

Total Pressure Variation Determination of Reaction Rates at Constant Reactant Pressure

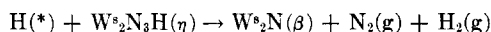
Catalytic Decomposition of Ammonia by Tungsten

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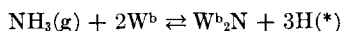
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Confirmation of a mechanism for the catalytic decomposition of ammonia by tungsten deduced from thermal desorption results requires measurements of the overall rate of reaction over a wide range of reactant pressures. Total pressure variation measurement of the rate is complicated by slow desorption of the reactant from the reaction vessel wall. A manostat is described which eliminates these problems. The rate of reaction has been determined for constant ammonia pressures in the range 9.10^{-3} to 6 torr and temperatures varying from 825° to 1050°K. The reaction is zero order for nitrogen and hydrogen. At 1050°K, the order for ammonia is zero at low pressure with a transition at 10^{-1} torr, as expected for a surface saturated with δ -nitrogen, $W^{\delta}N$, at low pressure and formation of η -species, $W^{\eta}N_3H$, above 10^{-1} torr. However, for pressures above 10^{-1} torr the order remains constant at $\frac{1}{3}$ even above the pressures required for η -saturation. It is proposed that absorbed hydrogen, $H(^*)$, participates in desorption of the η -species,



and that the absorbed hydrogen is in equilibrium with gas phase ammonia, to



account for the $\frac{1}{3}$ order for the reaction. The activation energy for the reaction has been determined at pressures varying from 10^{-2} to 2 torr and all values fall in the range 35.9 to 39.7 Kcal mole⁻¹ in agreement with the activation energies for δ - and η -desorption. The activation energy falls, as predicted, at the transition pressure of 10^{-1} torr. An increase at high pressure can be explained if the hydrogen absorption reaction is endergonic. Reasons are suggested for the lack of agreement between these results and recently published data.

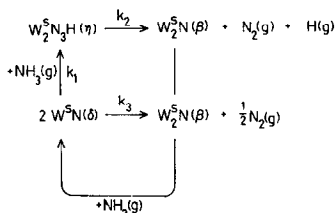
For a generalized chemical reaction, $\sum_i \nu_i M_i = 0$, where ν_i is the stoichiometric coefficient of chemical species M_i , for which $\sum_i \nu_i \neq 0$ and all M_i are gas phase species which can be considered perfect, the rate of reaction can be determined from the variation in the total pressure of the gas mixture. For example, consider the decomposition of ammonia reaction,



In this case, the rate of increase in total

pressure will be equal to the rate of decrease in the reactant pressure. This has been the method used almost exclusively in studies on the kinetics of this reaction catalysed by tungsten surfaces (1-6). The interpretation of the results as indicating a reaction which is zero order in the ammonia concentration has led to this reaction becoming a favorite textbook example. More recently we have studied this reaction using field electron emission microscopy (7, 8) and thermal desorption

mass spectrometry (8-11) and have concluded that there are two competing pathways for the reaction, involving two surface intermediates, δ -nitrogen, $W^{\delta}N$, and the η -species, $W^{\eta}N_3H$, schematically;



For simplicity, the reaction steps have not been balanced. Such cyclic paths only apply when the system is far from equilibrium; close to equilibrium, i.e., almost complete decomposition, the reverse reactions must also be considered.

The rate constants for reactions (1), (2), and (3) are (8, 10)

$$k_1 = 3.10^{18} \exp - [12000/RT] \text{ molecules cm}^{-2} \text{ sec}^{-1} \text{ torr NH}_3^{-1}$$

$$k_2 = 4.10^7 \exp - [35000/RT] \text{ sec}^{-1}$$

$$k_3 = 10^8 \exp - [(44700 - 8000\theta)/RT] \text{ sec}^{-1}$$

and all other reactions are considered fast. Reaction (1) is slow but dependent on the ammonia pressure so we predict two zero-order regimes for the decomposition mechanism determined by competition between reactions (1) and (3). At high reactant pressure, reaction (2) should be rate limiting whereas at low reactant pressure, reaction (3) will be rate limiting. The above kinetic parameters determined by thermal desorption studies on the individual reaction steps indicate that the transition pressure should be in the vicinity of 10^{-1} torr for a tungsten catalyst at a temperature of 1000°K . In order to confirm these predictions it is necessary to measure the overall rate of reaction over a wide range of pressure extending down to pressures below 10^{-1} torr.

