results as well as an extension into the area of the gas-in-liquid spray tower.

ACKNOWLEDGMENT

The financial support of the Monsanto Chemical Company in the form of a fellowship to R. E. C. Weaver during a part of the period covered by this investigation and of the California Research Corporation for a grant-in-aid is gratefully acknowledged. The present work was made possible through this support.

NOTATION

$1 - \epsilon$ = volumetric holdup
V_S = slip velocity, ft./sec. = vectorial difference between the average discontinuous fluid velocity and the average continuous velocity.
V_T = droplet terminal velocity, ft./sec.
Re = Reynolds number
C_D = drag coefficient

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Reaction Rates in the Synthesis of Ammonia

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A study has been made of the reaction rates of mixtures of hydrogen and nitrogen to form ammonia over a doubly promoted iron catalyst at 400° and 450°C. and at pressures up to 1,000 atm. In this work particular care has been taken to obtain data representing the true kinetics of the reaction. The reactor used was essentially isothermal, and the effects of diffusion have been reduced to a minimum. The results have been correlated by the use of the mechanism proposed by Temkin and Pyschev (*19*) with moderate success.

The kinetics of the ammonia synthesis reaction have been the subject of many investigations, and results have been published by Adams and Comings (*1*), Uchida and Kuraishi (*21*), Bokhoven and van Raayen (*3*), Siderov and Livshits (*17*, *18*), Nielsen (*14*), Emmett and Kummer (*6*), Almquist and Crittenden (*2*), and Larson and Tour (*13*). Of these investigations only three (*1*, *17*, *18*) make a claim to an essentially isothermal catalyst bed; the others report temperature variations in the bed, running as high as 15° in one case (*14*). Siderov and Livshits (*18*) report the highest pressure (500 atm.), and in no case has the entire diffusion problem been analyzed, although Bokhoven and his associates (*3*, *8*) have done valuable work on the question of diffusion within the catalyst pores, and Adams and Comings (*1*) report a calculation for the effect of diffusion between the bulk of the gas and the surface of the catalyst.

APPARATUS

Figure 1 shows the general flow diagram for the process. The mixture of hydrogen and nitrogen was compressed over mercury in the *U*-tube made from two 3-liter vessels, *E*. The pump, *B*, pumped oil into one leg of the *U*-tube and could develop a pressure of 20,000 lb./sq. in. The compressed synthesis gas was stored in the two 3.5-liter vessels, *H*; these vessels could store enough gas for about a week of continuous running at about 400 atm. pressure in the reactor.

During a run the gases passed from the storage vessels, *H*, through the clean-up train (*14*, *13*, *8*, *12*, *11*) to the reactor, *R*. This train consisted of a 1-liter vessel filled with sodium hydroxide pellets and activated carbon; here carbon dioxide and possibly oil mist were removed. Next came a 300 cc. vessel containing finely divided copper maintained at 300°C.; the copper was made from the reduction of copper hydroxide in a stream of hydrogen or synthesis gas. This vessel was intended to remove oxygen. Any water formed was removed in the condenser and separator (*8*, *12*) followed by the vessels, *M*, containing silica gel.

After passing through the reactor the gases were expanded to atmospheric pressure in the heated valve, *S*; the ammonia was absorbed in the sulfuric acid bubblers, *T*, and the rate of flow of the residual hydrogen-nitrogen was obtained by the wet test meter, *U*.

The reactor itself (Figure 2) was made from a 14-in. length of standard 9/16 × 3/16 in. tubing. 1.625 g. of unreduced catalyst were contained in a 5-cm. length of this tube, and three thermocouples were placed in the bed. In no case was the variation in temperature among these thermocouples more than 3°C., and in most cases it was less than 1°C. The catalyst occupied a space of 0.602 cc., not counting the thermocouple wires (30-gauge iron constantan); the void fraction was 0.46. The particles in the bed were roughly 2 mm. in diameter (9–10 mesh). The catalyst was activated by the standard procedure (*14*). Several external heaters were installed to control the longitudinal temperature variation within the bed.

The design of the reactor described above was determined by the following factors. (1) The large length-to-diameter ratio insured the highest possible linear velocity past the pellets, thus reducing the effect of longitudinal diffusion and diffusion to the catalyst surface to a minimum. (2) The small pellet size reduced the effect of diffusion within the catalyst pores to a minimum. (3) The whole arrangement, with several separately controlled heaters, resulted in very good control of temperature in the bed. (4) The small diameter held the radial temperature differences to minimum values. Usually a bed diameter to pellet diameter of at least ten is used to reduce

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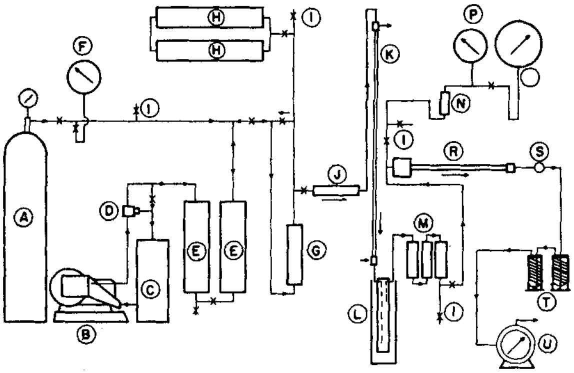

Fig. 1. Flow diagram.

