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# Ammonia Decomposition in the Presence of Water Vapor

## II. Kinetics of the Reaction on Nickel Catalyst

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The kinetics of ammonia decomposition on alumina-supported nickel catalyst in the presence of excess of water have been investigated. Experiments on the influence of the partial pressure of ammonia, hydrogen and steam and of contact time have been conducted. A kinetic expression is proposed to fit all the experimental results. It implies a first order for ammonia, and a negative first order for hydrogen, which exerts an inhibiting influence. This expression is in accordance with the general kinetic expression proposed by Temkin, which takes this quite simple form for sufficient low pressures of reactant and products. Steam seems to exert an influence on the steady state of reduction of the nickel compounds, whose reduced fraction appears to be the active species.

## INTRODUCTION

In Part I (*1*) has been described the activity of supported nickel and ruthenium catalysts for the decomposition of ammonia in the presence of water, and the influence of different preparation conditions of these catalysts. The kinetics of the ammonia decomposition for nickel catalyst are now presented; results obtained with ruthenium are described elsewhere (*2*).

A great deal of research has been done on the kinetics of ammonia decomposition on different metals. Much of it has obviously to do with $NH_3$ synthesis catalysts, i.e., diversely promoted iron, as well as ruthenium. Some excellent reviews have been published (*3–5*) mainly concerning $NH_3$ synthesis, but necessarily involving both the forward and the reverse reaction. In this Introduction, we limit ourselves mainly to the literature on the kinetics of decomposition, especially on Fe, Ru, Ni and Pd.

Historically, it was the Temkin–Pyzhev equation (*6*) that was first proposed (in 1940) to express the experimental results, on iron, of the synthesis and decomposition reactions in the case of relatively high conversions

$$r = k_1 P_{N_2}\left[\frac{P_{H_2}{}^3}{P_{NH_3}{}^2}\right]^{\alpha} - k_2\left[\frac{P_{NH_3}{}^2}{P_{H_2}{}^3}\right]^{(1-\alpha)}$$

with

$$\alpha = \frac{\Delta E_a}{\Delta Q},$$

where $\Delta E_a$ = variation in activation energy for $N_2$ chemisorption vs coverage; and $\Delta Q$ = variation in heat of $N_2$ chemisorption vs coverage.

Other authors, such as Brunauer *et al.* (*7*), confirmed the validity of the physicochemical basis for this equation advanced by Temkin, which implied in particular a variation in the properties of nitrogen chemisorption with surface coverage.

Amano and Taylor (*8*) checked the validity of Temkin's equation for $NH_3$ decomposition on $Ru/Al_2O_3$. Logan and Kemball (*9*) compared the performances and

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decomposition kinetics of $NH_3$ on different metals in the form of wires, and also confirmed Temkin's equation. Temkin *et al.* (*10*) then demonstrated that a general expression (given below) for the $NH_3$ synthesis rate could be established. Tamaru *et al.* (*11, 12*) tried to determine the main chemisorbed forms ($NH_2$, NH, and even N, over Ni) for $NH_3$ decomposition. In addition, they assembled the findings of Logan and Kemball, as well as those of other authors, so as to reveal some remarkable correlations.

A more complex kinetic expression has been proposed by Mardaleishvili *et al.* (*13*) for the decomposition of $NH_3$ on Pd and Ni. In the case of Ni, these authors were led to consider two types of equations depending on whether the catalyst is fresh or has been operating for some time, and which are different from the previous ones. Takezawa and Mezaki (*14*) examined the decomposition of $NH_3$ on iron and hesitated between two rate equations, namely the equation,

$$r = k_1 \left[\frac{P_{NH_3}}{P_{H_2}{}^{1.5}}\right]^2 \frac{1}{\left[1 + K_1 \dfrac{P_{NH_3}}{P_{H_2}{}^{1.5}}\right]^2},$$

and that of Temkin. They finally came round to accept the latter.

Aika *et al.* (*15, 16*) mainly examined the synthesis of $NH_3$, particularly on Ru, and on Ru modified by alkaline additives. Many other investigations [e.g., (*17–19*)] have been published, but are of less interest for our work.

In conclusion, an agreement does not appear to have been reached with regard to the form of the kinetic equation. Therefore, we have tried to look for an equation valid for our experimental conditions.

## EXPERIMENTAL RESULTS

One delicate problem concerns the possible change of the fraction of reduced nickel: (a) all along the catalytic bed, (b) through the pellet and (c) as a function of the composition of the feed. Fortunately, however, it was possible to perform the kinetic investigation under conditions where nickel is practically all reduced. Such conditions are obtained when starting from previously reduced catalyst, and when adding hydrogen to the introduced ammonia and water mixture. So the kinetic investigation has been done here with the so-called Ni catalyst (*1*). Identical results have been obtained with the so-called NiO-oxidized Pd catalyst (*1*), which is easily activated (e.g., reduced) by the reacting feed, and for which Pd exerts no activity.