For reaction mixtures containing gases which are strongly and yet reversibly adsorbed on the reaction vessel walls the simple calculation of the reaction rate from the variation in total pressure is invalid. Desorption of a reactant or adsorption of a product as the conversion increases neces-

sitates a correction which, for rates measured in a stepwise fashion, can only be calculated if the equilibrium adsorption isotherm is known. If the reaction is carried out in a continuous manner, then the rates of adsorption or desorption must be available. Ammonia gas adsorbs to a considerable extent on glass surfaces at room temperature; furthermore adsorption and desorption are slow processes. This complicates the determination of reaction rates, particularly at low reactant pressure where more ammonia can desorb from the wall than originally present in the gas phase (θ). In this work we have decided to avoid all of these complications by maintaining a constant reactant pressure throughout the course of the reaction. Hailes used this technique for two particular ammonia pressures of 7 and 37 torr using ammonia condensed in a cold finger immersed in cooling mixtures (4). In the present experiments we needed to be able to control the ammonia pressure over a wide range and have designed an appropriate cryogenic evaporation source.

EXPERIMENTAL METHOD

A schematic diagram of the apparatus used is shown in Fig. 1. The catalyst is a 24-cm length of 0.025-cm diameter tungsten wire, W , stretched horizontally between two of the 0.15 cm diameter Kovar leads of a four-lead press seal; the remaining leads are used to tap off a 15-cm centre section of the sample filament, via 0.008-cm tungsten leads, to allow temperature measurement and control. The glass reaction vessel, 50 mm in diameter, is pumped through a 1-inch all-metal valve V_1 by a 20 l sec^{-1} ion pump, I .

The evaporation source, S , is connected directly to the reaction vessel through 16-mm diameter glass tubing. The two limbs of the evaporation source terminate in $\frac{1}{4}$ inch Kovar tubes which are brazed into the top of a heavy 1 inch diameter by $1\frac{1}{2}$ inch long copper block which is also bored to contain a snugly fitting 30Ω heater, H . The block and limbs are enclosed in an evacuated glass jacket which is surrounded by liquid nitrogen in the Dewar vessel, D . Thermal connection between the copper

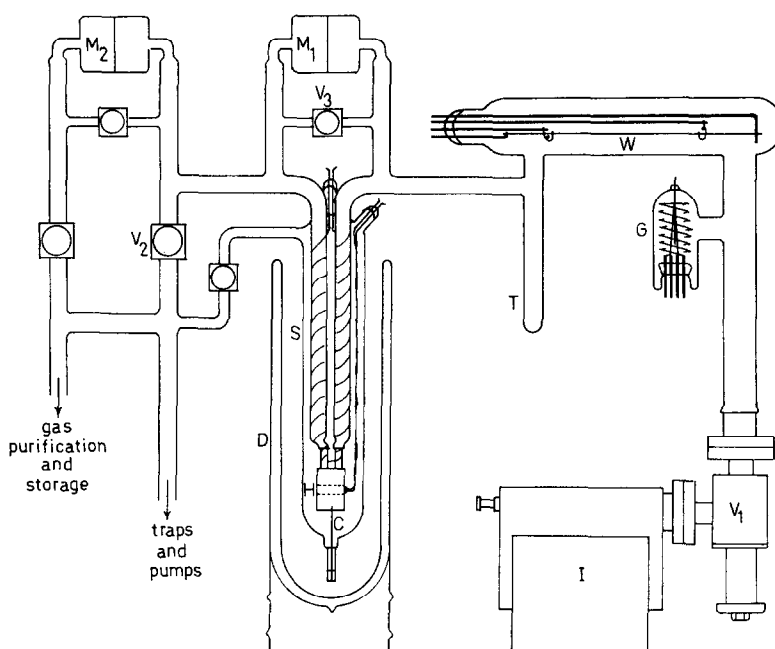


FIG. 1. Hot-wire reactor with manostat.