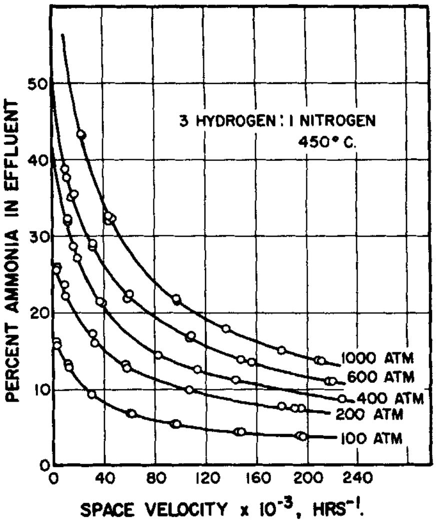

Fig. 3. The effect of space velocity on the ammonia concentration in the product.

radial gradients of temperature, velocity, and composition; however even a rather large temperature gradient over the 2.38-mm. radius of the present reactor does not give a large temperature difference.

RESULTS

The data were obtained directly as a precentage ammonia in the gas leaving the reactor as a function of space velocity, pressure, temperature, and composition of the feed. Figure 3 illustrates the data obtained for the 3 : 1 hydrogen-nitrogen feed mixture. Wherever possible the curves have been extrapolated to the equilibrium composition (*12*, *11*) at a zero space velocity.

The usual method of obtaining the rate of reaction from information on the composition of the gas leaving the reactor is based on the equation

$$r = \frac{dx}{d\left(\frac{1}{S_0}\right)} \tag{1}$$

derived from the basic definitions (*9*)

$$r\,dV = F\,dx \tag{2}$$

and

$$S_0 = \frac{F}{V} \tag{3}$$

The space-time yield is related to the degree of conversion by

$$x = \frac{\sigma}{S_0} \tag{4}$$

for the reaction being considered. Thus the rate can be calculated from data on the space-time yield by the equation

$$r = \sigma - S_0 \frac{d\sigma}{dS_0} \tag{5}$$

Curves of the space-time yield as a function of space velocity are given in Figure 4. These curves are easily plotted from the original experimental data, and they have the advantage of permitting a more reliable curve to be drawn in the region of low S_0 than could be done by the use of x vs. $1/S_0$ [refer to Equation (1)]. All the curves must pass through the origin, and in addition

$$\left(\frac{d\sigma}{dS_0}\right)_{S_0=0} = \left(\frac{Z_{NH_3}}{1 + Z_{NH_3}}\right)_{equilibrium} \tag{6}$$

The precision of the points obtained at high S_0 is considerably higher than that for the points at low S_0, so it is very helpful to know how the curves begin.

The determination of r from the experimental data as described above is based on the assumption of plug flow through the reactor with no longitudinal diffusion. It will be shown below that longitudinal diffusion is not significant, and the shape of the reactor makes the assumption of plug flow at least more plausible than the assumption would be for a short, fat reactor. Incidentally, for a reactor with complete internal mixing Equation (5) should be replaced by $r = \sigma$.

Equation (5) can be used with the data of Figure 4 to obtain the reaction rates as a function of pressure, temperature, initial composition, and mole-fraction ammonia. The rates for all the conditions investigated are given in Figures 5 to 8; the procedure used involved the finding of an empirical, analytical expression for σ as a function of S_0. An advantage of reporting the rate in this form is that it is independent of any assumed mechanism of reaction; it can be directly used for the design of a reactor.

INTERPRETATION OF THE DATA BY THE TEMKIN MECHANISM

The most plausible explanation of the kinetics of the ammonia synthesis reaction is usually accepted as that of Temkin

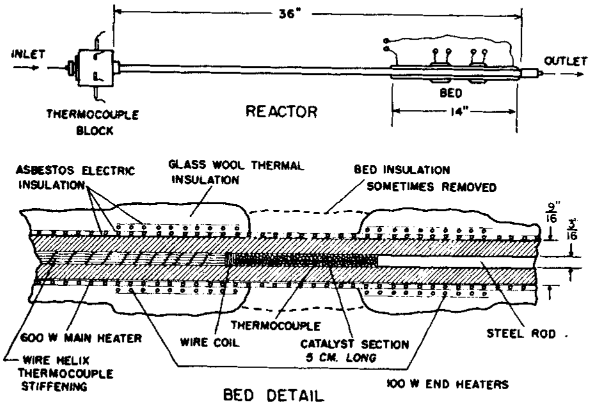

Fig. 2. Reactor details.