In view of this, the kinetic results obtained, and their interpretation, only concern the catalytic activity of reduced nickel. However, we shall see that the general interpretation of our results leads us to assume that steam just acts to determine the state of reduction of the nickel and can be considered as an inert diluent for the catalysis.

The apparatus and mode of experimentation have previously been described (*1*). We may recall that the catalyst consists of 14% nickel on alumina carrier of 8 $m^2/g$ and 45 $cm^3/g$.

The possible influence of diffusional limitation was first examined. Variation of linear gas velocity, for a constant contact time, did not induce a conversion change, which proves that there is practically no diffusionnal limitation in the homogeneous phase. Figure 1 shows the influence of pellet dimension on conversion. For pellets of diameter 2.4 to 4 mm, diffusional limitation in pores, appeared only at temperatures higher than 430°C, or more precisely when conversion, *for the experimental chosen conditions*, was higher than 50%. The following experiments were performed with pellets of this dimension (which correspond to industrial catalysts) to avoid too high a pressure drop, with a GHSV of 20,000 $hr^{-1}$. Chemical limitation will be observed only

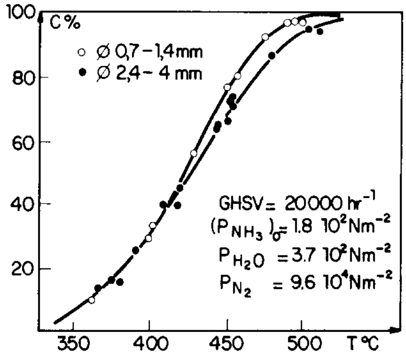

FIG. 1. Influence of diffusional limitations in the catalyst grain.

at lower temperature, or in the presence of hydrogen, which exerts an inhibiting effect.

With such precautions in mind, the investigation has concerned:

1. The influence of ammonia partial pressure.
2. The influence of hydrogen partial pressure.
3. The influence of steam.
4. The influence of contact time.

Nitrogen influence has not been investigated. Since in this work this gas is used in great excess, its kinetic influence does not appear.

### *1. Influence of Ammonia Partial Pressure*

The influence of this parameter was examined by feeding the reactor with a constant flow rate of solutions containing different ammonia concentrations. Consequently (due to the low partial pressure of ammonia in the reactor) the NTP flow rate ($F_a$) of ammonia gas is proportional to the partial pressure of ammonia ($P_a$) at the entrance of the reactor:

$$P_a = \alpha F_a \qquad \alpha = \text{constant.}$$

This property will be used further. Figure 2a gives the variation of conversion versus temperature, for different initial partial pressures of ammonia $(P_{\mathrm{NH_3}})_0$. Conversion decreases when $(P_{\mathrm{NH_3}})_0$ increases.

### *2. Influence of Hydrogen Partial Pressure*

According to the classical method, we used synthetic mixtures of $NH_3 + H_2$ to study the effect of the reaction product, i.e., $H_2$. The results presented in Fig. 3a show a large inhibiting effect of the hydrogen, which apparently decreases when the temperature increases. Moreover, Fig. 3b shows that the conversion is independent of the ammonia partial pressure, as soon as the initial hydrogen partial pressure reaches a sufficient level, i.e., $5 \times 10^2$ N m$^{-2}$ at 426°C. We must emphasize that the thermodynamics remain quite favorable for this range of initial partial pressure of hydrogen.

### *3. Influence of Steam*

To measure the activity of different catalysts in the absence of steam, we used

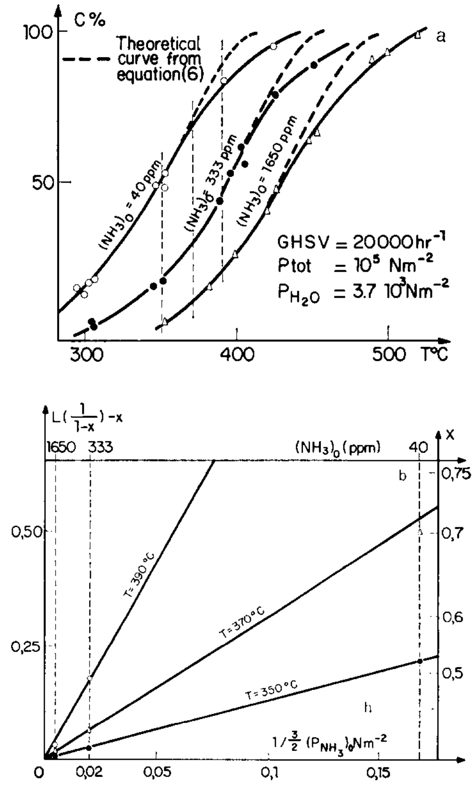

FIG. 2(a) Influence of ammonia partial pressure and of temperature on the conversion. (b) Influence of ammonia partial pressure, according to the linear form (6) of the basic Eq. (3).

a $N_2$–$NH_3$ gaseous mixture having a similar mole ratio, 1:540, for $NH_3/N_2$.

