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A KINETIC EXPRESSION WITH DIFFUSION CORRECTION FOR AMMONIA SYNTHESIS ON INDUSTRIAL CATALYST

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The expression for the rate of formation of ammonia at pressures from 150 to 300 atm. derived here is the simplest available for a modern catalyst, is suitable for design, optimization, and control studies, and is believed to be as accurate as the most complex expressions in the composition, temperature, and pressure regions of commercial importance. The rate expression is based on the Temkin and Pyzhev expression corrected for high pressures and fitted to recently reported kinetic measurements of Nielsen, Kjaer, and Hansen for an industrially used catalyst. In addition, simple expressions permit rapid calculation of effectiveness factors for 6- to 10-mm. particles for the process conditions found in modern synthesis units.

MANY workers have sought a reaction rate expression which not only correlates experimental data but is also satisfactory from the mechanistic standpoint. Since a prohibitive amount of evidence is required to determine the mechanism uniquely (Nielsen *et al.*, 1964; Petersen, 1965) and the expressions involved are inherently complex, it is expedient to find a simpler expression, which adequately represents experimental equilibrium studies and packed-bed kinetic studies.

The need for a simple rate expression becomes apparent when one considers that the computation time required even for steady-state design calculations is highly dependent on the complexity of the rate expression. For recycle studies which involve the solution of nonlinear equations, or for optimization studies in which parameters are varied and calculations are repeated many times, the use of a simple rate expression is essential.

The literature contains innumerable rate expressions and several of these could be used after slight modification for calculating industrial converters. The range of applicability of these expressions must always be carefully recognized and one must note as well (if stated) the type and size of the catalyst. Adams and Comings (1953), Annable (1952), Hays *et al.* (1964), Kubota and Shindo (1959), and Nielsen (1956) give information and rate expressions useful for converter calculations.

A pseudo-homogeneous expression is developed for a bed packed with fine (laboratory size) catalyst, and an effectiveness factor is developed for industrial size catalyst pellets by integrating the transport equations for spherical particles.

Pseudo-Homogeneous Expression for a Bed Packed with Fine Catalyst

The only experimental kinetic data we consider are those of Nielsen *et al.* (1964). This is the most recent set of kinetic data

for commercially available ammonia synthesis catalyst and the experimental conditions are representative of process conditions. These data can be correlated fairly well by a slightly modified form of the simple Temkin (1950) expression

$$V_3 = 2k \left[K_a^2 a_1 \left(\frac{a_2^3}{a_3^2} \right)^\alpha - \left(\frac{a_3^2}{a_2^3} \right)^{1-\alpha} \right] \quad (1)$$

Subscripts designate components; nitrogen is considered as component 1, hydrogen as component 2, ammonia as component 3, and all inert components in the system, taken collectively, as component 4. Parameter α has been used by investigators of ammonia synthesis kinetics to correlate kinetic data (Bokhoven *et al.*, 1955). Both $\alpha = 0.5$ and $\alpha = 0.75$ are used in this paper to determine if one of these yields a better fit of the data. The more complicated expression used by Nielsen *et al.* (1964) fits their data only slightly better (see Figure 4).

Some thermodynamic data are required to relate activities a_1 , a_2 , and a_3 to the composition, pressure, and temperature. To this end we use:

1. The equation of Gillespie and Beattie (1930):

$$\log_{10} K_a = -2.691122 \log_{10} T - 5.519265 \times 10^{-5} T + 1.848863 \times 10^{-7} T^2 + \frac{2001.6}{T} + 2.6899 \quad (2)$$

For this equation the temperature, T , is in degrees Kelvin and K_a replaces Gillespie and Beattie's K_p^* .

2. The Lewis and Randall rule (1961): This is known to be valid in the T, P range we are considering (Denbigh, 1964; Kazarnovskii, 1945).

The activity of a component is given by definition as

$$a_i = \frac{f_i}{f_i^*} \quad (3)$$

where f_i^* is the fugacity of component i at a particular arbitrarily chosen standard state. Choosing f_i^* as equal to the fugacity

of pure component i at a pressure of 1 atm. and a temperature equal to the temperature of the system, one may write

$$a_i = f_i = X_i f_i^\circ \quad (4)$$

where f_i° is the pure component fugacity at the temperature and pressure of the system.