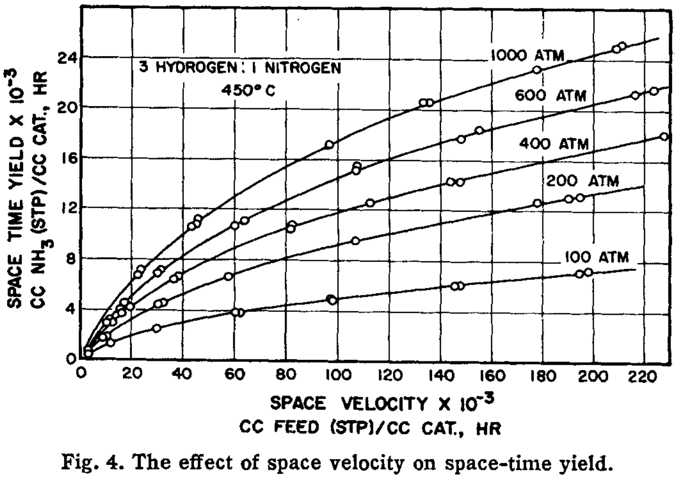

Fig. 4. The effect of space velocity on space-time yield.

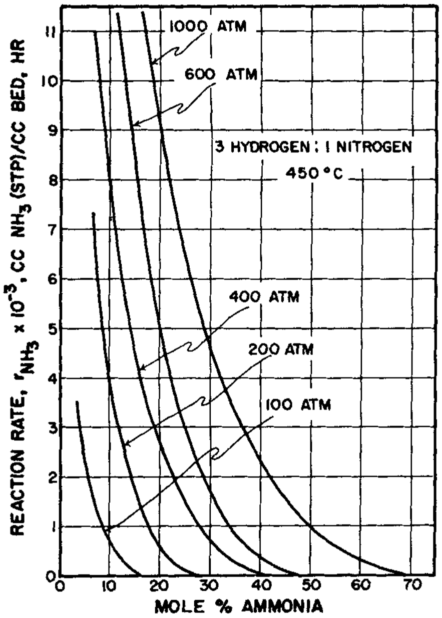

Fig. 5. Reaction rates for the 3:1 mixture at 450°C.

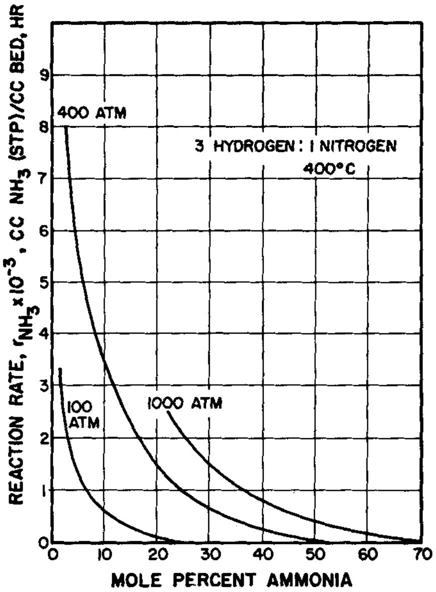

Fig. 6. Reaction rates for the 3:1 mixture at 400°C.

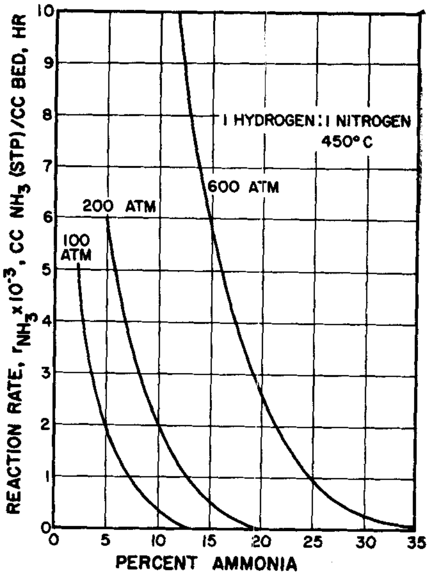

Fig. 7. Reaction rates for the 1:1 mixture at 450°C.

and Pyzhev (*20*). Among the assumptions involved in this mechanism are:

1. The rate of adsorption of nitrogen on the surface of the catalyst is the rate-controlling step. From this it follows that the adsorbed nitrogen is in equilibrium with the hydrogen and ammonia in the gas phase.
2. The adsorption of nitrogen is described by the Temkin isotherm, which is based on a linear variation of activation energy of adsorption and heat of adsorption with the fraction of available surface covered.
3. The nitrogen adsorption phenomena are not affected by the presence of varying amounts of hydrogen and ammonia.