Steam has a slight "inhibiting" influence which seems to be relatively independent of the temperature. For example, for a $(P_{H_2O})/(P_{NH_3})_0$ ratio $\simeq 20$, the decrease in conversion is only 20% (Fig. 4a). We also performed a few tests at 440°C, in the presence of varying amounts of water. The results (Fig. 4b) show that the presence of traces of water already have an effective inhibiting action. When steam pressure attains $2 \times 10^3$ N m$^{-2}$, i.e., $(P_{H_2O})/(P_{NH_3})_0 = 12$, there is a leveling-off of inhibition.

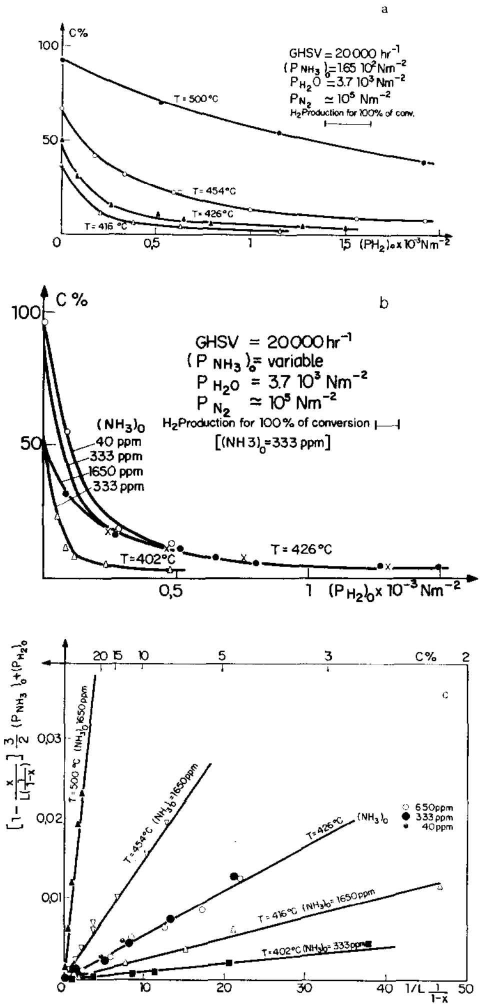

FIG. 3(a) Influence of initial hydrogen partial pressure on the conversion, for different temperatures. (b) Influence of initial hydrogen partial pressure on the conversion, for three initial ammonia partial pressures and two temperatures. (c) Influence of initial hydrogen partial pressure, according to the linear form (5) of the basic Eq. (3).

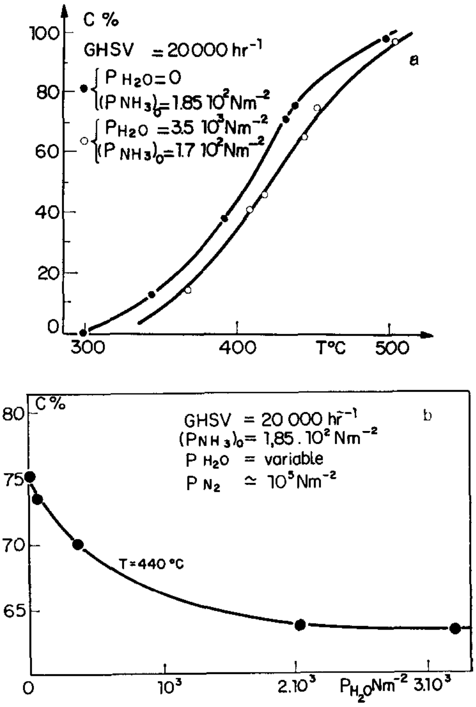

FIG. 4. (a) Influence of water vapor on the conversion. (b) Influence of water vapor partial pressure on the conversion.

## *4. Influence of Contact Time*

The influence of this parameter was studied by varying the total flow rate of the gaseous mixture being fed to the reactor, while the catalyst mass remained constant. Figure 5a gives the results obtained at 3 temperatures (371, 402 and 452°C). In addition to the experimental curve, the broken curve plots the theoretical variation curve, passing through the origin and the first experimental point, and corresponding to a first order relative to ammonia, without any other kinetic influence. It appears that these theoretical

