

V. PHYSICAL ELECTRONICS AND SURFACE PHYSICS*

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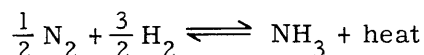
A. SYNTHESIS OF AMMONIA UNDER HIGH-VACUUM CONDITIONS

1. Introduction

The specific objective of this program is to study the role of iron as a catalyst in the synthesis of ammonia by using high vacuum techniques and a mass spectrometer. More generally, we hope to demonstrate the value of high-vacuum surface studies to the field of heterogeneous catalysis.

This first progress report describes the problem, the experimental apparatus, and some preliminary data.

2. Equilibrium



Equilibrium data for this reaction was first obtained by Haber and Van Oordt in 1905¹ and is now established over a wide range of temperatures.² The reaction is clearly favored by low temperatures and high pressures.

The experimental equilibrium data can be fitted closely through statistical mechanics by using an energy of formation, ΔE , of -9400 cal/gm-mole; for temperatures in the vicinity of 300 to 600°K, the equilibrium constant varies in proportion to $T^{-3} \exp\left(-\frac{\Delta E}{RT}\right)$, hence increases strongly for a decrease in temperature. However, for an industrially-useful reaction rate, a temperature of at least 625 to 700°K is required. Thus a sharp conflict exists between the demands for a useful rate and for higher production concentrations.

Even if the reaction would proceed at room temperature (this has not been observed), the equilibrium partial pressure of ammonia formed from reactants at pressures directly observable with a spectrometer would be small. For example, at 300°K

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with $P_{N_2} = P_{H_2} = 10^{-5}$ Torr, $P_{NH_3} \approx 10^{-10}$ Torr at equilibrium. Yet ammonia was recently synthesized at pressures greater than 10^{-7} Torr under nonequilibrium conditons

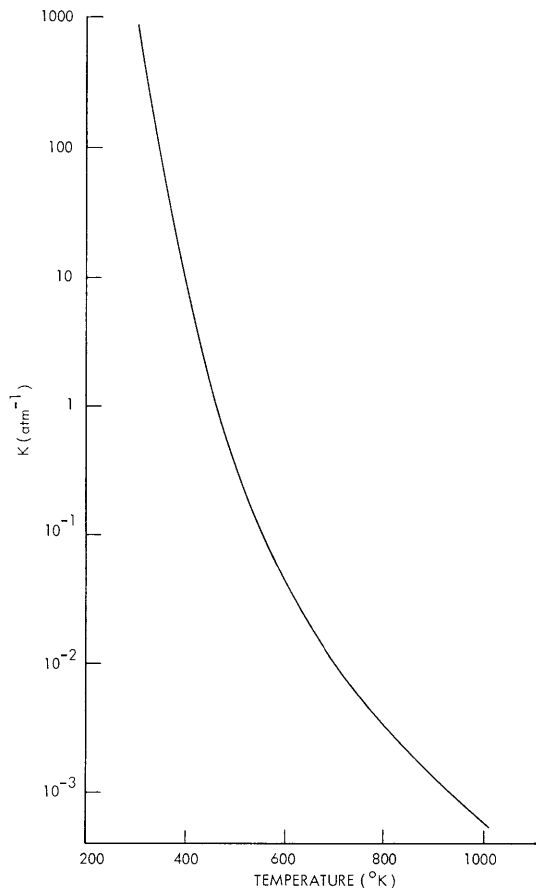


Fig. V-1. Equilibrium constant, K , as a function of temperature for the reaction $\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightleftharpoons NH_3$.

by G. E. Moore who used a molybdenum ribbon as his catalyst.³ Moore pulsed the ribbon's temperature, thereby probably increasing the surface "pressure" or concentration of one or both of the reactants considerably above equilibrium. He noted that at these low pressures, diffusion effects seem to be of importance comparable to surface effects.

