

metal membrane at temperatures of 225°–275° and the HCOOH partial pressures of 0.01–0.1 atm., using a recycle-continuous unit. The reaction rate is proportional to  $P_{\text{HCOOH}}^{0.66}$  and the energy of activation is 16.2 kcal/mol. The data of volatility of the hydrogen on the palladium surface and of the hydrogen delivery rates through the palladium membrane, preclude the possibility of the reaction course via a chain mechanism.

**Determination of Kinetics of Heterogeneous Catalytic Reactions, Based on the Critical Ignition Conditions: Synthesis of Alcohols from Carbon Monoxide and Hydrogen**

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A method, employing a differential-type reactor, was developed to determine the temperatures of the gases at the critical conditions of ignition. The kinetic parameters of the reactions of this type were determined with the aid of the method described in an earlier paper (1, 2), which correlates the critical parameters of strongly exothermal reactions with the critical conditions of ignition on the surface of a catalyst. The effectiveness of the latter method was demonstrated, by way of an example, in synthesizing alcohols from CO and H<sub>2</sub> over a fused iron catalyst.

**Kinetics of Ammonia Synthesis at Non-Equilibrium Conditions**

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An investigation of the kinetics of ammonia synthesis at near-equilibrium conditions and at conditions far-away from the equilibrium, was carried out in a recycle-continuous operation over nickel and cobalt catalysts at atmospheric and sub-atmospheric pressures. Two derived equations are shown to calculate the reaction rates: one of these is to be used when the NH<sub>3</sub> concentrations are close to the equilibrium values; the other one, when concentrations of the NH<sub>3</sub> are small relative to those at the equilibrium. The magnitudes of the exponent in the two equations are identical. The values of  $m$  and of  $m'$ , (since  $m = m'$ ) are

0.32 with the nickel catalyst and 0.22 with the cobalt catalyst. The equality of the  $m$  and  $m'$  values corroborates the theoretical interpretation of the kinetics of ammonia synthesis at the conditions far away from the equilibrium.

**Mass-Spectrometric Determination of the Rate Constants of Elementary Reactions: Reaction of Atomic Hydrogen with Ethylene**

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The rate constant,  $k_1$ , of the addition of atomic hydrogen to ethylene was determined at continuous flow conditions, using the "diffusion flux" technique. At the  $P_{\text{total}}$  of 6.56 mm Hg and T of (297 ± 3)°K,  $k_1$  is [8.8(±20%)](10<sup>-19</sup>) cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>.

The atomic hydrogen was produced by passing a stream of helium with small amounts of admixed H<sub>2</sub> through a high-frequency electric discharge. The concentrations of the H and C<sub>2</sub>H<sub>4</sub> atoms were determined mass-spectrometrically. The gas from the reactor was introduced into the ion generator in the form of a modulated molecular beam. The mass spectrometer was of known sensitivity for atomic hydrogen.

**The Effect of Ammonia Preadsorption on Thin Coatings of Gold on the Visible-Region Adsorption Spectra of the Metal**

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The absorption spectra in the visible region of very thin granular coatings of gold were studied before and after preadsorption of ammonia. The results obtained were analyzed in the light of the theory of plasmic oscillation of the electrons of a source-metal. The study shows that the preadsorbed ammonia increases concentration of the electrons due to the metal, decreases the electron relaxation time, and increases dielectric permeability of the medium around the metal granules. These findings are attributed to the electron transfer from the adsorbed molecules of ammonia to the metal. Other experimental data show that the preadsorbed ammonia alters the adsorption spectrum of atomic gold covering the quartz surface.