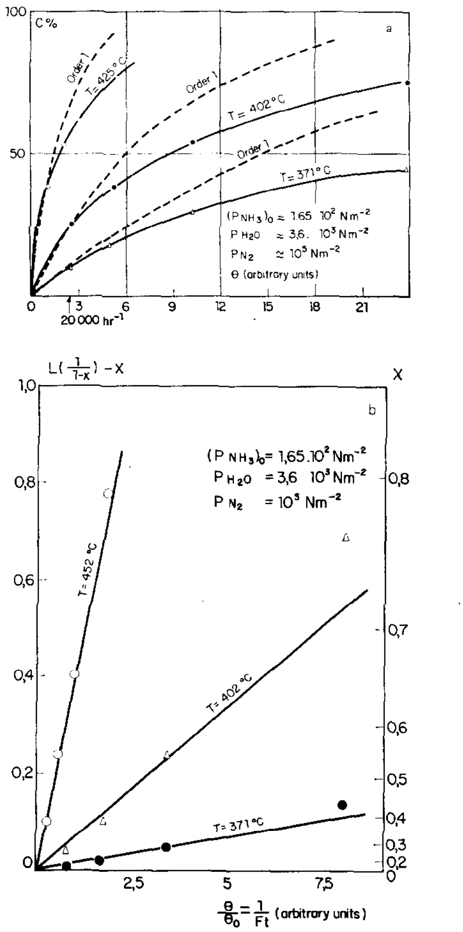

FIG. 5. (a) Conversion versus contact time for three temperatures. Experimental curves, and theoretical curves, for order one, relative to ammonia. (b) Influence of contact time on the conversion, according to the linear form (6) of the basic Eq. (3).

curves give higher conversion than the experimental ones. This phenomenon is interpreted below.

## INTERPRETATION: DETERMINATION OF THE KINETIC EXPRESSION

We have found it useful to distinguish successive steps in this determination:

1. A first approach, rather qualitative, leading to the proposal of a possible kinetic expression.
2. A second step, leading to quantitative determination of different parameters of this expression.
3. The final step, in which all the experimental results will be used to confirm the validity of the chosen expression and to give the most precise determination of the kinetic parameters.

### 1. FIRST APPROACH

a. Figure 3b shows, as already mentioned, that for a sufficient initial pressure of hydrogen, ammonia conversion becomes independent of its initial partial pressure. We can consider that when $(P_{NH_3})_0$ varies, all the other partial pressures remain unchanged; particularly $P_{H_2}$ remains practically constant because of the great excess of introduced $H_2$ in regard to the quantity produced by $NH_3$ conversion (which remains low). Considering the experimental technique used here, this result suggests the intervention of a first order relative to ammonia.

This affirmation can be easily understood if we consider, as already mentioned, that this experimental technique is characterized by proportionality between the partial pressure of ammonia at the reactor entrance and its feed rate.

In this case, from the balance equation:

$$F_a dx = r dm, \qquad (1)$$

where $x$ = $NH_3$ conversion, $r$ = rate of $NH_3$ decomposition and $m$ = catalyst weight, we find easily, that for a first order relative to ammonia, and so with

$$r = k_1 P_a(1 - x),$$

we obtain by integration of Eq. (1):

$$x = 1 - e^{-kam},$$

i.e., a conversion independent of ammonia pressure, as observed.

b. Figure 2a shows that when $(P_{NH_3})_0$ increases, the conversion decreases, results apparently in contradiction with the previous one. But we must consider that in this case $(P_{H_2})_0 = 0$, and that the production of hydrogen by $NH_3$ decomposition can exert a kinetic influence, which consequently would be an inhibition.

c. Figure 3a and b confirm then, as already invoked, the inhibiting influence of hydrogen. Figure 5a leads us also to invoke an inhibition by produced hydrogen to explain the lower conversion than those given by the sole influence of a first order law relative to $NH_3$.

So, we can propose expressions of the form:

$$r = k\frac{P_{NH_3}}{(P_{H_2})^\beta} \quad \text{or} \quad r = k\frac{P_{NH_3}}{(a + P_{H_2})^\beta}.$$

## 2. DETERMINATION OF $\beta$ AND a

The classical method is to plot $Lr$ versus $LP_{H_2}$. If the first equation is valid, we must observe a linear curve, whose slope gives $\beta$. The intervention of the term $a$ causes a deviation from linearity which can characterize the value of the parameter, $a$, relative to $P_{H_2}$. Figure 6 leads us to propose a small value for $a$, a value which, to a first approximation, can be neglected. Moreover, the slope of the straight line obtained being equal to one, it is possible to propose the expression:

$$r = k\frac{P_{NH_3}}{P_{H_2}}. \qquad (2)$$

It should be pointed out that Eq. (2) introduces an infinite rate at the initial conditions, when no hydrogen is added. However, from a formal point of view, this infinite value has an influence only during an infinitely short time and does not introduce any incoherence. Fundamentally, it is evident that the denominator of Eq. (2) should rather have the form $\epsilon + P_{H_2}$, with $\epsilon$ being a small term with respect to $P_{H_2}$.

