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# Kinetics of Ammonia Decomposition on Polycrystalline Tungsten

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The rates of ammonia decomposition on polycrystalline tungsten wires between 900 and 2200K and at pressures between 20 and 770 Torr are measured. All data can be fit accurately at all temperatures and pressures by a Langmuir–Hinshelwood unimolecular reaction rate expression. Comparison with previous results suggests that this rate expression can be used to approximate reaction rates at pressures down to $10^{-3}$ Torr. Thus a single rate expression describes the reaction over a range larger than $10^5$ in reactant pressure.

## INTRODUCTION

The catalytic decomposition of ammonia has been studied since the early days of heterogeneous catalysis. In fact, Dulong and Thenard (*1*) in 1823 wrote on the properties of some transition metals which decomposed ammonia when heated. The development of the ammonia synthesis process seventy years ago motivated many studies of the reverse reaction, continuing until our days. Bond (*2*) reviewed the literature on the subject prior to 1962, while Tamaru (*3*) comments on more recent contributions. Currently the catalytic decomposition of ammonia is carried out industrially in a process for heavy water separation.

Tungsten has been a much studied ammonia decomposition catalyst. However, we know of no experiments reported for reactant pressures higher than 350 Torr or over temperature ranges wider than 200K. In the work reported here we found that rates for ammonia decomposition on tungsten wires over a wide range of catalyst temperatures and gas pressures can be fit to a Langmuir–Hinshelwood (LH) rate expression,

$$R = k_0KP/(1 + KP), \tag{1}$$

where

$$k_0 = A_0 \exp(-E_0/RT) \tag{2}$$

and

$$K = A_K \exp(-E_K/RT). \tag{3}$$

Here $k_0$ is the reaction rate constant and $K$ is the adsorption constant for ammonia, with $E_0$ and $E_K$ the activation energy for reaction and the heat of adsorption of ammonia, respectively. A similar expression has been shown to fit data for ammonia decomposition on polycrystalline Pt, Pt single-crystal planes, and polycrystalline Fe (*4*).

While most industrial catalytic processes operate at a total pressure of 1 atm or higher, laboratory experiments concerning fast reactions are usually performed at pressures in the Torr range in order to avoid mass transfer resistances. It is conceivable, however, that the reaction mechanism or the surface structure of the catalytic material could change with pressure. The question about the relevance of reaction rate measurements under such idealized conditions is then justified. In the work reported here we show that, at least for ammonia decomposition on W, the kinetics can be fit both at high and low pressures by the simplest possible form for a surface rate expression.

## EXPERIMENTAL

The reaction was carried out in a Pyrex batch reactor. Total pressure was continu-

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ously monitored with a capacitance manometer. Refrigeration-grade (anhydrous) ammonia passed at atmospheric pressure through a bed of NaOH pellets before entering the reaction chamber. Catalysts were 0.0075, 0.0127, and 0.025-cm-diameter W wires of 99.98% purity. A 9-cm length of wire was welded to Ni leads and kept straight and horizontal along a diameter of a 1000-cm$^3$ flask. Temperatures were measured from the wire electrical resistance between 0.0075-cm potential leads, while a regulated power supply maintained specified temperatures constant to within a few degrees. Rates were calculated from the pressure changes observed in a set time interval. Conversions were always below 10% so that initial rates were measured.

After heating the catalyst at high temperatures (>2000K) for about 20 min in ammonia at 1 atm, reaction rates were reproducible. Heating in ammonia has been shown to render clean Pt and Fe surfaces (*4*).

Figures 1–3 show the measured rate of ammonia decomposition, $R$, versus temperature in pure ammonia for pressures between 20 and 770 Torr for the three wire diameters investigated. Rates no lower than $10^{16}$ molecules/cm$^2$ sec could be measured, and this sensitivity limited the minimum catalyst temperature to about 900K. The maximum temperature was limited by W evaporation above 2200K.

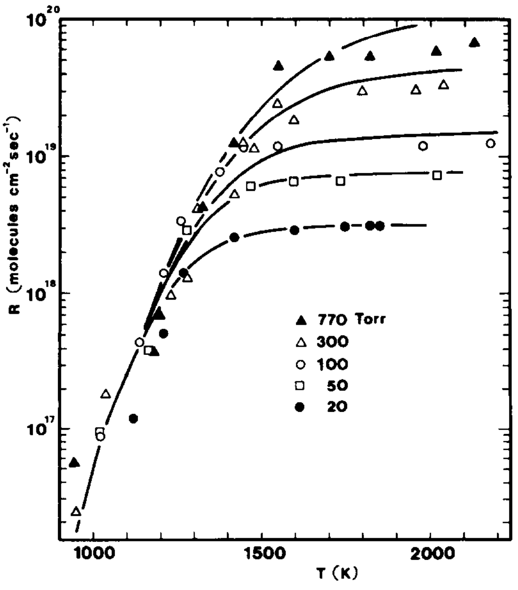

FIG. 1. Rate of reaction $R$ versus temperature on a 0.0075-cm-diameter tungsten wire for initial ammonia pressures indicated. Curves are calculated from Eq. (1) using parameters shown in Table 1.