3. For the pure component fugacities we write

$$f_i^\circ = \gamma_i P \quad (5)$$

and then use literature expressions for the activity coefficients as follows:

For hydrogen, from Cooper (1967) and Shaw and Wones (1964) we obtain

$$\gamma_2 = \exp \left\{ e(-3.8402T^{0.125} + 0.541)P - e(-0.1268T^{0.5} - 15.980)P^2 + 300 [e(-0.011901T - 5.941)](e^{-P/300} - 1) \right\} \quad (6)$$

For nitrogen and ammonia, the correlations of Cooper (1967) and Newton (1935) have been fitted accurately by the following expressions:

$$\begin{aligned} \gamma_1 = & 0.93431737 + 0.3101804 \times 10^{-3} T + \\ & 0.295896 \times 10^{-3} P - 0.2707279 \times 10^{-6} T^2 + \\ & 0.4775207 \times 10^{-6} P^2 \quad (7) \end{aligned}$$

$$\begin{aligned} \gamma_3 = & 0.1438996 + 0.2028538 \times 10^{-2} T - \\ & 0.4487672 \times 10^{-3} P - 0.1142945 \times 10^{-5} T^2 + \\ & 0.2761216 \times 10^{-6} P^2 \quad (8) \end{aligned}$$

In Equations 6, 7, and 8 the temperature, T , is in degrees Kelvin and the pressure, P , is in atmospheres. [The fugacity of a component may be calculated from an equation of state (Porcelli, 1967), but, unfortunately, no applicable volume-explicit equations of state have been found in the literature, so the procedure is relatively time-consuming. We have studied this method using both the Beattie-Bridgman and the Redlich-Kwong equations of state and have concluded that the simple equations given above are precise.]

To fit data of Nielsen *et al.* we assumed also that k is of Arrhenius form

$$k = H e^{-E/RT} \quad (9)$$

The frequency factor, H , and the activation energy of the reverse reaction, E , were estimated as detailed below.

The plug flow model is assumed for the laboratory converter whose feed contained no ammonia, so that we may write the fractional conversion of nitrogen at some cross section as

$$\eta = \frac{\text{molar flow of } N_2 \text{ at inlet} - \text{molar flow of } N_2 \text{ across section}}{\text{molar flow of } N_2 \text{ at inlet}} \quad (10)$$

The following expressions for the mole fractions of the individual components, in terms of the conversion and the inlet flow rates, F_i° , of the components, can be easily derived from the stoichiometry of the reaction

$$X_1 = \frac{F_1^\circ(1 - \eta)}{F^\circ - 2 F_1^\circ \eta} \quad (11)$$

$$X_2 = \frac{F_2^\circ - 3 F_1^\circ \eta}{F^\circ - 2 F_1^\circ \eta} \quad (12)$$

$$X_3 = \frac{2 F_1^\circ \eta}{F^\circ - 2 F_1^\circ \eta} \quad (13)$$

A mole balance for nitrogen applied to a differential element, dz , of the reactor gives the following result when expressed in terms of conversion