block and the liquid nitrogen is via a 0.10-cm diameter copper wire, C, brazed into the block at one end and soft soldered into a copper fitting within a $\frac{1}{4}$ inch Kovar tube at the other end. The limbs of the evaporation source are surrounded by tightly coiled nichrome wire. In operation, the heating currents to the block and limb heaters are provided by stable, well-regulated power supplies.

The differential pressure across the evaporation source could be accurately measured using the capacitance manometer, M_1 , which was an MKS model 90 with a bakeable ± 1 torr head surrounded by a thermostating jacket. The evaporation source was operated in a differential manner to avoid problems caused by any slight temperature variations in the copper block. Such a temperature variation would alter the equilibrium vapour pressure of ammonia gas in the reaction mixture. These changes would be too small to change the rate of reaction to a measurable extent but could make it impossible to measure accurately the small total pressure changes caused by decomposition. Small temperature fluctuations will change the ammonia pressure equally on both sides of the ma-

nometer and thus the change in differential pressure will accurately represent the change in pressure of reaction products. The reference ammonia pressure was also measured by a capacitance manometer, M_2 . This was a CGS Datametries model 1023 with a $523\text{H} \pm 10$ torr head. The reference side of manometer M_2 was continuously pumped during an experiment by a mercury diffusion pump backed by a rotary pump.

The apparatus is bakeable to permit ultrahigh vacua to be attained; however, in the present experiments the system has not been baked and the base pressure, indicated by the ion gauge, G, was 10^{-8} torr. In this way it will be possible to discover, by subsequent uhv experiments, whether such ultraclean conditions make any difference to the reaction kinetics.

Anhydrous ammonia gas (Matheson) was further purified by vacuum distillation and, after pump down and outgassing of the tungsten filament, could be introduced into the reaction vessel from storage bulbs via the O-ring valve V_2 and the all-metal valve V_3 . Slow adsorption of the ammonia on the walls of the reaction vessel necessitated a long equilibration time exceeding

one hour before a constant zero differential pressure was established.

The temperature of the tungsten filament was controlled by an automated Kelvin double bridge using a feedback circuit and differential amplifier. This allowed the filament to be raised to temperature in less than one second and held there automatically in spite of changes in power required as pressure and composition changes in the reaction mixture changed the thermal conduction of the gas. This is a considerable improvement in convenience and accuracy over earlier experiments in which the power was varied manually to keep a Wheatstone bridge circuit in balance. Moreover, the earlier procedure would require considerably more than one second to make the initial adjustment of temperature.

Most experiments were carried out in a stepwise manner; after heating for times varying from 15 to 300 sec, depending on

the reaction rate, the filament current was turned off and the gases allowed to cool to room temperature before measuring the new equilibrium pressure of the gas mixture. Some experiments were performed in a continuous fashion by measuring the pressure of the hot gas mixture as a function of time while the filament was continuously maintained at reaction temperature. For comparative purposes both stepwise and continuous experiments were carried out with the evaporation source in operation and also using the ammonia adsorbed on the reaction vessel wall as the only source of reactant gas.

RESULTS AND DISCUSSION

Pressure Variation during Heating, Decomposition and Cooling of the Reaction Mixture