The above factors have been extensively discussed in the literature, and much experimental evidence exists in support of these ideas. As an example of such a discussion the recent work edited by Emmett may be cited (*5*).

The rate equation was originally proposed (*20*) with partial pressures used as a measure of concentration, but more recently the equation has been revised for use at high pressures by the introduction of fugacities and an additional correction term (*19*). This latter equation is

$$r = \left(k_1 f_{N_2}\left[\frac{f_{H_2}^{3}}{f_{NH_3}^{2}}\right]^{\alpha} - k_2\left[\frac{f_{NH_3}^{2}}{f_{H_2}^{3}}\right]^{1-\alpha}\right)_e \exp\frac{(\alpha \bar{V}_S - \bar{V}_a)P}{RT} \quad (7)$$

where k_1 and k_2 are related by

$$k_1 = k_2 K_e \quad (8)$$

Let us define

$$\psi = \exp\frac{(\alpha \bar{V}_S - \bar{V}_a)P}{RT} \quad (9)$$

and rearrange Equation (7) to give

$$r = k_2\left(\left[K_e \frac{f_{N_2} f_{H_2}^{3}}{f_{NH_3}^{2}} - 1\right] \cdot \left[\frac{f_{NH_3}^{2}}{f_{H_2}^{3}}\right]^{1-\alpha}\right)\psi \quad (10)$$

According to the theory on which Equation (10) is based, k_2 should be a function of temperature only, and ψ should be a function of temperature and pressure only. From experimental data the best values of $k_2\psi$ and α can be found. The quantity ψ can be calculated, although there is difficulty in estimating the values of $\bar{V}_S$ and $\bar{V}_a$. Temkin (*19*) suggests using the molar value of solid nitrogen, 27 cc./g. mole, for both $\bar{V}_S$ and $\bar{V}_a$.

The value of $k_2\psi$, or k_2, if the above values of $\bar{V}_a$ and $\bar{V}_S$ are used, as well as the value of α can be found from the data on reaction rate vs. composition at various constant pressures and temperature. It will be seen that α is fairly independent of pressure and temperature but that k_2 is not independent of pressure, as required by the ideas leading to Equation (*10*). The constants are con-

Table 1. Experimental Values of the Temkin Rate Constant

Temperature and initial composition	Pressure, atm.	ψ	$k_2 \times 10^{-4}$ cc. S.T.P. NH_3/hr. cc. atm.$^{-1/2}$
450°C. 3H$_2$:1N$_2$	100	0.978	1.82
	200	0.956	2.19
	400	0.913	1.10
	600	0.874	0.830
	1000	0.798	0.396
400°C. 3H$_2$:1N$_2$	100	0.976	0.282
	400	0.906	0.110
	1000	0.783	0.025
450°C. 1H$_2$:1N$_2$	100	0.978	1.41
	200	0.956	1.23
	600	0.874	0.690
450°C. 2H$_2$:1N$_2$	100	0.978	1.78
	200	0.956	1.58
	600	0.874	0.95

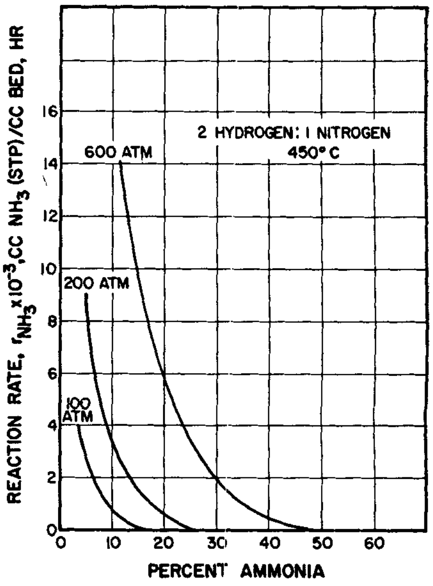

Fig. 8. Reaction rates for the 2:1 mixture at 450°C.

veniently evaluated if Equation (10) is put into the form

$$\log\left[\frac{r}{K_e\,\dfrac{f_{N_2}f_{H_2}^{\;3}}{f_{NH_3}^{\;2}}}\right] = \log k_2\psi + (1-\alpha)\log\left(\frac{f_{NH_3}^{\;2}}{f_{H_2}^{\;3}}\right) \qquad (11)$$

or

$$\log Y = \log k_2\psi + (1-\alpha)\log X \qquad (12)$$

The values of $k_2\psi$ and $(1-\alpha)$ can be found from a plot of log Y vs. log X, (Figures 9 to 12). However the choice of a method for the calculation of Y and X from the composition of the gas from the reactor presents a difficult problem.

