

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## The Decomposition of Deutero-ammonia on Tungsten Filaments

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From the researches of Hinshelwood and Burk<sup>2</sup> it is known that the decomposition of ammonia on a hot surface of tungsten is a nearly "zero-order" reaction, largely independent of ammonia pressure between the limits of 50–200 mm. The reaction appears, moreover, to be independent of the pressures of nitrogen and hydrogen. Such zero-order heterogeneous reactions are usually interpreted as processes in which the reaction surface is practically saturated with the reactant gas. It is also assumed that if the simple zero-order characteristics are maintained over a range of temperature, the surface area of reaction remains unchanged and "the variation of the observed reaction velocity is due entirely to the changing rate of the actual chemical transformation." For these reasons an examination of the catalytic decomposition of deutero-ammonia on tungsten was of interest, since if it were found to be, like ammonia, of zero order, the effect of temperature would immediately reveal the stability of the molecule in question on such surfaces compared with the stability of ordinary ammonia. We have, therefore, made comparative studies of the decompositions of ammonia and deutero-ammonia on tungsten filaments in the neighborhood of 1000°K.

### Experimental

The reactions were followed in a 150-watt Mazda tungsten filament lamp of 325-cc. capacity suitably modified to permit evacuation, admission of gas and measurement of pressure on a mercury manometer. The lamp was immersed in a cold water bath at a temperature of approximately 20°. Experiment showed that the pressure measurements were insensitive to the observed variations of bath temperature. The tungsten wire was kept at constant temperature (~950°K.) by maintaining a constant resistance of the wire, the energy being supplied from a d. c. source at 110 volts, operated with suitable external resistance. The constancy of resistance in the wire was secured by a Wheatstone bridge arrangement coupled with a galvanometer set to zero position, the external resistance being adjusted by hand

control as required. The activity of the wire was controlled by duplication of experimental runs and by interposing runs with the deutero-ammonia between groups of runs with ammonia. Throughout the whole series of fifty experiments there was no important change in catalytic activity.

The gases employed were pure NH<sub>3</sub>, pure ND<sub>3</sub> and a deutero-ammonia (48% D), prepared as in our earlier work,<sup>3</sup> both light and heavy ammonias being specially purified and introduced into the reaction system after condensation in liquid air, evacuation and subsequent evaporation.

### Experimental Results

**The Order of Reaction.**—With both ammonias, NH<sub>3</sub> and ND<sub>3</sub>, examined in a pressure range of 3 to 15 cm., the reaction, at a given wire resistance, proved to be of zero order, the curves for decomposition as a function of pressure being in every way similar to those obtained for ammonia by Hinshelwood and Burk.<sup>2</sup> This can be seen from the curves in Figs. 1 and 2, for NH<sub>3</sub> and ND<sub>3</sub>, respectively, which show little change in initial slope (pressure increase *versus* time) for a four-fold variation in operating pressure. The curves in Fig. 1 at 3.5 and 7 cm. pressure are constructed from two separate experiments each of which gave coincident results. This confirms the reproducibility of the data.

**Comparative Velocities of Decomposition.**—The data of the preceding section and data from additional experiments, specially designed to test the comparative rates, reveal that, at a given temperature of wire, the relative velocities of decomposition of NH<sub>3</sub> and ND<sub>3</sub> are in the ratio 1.6:1. Thus, in a pair of experiments (Nos. 39 and 40) at 7 cm. pressure the ratios of the two velocities are 1.56, 1.59, 1.62 and 1.59 at 15, 30, 50, 70% decomposition. Similarly in Experiments 46 and 47 at the same pressure the ratios were 1.56, 1.57, 1.62 and 1.61 for similar intervals of decomposition. In Experiments 30 and 31 at 3.5 cm. pressure the ratios are 1.58, 1.60 and 1.56. Further values of this ratio are shown in Fig. 3.

**Comparative Temperature Coefficients.**—Experiments were carried out at three different wire resistances with NH<sub>3</sub> and ND<sub>3</sub>. In the tem-

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(2) Hinshelwood and Burk, *J. Chem. Soc.*, 127, 1116 (1925).(3) Taylor and Jungers, *J. Chem. Phys.*, 2, 373 (1934).

perature interval in question the velocity of decomposition increased ten-fold. Within the experimental error the temperature coefficient as measured was identical in the case of the two gases. This could readily be demonstrated by adjusting the comparative rates with the factor 1.6 already attained. Plots of the data for both gases so adjusted fell approximately on the same curves. The deviations from identity of the curves were definitely in the direction of a larger temperature coefficient for the deuterio-ammonia.