The pressure variation was recorded directly using the DC output of manom-

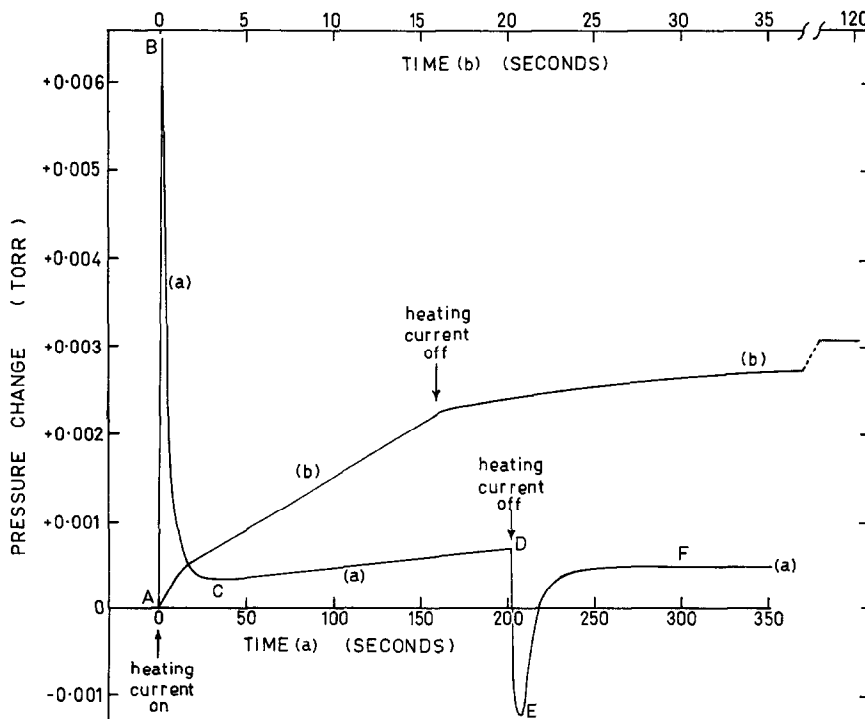


FIG. 2. Pressure response of the reaction mixture during a heating, decomposition, cooling, equilibration cycle. (a) ammonia pressure, 0.38 torr; filament temperature, 825°K; stepwise decomposition rate, 2.5×10^{-6} torr sec $^{-1}$. (b) ammonia pressure, 0.011 torr; filament temperature, 1050°K; stepwise decomposition rate, 2.1×10^{-4} torr sec $^{-1}$.

eter M_1 ; two examples are shown in Fig. 2. For Fig. 2a, the temperature of the evaporation source was adjusted to maintain an equilibrium ammonia pressure of 0.38 torr and the tungsten filament was heated to 825°K. The Kelvin double bridge was turned on at A and from A to B the dominant effect resulting in the sharp pressure rise is the heating of the reaction mixture by the hot filament. In the region BC the dominant effect is the condensation of ammonia gas on the evaporation source to counteract the pressure increase, resulting from the temperature increase of the gas, and restore an equilibrium pressure of 0.38 torr. For region CD the dominant effect is the pressure increase produced by decomposition of ammonia. At D the heating current is turned off and from D to E the dominant effect is cooling of the reaction mixture, whereas in the period EF ammonia evaporation to restore the equilibrium value for the ammonia pressure dominates. The reaction rate can be calcu-

lated most accurately from the equilibrium pressure change at F and is 2.5×10^{-6} torr sec^{-1} for these reaction conditions. The pattern of the pressure variation depends markedly on the reaction conditions. In Fig. 2b, the ammonia pressure is 0.011 torr and the filament temperature is 1050°K. The decomposition rate is 2.1×10^{-4} torr sec^{-1} , almost 100 times faster than for experiment (a), whereas the heating effect is much reduced at the lower reactant pressure. The ammonia condensation effect, BC in experiment (a), can not be detected; moreover the steady-state rate is approximately one-half of the stepwise rate which is just what would be expected if a negligible amount of the ammonia decomposed was replaced by evaporation during the 15-sec heating period. The cooling effect, DE in experiment (a), can not be detected but is dominated by the replenishment of the ammonia which has been lost by decomposition. The steady-state rate in experiment (a) is also less than the stepwise

