2COEFM(I,J)=(DFOM(I,J)+DWM(I,J)*DF1M(I,J)+DF2M(I,J))
     *              *83.1439*DTCM(I,J)/DPCM(I,J)
   50       CONTINUE
   40 CONTINUE
C
C
      FRAC(1)=Y(1)/(Y(1)+Y(2)+Y(3)+Y(4))
      FRAC(2)=Y(2)/(Y(1)+Y(2)+Y(3)+Y(4))
      FRAC(3)=Y(3)/(Y(1)+Y(2)+Y(3)+Y(4))
      FRAC(4)=Y(4)/(Y(1)+Y(2)+Y(3)+Y(4))
      D2MIX  =FRAC(1)**2*D2COEF(1)+
     *         FRAC(2)**2*D2COEF(2)+
     *         FRAC(3)**2*D2COEF(3)+
     *         FRAC(4)**2*D2COEF(4)+
     *         2.0*FRAC(1)*FRAC(2)*D2COEFM(1,2)+
     *         2.0*FRAC(1)*FRAC(3)*D2COEFM(1,3)+
     *         2.0*FRAC(1)*FRAC(4)*D2COEFM(1,4)+
     *         2.0*FRAC(2)*FRAC(3)*D2COEFM(2,3)+
     *         2.0*FRAC(2)*FRAC(4)*D2COEFM(2,4)+
     *         2.0*FRAC(3)*FRAC(4)*D2COEFM(3,4)
      DPRESS=DPTOT/1.0E5
      V=83.1439*DTEMP/DPRESS
      DZMIX=1.0+D2MIX/V
      DFAT=DEXP(2.0/V*(FRAC(4)*D2COEFM(1,4)+FRAC(3)*D2COEFM(1,3)+
     *                 FRAC(2)*D2COEFM(1,2)+FRAC(1)*D2COEFM(1,1))
     *                 -DLOG(DZMIX))
      DFNT=DEXP(2.0/V*(FRAC(4)*D2COEFM(2,4)+FRAC(3)*D2COEFM(2,3)+
     *                 FRAC(2)*D2COEFM(2,2)+FRAC(1)*D2COEFM(2,1))