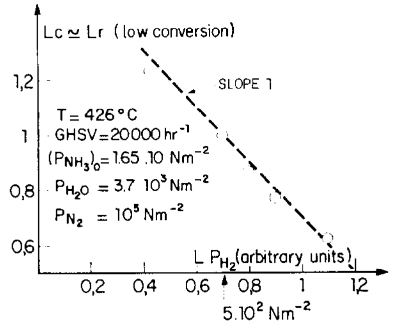

FIG. 6. Determination of $a$ and $\beta$, coefficients of the rate equation, from the curve at 426°C of Fig. 3a or b, with $(NH_3)_0$ = 1650 ppm.

## 3. EXPLOITATION OF THE TOTALITY OF RESULTS

On the basis of the kinetic Eq. (2), the integration of the balance equation enables us to apply the results obtained for any conversion. The rate equation for a given conversion $x$ becomes:

$$r_{(x)} = k\frac{(P_{NH_3})_0(1 - x)}{(P_{H_2})_0 + \frac{3}{2}(P_{NH_3})_0 x}.$$

Integration leads to the basic equation:

$$(P_{H_2})_0 L\frac{1}{(1 - x)} + \tfrac{3}{2}(P_{NH_3})_0 \times \left[L\frac{1}{1 - x} - x\right] = k22.4\frac{m}{F_t}. \qquad (3)$$

$F_t$ represents the total entrance flow-rate and we have:

$$F_a = \frac{F_t}{22.4}\frac{(P_{NH_3})_0}{P_{\text{total}}}$$

$$P_{\text{total}} = 1 \text{ bar} = 10^5\, N\, m^{-2}$$

This general equation makes use of the term $m/F_t = \theta$ (contact time), which can be easily related to the GHSV by use of the bed density of the catalyst $\rho_b$:

$$m = \rho_b V_b \ (V_b \text{ catalytic bed volume})$$

and

$$\text{GHSV} = \frac{F_t}{V_b} = \frac{F_t}{m}\rho_b \qquad (4)$$

The basic equation will be applied to the three types of experimental investigation:

a. The variation of $x$ as a function of $(P_{H_2})_0$ for different temperature.

b. The variation of $x$ as a function of $(P_{NH_3})_0$, for different temperatures.

c. The variation of $x$ as a function of contact time, $\theta = m/F_t$, for different temperatures.

Since the experiments were performed with grains measuring from 2.4 to 4 mm, corresponding to industrial catalysts, diffusion phenomena may occur in cases of the highest rate. But for experiments performed in the presence of hydrogen, the inhibiting effect of this molecule reduces the chemical rate of reaction. As the diffusion rate is unaffected, the presence of hydrogen permits the activity to remain under conditions where there is no diffusional limitation, even at relatively high temperatures. Moreover, experiments in the presence of $H_2$ ensure an almost entirely reduced catalyst, thus having the same composition all along the catalytic bed.

*a. Influence of $(P_{H_2})_0$ for $(P_{NH_3})_0$ = Constant (Fig. 3a and b).*

Equation (3) can be applied in different ways. In the present case, we will apply it in the form:

$$\tfrac{3}{2}(P_{NH_3})_0\left[1-\frac{x}{L\dfrac{1}{(1-x)}}\right]+(P_{H_2})_0 = k22.4\frac{m}{F_t}\frac{1}{L\dfrac{1}{(1-x)}}. \quad (5)$$

By plotting the first term as a function of $1/1/L[1/(1-x)]$, we should obtain a straight line, passing through the origin, and having a slope equal to $k$ (multiplied by a constant term). This operation has been done in Fig. 3c:

α. At 500, 454, 416, and 402°C, a single pressure of $(P_{NH_3})_0$ being used.

β. At 426°C, for three different pressure $(P_{NH_3})_0$.

For each temperature, we effectively obtain a straight line passing through the origin, thus illustrating the validity of the model chosen and giving the value of $k$. Emphasis should be placed on the good linearity obtained at 426°C, with three different values of $(P_{NH_3})_0$. The values of $k$, plotted in Arrhenius coordinates (Fig. 7), give a linear curve, thus providing a further confirmation of the validity of the model and giving the activation energy:

$$E = 185 \text{ kJ mole}^{-1}.$$

*b. Influence of $(P_{NH_3})_0$ for $(P_{H_2})_0 = 0$ (Fig. 2a)*

The basic Eq. (3) could be used in the form (5). But in the particular case $(P_{H_2})_0 = 0$, we choose the form (6) which is simpler:

$$\left[L\frac{1}{1-x}\right]-x = k22.4\frac{m}{F_t}\frac{1}{\tfrac{3}{2}(P_{NH_3})_0}. \quad (6)$$

By plotting the first term of Eq. (6) as a function of $1/(P_{NH_3})_0$, a straight line should be obtained of slope equal to $k$.

α. *Results obtained at low temperatures (without limitation by diffusion).* Figure 2b effectively gives straight lines, thus confirming the validity of the model chosen and giving the values of $k$. For three considered temperatures (among the infinite possibility of choice in Fig. 2a), the corresponding values of $k$ are also plotted in Arrhenius coordinates in Fig. 7.

