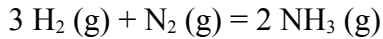
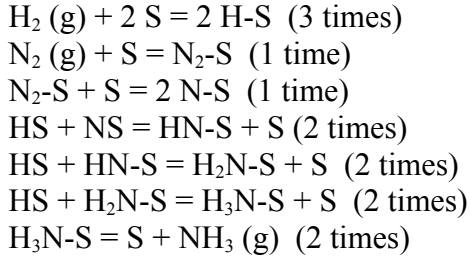


Ammonia Synthesis - Derivation of Rate Equations

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Ammonia synthesis mechanism over iron catalyst surface (Ertl, 1991):



In parentheses are number of times an elementary step occurs so that list of elementary steps sum to the stoichiometric equation for the reaction pathway:

This mechanism has many more steps than the general 2-step mechanism in my surface kinetics notes. Starting from the ODEs for a batch reactor and applying the steady-state approximation (SSA) to all surface species results in algebraic equations that look very difficult to get into a single equation. So I decided to consider a steady-state reactor, assume step (3) is the rate determining step, then apply the partial equilibrium approximation (PEA) to all other steps. The same result for the overall rate should be also obtained for a batch reactor with the SSA applied to all surface species and the PEA applied to all steps other than step (3).

For a reactor at steady-state, we make the assumption that step (3), dissociation of adsorbed N_2 , is the "rate determining step."

$$r_{\text{nh3}} = -2 r_{\text{n2}} = 2 k_{3f} C_{\text{n2}}^{\text{S}} C_{\text{v}}^{\text{S}} - 2 k_{3b} (C_{\text{n}}^{\text{S}})^2$$

We assume that all surface sites are identical and that rate coefficients do not vary with surface coverages. Then we apply the "partial equilibrium approximation" to all steps other than (3) in the mechanism. Doing the algebra to express all surface concentrations, except the total concentration of active sites, in terms of the partial pressure of gaseous species, I obtain

$$r_{\text{nh3}} = \frac{K_a P_{\text{n2}} - K_b \left(\frac{P_{\text{nh3}}^2}{P_{\text{h2}}^3} \right)}{B^2}$$

where

$$B = 1 + K_c P_{h2}^{0.5} + K_d P_{n2} + K_e \left(\frac{P_{nh3}}{P_{h2}^{1.5}} \right) + K_f \left(\frac{P_{nh3}}{P_{h2}} \right) + K_g \left(\frac{P_{nh3}}{P_{h2}^{0.5}} \right) + K_h P_{nh3}$$

$$K_j = \frac{k_{jf}}{k_{jb}} \quad \text{for } j = 1 \text{ to } 7$$

$$K_a = 2 (C_{tot}^s)^2 k_{3f} K_2 RT$$

$$K_b = \left(\frac{2 (C_{tot}^s)^2 k_{3b}}{K_1^3 K_4^2 K_5^2 K_6^2 K_7^2 RT} \right)$$

$$K_c = K_1^{0.5} (RT)^{0.5}$$

$$K_d = K_2 RT$$

$$K_e = \left(\frac{1}{K_1^{1.5} K_4 K_5 K_6 K_7 (RT)^{0.5}} \right)$$

$$K_f = \left(\frac{1}{K_1 K_5 K_6 K_7} \right)$$

$$K_g = \left(\frac{(RT)^{0.5}}{K_1^{0.5} K_6 K_7} \right)$$

$$K_h = \left(\frac{RT}{K_7} \right)$$

(5a-5h)

If we are fitting Equation 2 to rate data, we have eight adjustable parameters, K_a through K_h (possibly only seven, since making the rate equation consistent with the equilibrium relationship with a known equilibrium constant may eliminate one of the eight). With this many adjustable parameters, we should be able to fit almost anything!

This rate equation is for a steady-state reactor. It would apply to a transient batch reactor when the amount of catalyst surface atoms is small relative to the amount of gaseous molecules such that the SSA applies to all surface species.

The first term of Eqn 2 is the rate of production of ammonia by the forward reaction of step (3). The second term is the rate of consumption of ammonia by the reverse reaction of step (3).