Three methods for the calculations of the fugacities were considered: ideal solutions, Joffe's method (*10*), and the method of Redlich, *et al.* (*15*). The last method listed had to be abandoned as impractical when it was found impossible to fit the Redlich and Kwong (*16*) equation of state to data on pure ammonia with a reasonable precision. In order to test the other two methods values of the fugacity ratio at equilibrium were calculated at a series of pressures and compared to the experimental results obtained from the data of Larson and Dodge (*12*) and the equations

$$K_e = K_\nu K_z p^{-2} \qquad (13)$$

$$\Delta G^0 = -RT\ln K_e \qquad (14)$$

$$K_z = \frac{Z_{NH_3}^{\;2}}{Z_{N_2}Z_{H_2}^{\;3}} \qquad (15)$$

The results are shown in Figure 13. In all cases the generalized charts of Hougen and Watson (*9*) were used, and Kay's rule was used with Joffe's method. Although Method 4 is the best, Method 2 works suprisingly well, and since it is so much simpler to use, this method was chosen for succeeding calculations. In addition Figure 14 points out another reason for being content with the ideal-solution method. At a given pressure and temperature the ν ratio is a constant for ideal solutions. The value of this ratio is the experimental one obtained from Equation (13) and does not involve the use of the generalized charts. Now for a nonideal solution the changing of the composition at constant temperature and pressure results in a change in the ν ratio; it no longer equals K_ν. The extreme sensitiveness of Joffe's method to the way in which the generalized charts are used is illustrated. In view of this behavior it was decided that the ideal-solution method was about as reliable as that of Joffe. If it turned out that the kinetic data were accurate and faithfully represented by Equation (10), at least at constant temperature, pressure, and initial composition, it would be required that the ν ratio vary as given by the dotted curve in Figure 14. It would be very interesting to know the P-V-T relations of suitable mixtures in order to be able to calculate the actual values of the ν-ratio.

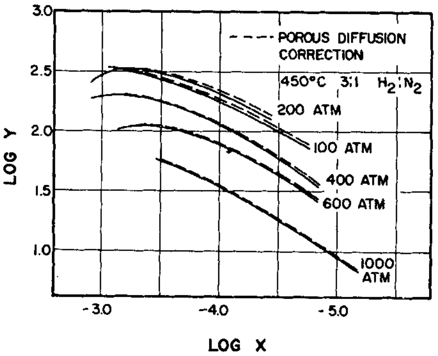

Fig. 9. Test of the Temkin and Pyshev equation for the 3:1 mixture at 450°C.

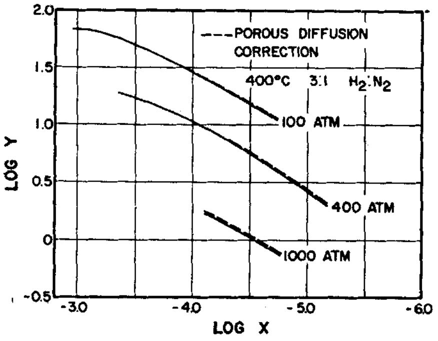

Fig. 10. Test of the Temkin and Pyshev equation for the 3:1 mixture at 400°C.

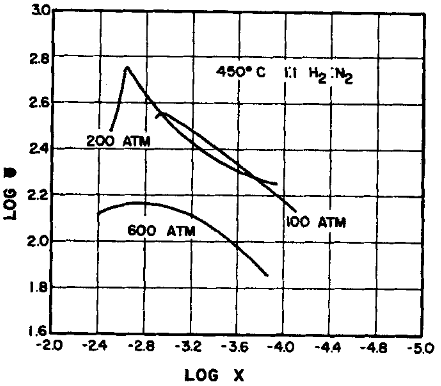

Fig. 11. Test of the Temkin and Pyshev equation for the 1:1 mixture at 450°C.

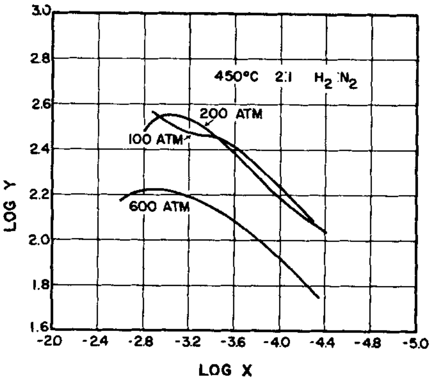

Fig. 12. Test of the Temkin and Pyshev equation for the 2:1 mixture at 450°C.

