

Another Rate Equation for the Catalytic Synthesis of Ammonia

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A rate equation for the ammonia synthesis is given based on the assumption that the adsorption of molecular nitrogen on one site is the rate-determining step. The equation represents satisfactorily the experimental data.

Ozaki *et al.* (1) gave a rate equation for the NH_3 Synthesis (2)

$$\frac{dp_{\text{NH}_3}}{dt} = k_1 p_{\text{N}_2} (1 - \Theta)^2 - k_2 \Theta^2, \quad (1)$$

assuming a Langmuir equation for Θ :

$$\Theta = \frac{K p_{\text{NH}_3} / p_{\text{H}_2}^{1.5}}{1 + K p_{\text{NH}_3} / p_{\text{H}_2}^{1.5}}, \quad (2)$$

K = adsorption equilibrium constant for the reaction $\text{N}_a + 1.5\text{H}_2 \rightleftharpoons \text{NH}_3$; N_a = adsorbed N-atom.

With $x = p_{\text{NH}_3} / p_{\text{NH}_3, \text{eq.}}$ the integration of Eq. (1) gives

$$k_1 = (p_{\text{NH}_3, \text{eq.}} / p_{\text{N}_2}) t^{-1} \left\{ \frac{1}{2} (1 + a_1^2) \ln \frac{1 + x}{1 - x} - a_1 \ln (1 - x^2) - a_1^2 x \right\} \quad (3)$$

$$a_1 = (K / p_{\text{H}_2}^{1.5}) p_{\text{NH}_3, \text{eq.}}$$

Brill *et al.* (3) showed that the adsorption of nitrogen on iron preferentially takes place on the 111 faces of the iron crystals of the catalyst. The theory, according to Ruch, requires in this case adsorption of N_2 -molecules oriented perpendicular to the surface. A number of experiments were carried out to verify this theory. Schmidt (4) showed that N_2H seems to be the first product formed at synthesis, Brill *et al.* (5) found, by infrared adsorption studies, surface complexes containing N_2 ; and Taube and Zimmermann (6) tried to perform NH_3 synthesis on iron whiskers consisting of 100- and 110-faces exclusively. The yield per cm^2 and sec was at least 100 times less than that of an ordinary am-

monia catalyst. Molière and Berndt (7) investigated the surface of these whiskers by means of LEED and found no adsorption of nitrogen. Furthermore Scholten *et al.* (8), as well as Morikawa and Ozaki (9) and also Takezawa and Emmett (10) showed that molecular nitrogen is present at the surface of ammonia catalysts at least at temperatures lower than 400°C .

Now, if the theory of Ruch is right, the fact that Eq. (1) represents the experimental data rather well seems to be in contradiction to this theory. It appeared to be worthwhile to investigate whether a rate equation can be derived which assumes the hydrogenation of molecular nitrogen. In this case, with nitrogen molecules oriented perpendicular to the surface, only one site would be required per N_2 at adsorption. Consequently Eq. (1) should be replaced by

$$\frac{dp_{\text{NH}_3}}{dt} = k_1 p_{\text{N}_2} (1 - \Theta) - k_2 \Theta. \quad (4)$$

In this case it is

$$\Theta = \frac{c p_{\text{N}_2}}{1 + c p_{\text{N}_2}} = \frac{c K^{-1} p_{\text{NH}_3}^2 / p_{\text{H}_2}^3}{1 + c K^{-1} p_{\text{NH}_3}^2 / p_{\text{H}_2}^3}, \quad (5)$$

K = equilibrium constant for the reaction $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$ in the gas state. As usual, the nitrogen pressure is replaced by its fugacity (11). Integration of Eq. (5) gives

$$k_1 = (p_{\text{NH}_3, \text{eq.}} / p_{\text{N}_2}) t^{-1} \times \left\{ \frac{1}{2} (a + 1) \ln \frac{1 + x}{1 - x} - ax \right\}, \quad (6)$$

$$a = c K^{-1} p_{\text{NH}_3, \text{eq.}}^2 / p_{\text{H}_2}^3.$$

TABLE 1^a
COMPARISON OF k -VALUES ACCORDING TO Eqs. (3) AND (6)

t	x	k_1 [Eq. (3)]	k_1 [Eq. (6)]	
.259	.396	.407	5.70	a_1 [Eq. (3)] = 701
.180	.342	.412	5.65	
.121	.286	.415	5.59	a [Eq. (6)] = 46.0
.0953	.257	.416	5.60	
.0723	.225	.420	5.67	
.0584	.198	.403	5.51	
.0402	.163	.409	5.77	
		$412 \pm 1.4\%$	$5.64 \pm 1.5\%$	

^a Catalyst: Fe; temp.: 340°C.