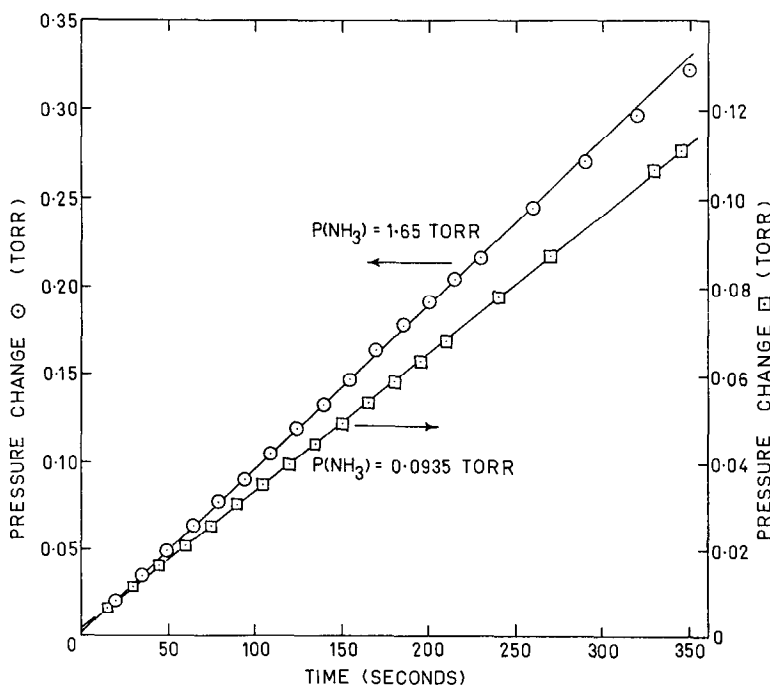


FIG. 3. Rate of decomposition of ammonia for a tungsten filament temperature of 1050°K. The evaporation source was used to maintain the ammonia pressure constant at either 0.0935 or 1.65 torr. The pressure change was determined in a stepwise manner allowing 180 sec for equilibration. The rate is zero order in N_2 and H_2 , but not NH_3 .

rate by 10% and probably the replenishment of ammonia is also incomplete during this experiment. Clearly the interpretation of the steady state rates is difficult and the stepwise rate measurements are much more reliable. For high reaction rates the ammonia pressure will not be constant during a heating period and the rate will vary slightly as a consequence. However, a constant reactant pressure will be established before the commencement of each heating period. Thus, by decomposing only a small fraction of the ammonia in each heating period the effect will be small and the stepwise rate will approximate the correct rate for that ammonia pressure.

Order of Reaction

These experiments were all carried out in a stepwise manner using the evaporation source and a tungsten filament temperature of 1050°K. The measurements were carried out at 24 reactant pressures varying from 9.6×10^{-3} to 6.07 torr. Typical results are shown in Fig. 3 for reactant pressures of 9.35×10^{-2} and 1.65 torr and it can be seen that the reaction rate is uninfluenced by

the buildup of reaction products; for the low pressure experiment, this is the case even where the pressure of products exceeds that of the reactant. Thus the reaction is zero order in the nitrogen and hydrogen pressure, agreeing with the results obtained by Hailes (4). The rate is influenced by the ammonia pressure; the rate at the higher reactant pressure is three times greater.

A plot of log (reaction rate) against log (reactant pressure) will have a slope equal to the order of reaction. Such a plot is shown in Fig. 4. As predicted, the reaction is zero order at low pressure, corresponding to a saturated δ -nitrogen adlayer; the rate is constant at $(3.6 \pm 0.4)10^{-4}$ torr sec⁻¹, a value in excellent agreement with that calculated from the rate constant for δ -nitrogen desorption, k_3 . There is a transition in the vicinity of 10^{-1} torr, as predicted, to an order of 0.35. The reaction order remains constant at this value up to the highest pressures used; there is no sign of a trend towards zero order as would be expected if the surface coverage of the η -species were to increase and saturate.