Figures 9 to 12 show that Equation (10) gives a fairly reasonable representation of the data at a given pressure, temperature, and initial composition. Most of these figures do not include a small correction due to diffusion within the catalyst pores to be discussed below. By the statement that the ψ correction is not included, it is emphasized that log Y rather than log Y/ψ is plotted vs. log X. Supposedly all the lines in Figure 13 should be bought into one if log (Y/ψ) were used, but actual use of the ψ term does not bring the lines much closer together; the variation in ψ is much too small.

The value of α was estimated from the slopes of the lines over their right-hand portions, where they approximate straight lines. Rather than obtain a separate α value for each curve a mean value of 0.5 is proposed for all curves. It is of interest to observe that this value of α, and in fact the whole Temkin-Pyzhev expression, can be obtained by the simplified treatment proposed by Weller (*22*) and by Boudart (*3a*). The straight line defined by the value of α is then considered to coincide with the experimental curve at a point about in the middle of the fairly straight portion of the curves. In this way the values of k_2 given in Table 1 were obtained.

From the values of k_2 given for 400° and 450°C. there can be calculated the following energies of activation:

Pressure	Energy of activation
100	36,000 cal./g. mole
400	44,000 cal./g. mole
1000	53,000 cal./g. mole

Since these values are based on only two temperatures, they are not very precise; indeed the value at 100 atm. is substantially lower than that found by Emmett and Kummer (*6*).

Diffusion Effects

The accuracy of the preceding treatment depends on the absence of diffusion effects of any kind. It will now be shown that under the experimental conditions of this investigation these effects were indeed small.

Diffusion into the Catalyst Pores

The methods of Bokhoven and van Raayen (*3*) will be followed, and the calculations will be based on the rate of transfer of ammonia from the interior of a spherical catalyst pellet to the surface. The rate of reaction will be expressed in terms of a pseudo first-order rate constant defined by the expression

Reaction rate, g.mole NH_3/cc.

catalyst sec. $= k'\rho_M(Z_e - Z)_{NH_3}$ (16)

In terms of the value of r reported in Figures 5 to 8

$$k' = \frac{r}{(22{,}400)(3600)} \cdot \frac{\rho_c}{\rho_B \rho_M (Z_e - Z)_{\mathrm{NH_3}}} \qquad (17)$$

$$k' = 2.29 \times 10^{-8} r/\rho_M \phi \qquad (18)$$

where

$$\phi = (Z_e - Z)_{\mathrm{NH_3}} \qquad (19)$$

Now the rate of diffusion will be defined by

$$\text{Diffusion rate, g.moles } \mathrm{NH_3}/\text{sq. cm. sec.} = -D_{eff}\rho_M (dZ_{\mathrm{NH_3}}/dr_c) \qquad (20)$$

If a mass balance is made over a spherical shell of thickness dr, there is obtained

$$\frac{d^2\phi}{dy^2} + \frac{2}{y}\frac{d\phi}{dy} = h^2\phi \qquad (21)$$

where

$$r_c = yR \qquad (22)$$

and

$$h^2 = \frac{k'R^2}{D_{eff}} \qquad (23)$$

Integration of Equation (21) gives

$$\phi = \frac{\phi_s \sinh hy}{y \sinh h} \qquad (24)$$

$$\phi_s = \phi \quad \text{at} \quad y = 1.0$$

If an effectiveness factor is defined as the ratio of the reaction rate per pellet to that which would be obtained if the diffusion from the interior were very fast, one gets

$$E = \frac{4\pi \rho_M k' R^3 \int_0^1 \phi y^2 \, dy}{\frac{4}{3}\pi R^3 \rho_M k' \phi_s} \qquad (25)$$

and

$$E = \frac{3}{h}\left[\coth h - \frac{1}{h}\right] \qquad (26)$$

Values for k' were calculated from the data of Figures 9 to 12 by the use of Equation (18) with ϕ equal to ϕ_s. This result is of course very approximate, for the data do not actually follow Equation (18). Values for D_{eff} were calculated by the assumption, for the purpose of estimating the diffusivity, that ammonia was an ideal gas and by the use of the data of Bokhoven and van Raayen (*3*) for diffusion rates through porous catalyst pellets.

The effect of porous diffusion is shown graphically by the dashed lines of Figures 9 and 10. At 400°C. the lowest value of E is 0.90, and at 450°C. the lowest values of E is 0.88; both are for the lowest pressure, 100 atm. As is to be expected the value of E is smaller when the reaction rate is larger, that is away from equilibrium, at the right-hand extremities of the curves of Figures 9 and 10. There appears to be no way to tell from these data whether surface migration of the ammonia or other adsorbed fragments adds to the rate of transfer within the catalyst pellets at the highest pressures.