     *                 -DLOG(DZMIX))
      DFHT=DEXP(2.0/V*(FRAC(4)*D2COEFM(3,4)+FRAC(3)*D2COEFM(3,3)+
     *                 FRAC(2)*D2COEFM(3,2)+FRAC(1)*D2COEFM(3,1))
     *                 -DLOG(DZMIX))
      DFIT=DEXP(2.0/V*(FRAC(4)*D2COEFM(4,4)+FRAC(3)*D2COEFM(4,3)+
     *                 FRAC(2)*D2COEFM(4,2)+FRAC(1)*D2COEFM(4,1))
     *                 -DLOG(DZMIX))
C
      DPRESS=DPTOT/1.0E5*DPR
      FRAC(5)=Y(5)/(Y(5)+Y(6)+Y(7)+Y(8))
      FRAC(6)=Y(6)/(Y(5)+Y(6)+Y(7)+Y(8))
      FRAC(7)=Y(7)/(Y(5)+Y(6)+Y(7)+Y(8))
      FRAC(8)=Y(8)/(Y(5)+Y(6)+Y(7)+Y(8))
```

```
      D2MIX =FRAC(5)**2*D2COEF(1)+
     *        FRAC(6)**2*D2COEF(2)+
     *        FRAC(7)**2*D2COEF(3)+
     *        FRAC(8)**2*D2COEF(4)+
     *        2.0*FRAC(5)*FRAC(6)*D2COEFM(1,2)+
     *        2.0*FRAC(5)*FRAC(7)*D2COEFM(1,3)+
     *        2.0*FRAC(5)*FRAC(8)*D2COEFM(1,4)+
     *        2.0*FRAC(6)*FRAC(7)*D2COEFM(2,3)+
     *        2.0*FRAC(6)*FRAC(8)*D2COEFM(2,4)+
     *        2.0*FRAC(7)*FRAC(8)*D2COEFM(3,4)
      V=83.1439*DTEMP/DPRESS
      DZMIX=1.0+D2MIX/V
      DFAS=DEXP(2.0/V*(FRAC(8)*D2COEFM(1,4)+FRAC(7)*D2COEFM(1,3)+
