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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 decomposition of molecular complexes and usefulness of Transition State Theory in calculating the reaction rate.

Empirical Determination of Mechanism of Interaction of "Hot" Atoms and Hydrocarbon Molecules

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Based on kinetic calculations, different experiments are outlined to determine reaction kinetics of "hot" atoms with hydrocarbon molecules. As a result, valuable information is obtained regarding the mechanism of individual collisions. The experiments involving heterogeneous reactions yield the greatest amount of information of this type—particularly so, when employing inert moderators with atomic weights appreciably smaller than those of the hot atoms. In the latter case, experimental determinations of reaction rates between "hot" atoms and the surface—as a function of the inert gas layer thickness, serve to re-establish the functional dependence of energetics of these reactions.

Mechanism and Kinetics of Interruption of Chain Oxidation Reactions

By M. S. Khlopl'yankeena, A. L. Boochachenko, M. B. Neiman, A. G. Vaseel'yeva

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Chain oxidation reactions can be interrupted by aliphatic nitrate radicals, with resulting addition of the alkyl radicals. The effectiveness of interruption depends on availability of alkyl radicals in a reaction due to competition for them by the nitrate radicals and oxygen. At a temperature of 60° the ratios of the rate constants of the two competing reactions are 26 ± 3 for ethyl benzene and 1.4 ± 0.2 for diphenyl benzene.

The nitrate radicals are very convenient "counters" of the radicals present at the inception of radical polymerization reactions. For this reason, the nitrate radicals are useful quantitative indicators in determining the rates to initiate the reactions of ths type and in studying the "cage" effect in liquid phase reactions of radicals.

Kinetics of Thermal Decomposition of Methane

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Analytical methods were developed to solve kinetic equations for isothermal decomposition of methane and to evaluate its optimum conversion to acetylene at different reaction temperatures. Numerical solutions of the equations are presented when processing at different isoenthalpic conditions. The reaction time for the maximum yields of acetylene (70–80%) is shown to be 10^{-4}–10^{-3} sec.

The rate of heat abstraction to quench the acetylene and other reaction products exceeds 2,000 kcal/sec per mole of methane charge.

Low Temperature Halogenation of Simplest Olefins in Solid Phase

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Using suitable melting point curves, thermographic studies were made of low temperature chlorination and bromination of ethylene, propylene, and isobutylene—as solid nomogeneous mixtures at the reaction conditions. For equimolecular mixtures of these hydrocarbons at temperatures below −180°C, the reactions are practically instantaneous and occur near the melting points of the olefins studied. Isobutylene is rapidly halogenated at a temperature of −196°C, during condensation of gaseous reaction mixtures. It appears that exothermal formation of molecular complexes—with accompanying transfer of electrical charge—represents the initial stage of reactions of this type.

A qualitative comparison of relative reactivities of olefins with halides is presented in a tabulated form. The courses of these reactons in solid, liquid, and gaseous states are compared qualitatively.

Based on the results of this study and the published data, presence of negative temperature coefficient is hypothesized for the reactions in liquid phase.

Alteration of Physico-Chemical Properties of Solids by Additives: Thermal Decomposition of Silver Oxalate

By Yu. A. Zakharov, G. G. Sav'yel'yev, V. K. Jooravl'yov, V. V. Boldir'yev

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The effect of addition of Cd^{++}, Hg^{++}, and Pb^{++} on some of the properties of silver oxalate was studied in the light of some of the properties of these ions. The results show that at similar conditions these ionic additives alter to a quantitatively different degree the electrical properties and thermal stablity of $Ag_2C_2O_4$. Thermal decomposition of silver oxalate is increasingly re-