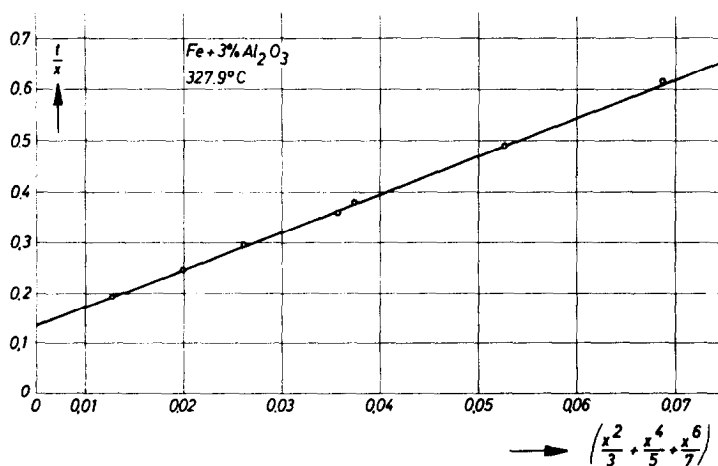
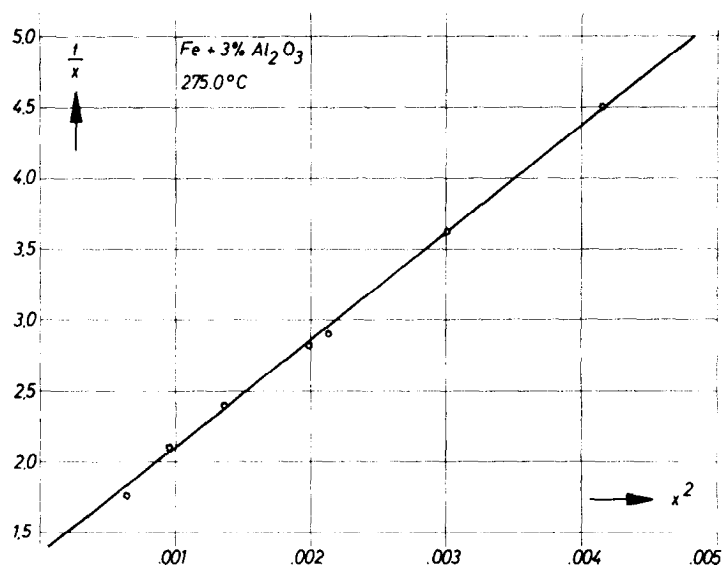


FIG. 1. Graphs according to Eq. (7).

Equation (6) is simpler than (3) and represents the experimental data also rather well (see Table 1). Expanding the \ln in Eq. (6) in a series and rearranging gives

$$t/x = \text{const.} \{1 + (a+1)(x^2/3 + x^4/5 + \dots)\}, \quad (7)$$

i.e., t/x is a linear function of the series $x^2/3 + \dots$.

Figure 1 shows two examples of the graphic representation of measurements according to Eq. (7) at two different temperatures. One sees that the first term of the series is sufficient for small values of x at the lower temperature, whereas the term with x^6 has to be included for higher yields at the more elevated temperature, where also the measurements are more accurate.

From Eq. (5) it follows that c contains a heat of adsorption. Consequently $\log c$ is supposed to be a linear function of $1/T$. That this is actually the case is shown in Fig. 2. The same linear relation is found for partly poisoned catalysts. In both cases the same value results for this heat of adsorption: 50 kcal/mole.

A similar evaluation of a -values determined by means of Eq. (3) does not lead to a satisfactory linear dependency of \log

K [Eq. (2)] versus $1/T$, where K is supposed to contain an equilibrium constant besides a heat of adsorption.

In both cases, for Eqs. (3) and (6), a increases as the yield of ammonia decreases, i.e., for partly poisoned catalysts larger a -values are found than for unpoisoned ones. This results in increasing "frequency factors" in the plot $\log c$ versus $1/T$ and is in strong contradiction to the expectation. Formally, it might be explained by the assumption that the rate constant for NH_3 -desorption is relatively much smaller for partly poisoned than for unpoisoned catalysts.

Kiperman and Granovskaja (12) showed that at yields of NH_3 smaller than 1% of the equilibrium value, Eq. (8) holds.

$$k_1 = (x/t)p_{\text{NH}_3, \text{eq.}}/p_{\text{N}_2} \quad (8)$$

This equation is approximated for small x -values by both Eqs. (3) and (6). However the limit up to which the approximation is good enough is quite different for Eqs. (3) and (6). This is shown by the data of Table 1 which simultaneously illustrates the application of Eqs. (3) and (6).

Expanding the logarithms in Eq. (3) leads to

$$\{ \} = \{x + (a_1^2 + 1)(x^3/3 + x^5/5 + \dots) + a_1(x^2 + x^4/2 + \dots)\}. \quad (9)$$

If Eq. (8) is supposed to hold for $x < 0.01$ the condition

$$x \gg a_1 x^2 + a_1^2 x^3/3, \quad (10)$$

must be fulfilled. An analogous consideration leads for Eq. (6) to:

$$x \gg ax^3/3. \quad (11)$$

It is obvious that even for $a_1 = a$ Eq. (11) is easier to be satisfied than Eq. (10).

Inserting the experimentally determined values gives for $x = 0.01$:

$$c_1 x^2 + a_1^2 x^3/3 = 0.07 + 0.15 > x,$$

and

$$ax^3/3 = 0.14 \times 10^{-4} \ll x.$$

Therefore, the equation of Kiperman and Granovskaja is an approximation of Eq. (6) rather than (3).

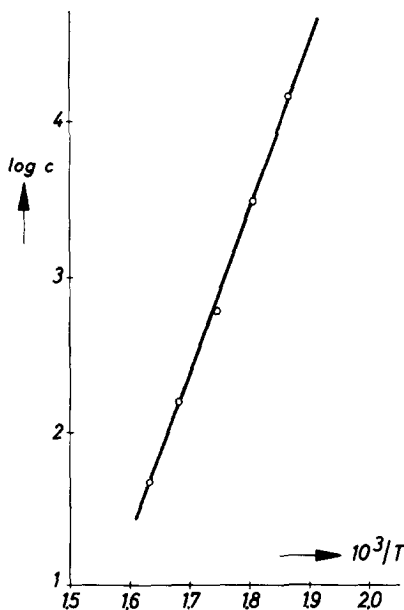


FIG. 2. Logarithmic plot of c [Eq. (5)] versus $10^3/T$.

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