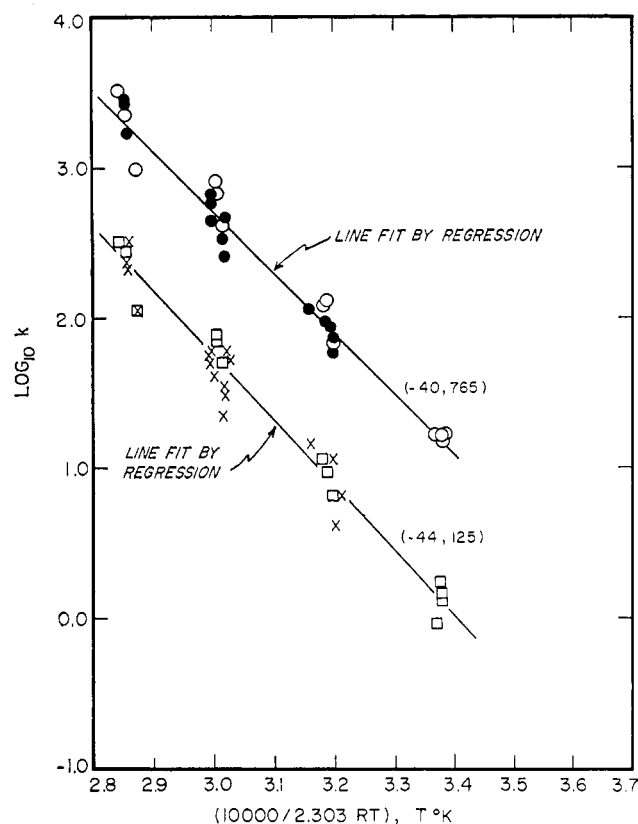


Figure 1. Plots of $\log_{10} k$ against $10^4/2.303RT$

Values of $\log_{10} k$ determined for values of $10^4/2.303RT$ from experiments of Nielsen *et al.* by evaluation of Expression 16: \circ $P = 150$ atm. \bullet $P = 300$ atm. Corresponding values for development of Equation 1 with $\alpha = 0.75$: \square $P = 300$ atm. \times $P = 150$ atm.

$$\frac{d\eta}{dz} = -\frac{A}{F_1^\circ} V_1 \quad (14)$$

The rate of formation of nitrogen is of course related to the rate of formation of ammonia by

$$V_1 = -1/2 V_3 \quad (15)$$

Substitution of Equation 1 with $\alpha = 0.5$ into Equation 15 and the subsequent substitution of this result into Equation 14 give, after a slight rearrangement and integration between the limits $z = 0$ and $z = L$, the following integral expression for k :

$$k = \frac{F_1^\circ}{AL} \int_{\eta=0}^{\eta=\eta_e} \frac{d\eta}{\left[K_a^2 X_1 f_1^\circ \left(\frac{f_2^{\circ 3/2} X_2^{3/2}}{f_3^\circ X_3} \right) - \left(\frac{f_3^\circ X_3}{f_2^{\circ 3/2} X_2^{3/2}} \right) \right]} \quad (16)$$

The exit conversion, η_e , may be expressed in terms of the measured exit mole fraction of ammonia, X_{3e} , by rearrangement of Equation 13:

$$\eta_e = \frac{X_{3e} F^\circ}{2 F_1^\circ (1 + X_{3e})} \quad (17)$$

The integration of Equation 16 has been carried out using the Romberg integration procedure (Conte, 1965; Henrici, 1964).

In addition to the results of integrating Equation 16, the results of integrating the corresponding expression for k which arises when $\alpha = 0.75$ are displayed in Figure 1. Both lines fit the data reasonably well and it is difficult to ascertain whether the scatter of the points is due to experimental error or the lack

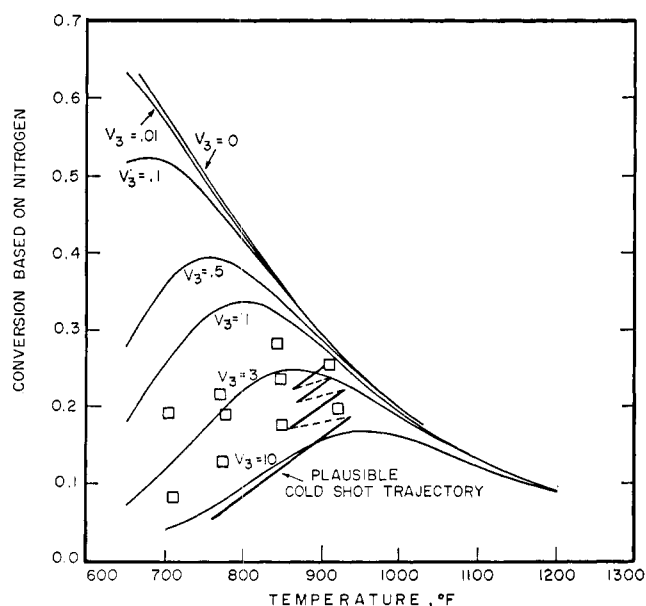


Figure 2. Contours of constant reaction rate V_3 (pound moles of ammonia per cubic foot of catalyst bed per hour) in plane of conversion and temperature for a stoichiometric, inert-free reaction mixture at a total pressure of 150 atm.