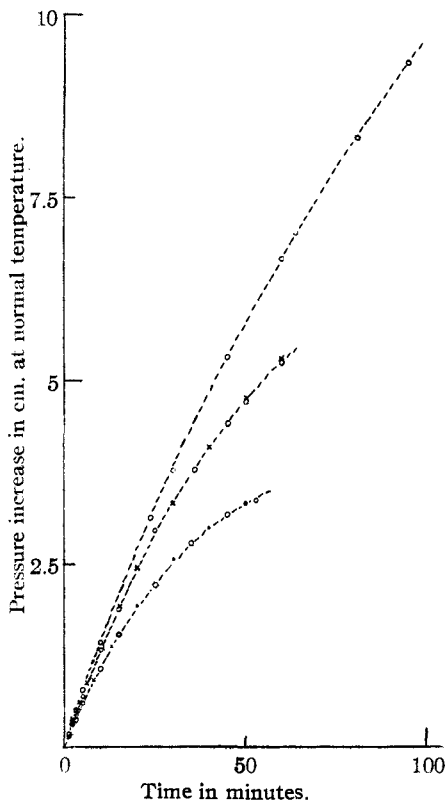


Fig. 1.—Velocity of decomposition of  $\text{NH}_3$  at 3.5, 7 and 15 cm. pressure: circles and crosses indicate reproducibility of experiments.

The temperature range in which these experiments were made was not accurately determined since we were only interested in relative values. Our data on the resistivity of the tungsten wire indicate, however, that the three temperatures employed in these measurements were approximately  $900, 950$  and  $1020^\circ\text{A}$ . The velocity data obtained with ammonia show a variation with the temperature similar to that obtained by Hinshelwood and Burk<sup>2</sup> and by Hailes.<sup>4</sup> The activation energy for the process in this range

(4) H. R. Hailes, *Trans. Faraday Soc.*, **27**, 601 (1931).

of temperature and pressure is about 35,000 calories.

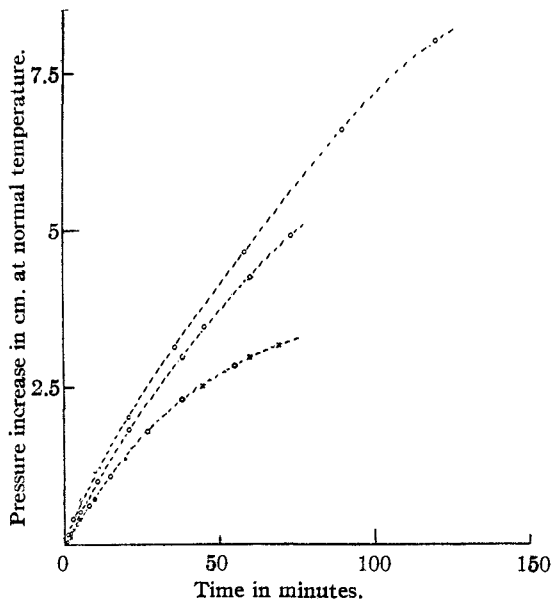


Fig. 2.—Velocity of decomposition of  $\text{ND}_3$  at 3.5, 7 and 15 cm. pressure: circles and crosses indicate reproducibility of experiments.

**Influence of Deuterium Concentration.**—A mixed deuterio-ammonia preparation, containing all the ammonias in equilibrium, 48% of all the

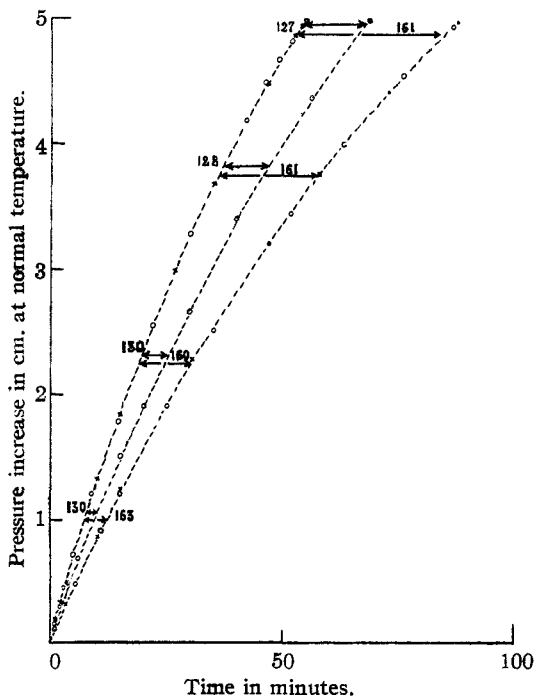


Fig. 3.—Velocity of decomposition of  $\text{NH}_3, \text{ND}_3$  and  $\text{NH}_{1.5}\text{D}_{1.5}$  (equilibrium mixture) at 7 cm. pressure.