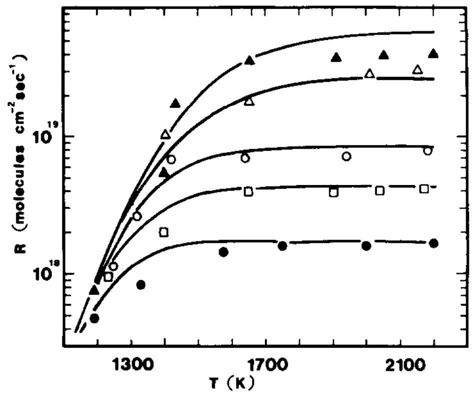

FIG. 2. Rate of reaction $R$ versus temperature on a 0.0127-cm-diameter tungsten wire. Symbols denote pressures as indicated in Fig. 1. Curves are calculated from Eq. (1) using parameters shown in Table 1.

Data shown on each figure were obtained on several (between 5 and 10) wires cut from the same spool. No systematic deviations from the mean can be observed for any particular wire. All data could be fit by LH kinetics, Eq. (1), with parameters shown in Table 1. While Figs. 1–3 show that the activation energy for the first-order regime (high-temperature data) is clearly zero, the activation energies for the zeroth-order regimes (low-temperature data) can be obtained from the Arrhenius plots in

TABLE 1

Parameters for Langmuir–Hinshelwood Kinetics (Eq. (1))

| Wire diameter (cm) | $E_0 = E_K$ (kcal/gmol) | $\log A_0$ (molec./cm$^2$ sec$^{-1}$) | $\log A_K$ (Torr$^{-1}$) |
|---|---|---|---|
| 0.0075 | 38.0 | 24.93 | −7.72 |
| 0.0127 | 40.0 | 25.24 | −8.30 |
| 0.025 | 44.4 | 25.65 | −9.09 |

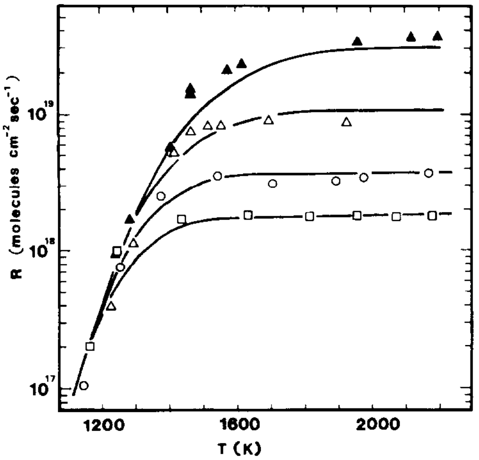

FIG. 3. Rate of reaction $R$ versus temperature on a 0.025-cm-diameter tungsten wire. Symbols denote pressures as indicated in Fig. 1. Curves are calculated from Eq. (1) using parameters shown in Table 1.

Figs. 4 and 5. Here points obtained from the zero-order asymptote in Figs. 1–3 give straight lines for rate variations by a factor of 1000, yielding the $A_0$ and $E_0$ values shown in Table 1.

Figure 6 shows a plot of rate versus ammonia pressure on all three wire diameters for $T$ = 2200K. All wires exhibit first-order kinetics at this temperature when reaction rates are lower than $2 \times 10^{19}$ molecules/cm$^2$ sec. Calculations indicate that mass transfer resistances should become noticeable for higher rates of reaction.

## DISCUSSION

As was found before for ammonia decomposition on Pt (polycrystalline and single-crystal planes) and on Fe (*4*), a LH unimolecular reaction rate expression can quantitatively fit the experimental data. Our results show that Eq. (1) is valid over a factor of almost 100 in pressure, at temperatures between 900 and 2200K, and at rates varying by a factor of 1000. No systematic deviations from the calculated curves are evident, except for those rates high enough for mass transfer resistances to become important.