□ Reported exit conversions from experimental converter of Nielsen *et al.* (1964)

of fit of the assumed form. Either form fits the data well enough, as calculations given below show, to be useful for the calculation of industrial converters. The form of the rate expression with $\alpha = 0.5$ is to be preferred, as it is the simpler of the two and fits the data in as consistent a manner as the more complicated expression. The rate constant, k , does not appear to be a function of pressure, which is as expected, considering the introduction of the component fugacities into the rate expression.

Regression has been used to fit straight lines through the points shown in Figure 1. The slope of the upper line which is the activation energy has been found to be $-40,765$ and the antilog of the intercept, which is the frequency factor, equal to 8.849×10^{14} . Hence, k as an explicit function of temperature is

$$k = 8.849 \times 10^{14} e^{-40,765/RT} \quad (18)$$

In Equation 18 the units of the temperature are degrees Kelvin and the appropriate value of R , the universal gas constant, is 1.987. The rate of formation of ammonia in kilogram-moles of ammonia formed per cubic meter of catalyst bed per hour is therefore

$$V_3 = 1.7698 \times 10^{15} e^{-40,765/RT} \left[K_a^2 X_1 f_1^\circ \left(\frac{f_2^{\circ 3/2} X_2^{3/2}}{f_3^\circ X_3} \right) - \left(\frac{f_3^\circ X_3}{f_2^{\circ 3/2} X_2^{3/2}} \right) \right] \quad (19)$$

Discussion of Rate Expression

Figures 2 and 3 display some reaction rate contours in the η, T plane. In both figures the inlet mixture to the reactor is considered to be an inert-free, stoichiometric mixture of hydrogen and nitrogen. The numbers used to label the contours are the corresponding reaction rates (pound moles of ammonia per cubic foot of catalyst bed per hour). In Figure 2 a trajec-

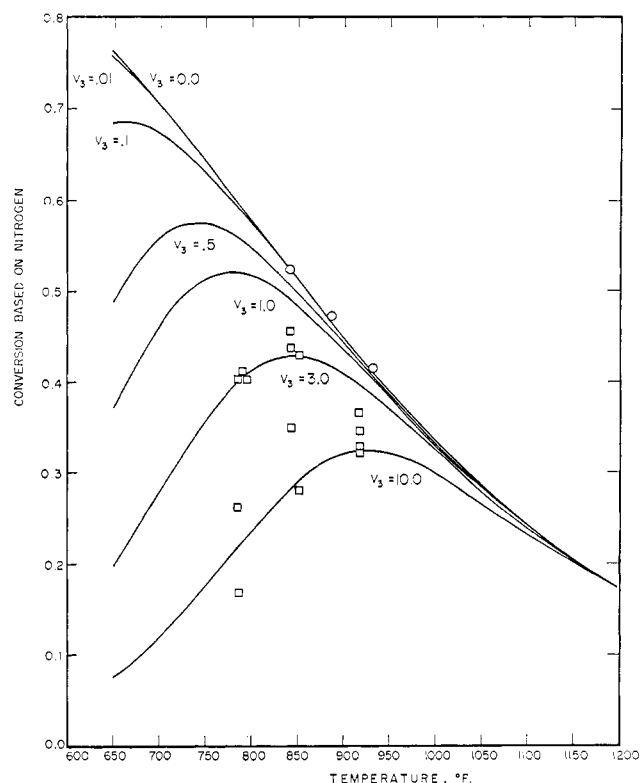


Figure 3. Contours of constant reaction rate V_3 (pound moles of ammonia per cubic foot of catalyst bed per hour) in plane of conversion and temperature for a stoichiometric, inert-free reaction mixture at a total pressure of 300 atm.

□ Reported exit conversions from experimental converter of Nielsen *et al.* (1964). ○ Equilibrium data of Larson (1924)

tory calculated for a plausible set of industrial conditions is displayed, so that one may observe the approximate region of the η, T plane which is of industrial importance. In both figures the isothermal kinetic experimental measurements are shown by small squares. The equilibrium line ($V_3 = 0$) lies very close to the equilibrium data of Larson (1924).