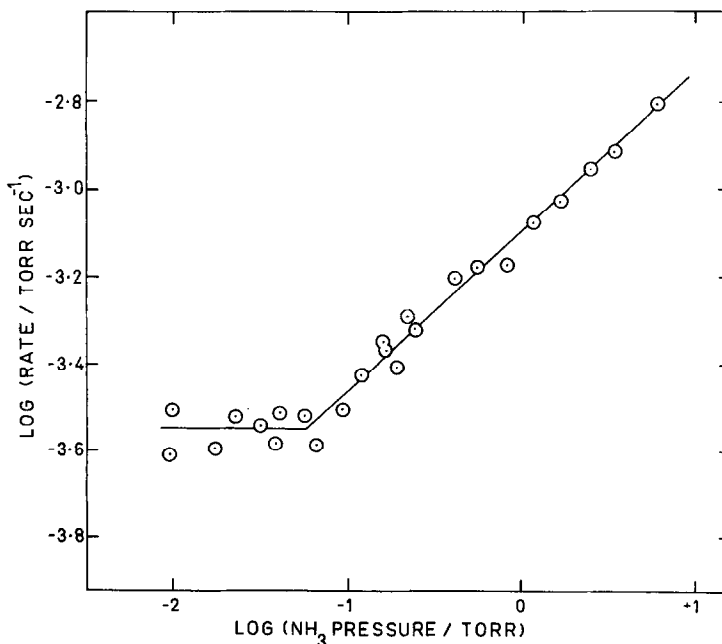


Fig. 4. Order of reaction in NH_3 as a function of ammonia pressure. The reaction is zero order below 10^{-1} torr and $\frac{1}{3}$ order at higher pressures.

McAllister and Hansen (12) have recently reported results for the catalytic decomposition of ammonia on tungsten single crystal faces which are in marked disagreement with the results presented here. The rates were measured for catalyst temperatures varying from 800° to 970°K and ammonia pressures varying from 5×10^{-4} to 10^{-1} torr; the rate of decomposition was interpreted by an expression, $\text{rate} = A + BP_{\text{NH}_3}^{2/3}$. In contrast, the results reported here show that the reaction rate is independent of the ammonia pressure, at least for the higher pressures studied by McAllister and Hansen. The reason for these conflicting results is not obvious. The sample used in these experiments is polycrystalline but this cannot account for the difference since McAllister and Hansen observed the same behavior for all crystal planes investigated. Ultrahigh vacuum conditions were not employed in the present experiments and yet the results at the lower pressures do agree with the predictions based on ultrahigh vacuum thermal desorption experiments. McAllister and Hansen determined the reaction rate from the rate of increase in partial pressure of products measured mass spectrometrically, and thus their data are free from the complications which can arise in the total pressure method. However, McAllister and Hansen relied entirely on desorption of ammonia from the reaction vessel walls to maintain a constant reactant pressure throughout their experiment. Since the steady state rates were constant for 100 sec or more, the pressure was probably constant during this period; however it is very possible that the steady state pressure was less than that measured before decomposition had commenced. In the discussion of Fig. 2 it has been pointed out that at steady state the replenishment of ammonia is incomplete, even when using an evaporation source. When ammonia adsorbed on the reaction vessel wall is used as the only source of reactant gas, the situation will be even worse. This is illustrated by the results shown in Table 1.

The ammonia pressures at the conclusion of each experiment, $p_{\text{NH}_3}^{\text{final}}$, were deter-

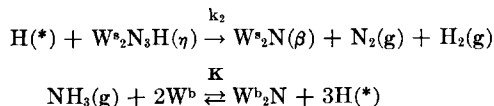
TABLE 1
APPARENT STEADY-STATE REACTION RATES
WITHOUT EVAPORATION SOURCE;
TUNGSTEN FILAMENT
TEMPERATURE, 1050°K