The identity of the straight line obtained for a different range of temperature than previously, confirms the validity of the model.

β. *Results obtained at high temperature (with possible limitation by diffusion).* In the temperature range of 390–430°C, for example, the kinetic Eq. (6) can be incorrect, in the absence of hydrogen in the feed. Thus the results will be exploited by a reverse process. On the basis of the values of $k$ previously obtained from the Arrhenius line (Fig. 7), it is possible to calculate the value of the "chemical" conversion, $x_c$ (in absence of limitation by diffusion), at any temperature. Calculated curves $x_c = f(T^{re})$ are represented in Fig. 2a as broken lines. We effectively observe coincidence of calculated and experimental curve for low temperature, but, $x_c > x_{\text{exp}}$, for high temperature. Moreover, for pellets of small dimensions (0.7–1.4 mm), the experimental and theoretical curves coincide in Fig. 1, showing in this case the absence of limitation by diffusion, for all the temperature range.

Exploitation of the variable $(P_{NH_3})_0$ can be done for any initial hydrogen pressure $(P_{H_2})_0$, for example by using the curves with a fixed $(P_{H_2})_0$ in Fig. 3b (at 426°C). In fact, this is merely another way of applying the results which have already been used with the variable $(P_{H_2})_0$ (straight line in Fig. 3c) and have already served to check the validity of the proposed model.

### c. *Influence of Contact Time;* $(P_{NH_3})_0$ *= Constant and* $(P_{H_2})_0 = 0$

The experimental curves in Fig. 5a can be exploited from Eq. (6), with the variation of $x$ being obtained in this case by the variation of $F_t$.

If the model is valid, by plotting the first term in the formula as a function of $1/F_t$ we should obtain a straight line passing through the origin and having the slope $k$. Figure 5b shows that a linearity is effectively observed; the values of $k$ obtained for the three temperatures are also on the same Arrhenius plot in Fig. 7.

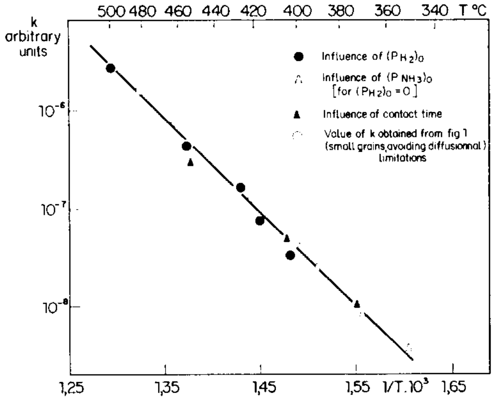

FIG. 7. Arrhenius representation of the rate constant for Ni catalyst.

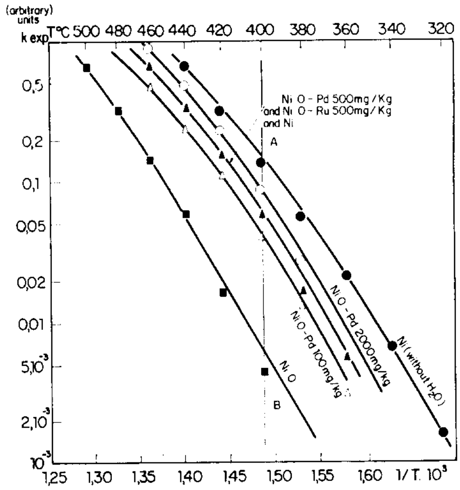

FIG. 8. Arrhenius representation of experimental rate constant for several nickel catalysts.

It is interesting to come back to the apparent decrease in the inhibiting effect of hydrogen with temperature (Fig. 3a), a result apparently in contradiction with Eq. (2), in which the effect of $H_2$ does not depend on the temperature.

This apparent effect results from the intervention of high conversions. At 500°C for example, where conversion with $(P_{H_2})_0 = 0$ is very high (94%), the hydrogen *already produced* exerts a great inhibiting effect and the hydrogen *added* to the feedstock brings only a further reduced inhibition. On the other hand, at 426°C, where conversion with $(P_{H_2}) = 0$ is only 50%, the inhibition resulting from the hydrogen *produced* is less, and the system is more sensitive to the amount of hydrogen introduced with the feedstock.

## 4. COMPARISON WITH THE RESULTS IN THE LITERATURE

The kinetic equation that we have proposed appears to be different from the one generally accepted, which has the form:

$$r = k\left[\frac{P_{NH_3}{}^2}{P_{H_2}{}^3}\right]^{(1-\alpha)}, \qquad (7)$$

$\alpha \simeq 0.5$ for Ni.