Figure 4 demonstrates the ability of the proposed rate expression to fit the kinetic data. It is a plot of the calculated minus the measured per cent of ammonia at the outlet of the experimental reactor *vs.* the measured outlet per cent of ammonia. The calculated outlet per cent of ammonia is determined by numerical integration of the differential equation which results from a mole balance taken on a differential element of the reactor. The mole balance differential equation is solved for both the rate expression given by Nielsen *et al.* and that presented in this paper. The Kutta-Merson algorithm (Fox, 1962; Lance, 1960) was employed at each set of experimental conditions.

Effectiveness Factor

The rate expression presented in Equation 19 adequately describes the experimental situation under which the reaction data were taken. The particle size was sufficiently small to exclude the possibility of interaction of kinetic and transport effects. Particles of 6- to 10-mm. size [used in some current converter designs (*Chemical Week*, 1966)] are, however, subject to diffusion restriction in their pore structure.

The classical approach to this problem is to calculate the effectiveness factor, ξ , which is defined as the rate at which the reaction occurs in a pellet divided by the rate at which the reac-

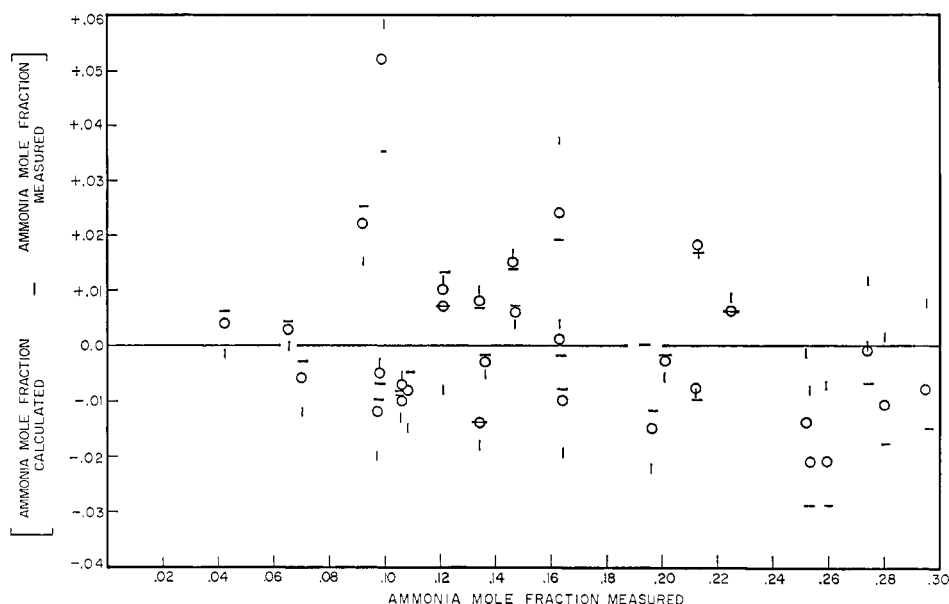


Figure 4. Comparison of three reaction rate expressions for fine catalyst with experimental points of Nielsen *et al.* (1964)

— Our expression (with $\alpha = 0.5$). — Expression which can be developed from Equation 1 with $\alpha = 0.75$.
 ○ Expression of Nielsen *et al.* (1964)

tion would occur if the concentration and temperature throughout the pellet were the same as those at the surface—i.e.,

$$\xi = \frac{\left(\text{molar flux of component } i \text{ across surface} \right) \times \left(\text{surface area of pellet} \right)}{\left(\text{vol. of pellet} \right) \times \left(\text{rate of formation of component } i \text{ at surface comp., } T, P \right)} \quad (20)$$

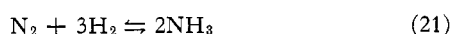
This factor has been calculated for different kinetic expressions by several authors (Akehata *et al.*, 1961; Bokhoven and van Raayen, 1954; Kubota and Shindo, 1956; Kubota *et al.*, 1959; Nielsen, 1956), but in all calculations which have appeared either pseudo-first-order kinetics were used, or the bulk flow terms in the equations for the transport within the catalyst pellets were omitted.