Diffusion to the Catalyst Surface

In order to evaluate the effect of diffusion between the bulk of the gas and the surface of the catalyst pellets the partial pressure drop for nitrogen necessary to give the observed reaction rate was calculated. The basic equation is

$$r = 2\rho_B (22{,}400) k_g a_m \, \Delta P_{N_2} \qquad (27)$$

For these rough estimates ideal gases are assumed. The factor of two appears in Equation (27), since r refers to the rate of reaction of ammonia. The coefficient k_g was found from the j_D factors published by Gamson, Thodos, and Hougen (*7*). The Schmidt number used was 1.08, based on diffusion in the system hydrogen-nitrogen. After one uses the equation given by these authors for j_D and suitable values for the constants, Equation (27) becomes

$$\Delta P_{N_2} = 0.0190 r / S_0^{0.49} \qquad (28)$$

Calculations with Equation (28) show that even at the lowest space velocities and conversions the value of $\Delta P_{\mathrm{N_2}}$ is a small fraction of the total nitrogen partial pressure.

Longitudinal Diffusion

A material balance on the hydrogen entering and leaving a differential length of the reactor gives

$$r = -\tfrac{2}{3}(22{,}400)(3600)\frac{d(Z_{\mathrm{H_2}} G_M)}{dl} + \tfrac{2}{3}(22{,}400)(3600) D_e \rho_M \frac{d^2 Z_{\mathrm{H_2}}}{dl^2} \qquad (29)$$

where

$$G_M = \frac{S_0 L}{(22{,}400)(3600)}\left(\frac{1}{1 + Z_{\mathrm{NH_3}}}\right) \qquad (30)$$

In the above equation S_0 is a constant corresponding to a certain feed rate. If the second term in Equation (29) is omitted, the first term becomes simply r as defined by Equation (2). The value of $d^2Z_{\mathrm{H_2}}/dl^2$ and thus the second term of Equation (29) can be approximated from the rate data already obtained by neglecting the second term. If this term is only a small fraction of the first, that is of the value of r, it may be concluded that longitudinal diffusion is not important. If the second terms is an appreciable fraction of the first, the simple procedure for the calculation of $d^2Z_{\mathrm{H_2}}/dl^2$ to be given below becomes invalid.

In the absence of mass transfer effects the reaction rate at any point in the reactor will be a function of Z only at a given pressure, temperature, space velocity, and initial composition. The de-

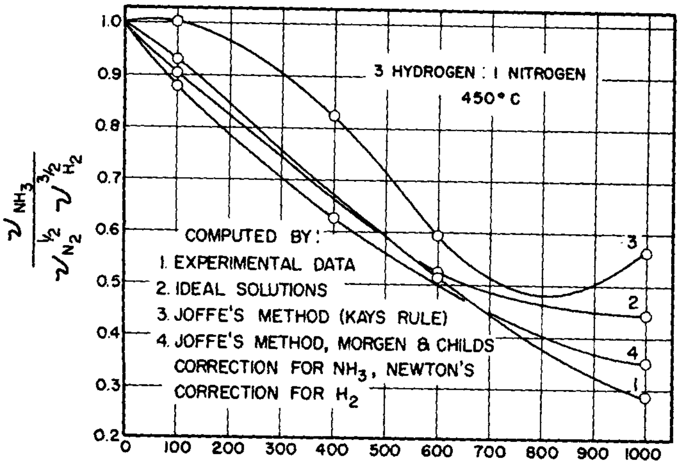

Fig. 13. Test of alternate methods of calculating fugacities at equilibrium.

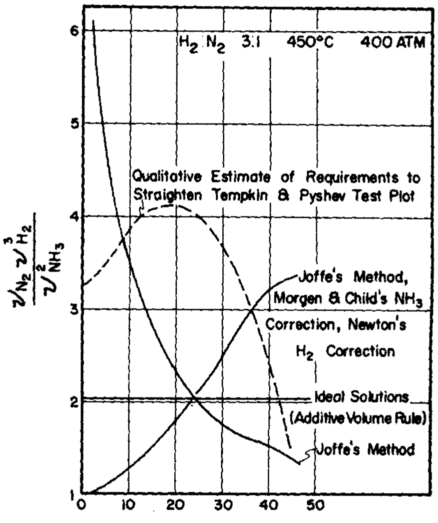

Fig. 14. Variation of fugacity-coefficient ratio with conversion.

gree of conversion will depend only on the time of contact, so that the composition at a point one tenth of the way through the reactor at an S_0 of 10,000 will correspond to the composition at the exit of the reactor at an S_0 of 100,000. In this way a curve is obtained of Z_{H_2} as a function of l, and thus $d\,Z_{H_2}/dl^2$ can be obtained. The value of D_e is difficult to estimate. The work of Deisler and Wilhelm (*4*) and of McHenry and Wilhelm (*13a*) indicate that D_e is two or three times the ordinary molecular diffusivity at much higher Reynolds numbers than those used in this work. In view of this uncertainty a value of D_e equal to three times the molecular diffusivity has been used here.