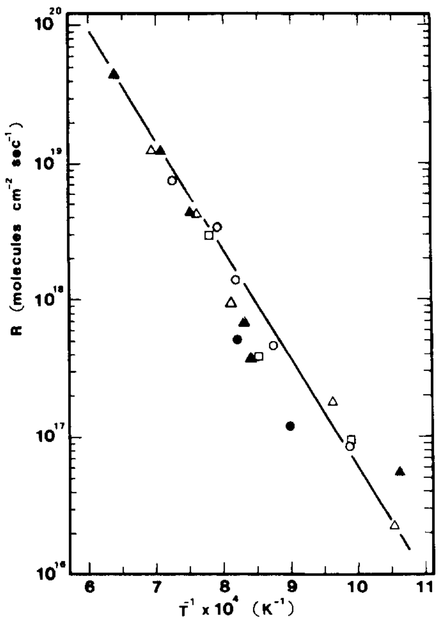

FIG. 4. Plot of log $R$ versus $1/T$ for the data of Fig. 1 in the zero-order regime. The slope and intercept of this line give $k_0$ as shown in Table 1. Diameter of tungsten wire is 0.0075 cm.

The LH kinetic parameters given in Table 1 seem to be consistent for the three wire diameters investigated. However, the observed reaction rates vary with diameter

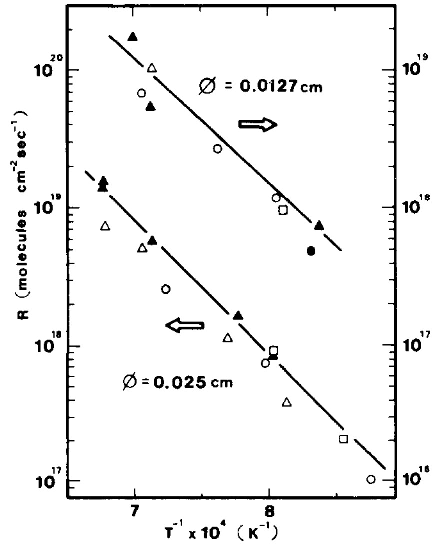

FIG. 5. Plot of log $R$ versus $1/T$ for the data of Figs. 2 and 3 in the zero-order regime. The slope and intercept of this line give $k_0$ as shown in Table 1.

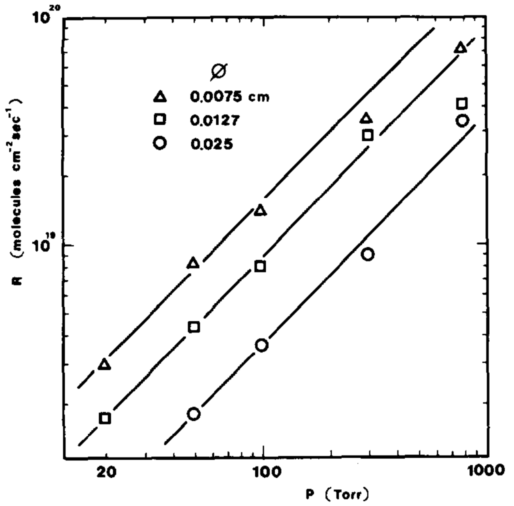

FIG. 6. Plot of log $R$ versus log $P$ for temperature indicated. For rates lower than $2 \times 10^{19}$ molec./cm$^2$ sec$^{-1}$ the reaction is first order in $P$. At higher rates mass transfer resistances become important. $T$ = 2200K.

in the order 0.0075-cm diameter > 0.0127 > 0.025. Reproducibility of results on many different wires after the high-temperature treatment suggests that the surface should be free of gross contamination, leading us to believe that surface heterogeneity may be the cause of the activity variation. It has been shown (5) that different tungsten crystal planes present activities for ammonia decomposition varying by a factor of 10. If the crystal planes exposed on a surface vary with surface curvature, then reaction rates will be a function of wire diameter.

### *Kinetics and Mechanisms*

The results of the present investigation are most simply interpreted assuming single rates, coverage-independent parameters, and adsorption–desorption equilibrium. These are the LH assumptions which, for the reaction steps

$$NH_{3(g)} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} NH_{3(s)}, \quad (4)$$

$$NH_{3(s)} \xrightarrow{k_0} \tfrac{1}{2}N_{2(g)} + \tfrac{3}{2}H_{2(g)}, \quad (5)$$

yield the reaction rate expression

$$R = [k_0k_a/(k_d + k_0)]P/[1 + k_a/(k_d + k_0)P], \quad (6)$$

where $k_a$, $k_d$, and $k_0$ are rate constants for adsorption, desorption, and reaction, respectively. If $k_0 \ll k_d$, then $K$ in Eq. (1) will be a true adsorption–desorption equilibrium constant. The preexponential factor $A_K$ for localized adsorption of nondissociated ammonia is

$$A_K = s_0/\nu_0(2\pi MRT)^{1/2} \approx 10^6 s_0/\nu_0 \ (\text{Torr}^{-1}) \quad (7)$$

and, if $\nu_0$ is a vibrational frequency $\nu_0 \approx 10^{13\pm1}$ sec$^{-1}$, for the sticking coefficient at zero coverage $s_0 \approx 10^{-1\pm1}$ we obtain

$$-10 < \log A_K < -6.$$

Thus our measured $A_K$ values (Table 1) are within the expected range for the classical LH unimolecular rate expression.