The following assumptions are made:

1. The catalyst particles may be considered to be spheres.
2. The diffusion coefficients of each component are independent of position within a particle.
3. The particles are isothermal.
4. Knudsen diffusion is not experienced.

Assumption 1 is discussed by Nielsen (1956). Assumption 2 is believed to be reasonable in view of the accuracy to which the diffusion coefficients in a porous medium can be estimated. As a result of this assumption a small error is introduced into the calculated gas compositions in a particle (Delbridge, 1968; Wei, 1963). (The mole fractions do not sum to 1 inside the particle; however, at the center this sum varied over the narrow range 0.97 to 1.03.) The third assumption may be easily validated by application of the relation derived by Prater (1958) for the temperature difference between the bulk phase and a region interior to the pellet surface. The maximum temperature difference calculated from this relation is approximately 2.5° C. Assumption 4 is based on the paper by Bokhoven and van Raayen (1954).

We may now develop the equations for the molar flux of a reference substance across the surface. The reaction under consideration is



In the ensuing discussion the symbol ν_i represents the stoichiometric coefficient of the i th component in the reaction scheme given in Equation 21. Following the ordinary convention, ν_i is positive if the component is a product, negative if the component is a reactant, and zero if the component is an inert substance.

A mole balance for component i gives

$$\frac{1}{r^2} \frac{d}{dr} (r^2 N_i) = V_i \quad (22)$$

where N_i is the molar flux of the i th component in the r -direction and V_i is the rate of formation of component i . The rate of formation, V_i , is the rate of formation of component i per unit volume of catalyst pellet. (It is found from the rate expression developed above by dividing by $1 - \epsilon$, where ϵ is the void fraction for the laboratory packed bed.)

The molar flux, N_i , may be related to the concentration gradient by

$$N_i = -CD_{ie} \frac{dX_i}{dr} + X_i \sum_{j=1}^4 N_j \quad (23)$$

The following relation exists between the molar fluxes at steady state of any two components i and j

$$\nu_i N_j = \nu_j N_i \quad (24)$$

Equation 24 implies that the molar flux of any inert component is equal to zero.

The boundary conditions for Equation 22 are

$$\begin{aligned} N_i &= 0 \quad \text{at } r = 0 \\ X_i &= X_{i0} \quad \text{at } r = R' \end{aligned} \quad (25)$$

where X_{i0} is the mole fraction at the surface and this will be assumed to be the same as in the gas phase. (Such an assumption is valid at the high gas velocities found in present-day plant converters.)

Substitution of Equation 24 into Equation 23 and utilization of the relationship

$$\sum_{j=1}^3 \nu_j = -2 \quad (26)$$

give

$$N_i = \frac{-CD_{ie} \frac{dX_i}{dr}}{1 + 2 \frac{X_i}{\nu_i}} \quad (27)$$

If Equation 24 is employed again, this time in conjunction with the just-derived result, Equation 27 yields

$$\frac{-CD_{je} \frac{dX_j}{dr}}{1 + 2 \frac{X_j}{\nu_j}} = \frac{\nu_j}{\nu_i} \left[\frac{-CD_{ie} \frac{dX_i}{dr}}{1 + 2 \frac{X_i}{\nu_i}} \right] \quad (28)$$

Integrating this equation twice leads to

$$X_j = -\frac{\nu_j}{2} + \frac{1}{2}(\nu_j + 2X_{j0}) \left(\frac{\nu_i + 2X_i}{\nu_i + 2X_{i0}} \right)^{D_{ie}/D_{je}} \quad (29)$$

As a consequence of this relation, the solution of only one mole balance (Equation 22) need be considered.