The longitudinal diffusion term in Equation (21) has been calculated at several positions in the bed and for several space velocities. Even at the lowest space velocity and at points very near the entrance to the bed longitudinal diffusion is not important.

CONCLUSIONS

As a result of the tests of the Temkin mechanism it can be stated that the method correlates data at any one temperature, pressure, and initial composition fairly well at degrees of conversion not too close to equilibrium. It may be remarked that most of the erratic behavior of the curves of log Y vs. log X, particularly noticeable in Figures 11 and 12, can probably be explained by the fact that, as equilibrium is approached, both the numerator and the denominator in the expression for Y [Equation (11)] are approaching zero. An error of only a few per cent in the reaction rate is multiplied as much as one hundred fold in the value of Y at conversions near equilibrium.

Although the effect of space velocity may be considered as fairly well accounted for by the Temkin mechanism, the effect of pressure is not predicted so well. In order to account for the separation of the curves in Figure 9 for instance, the partial molar volumes of the adsorbed nitrogen would need to be in the order of 200 to 500 cc./g. mole, rather that 20 to 50 cc./g. mole as is more probably the case. As a matter of fact the effect of ψ when one uses the latter values is so small that the curves for 100 and 200 atm. may be considered roughly in accord with the theory; similar remarks apply to Figures 11 and 12.

The available P-V-T- data on mixtures of hydrogen, nitrogen, and ammonia have been used recently to show qualitatively the effect on the reaction rates of using the correct fugacities instead of those predicted by ideal solutions (*2a*). Although the range of the P-V-T data does not permit a quantitative comparison with the data of the present work, the results of reference (*2a*) indicate that the curves of Figures 9 to 12 would not be straightened by the use of the correct, real-solution fugacities.

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NOTATION

D_e = longitudinal eddy diffusivity, sq. cm./sec.
D_{eff} = effective diffusivity through porous catalyst, sq. cm./sec.
E = effectiveness factor
F = feed rate, cc. at standard temperature and pressure/hr.
G_M = gas mass velocity at a point in the reactor, g. mole/sec. sq. cm.
L = length of reactor, 5.0 cm.
K_e = equilibrium constant, $f_{NH_3}{}^2/f_{H_2}{}^3 f_{N_2}$
K_Z = ratio of mole fraction at equilibrium $Z_{NH_3}{}^2/Z_{H_2}{}^3 Z_{N_2}$
K_ν = ratio of fugacity coefficients at equilibrium, $\nu_{NH_3}{}^2/\nu_{N_2}\nu_{H_2}{}^3$
R = radius of spherical catalyst pellet. cm.
S_0 = space velocity, cc. S.T.P. feed/(hr.)(cc. bed)
V = volume of bed, cc.
X = $f_{NH_3}{}^2/f_{H_2}{}^3$

$$Y = r \Big/ \left[K_e \frac{f_{N_2} f_{H_2}{}^3}{f_{NH_3}{}^2} - 1 \right]$$

Z_i = mole fraction
a_m = surface of catalyst per unit mass, 8.3 sq. cm./g.
f_i = fugacity, atm.

$$h = \sqrt{\frac{k'R^2}{D_{eff}}}$$

j_D = Chilton and Colburn mass transfer factor
k_1 = forward reaction rate constant, cc. S.T.P. NH_3/hr. cc. bed (atm.)$^{3/2}$
k_2 = reverse reaction rate constant, cc. S.T.P. NH_3/hr. cc. bed (atm.)$^{-1/2}$
k' = pseudo first-order reaction rate constant, cc. gas mixture/sec. cc. catalyst
k_g = mass transfer coefficient, g. mole N_2/hr. sq. cm. atm.
l = distance from reactor inlet, cm.
p = pressure, atm.
r = reaction rate, cc. S.T.P. NH_3/hr. cc. bed
r_c = distance from center of catalyst pellet, cm.
$\bar{V}_a$ = partial molal volume of nitrogen activated complex adsorbed, cc./g. mole
$\bar{V}_s$ = partial molal volume of nitrogen adsorbed, cc./g. mole
x = degree of conversion, cc. S.T.P. NH_3 formed/cc. S.T.P. feed
y = r_c/R

Greek Letters

α = constant, 0.5
ϵ = void fraction bed, 0.40
ν_i = fugacity coefficient, f_i/p
ϕ = $(Z_e - Z)_{NH_3}$
ψ = $\exp\,(\alpha\bar{V}_s - \bar{V}_a)p/RT$
ρ_M = molar density of gas, g. mole/cc.
ρ_B = density of bed, 2.7 g. catalyst/cc. bed
ρ_c = density of catalyst, 5.0 g. catalyst/cc. catalyst
σ = space-time yield, cc. S.T.P. NH_3/hr. cc. bed

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