The Kinetics of the Decomposition of Ammonia on Platinum at Low Pressures

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THE decomposition of ammonia into nitrogen and hydrogen was studied, at pressures of 10^{-4} torr and below, on electrically-heated platinum filaments using both conventional (c.v.) and ultra-high-vacuum (u.h.v.) techniques. The probability P of reaction when an ammonia molecule collides with the catalytic surface was found, and represented (when possible) by $P = B \exp(-E/\boldsymbol{R}T)$. With the u.h.v. apparatus, final pressures of 2×10^{-9} torr (measured by a Bayard–Alpert gauge) were readily achieved. Pressures ten times less were measured after long pumping and with the ion gauge used as an additional secondary pump.

A filament outgassed for 30 min. near the m.p. and flashed in ammonia at the reactant pressure (or a higher pressure) before each measurement gave in the u.h.v. apparatus reproducible values of P with $B = 10^{-1\cdot7}$ and $E = 4\cdot1$ kcal. mole^{-1} from 750—1830° K in general agreement with Apel'baum and Temkin.[1] Pre-treatment of the filament with hydrogen under various conditions did not alter the ammonia kinetics.

The c.v. apparatus gave far more complex results. After flashing in the vacuum a filament had at about 900° K a greater initial activity, and P above 900° K had a marked negative temperature-coefficient. However, after some minutes of reaction of ammonia, a steady state was reached with kinetics above 670° K similar to those in the u.h.v. apparatus. Initial rates in the c.v. apparatus were very dependent on the pre-treatment of the wire; great loss of activity arose from flashing in hydrogen at 10^{-2} torr, by heating at 1160° K in the residual gases, by leaving in the residual gases at room temperature, and by heating at 1900° K in propene. Generally the activity could be restored by treatment with ammonia at high temperature.

Many of the complications observed in c.v., including the negative temperature coefficient and high initial activity, were reproduced in u.h.v. by a wire pre-treated with 2,2,4-trimethylpentane. The wire was used in the freshly-baked apparatus to show that the complex kinetics arose from dissolved matter (very probably carbon) in the wire and not simply from outgassing residual hydrocarbon. The high activity ascribed to carbon impurity could exceed the normal u.h.v. activity by over 50 times. But in excessive amounts the carbon poisoned the filament.

We suggest that ammonia on platinum rapidly produces a surface covered by a nitrogen-containing layer (perhaps a surface nitride), which can be removed as a volatile product by reaction with carbon diffusing from the interior of the metal, to give a very active metal surface. But excessive carburization of the platinum is considered to give an inactive carbon-covered surface, from which carbon can be removed as a volatile product by reaction with ammonia. On this basis equations are deduced explaining in general terms the complex kinetics. The steady-state high-temperature reaction is considered (in agreement with Apel'baum and Temkin[1]) to have a slow step involving NH_2(ads) formation. This is supported by measurements of a reversible inhibition by hydrogen (order $-0\cdot25$), by calculation of B and by consideration of the possible rate of evaporation of nitrogen from the surface.

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[1] L. O. Apel'baum and M. I. Temkin, *Russ. J. Phys. Chem.*, 1959, **33**, 585.