To discuss this apparent discrepancy, we will consider the general equation proposed by Temkin for the iron catalyst of ammonia synthesis, and involving both reverse and forward reactions (*10*):

$$r = \frac{(k_\pm)P_{N_2}{}^{(1-\alpha)}\left[1 - \dfrac{1}{K}\dfrac{P_{NH_3}{}^2}{P_{N_2}\cdot P_{H_2}{}^3}\right]}{\left[\dfrac{\rho}{P_{H_2}} + \dfrac{1}{K}\cdot\dfrac{P_{NH_3}{}^2}{P_{N_2}P_{H_2}{}^3}\right]^{\alpha}\left[\dfrac{\rho}{P_{H_2}} + 1\right]^{(1-\alpha)}}, \qquad (8)$$

$k_\pm$ = rate constant of the synthesis reaction

$K$ = thermodynamic constant for the synthesis: $N_2 + 3H_2 \rightleftarrows 2\ NH_3$

$\alpha$ = term characterizing the influence of coverage for the chemisorption of nitrogen, $\alpha = \Delta E_a/\Delta Q$, in which $\Delta E_a$ is the variation in the activation energy and $\Delta Q$ is the variation in adsorption heat for the chemisorption of nitrogen, with degree of coverage.

$\rho$ = ratio of the desorption rate constant for chemisorbed nitrogen to its hydrogenation rate constant.

For the iron catalyst, Temkin proposed the value $\rho = 1.77 \times 10^{-2}$ bar at 450°C (*10*), or $\rho = 1.77 \times 10^{3}\ \mathrm{N\ m^{-2}}$.

*a. Application to our Results*

We have to examine the form taken by the general expression for ammonia decomposition, under our conditions of very low pressure of ammonia and hydrogen. We will consider:

1. The value taken by the term $\rho/P_{H_2}$, relative to one.
2. The value taken by the ratio $R$, relative to one:

$$R = \frac{\dfrac{1}{K}\dfrac{P_{NH_3}{}^2}{P_{N_2}P_{H_2}{}^3}}{\dfrac{\rho}{P_{H_2}}} = \left[\frac{1}{K\rho P_{N_2}}\right]\left[\frac{P_{NH_3}}{P_{H_2}}\right]^2. \qquad (9)$$

1. Comparison of $\rho/P_{H_2}$ in relation to one. By considering only the cases where $(P_{NH_3})_0 \leqslant 2 \times 10^2\ N\ \mathrm{m}^{-2}$ and $P_{H_2} \leqslant 5 \times 10^2\ N\ \mathrm{m}^{-2}$, and by taking the value of $\rho$ given for iron at 450°C, we obtain $\rho/P_{H_2} \gg 1$, or at least, $\rho/P_{H_2} > 1$.

2. Comparison of $R$ in relation to one. For 450°C, $K \approx 5 \times 10^{-15}\ (N\ \mathrm{m}^{-2})^2$. Here $P_{N_2} \approx 10^5\ N\ \mathrm{m}^{-2}$ and we will take $\rho = 1.77 \times 10^3\ N\ \mathrm{m}^{-2}$. So:

$$R = 1.1 \times 10^6\left[\frac{P_{NH_3}}{P_{H_2}}\right]^2;$$

and, introducing the conversion $x$,

$$R = 1.1 \times 10^6\left[\frac{1 - x}{(P_{H_2})_0/(P_{NH_3})_0 + \frac{3}{2}x}\right]^2. \qquad (10)$$

a. If $(P_{H_2})_0 = 0$, the expression of $R$ becomes:

$$R = 5 \times 10^5\left(\frac{1 - x}{x}\right)^2.$$

For $x = 0.9$, $R = 6 \times 10^3$; and $R$ decreases to one solely when $x \approx 0.9985$. Then, considering that $\rho/P_{H_2} \gg 1$ and $R \gg 1$, the equation for ammonia decomposition deduced from the general Eq. (8) (with the synthesis contribution being negligible) is reduced to the form:

$$r = \frac{(k_\pm)}{(K\rho)^{(1-\alpha)}}\left[\frac{P_{NH_3}}{P_{H_2}}\right]^{2(1-\alpha)}, \qquad (11)$$

which is the kinetic expression deduced from our experiments if we take $\alpha = 0.5$.

b. If $(P_{H_2})_0 \neq 0$, the value of $R$ is lowered by the intervention of $(P_{H_2})_0/(P_{NH_3})_0$ in its denominator, but we can again consider that $R \gg 1$ for the experimental conversion obtained.

Indeed, for the most extreme cases in this paper, namely, $(P_{NH_3})_0 = 33.3\ N\ m^{-2}$ and, for example, $(P_{H_2})_0 = 10^3\ N\ m^{-2}$ in Fig. 3b, we easily find that for $x = 0$, $R \approx 1200$, and that $R$ decreases to 1 solely when $x \approx 0.97$. On the other hand, we are just at the limit for the condition $\rho/(P_{H_2})_0 > 1$.