3. Design of Experiment

The heart of the experiment is a thin-walled iron tube commercially produced as a nitrogen diffusion leak for vacuum studies. The heating mandrel and filament normally surrounding the tube have been removed for our study. We reduced the wall thickness of the tube to about 5 mils to allow higher diffusion rates and direct resistance heating.

The mass spectrometer is placed close to the tube so that atoms, molecules, or free radicals leaving the iron surface can travel directly into the analyzer. The temperature

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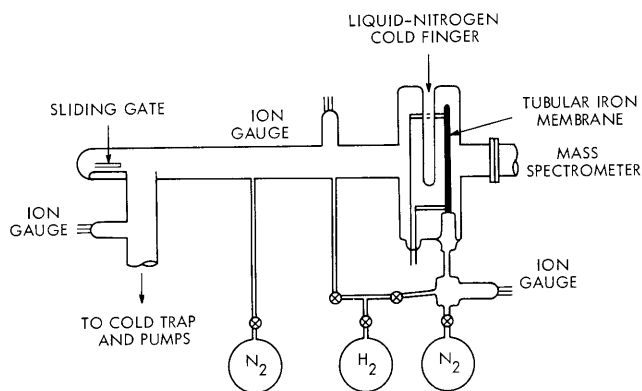


Fig. V-2. Schematic of experimental apparatus for studying NH₃ catalysis.

With the arrangement shown above, there are four possibilities for studying ammonia synthesis:

1. Both reactants supplied to the outer surface of the tube by chemisorption from the surrounding gas.
2. Both reactants supplied to the outer surface by diffusion from the interior of the iron membrane.
3. and 4. One reactant supplied through chemisorption and other through diffusion.

4. Results

We recently produced ammonia at easily measurable pressures. This was first accomplished by surrounding the iron catalyst, inside and out, with hydrogen and

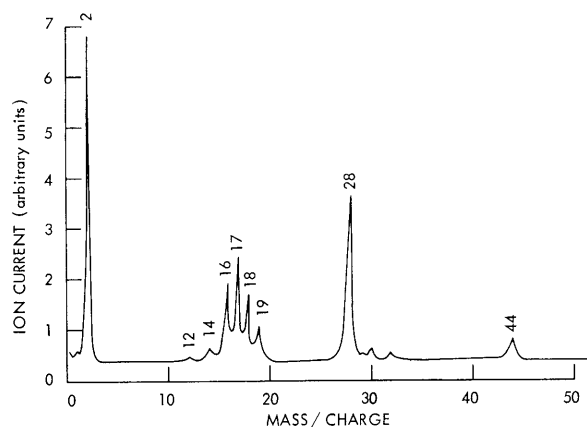


Fig. V-3.

Spectrum obtained following overnight of pumping with controlled nitrogen and hydrogen leaks. The iron tube was unheated. Total pressure, 3×10^{-7} Torr. Peak 44 is CO₂; peak 28 is N₂ and CO; 19 is fluorine (from the glass); 18 is H₂O; 17 is NH₃ with some OH from H₂O cracking; 16 is mostly NH₂ from NH₃ cracking; 14 is N; 12 is C from CO₂ and CO cracking; and 2 is H₂.

nitrogen at 10^{-4} Torr, then pulsing the membrane while the cold finger was filled with liquid nitrogen. On warming the finger, ammonia desorbed from its surface and was

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thereafter present in the system in varying amounts until the next bakeout.

Following bakeout and before breaking the flasks, we unsuccessfully attempted to outgas the iron of CO. Carbon monoxide continues to be produced conspicuously whenever the iron is heated. The tenacity and continued presence of CO with molybdenum and tungsten was recently pointed out as a possible source of error in hydrogen exchange studies not employing a mass spectrometer.⁴

The introduction of hydrogen to the system was accompanied by what appears to be the three lightest paraffins, methane being most prominent. We are now attempting to eliminate these undesirable products before continuing with our investigation of ammonia synthesis.

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