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Unidimensional Model of Reaction of Diatomic Radicals With Solid Surfaces

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The exchange energy between diatomic radicals and a solid surface was analyzed with the aid of a unidimensional mathematical model based on a harmonic approximation. A relationship was established between the critical dissociation energy of the radicals and their energy of bonding with the "wall." The results show that well potentials have practically no effect on the energy transfer from a diatomic radical to a solid. The probability of dissociation of diatomic molecules was evaluated in "one-point" adsorption.

Phenomenology of Atomic Oxygen Flames

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For atomic oxygen flames a correlation was established between conversion and the ratios of the initial reaction rates, W, of atomic oxygen to the critical auto-heating rates, W_{crit}. The conversion increases with increasing ratio values. Formation of atomic flames and the extent of conversion within them can be explained in terms of the limiting thermal phenomena.

The Upper Ignition Limit in Fluorine-Hydrogen Reaction

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In fluorine-hydrogen reactions the upper limit of ignition varies with pressure. It is concluded that the reaction proceeds along a branched-chain route. Apparently, the branching is associated with the dissociation of the fluorine due to oscillating energy of the excited HF molecules.

Photochemical Oxidation of Propane in Presence of Cl_2

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The nature of the initiators has but little effect on the mechanism of oxidation of propane when the reaction is photoinitiated by excited atomic Hg or by decomposition of NH_3, H_2S, and Cl_2. In the case of Cl_2, some decrease in formaldehyde yield is attributed to competition between the iso-C_3H_7 and the n-C_3H_7 radicals in the reactions below:

$$C_3H_7 + Cl_2 \rightarrow C_3H_7Cl + Cl \qquad (2)$$

$$C_3H_7 + O_2 \rightarrow C_3H_7O_2 \qquad (3)$$

At a temperature of 180°, the ratio k_2/k_1 is 13. Since n-$C_3H_7O_2$ radical is present in only relatively small concentrations, the ratio of the reaction constants, k_2/k_1, can be evaluated for the reactions below:

$$\text{iso-}C_3H_7O_2 + C_3H_8 \rightarrow \text{iso-}C_3H_7O_2H + C_3H_7 \qquad (4')$$

$$\text{iso-}C_3H_7O_2 + CH_3CHO \rightarrow CH_3O \qquad (5')$$

Here, $k_2/k_1 = 10^{24.3} \exp\left(\frac{-13{,}200 \pm 1{,}000}{RT}\right)$ molecules/cm^3.

Use of Chemiluminescence Technique in Study of Decomposition of Azo-bis-Isobutyronitrile in Presence of Oxygen

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The quantities of decomposed azo-bis-isobutyronitrile (AIBN) and of the O_2 reacting with the radicals produced in the decomposition were compared by observing the "oxygen decreases" due to the chemiluminescence. The cyanisopropyl radical was found to react faster with the O_2 than with the hydrocarbon. In inert solvents, all of the oxygen consumed in oxidizing the cyanisopropyl radical is found in the reaction products. The product radical from oxidation of the cyanisopropyl radical is more active in splitting off atomic hydrogen from the hydrocarbon than the peroxide radical of the hydrocarbon. With the aid of the chemiluminscence technique, evaluations were made of the decomposition rate constant of AIBN, the probability of escape of the primary radicals from the "cage," and the activation energy of AIBN decomposition.

Heterogeneous Recombination of Free Radicals and Their Interaction With Adsorbed Layer

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Heterogeneous recombination of free methyl radicals over different surfaces (glass, quartz, metals, metal oxides) was studied with the aid of a semiconductor sounding technique. The results show that the recombination obeys the first order reaction law. Based on these data, a hypothesis is proposed that in the recombination process the free radicals interact with the radicals adsorbed on the surface. The rate constant of the interaction process is proportional to that of the heterogeneous recombination.

The techniques developed in the course of this work can be utilized to study important processes, such as interaction of free active particles with any adsorbed layer. These processes play an important role in heterogeneous radiation and catalytic reactions, involving participation of free radicals.

Kinetics of Radiation Isotopic Exchange of Deuterium With Hydroxyl Groups of Silica Gel

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A study was made of the kinetics of radiation isotopic exchange of D_2 with the OH groups of silica gel. A kinetic equation developed is in good agreement with the experimental data. Solution of the equation involves numerical integration by the method of terminal differences. The number of exchangeable hydroxyl groups on the surface is 1.2×10^{14} cm^{-2}. A mechanism is proposed to describe the radiation isotopic exchange reaction.

Kinetics of Dehydration of Formic Acid Over Nickel Catalysts

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Kinetic data were obtained for dehydration of formic acid over nickel catalysts in non-gradient and in continuous-flow systems. At volumetric space velocities of 1,075–33,500 hr^{-1}, partial pressures of 40–400 mm Hg, and temperatures of 77°–110°, the reaction in the non-gradient systems proceeds according to the equation for the zero order reactions. In the continuous-flow systems and at somewhat higher temperatures, the reaction rate obeys the equation for the half-order reactions.

Based on the results obtained and on published data, a mechanism is considered for the reaction. The results of determination of the isotopic kinetic effect in the HCOOH-to-HCOOD exchange validate the assumptions used to develop the reaction mechanism.

Changes in Emanation Capacity of Oxide Catalysts in Chemisorption and Catalysis

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The changes in emanation capacity of different oxide catalysts (TiO_2; ZrO_2; MgO; ZnO; ZnO + 0.22% Na_2O; ZnO + 2% $ZnSO_4$) tagged with radioactive thorium were determined in chemisorption of the gases and vapors from decomposition of isopropyl alcohol. Concurrently, changes in emanation were determined in decomposition of the alcohol over a TiO_2 catalyst. The changes in emanation in chemisorption of acetone and of water on the surface of the oxide catalysts are associated with formation of surface chemical compounds. The results with the zinc oxide samples show that incorporation of modifiers into ZnO, which alter catalytic selectivity and the rates of chemisorption and desorption of acetone, changes its emanation capacity.

Mechanism and Kinetics of Oxidative Ammonalysis Reactions and of Partial Oxidation of Propylene Over Bismuth-Molybdenum Catalysts

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