$P_{\text{NH}_3}^{\text{initial}}$ (torr)	Apparent rate (torr sec ⁻¹)	$P_{\text{NH}_3}^{\text{final}}$ (torr)
0.082	1.8×10^{-4}	0.057
0.050	1.8×10^{-4}	0.022
0.011	6.5×10^{-5}	0.0014

mined by quenching the ammonia in cold finger T (Fig. 1) and measuring the change in pressure. A check on this value was made by pumping out the reaction products and then allowing the ammonia to warm and equilibrate with the reaction vessel wall at room temperature. The results were in excellent agreement. For ammonia pressures prior to decomposition in this range, $10^{-2} < P_{\text{NH}_3}^{\text{initial}} < 10^{-1}$, the stepwise rates using the evaporation source are $(3.6 \pm 0.4)10^{-4}$ torr sec⁻¹ and independent of ammonia pressure (Fig. 4). This rate cannot be compared directly with the apparent rates of Table 1. The difference between $P_{\text{NH}_3}^{\text{initial}}$ and $P_{\text{NH}_3}^{\text{final}}$ clearly demonstrates that the replenishment of ammonia is incomplete during the experiment. If it is assumed that no replenishment occurs, then the apparent rates must be doubled for comparison with the stepwise rate for which replenishment is complete. Thus the rates for initial pressures of 0.082 and 0.050 torr compare very well with the stepwise rate; this suggests that the decrease in pressure at steady state during decomposition is insufficient to take the system out of the zero-order regime. However at an initial pressure of 0.011 torr the rate has fallen off considerably. The steady state reactant pressure will be less than 0.0014 torr, since some ammonia evaporation will have occurred prior to measurement of $P_{\text{NH}_3}^{\text{final}}$; presumably the reactant pressure is too low to maintain a saturated δ -nitrogen adlayer, satisfactorily accounting for the decrease in rate. In this way it appears quite possible that the rates measured by McAllister and Hansen are correct but the reactant pressures erroneous. The

isotope effect which they observe could be an isotope effect on the rates of desorption of NH_3 and ND_3 from the reaction vessel walls.

The constant order for the reaction of 0.35 observed at pressures varying from 10^{-1} to 6 torr does not agree with the predictions of the δ/η competitive mechanism; this mechanism requires a variable order between 10^{-1} and 1 torr and a return to zero-order kinetics at about 1 torr, corresponding to a saturated η -species. Preliminary experiments, performed without the evaporation source, in the pressure range 10 to 300 torr suggest that the order remains constant at about $1/3$ at these higher pressures. Indeed a close examination of the early data of Hinshelwood and Burke (1) and Hailes (4) confirms this conclusion. A constant order of reaction over more than three orders of magnitude variation in reactant pressure is quite remarkable. A Langmuir-Hinshelwood mechanism cannot account for this behaviour, unless a very small change in the concentration of the adsorbed intermediate (η -species) accompanied this wide variation in reactant pressure; this would contradict the thermal desorption results (8, 9). The only known process not included in the δ/η competitive mechanism is the diffusion of nitrogen and hydrogen into the bulk of the metal. Tungsten nitriding by ammonia gas has been described by several workers (13-15); we have also observed (8, 9) that absorption of hydrogen accompanies this nitriding in the pressure and temperature range of the constant $1/3$ order reaction. The following mechanism satisfies all the experimental observations.



where W^{b} and $\text{W}^{\text{b}}\text{N}$ are bulk tungsten and nitride, respectively, and H^* represents subsurface or dissolved atomic hydrogen. This mechanism is speculative, but is supported by the following observations. First, in the absence of any nitrogen and hydrogen absorption there is a tendency for the

η -species to desorb hydrogen in the atomic state (8, 9, 16). Thus in the presence of subsurface hydrogen a reaction permitting desorption in the molecular state might be anticipated. Second, the amount of absorbed nitrogen and hydrogen increases with increasing ammonia pressure and removing ammonia before cooling the tungsten reduces the amount absorbed (17). These observations are consistent with the above equilibrium.

If the bulk tungsten and nitride are both at unit activity and the surface is saturated with the η -species, then

$$\frac{d[\text{N}_2(\text{g})]}{dt} = k_2[\theta_\eta][\text{H}^*] = k_2\{\text{K}[\text{NH}_3(\text{g})]\}^{1/3}$$

satisfactorily accounting for the $1/3$ -order reaction.