If $k_0 \gg k_d$, $K \approx k_a/k_0$ and the rate constant at high temperature is $k_a$. This may well be the case for our reaction, since the observed zero activation energy for the first-order process will correspond to unactivated adsorption, not an unlikely occurrence on metal surfaces. We can then write, for the high-temperature experiments,

$$R = k_aP = \frac{N_AsP}{(2\pi MRT)^{1/2}}, \quad (8)$$

where $N_A$ is the Avogadro number, $s$ is the sticking coefficient for ammonia, and $N_AP/(2\pi MRT)^{1/2}$ is the flux of reactant to the surface.

Introducing in (8) our experimentally measured reaction rate constants for the first-order regime, we obtain, after rearranging, $s = 3.29 \times 10^{-4}$, $1.77 \times 10^{-4}$, and $0.74 \times 10^{-4}$ for the 0.0075-, 0.0127-, and 0.025-cm-diameter wires, respectively. These figures are on the lower end of the range of expected values for sticking coefficients on metals. Now Eq. (6) reduces to

$$R = k_aP/(1 + k_0/k_aP), \quad (9)$$

TABLE 2

Comparison of Reaction Rates

| Investigators | Pressure (Torr) | Temperature (K) | $R$ observed (molec./cm$^2$ sec$^{-1}$) | $R$ calculated with Eq. (1) |
|---|---|---|---|---|
| Dawson (*6*) | 0.082 | 1050 | $2.1 \times 10^{15}$ | $2.7 \times 10^{15}$ |
| | 0.050 | 1050 | $2.1 \times 10^{15}$ | $1.7 \times 10^{15}$ |
| | 0.011 | 1050 | $7.6 \times 10^{14}$ | $3.9 \times 10^{14}$ |
| McAllister | | | | |
| and Hansen (*5*) | 0.001 | 960 | $2.0 \times 10^{15}$ | $2.4 \times 10^{15}$ |
| crystal | 0.008 | 924 | $7.3 \times 10^{14}$ | $1.6 \times 10^{15}$ |
| plane (100) | 0.008 | 863 | $5.3 \times 10^{14}$ | $3.0 \times 10^{14}$ |

where $k_a$ and $k_0$ can be calculated from the data presented in Table 1, with $k_0$ as in Eq. (2) and $k_a = A_0 A_K$.

### *Comparison with Other Authors' Results*

Most previous studies of ammonia decomposition kinetics on tungsten report reaction orders and activation energy measurements. Few investigators have specified surface area or reactor conditions sufficiently to permit comparison of rates per unit area. McCallister and Hansen (*5*) measured specific rates on single-crystal planes at pressures of the order of $10^{-3}$ Torr, while Dawson (*6*) described a study of the decomposition kinetics on a 0.025-cm-diameter wire at 1050K and at the same pressures. This author reports pressure variations with time; however, reaction rates per unit catalyst area can be calculated from the dimensions of the experimental system. As indicated in Table 2, our rate expression fits those authors' data remarkably well (within a factor of less than 2). Agreement implies that a single rate expression describes the reaction between $10^{-3}$ and 770 Torr, a range of over $10^5$ in reactant pressure.

As summarized by Bond (*2*), most investigators obtain activation energies between 38 and 45 kcal/mole for the zero-order regime, in good agreement with our $E_0$ values listed in Table 1. The order with respect to ammonia has been shown to vary between 0 and $\frac{2}{3}$ for temperatures varying between 900 and 1100K. All previous workers found the reaction to be independent of hydrogen and nitrogen pressure.

The formation of surface tungsten nitrides has been postulated in the literature (*3*), while surface species with various stoichiometries of the form $W_xN_nH_m$, $x$, $n$, and $m$ being integers, have been proposed to account for ammonia dissociation mechanisms. However, hydrogen partial pressure does not influence the rate of reaction. This is a distinct difference from the effects observed on iron surface nitrides, where the presence of hydrogen strongly influenced the rate of reaction (*4*). If a surface tungsten nitride was formed in our experiments, it showed no effect on the reaction rate expression. Since the electrical resistivity of the wires at room temperature did not change after reaction, we believe that no bulk nitrides were formed.

## SUMMARY

Our measured rates of ammonia decomposition on tungsten require only the simple LH unimolecular reaction rate expression for their complete description, although we covered temperature and pressure ranges wider than those investigated by previous workers. This rate expression can be extrapolated more than three orders of magnitude in pressure to fit other authors' data,

thus describing the kinetics of the reaction over a pressure range greater than $10^5$. This implies that, for this reaction, data obtained at low pressures can be simply extrapolated to conditions of technical catalysis.

## ACKNOWLEDGMENTS

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