Finally, for sufficiently small values of $P_{H_2}$, the general kinetic equation can be reduced to the simplified form Eq. (11) corresponding to the one deduced from our experiments.

### b. *Comparison with Published Results on Ammonia Decomposition*

Generally, conditions are such that $P_{H_2}$ has high values, which leads to:

$$\frac{\rho}{P_{H_2}} \ll 1.$$

$R$ remains higher than 1 if the conversion is not too close to equilibrium. Consequently, if the rate of the reverse reaction (synthesis) remains negligible, the decomposition rate deduced from Eq. (8) is reduced to:

$$r = \frac{(k_\pm)}{K^{(1-\alpha)}} \left[ \frac{P_{NH_3}}{P_{H_2}{}^{1.5}} \right]^{2(1-\alpha)}. \qquad (12)$$

This expression is different from Eq. (11) and corresponds to published experimental results for such a hydrogen pressure range.

Some authors, such as Logan and Kemball (*9*), have used intermediate hydrogen pressure conditions, for example $(P_{H_2})_0$ varying between $10^3$ and $7 \times 10^3\ N\ m^{-2}$. In such cases $0.25 \leqslant \rho/(P_{H_2})_0 \leqslant 2$. We have again $R \gg 1$. We must then apply an intermediate kinetic equation between (*11*) and (*12*). Logan and Kemball proposed Eq. (12), but pointed out that their operating method does not enable the order to be determined accurately relative to $H_2$.

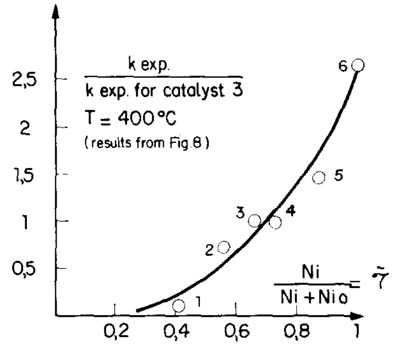

FIG. 9. Correlation between experimental rate constant at 400°C (from Fig. 8) and mean reduced fraction of different nickel catalysts [from Fig. 7 of Ref. (*1*)].

Of course, our comparative analysis of the kinetics problems implies the intervention of results relative to iron catalyst, but this sort of approximation seems acceptable in the actual state of our knowledge.

This analysis shows then that Temkin's general equation appears quite valid, but that care must be taken in examining the values taken by the different terms, depending on the operation range used.

## 5. INFLUENCE OF CATALYST PREPARATION OR COMPOSITION

Use of a kinetic expression makes possible the comparison of catalysts from their rate constants and their variation with temperature. Hence Fig. 8 presents in Arrhenius coordinates the rate constants for six catalysts of Part I (*1*). We observe:

1. A linear variation in the low temperature range, for which diffusional limitation does not occur.
2. That the activation energy is around 170 kJ mole$^{-1}$ for catalysts working essentially in a reduced state (Ni, NiO-oxidized Ru and NiO-oxidized Pd catalysts). For

NiO catalyst, the apparent activation energy is different (a little higher).

For an easy presentation of the problem we will first consider formally two arbitrary simplifications:

1. One by which the reduction degree would be the same for bulk and surface of nickel compound crystallites.
2. A second by which the turnover number of reduced nickel sites would be independent of the degree of reduction, i.e., of the presence of NiO.

If these formal simplifications were justified, the balance Eq. (1) could be written:

$$F_a dx = r_{(x)} dm\tau,$$

$\tau$ being the degree of reduction of the considered element $dm$, and $r_{(x)}$ being the same expression as previously. The integration would lead to an equation similar to (3), but in which $m$ would be substituted by:

$$m \int_{\text{entrance}}^{\text{exit}} d\tau = m\bar{\tau} (\bar{\tau} \text{ mean value of } \tau),$$

and in which, finally, the slope $k_0$ of the straight line, in the linear exploitation, would be substituted by:

$$k_{\text{exp}} = k_0\bar{\tau}.$$

$k_0$ being relative to pure Ni ← $k_0$ being relative to pure Ni.

In other words, such simplifications would imply a linear variation law for the experimental rate constant, as a function of $\bar{\tau}$. Figure 9 shows the values of $k_{\text{exp}}$ for the six catalysts of Fig. 8 at 400°C (values given by intersection with AB). A clear correlation is observed, but not a linear law. So the formal simplifications are not obeyed; however, it is difficult to disentangle the two causes of complexity. The sign of the observed curvature leads us to suppose either that the reduction degree is lower for the surface than for bulk, or that the turnover number of nickel sites decreases in the presence of oxidized nickel. These points merit further investigation.

## CONCLUSION

Under conditions existing in exhaust gases, the best kinetic equation, for fundamental or applied research, or for reactor designing, seems to be the one proposed from our experimental results, as long as nickel is mainly in a reduced state. Under conditions where large fractions of oxidized nickel appear, kinetic analysis must help to find the influence of nickel oxide and water.

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