Activation Energy

The reaction rate has been measured for pressures in the range 10^{-2} to 2 torr at temperatures varying from 825° to 1050°K . These results are presented as Arrhenius plots in Fig. 5. All the activation energies fall in the range 35.9 to 39.7 kcal mole $^{-1}$ which is exactly the range expected for a surface saturated with either the δ - or η -species.

McAllister and Hansen (12) observe surprisingly low activation energies for ammonia decomposition on tungsten. This can be explained by the same effect suggested to account for the differences in order of reaction. The differences between initial and steady state reactant pressures will increase with increasing reaction rate, i.e., increasing temperature. Thus the rates at higher temperatures will be lowered to a greater extent than those at the lower temperatures as compared to the true rate at the initial reactant pressure. This will lead to activation energies which are too low.

There are definite trends in the activation energies shown in Fig. 5. As the reactant pressure increases through the transition regime around 10^{-1} torr there is a decrease in activation energy as expected for the change from δ - to η -desorption as

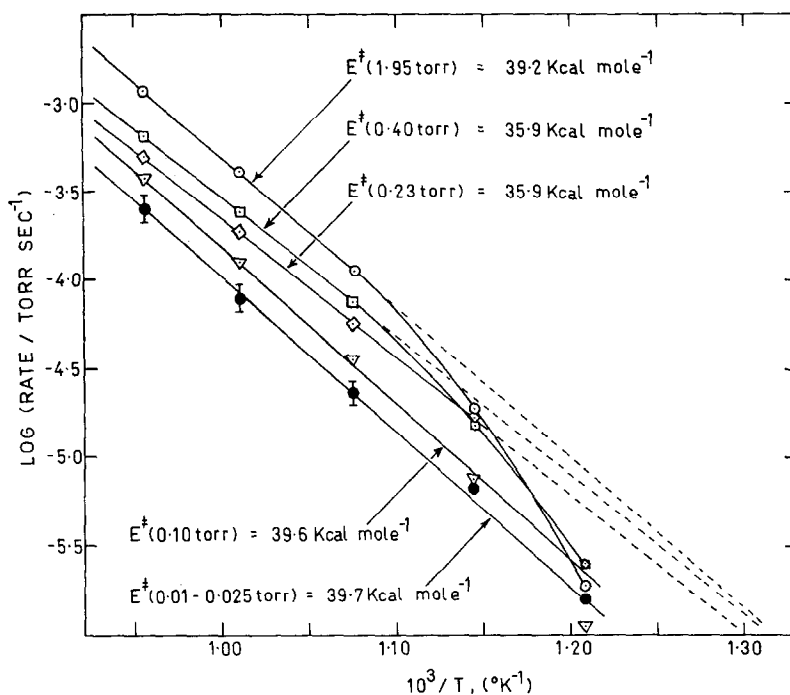


Fig. 5. Arrhenius plots for the decomposition of ammonia on tungsten at constant ammonia pressures varying from 0.01 to 1.95 torr. For pressures in the range 0.01 to 0.025 torr and temperatures from 930° to 1050°K five sets of data fell within the error bars shown.

rate limiting. At even higher pressures (1.95 torr) the activation energy again increases. If the incorporation of nitrogen and hydrogen into the bulk is an endergonic process, this can be understood since for participation of absorbed hydrogen in η -desorption the apparent activation energy will be $E_2^{\ddagger} + \frac{1}{3}\Delta G^{\circ}$, where ΔG° is the standard free energy change associated with equilibrium constant K . These conclusions are somewhat tentative and require confirmation with more extensive data.

Note that the rates at high reactant pressures fall off at temperatures below 930°K to values close to those for the low pressure experiments. The δ/η competitive mechanism discussed in the introduction to this paper predicts the opposite effect; i.e., the lower the temperature, the lower the pressure of ammonia required to sustain the η -species. At temperatures below 900°K little bulk incorporation of nitrogen or hydrogen has been detected. Thus the observed fall-off in rate at low tempera-

tures is consistent with the mechanism proposed to interpret the $\frac{1}{3}$ order of reaction.

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