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The Adsorption of Hydrogen and Nitrogen on the Iron Catalyst

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The adsorption of hydrogen and nitrogen on the oxidized and on the reduced iron catalysts has been kinetically studied under constant pressures in the range between 50 and 400 mmHg, and the following results found:

(1) In the case of the adsorption of hydrogen on the oxidized catalyst, the rate at first stays constant to some extent of coverage; thereafter it proceeds according to the first order kinetics, in which a complicated pressure dependency occurs.

(2) In the case of the adsorption of hydrogen on the reduced catalyst, the rate follows the Bangham-type rate formula, modified by the Langmuir-type pressure dependency in the constant terms.

(3) In the case of the adsorption of nitrogen, on both the oxidized and the reduced catalyst, the rate follows the Zeldowich-type rate equation as modified by the initial adsorption term, which features a pressure dependency of the Langmuir type.

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The Mechanism of the Base-Catalyzed Decomposition of Hydrogen Peroxide

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The base-catalyzed decomposition of hydrogen peroxide has been studied kinetically over an alkaline range of pH and at several temperatures. Since the decomposition is known to be strongly accelerated in the presence of a metal ion, the experiments were performed with or without adding EDTA, a reagent by which to form a strong chelate with a metal ion. Without EDTA, the first-order rate constant reached a maximum value near 13.4, with a slope of 1, when plotted against pH; this is in close agreement with the finding of Ohki and Kaneko. With EDTA, the maximum rate constant was near 13.8, with a slope of 2 below and above this pH value. This pH–rate profile was not that expected from the theory proposed by Duke and Haas. A chain reaction mechanism has been presented for the system without EDTA, in which a metal ion is involved as an effective catalyst. On the other hand, a cyclic bimolecular mechanism has been proposed when EDTA is present; in this mechanism a hydrogen peroxide molecule and its conjugate base combine to form a six-membered ring in the transition state.

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A Model of Complex Molecules Based on Theory of Chemical Reactions

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A non-adiabatic reaction mechanism is discussed, involving formation of long-lived complex intermediate molecules. The processes of this type are satisfactorily described by use of approximated values for the non-overlapping resonance levels of the complex molecules. The capture rate constants of reactions characterized by reversible spontaneous dissociation and the life spans of the complexes were calculated for the oscillation models of Sleighter and Kassel type.

The discussion also covers the effect of different degrees of freedom on the rates of decom-