Combination of Equation 22 with Equation 27 and performance of some differentiation and manipulation lead to

$$\frac{d^2X_i}{dr^2} - \left(\frac{2}{\nu_i + 2X_i} \right) \left(\frac{dX_i}{dr} \right)^2 + \frac{2}{r} \frac{dX_i}{dr} = - \left(\frac{\nu_i + 2X_i}{CD_{ie}} \right) f \quad (30)$$

In writing this equation the symbol f has been introduced to represent the rate of reaction, a quantity related to the rate of formation of a component i by

$$V_i = \nu_i f \quad (31)$$

Introducing $Z' = \frac{r}{R'}$ we obtain

$$\begin{aligned} \frac{d^2X_i}{dZ'^2} - \left(\frac{2}{\nu_i + 2X_i} \right) \left(\frac{dX_i}{dZ'} \right)^2 + \frac{2}{Z'} \frac{dX_i}{dZ'} = - \left[\frac{R'^2}{CD_{ie}} \right] (\nu_i + 2X_i) f; \\ \frac{dX_i}{dZ'} = 0 \text{ at } Z' = 0; \quad X_i = X_{i0} \text{ at } Z' = 1 \end{aligned} \quad (32)$$

This is a two-point boundary-value problem and may be treated numerically by a shooting technique—that is, one must either choose the unknown condition at the center ($Z' = 0$) and integrate Equation 32 toward the surface or choose the unknown condition at the surface ($Z' = 1$) and integrate toward the center. In either case, the value of the chosen quantity is varied and integration is repeated until the remaining boundary condition is satisfied. It is convenient to write Equation 32 for the product component ($i = 3$), thereby assuring that the denominator in the second term of Equation 32 cannot go to zero. If the integration is carried out from the center toward the surface, it is necessary on the first integration step to rewrite Equation 32 because of the third term. This type of problem has been treated by Weisz and Hicks (1962). We have found that one may use the inward integration procedure in the numerical solution of Equation 32, but the equations are slightly unstable, and it is necessary to determine the flux at the surface to within 1 part in 10^5 in order to satisfy the boundary condition at the center with tolerable accuracy (Simon, 1968). This surface flux may then be substituted into the following equation, yielding the effectiveness factor:

$$\xi = \frac{3 \left(\frac{-dX_3}{dZ'} \right)}{\frac{R'^2}{CD_{3e}} f(X_{i0}, T, P) (2 + 2X_{30}) \left(\frac{1}{1 - \epsilon} \right)} \quad (33)$$

Values of ξ calculated from Equation 33 are influenced by the origin of the quantities C , R' , D_{3e} , and ϵ . The values of D_{2e} and D_{1e} also enter into the calculations by virtue of Equation 29.

The total concentration, C , is found from

$$C = P/(\delta RT) \quad (34)$$

The radius, R' , for spheres equivalent to industrial size particles may be calculated from

$$R' = \Lambda/2 \psi \quad (35)$$

where Λ and ψ are the equivalent diameter and shape factor, respectively (Nielsen, 1956). For industrial particles of 6- to 10-mm. range the particle radius is 2.85 mm. Considering the effective diffusion coefficients one should note that the range of industrial operation is outside the region where Knudsen diffusion is important (Bokhoven and van Raayen, 1954) and therefore we use the relation given by Wheeler (1955):

$$D_{ie} = \frac{1}{2} \theta D_i \quad (36)$$

where θ is the intraparticle porosity and D_i is the bulk diffusion coefficient of component i . The porosity is approximately 0.52 according to Hoogschagen (1955). The value of D_i used in Equation 36 is found in the following manner (Fairbanks and Wilke, 1950). The bulk diffusion coefficient of component i at 0°C . and 1 atm. is given by

$$D_{i^\circ} = \frac{1 - X_{ig}}{\sum_{j=1}^3 \left(\frac{X_{jg}}{D_{ji^\circ}} \right) - \left(\frac{X_{ig}}{D_{ii^\circ}} \right)}, \quad i = 1, 2, 3 \quad (37)$$

The values used in the calculations are (Nielsen, 1956)

$$D_{31^\circ} = D_{13^\circ} = 0.161 \text{ sq. cm./sec.}$$

$$D_{21^\circ} = D_{12^\circ} = 0.571 \text{ sq. cm./sec.}$$

$$D_{32^\circ} = D_{23^\circ} = 0.629 \text{ sq. cm./sec.}$$

and (of course) the D_{ii° are not required.