     *                 FRAC(6)*D2COEFM(1,2)+FRAC(5)*D2COEFM(1,1))
     *                 -DLOG(DZMIX))
      DFNS=DEXP(2.0/V*(FRAC(8)*D2COEFM(2,4)+FRAC(7)*D2COEFM(2,3)+
     *                 FRAC(6)*D2COEFM(2,2)+FRAC(5)*D2COEFM(2,1))
     *                 -DLOG(DZMIX))
      DFHS=DEXP(2.0/V*(FRAC(8)*D2COEFM(3,4)+FRAC(7)*D2COEFM(3,3)+
     *                 FRAC(6)*D2COEFM(3,2)+FRAC(5)*D2COEFM(3,1))
     *                 -DLOG(DZMIX))
      DFIS=DEXP(2.0/V*(FRAC(8)*D2COEFM(4,4)+FRAC(7)*D2COEFM(4,3)+
     *                 FRAC(6)*D2COEFM(4,2)+FRAC(5)*D2COEFM(4,1))
     *                 -DLOG(DZMIX))
      RETURN
      END


      RETURN
      END
```

APPENDIX D

Equilibrium Constant and Reverse Reaction

The equilibrium conversion for the ammonia decomposition can be determined from the equilibrium constant.

$$K = \frac{(a_N)^{0.5}(a_H)^{1.5}}{(a_A)} \tag{31}$$

Where a_N , a_H, and a_A are the activities of nitrogen, hydrogen, and ammonia, respectively. The value of the equilibrium constant can be evaluated from the Gibbs free energy. Figure 26 and 27 show how the equilibrium constant and equilibrium conversion for this system vary with temperature.