The term B from the denominator of Eqn 2 is the denominator of the expression for C_v . An increasing value of B increases means that the concentration of vacant sites is decreasing. The fact that B is squared is from the fact that two surface sites participate in the rate determining step. All "Langmuir-Hinshelwood, Hougen-Watson" rate expressions for reactions on solid catalyst surfaces have a similar denominator term that is (1 + the sum of terms involving adsorption equilibrium constants and gas concentrations or pressures). The exponent on this sum is equal to the number of surface sites (both filled and vacant) that participate in the rate determining step. The denominator in "Langmuir-Hinshelwood, Hougen-Watson" rate equations describes "inhibition" of the reaction rate by adsorbed species covering the surface and blocking vacant sites and inhibiting further adsorption.

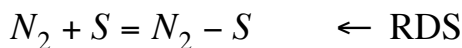
Making additional assumptions that the concentrations of some surface species are negligible would eliminate some of the terms from the B denominator term.

Note that Eqn 2 above is similar in form to the Temkin-Pyzhev rate equation. Re-arranging Eqn 6.7 in Gramatica and Pernicone's article (1991)

$$r_{nh3} = \frac{K_x P_{n2} - K_y \left(\frac{P_{nh3}^2}{P_{h2}^3} \right)}{\left(\frac{P_{nh3}^2}{P_{h2}^3} \right)^\alpha}$$

By adjusting the values of K_c through K_h in Eqn 2, one might be able to get the denominator to look similar to the denominator of the Temkin-Pyzhev equation, e.g., if the term involving K_c is much larger than the other terms in Eqn 2 (i.e., N_{ad} is the adsorbed species present in largest amounts) and α is close to 1 in Eqn 6 (which is the case when the rate coefficient of N_2 desorption is coverage invariant but the rate coefficient of N_2 adsorption decreases with increasing coverage). Remember that Eqn 2 is based on the assumption of identical sites with coverage-invariant properties, whereas the Temkin-Pyzhev equation, Eqn 6 here, was based on the Elovich adsorption isotherm, which assumes that the surface has sites with a distribution of properties.

Boudart and Djega-Mariadassou (1984) give another explanation of the derivation of Temkin's rate equation. Associative adsorption of N_2 is assumed to be the rate determining step, adsorbed N_2 is assumed to be the "most abundant reactive intermediate (mari)", and the PEA is applied to the reaction between H_2 and adsorbed N_2 :



where N_2-S is adsorbed N_2 . Over a uniform surface under these assumptions, the rate of ammonia formation is:

$$r_{nh3} = \frac{k_1 P_{n2} - \left(\frac{k_{-1}}{K_2} \right) \left(\frac{P_{nh3}^2}{P_{h2}^3} \right)}{1 + \left(\frac{1}{K_2} \right) \left(\frac{P_{nh3}^2}{P_{h2}^3} \right)} \approx \frac{k_1 P_{n2} - \left(\frac{k_{-1}}{K_2} \right) \left(\frac{P_{nh3}^2}{P_{h2}^3} \right)}{\left(\frac{1}{K_2} \right) \left(\frac{P_{nh3}^2}{P_{h2}^3} \right)} = \frac{(K_2 k_1) P_{n2} - k_{-1} \left(\frac{P_{nh3}^2}{P_{h2}^3} \right)}{\left(\frac{P_{nh3}^2}{P_{h2}^3} \right)} \quad \text{for } \theta_{n2} \rightarrow 1$$

However, Temkin assumed that there was a non uniform surface with a distribution of properties. Accounting for this distribution results in the parameter α in Temkin's rate equation.

Note that Eqn 6 predicts an infinite rate when no ammonia is present. That is not a problem in designing an industrial reactor since NH_3 removal from the product is not complete and NH_3 will always be present in the recycled gas fed to the reactor.

I can't think of any reason for the "virtual pressure" for N_2 that was mentioned in Gramatica and Pernicone's explanation of Temkin's rate equation.

References

Boudart, M. and Djega-Mariadassou, G., "Kinetics of Heterogeneous Catalytic Reactions," Princeton University Press (1984). (UCSD S&E Library, QD505.B6913.1984)

Ertl, G., "Elementary Steps in Ammonia Synthesis," pp. 109-132 in "Catalytic Ammonia Synthesis : Fundamentals and Practice," edited by J.R. Jennings. New York : Plenum Press (1991).

Gramatica, G. and Pernicone, N., "Kinetics of Ammonia Synthesis and Influence on Converter Design," pp. 211-252 in "Catalytic Ammonia Synthesis : Fundamentals and Practice," edited by J.R. Jennings. New York : Plenum Press (1991).