hydrogen atoms being the deuterium isotope, was decomposed and compared with the velocities of decomposition of the pure proto- and deuterio-ammonias. Over the whole range of decomposition the rate obtained was intermediate in value (see Fig. 3) and equal to that calculated on the mixture rule for 55%  $\text{NH}_3$  and 45%  $\text{ND}_3$ . We deduce, therefore, a practically linear relationship between decrease in reaction rate and deuterium content of the ammonia.

### Discussion

The zero-order decomposition of deuterio-ammonia over the pressure-temperature range studied, indicates reaction in a surface area practically saturated with reactant. From the close similarity of the physical properties of proto- and deuterio-ammonia molecules one is justified in assuming that the reaction area available to both types of molecule for reaction is the same under comparable operating conditions. Hence, we conclude that the slower rate of decomposition of the deuterio-ammonia is to be ascribed to the intrinsically greater stability of the molecule when in the adsorbed layer. For decomposition, the deuterio compound requires an activation energy in excess of that required for ammonia by an amount,  $\Delta E$ , such that, at the operating temperature,  $T$  ( $\sim 950^\circ\text{K}$ .), the ratio of reaction rates, 1.6, is equal to  $\exp(\Delta E/RT)$ . This requires that  $\Delta E = 900$  calories approximately, an activation energy difference which can well be ascribed to the zero-point energy differences of the proto- and deuterio-ammonia adsorption complexes with tungsten. It is evident that this difference of activation energies is sufficiently small to make a determination of its magnitude from the temperature coefficients of the two decompositions a severe experimental operation. Our experimental data on the effect of temperature are not adequate to reveal this small difference in activation energy but do indicate that the temperature coefficient of the deuterio-ammonia decomposition is slightly greater than that of ordinary ammonia. In respect to the magnitude of the difference in activation energies it is of interest to note that in our earlier work<sup>3</sup> on the photosensitized decomposition of the two ammonias by excited mercury the analysis of the experimental data by Evans

and Taylor<sup>5</sup> revealed that the relative probabilities of decomposition of the energy-rich molecules produced by transfer of energy from the excited mercury was 5:1. Since, in this case, the operating temperature was approximately  $300^\circ\text{K}$ ., the zero-point energy difference which would account for this is given by the expression  $5 = e^{\Delta E/600}$ , whence  $\Delta E = 960$  calories in excellent agreement with the value found for the catalytic decompositions on the tungsten wire. This result indicates that zero-order decompositions on catalytic surfaces can serve as an alternative method of securing data on differences in zero-point energies of compounds containing hydrogen isotopes. Further work in this field is being undertaken.

The conclusion thus confirmed by experiments with deuterio-ammonia that the rate determining process is the decomposition of the adsorbed molecule in a saturated surface layer is also in agreement with the observations of Hinshelwood and Burk that nitrogen and hydrogen are without effect on the reaction kinetics. On certain surfaces, notably iron, there is evidence that the controlling reaction involves evaporation of surface nitrogen. We can expect, in such cases, marked deviations from the relations here found with tungsten as to relative velocities of decomposition. Such tests are in progress.

### Summary

1. The decomposition of deuterio-ammonia on tungsten wires at about  $950^\circ\text{K}$ . is an approximately zero-order reaction in the pressure range 3.5-15 cm.
2. The zero-order decomposition in this temperature-pressure range is slower than that of ammonia under the same conditions in the ratio 1:1.6.
3. The decrease in decomposition rate in mixed ammonias is proportional to the D-content.
4. The temperature coefficients of decomposition of  $\text{NH}_3$  and  $\text{ND}_3$  are the same within experimental error.
5. A zero-point energy difference between the decomposing surface complexes of 900 calories will account for the difference in decomposition velocities. This difference is too small to detect by our experiments on temperature influence.

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(5) Evans and Taylor, *J. Chem. Phys.*, **2**, 732 (1934).