If we include the reverse reaction for ammonia decomposition in the model (Temkin and Pyzhev, 1940).

$$r_A = -k_1 \left[\frac{f_A^2}{f_H^3}\right]^{\beta} + k_2 f_N \left[\frac{f_H^3}{f_A^2}\right]^{(1-\beta)} \tag{60}$$

with

$$K^2 = \frac{k_1}{k_2} \tag{61}$$

The mole fraction of each gas component will never exceed equilibrium composition. At a pressure of 35.482E5 Pa and a feed gas composition of 0.3% NH_3, 20% H_2, 48% N_2, and

31.7% He, ammonia starts to decompose at temperature greater than 875 K. As shown in Figure 28, the fractional conversion for the membrane reactor is always greater than the conversion obtained in a plug flow of equal length when the reverse rate term is incorporated into the reaction rate expression. The reactor parameters are the same as those given in section 7.1
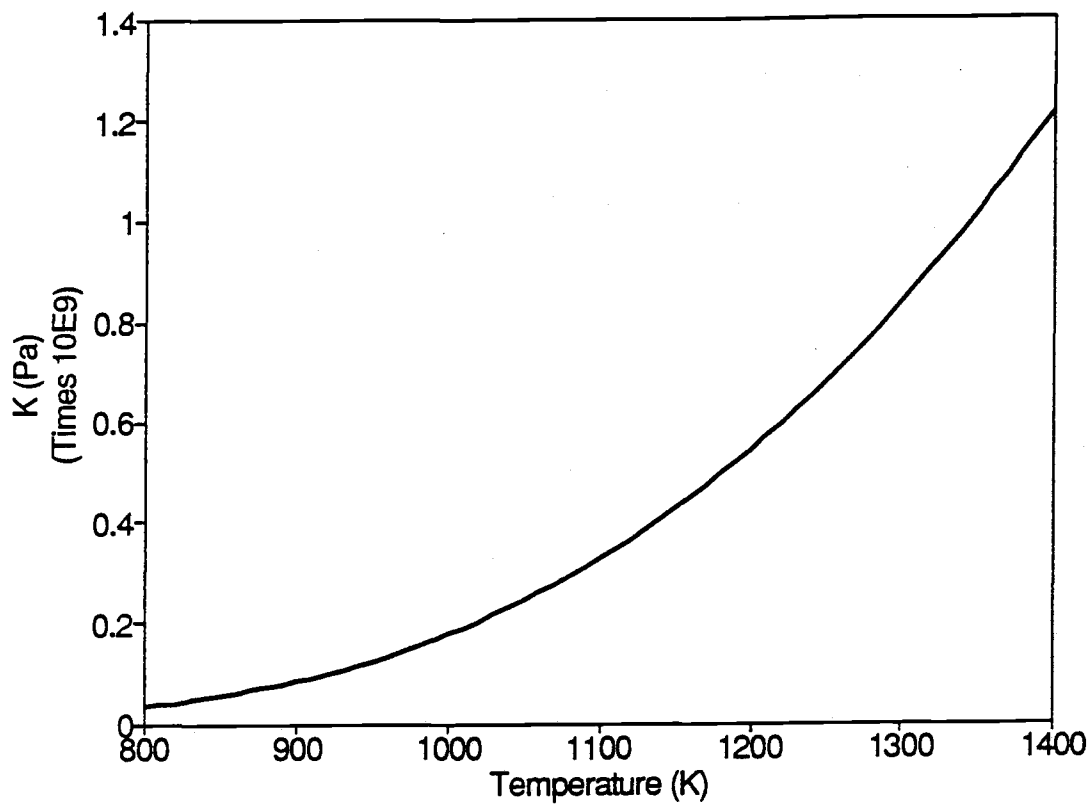
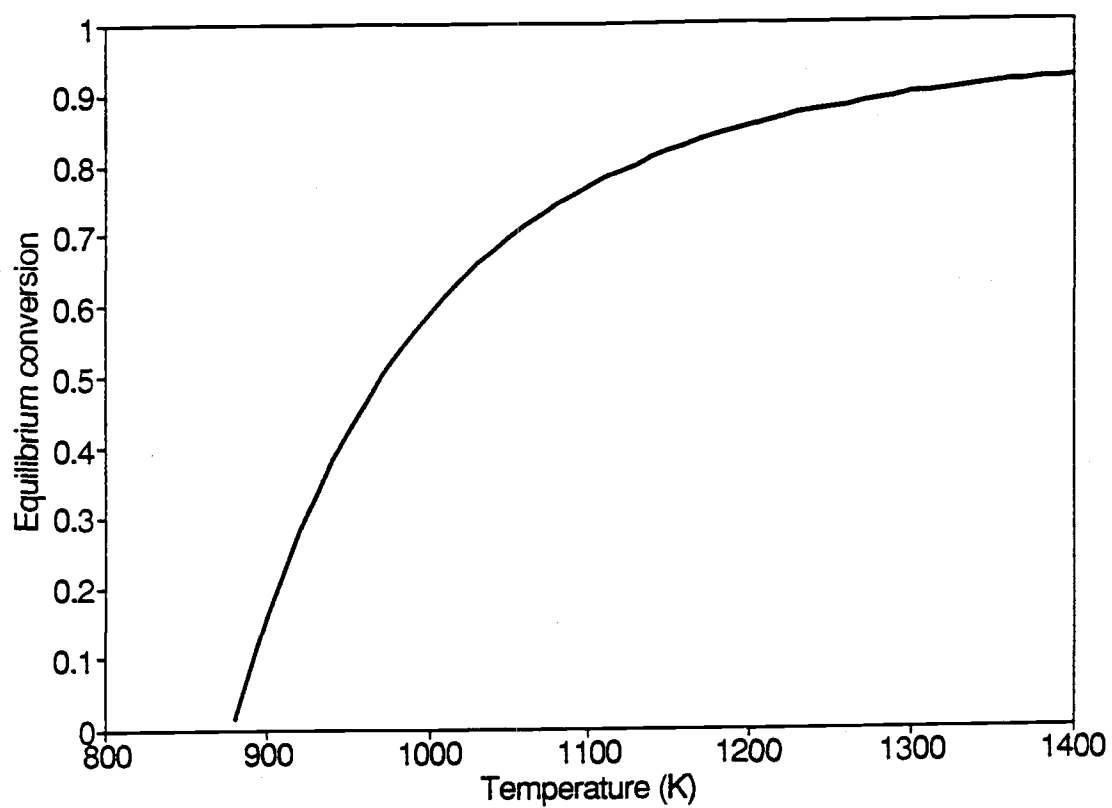Figure 26   Equilibrium constant at various temperature

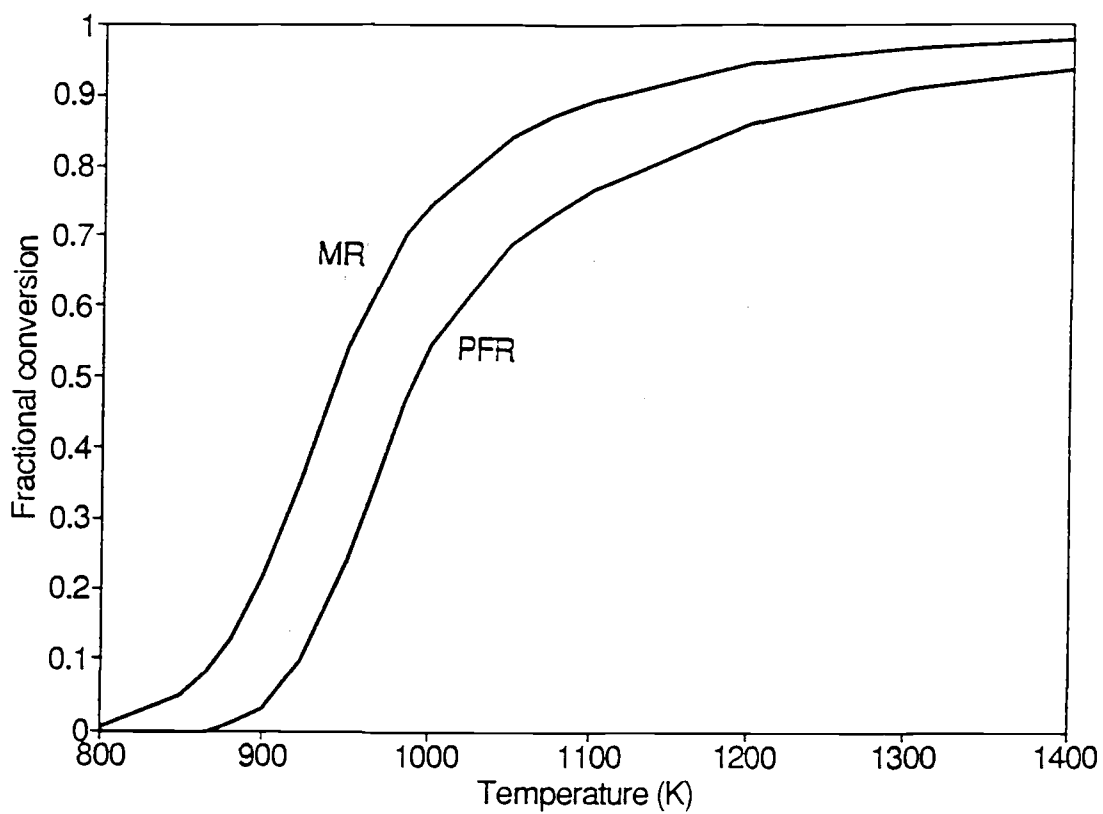Figure 27   Equilibrium conversion at various temperature

Figure 28 Fractional conversion of PFR and MR with include
reverse reaction