The diffusion coefficients calculated from Equation 37 are then corrected to the temperature and pressure at the surface of the catalyst pellet by Equation 38.

$$D_i = D_{i^\circ} \left(\frac{T}{273} \right)^{1.75} \frac{1}{P} \quad (38)$$

where P is in atmospheres.

The void fraction of the laboratory reactor, ϵ , was not reported. We have estimated it to be 0.46, approximately the same as the void fraction of an industrial converter charged with 6- to 10-mm. particles. The selection of a larger value of the void fraction (of the laboratory converter) would result in calculation of larger values of the effectiveness factors.

The results of numerous calculations of ξ for various values of P and T may be summarized in the form of a simple expression in which ξ is given as a function of η and T with P as a parameter,

$$\xi = b_0 + b_1 T + b_2 \eta + b_3 T^2 + b_4 \eta^2 + b_5 T^3 + b_6 \eta^3 \quad (39)$$

The conversion, η , refers to the conversion of nitrogen as measured from the reference mixture ($\eta = 0$) which has the following composition: a 3 to 1 H_2/N_2 ratio and 12.7% inerts. The temperature, T , is in degrees Kelvin, and the constants in Equation 39 are given for various pressures in Table I. The effect of pressure on the effectiveness factor is such that a higher pressure will cause a lower effectiveness factor. This is contrary to the results calculated by Bokhoven and van Raayen

Table I. Constants for Equation 39

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

(1954) by representing the rate as pseudo-first-order, but in agreement with the results obtained by Kubota and Shindo (1956). Similar calculations have been made for other H_2/N_2 ratios. There were variations of the resulting effectiveness factors from those given here, but the over-all effect on the design of converters for industrial use was negligible.

Conclusions

For fine catalyst with no diffusion restriction, the relation between the rate of formation of ammonia, V_3 , and the temperature, pressure, and composition in the bulk gas phase may be obtained from Equations 2, 5, 6, 7, 8, and 19.

For catalyst of 6- to 10-mm. particle size, the corresponding relation is

$$\text{Rate} = V_3 \cdot \xi \quad (40)$$

where ξ is as given in Equation 39. Several minor additional correction factors are necessary to correct this equation for the effects of particle size on reduction, poisoning, and catalyst aging (Nielsen, 1956).

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Nomenclature

A = cross-sectional area of experimental reactor
 a_i = activity of component i
 b_i = constants in Equation 39
 C = total concentration
 D_i = diffusion coefficient of component i
 D_i^0 = diffusion coefficient of component i at 0° C. and 1 atm.
 D_{ji} = diffusion coefficient of component j in component i
 D_{ie} = effective diffusion coefficient of component i
 E = activation energy for reverse reaction
 f = rate of reaction
 f_i = fugacity of component i in mixture
 f_i^* = fugacity of component i at standard state
 f_i^0 = fugacity of pure component i at temperature and pressure of system
 F^0 = total molar flow at reactor inlet
 F_i^0 = molar flow rate of component i at reactor inlet
 H = frequency factor for reverse reaction
 i, j = as suffixes: 1 refers to N_2 , 2 refers to H_2 , 3 refers to NH_3 , 4 refers to inerts
 k = rate constant for decomposition of ammonia
 K_a = equilibrium constant in terms of activities
 L = length of experimental reactor
 N_i = molar flux of component i in r direction
 P = pressure
 R = universal gas constant
 R' = radius of spherical particle
 r = radial coordinate of spherical particle
 T = temperature
 V_i = rate of formation of component i
 X_i = mole fraction of component i in catalyst pellet

X_{ig} = mole fraction of component i in gas (bulk) phase
 z = coordinate measuring distance along reactor
 Z' = dimensionless radial coordinate of a spherical particle

GREEK SYMBOLS

α = kinetic parameter
 γ_i = activity coefficient
 η = conversion based on nitrogen
 η_e = conversion of outlet mixture
 ξ = effectiveness factor
 ϵ = void fraction of laboratory reactor
 ν_i = stoichiometric coefficient of component i
 δ = compressibility factor
 Λ = equivalent diameter
 ψ = shape factor
 θ = intraparticle porosity

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