tion rate constants were calculated for several radiative reactions.

"Step-Wise" Recombination of Free Radicals in Irradiated Organic Compounds: Discussion of Proposed Formal Kinetic Model and of a Method to Evaluate Kinetic Constants

A. I. Meekhi'lov, Ya. S. L'yeb'yed'yev, and N. Ya. Booben

Institute of Chemical Physics of the Academy of Sciences of USSR

Several models of "step-wise" recombination of free radicals in solid phase are discussed. The results of formal kinetic calculations are compared with the experimental data. An experiment to evaluate spacial distribution of the free radicals is proposed.

Formation and Reactions of Free Radicals in Organosilicons Irradiated by Ultraviolet Rays: Polyphenylmethylsiloxane

E. L. Joojgov, N. N. Boobnov, and V. V. Voyevodsky

Institute of Chemical Kinetics and Combustion of Siberian Division of the Academy of Sciences of USSR

EPR studies were made to determine kinetics of formation and reactions of free radicals in polyphenylmethylsiloxane. At a temperature of 77°K the radicals identified were $\dot{C}H_3$ and $R—\dot{C}H_2$. A study of kinetic principles to correlate intensity of ultraviolet light with accumulation of the free radicals shows that the $\dot{C}H_3$ radical formation, due to rupture of the Si—C chemical bond, requires two quanta of radiation; on the other hand, formation of $R—\dot{C}H_2$, which involves rupture of the C—H chemical bond, requires only one quantum.

The rate constants of methyl radical in the reactions below were determined as follows:

$$\dot{C}H_3 + M^* \xrightarrow{k_0^{\text{eff}}} CH_4 + R - \dot{C}H_2; \quad k_0^{\text{eff}} = 2 \times 10^{-3}\ \text{sec}^{-3}$$

$$\dot{C}H_3 + M \xrightarrow{k_1} CH_4 + R - \dot{C}H_2; \quad k_1 = 3.5 \times 10^{-5}\ \text{sec}^{-1}$$

$$\dot{C}H_3 + \dot{C}H_3 \xrightarrow{k_2} C_2H_6; \ k_2 = 1.2 \times 10^{-21}\ \text{cm}^3/\text{sec}$$

Kinetics of Isotopic Exchange Between Hydrogen and Water Vapor Over Nickel Catalysts: Effect of Transfer Reactions on the Reaction Rates

E. S. N'yedoomova, G. K. Bor'yeskov, and M. G. Sleenko

D. I. Mend'yel'yeyev Chemico-Technological Institute of the City of Moscow;
Institute of Catalysis of Siberian Division of the Academy of Sciences of USSR

The isotopic exchange reaction, $HDO + H_2 \rightleftarrows HD + H_2O$, was studied over a nickel-chromium catalyst in a recycle-continuous and in a single pass-continuous operation. The effects of the catalyst particle size and of linear velocity of the gaseous reaction stream were determined and an equation to evaluate chemical kinetics of internal diffusion was derived. The results at a temperature of 130° show that with the catalyst particles larger than 0.1 mm in size the isotopic exchange reaction proceeds by internal diffusion.

Catalytic Properties of Rare Earth Oxides in Oxidation of Hydrogen

T. T. Bakoom'yenko

L. V. Peesarjevsky Institute of Physical Chemistry of the Academy of Sciences of Ukrainian SSR

Catalytic activities of oxides of lanthanum, serium, praseodymium, neodymium, samarium, dysprosium, holmium, ytterbium, and lutecium were determined in oxidation of hydrogen at temperatures of 300° to 500° and total system pressure of 550 mm Hg. The concentrations of oxygen in the oxygen-hydrogen mixtures employed were 2% and 98%.

The results of this study show that the rare earth oxides investigated are catalysts of medium quality compared to the oxides of the central elements of the 4th period of the Periodic Table. Except for the oxides of praseodymium and neodymium, the activities of these oxides are of a like order of magnitude; the activities of praseodymium and neodymium oxides are of the next higher order.

The heats of activation of the reaction over these catalysts were evaluated and found to change with changes in the composition of the reaction mixture. The composition changes are believed to affect the stationary state of the reaction and activity of the catalyst.

Kinetics of Ammonia Synthesis Over Alloys of Iron and Cobalt

N. M. Morozov, L. I. L'ook'yanova, and M. I. T'yomkeen

L. Ya. Karpov Physico-Chemical Institute

A study of kinetics of ammonia synthesis was made over iron-cobalt alloys. Increasing cobalt concentration in the alloy, decreases the power exponent, *m*, of the kinetic equation from 0.5 to 0.2.

Based on measurements of the reaction rates at equilibrium, catalytic activity per unit of surface of the alloys of widely different composition remains substantially constant despite changes in the crystal structure.

Catalytic Properties of Rare Earth Oxides in Conversion of *n*-Butane

KH. M. MEENACHEV AND YU. S. KHODAKOV

N. D. Z'yeleensky Institute of Organic Chemistry of the Academy of Sciences of USSR

Catalytic properties of oxides of La, Ce, Pr, Nd, Sm, Ho, Er, Dy, Yb, Tm, and Tb were investigated at temperatures of 400°–550° in a recycle-continuous unit, using statistical method of treatment of the experimental data. Catalytic properties of erbium oxide were also determined for conversion of ethylene, ethane, and propylene.

In all cases, the reaction kinetics were expressed by the first order equation. The specific reaction rate, pre-exponential factor, and activation energy were determined for each catalyst. Lack of correlation was noted between activation energy and magnetic properties of the rare earth oxides.

Electronic Factor in Kinetics of Chemisorption on Semi-Conductors

F. F. VOLKENSHTEIN AND O. P'YESHOV

Institute of Physical Chemistry of the Academy of Sciences of USSR; Department of Physics of M. V. Lomonosov State University of the City of Moscow

Kinetics of chemisorption on semi-conductor surfaces was investigated in the framework of the electronic theory, which takes cognizance of the electrically neutral and charged forms of chemisorption. Kinetics of each form are examined and the conditions to maintain electronic equilibrium on the surface of a semi-conductor are determined for the process. Activation energy of adsorption is calculated as a function of the parameters characterizing electronic state of a system considered. Characteristics of reversible and irreversible chemisorption processes are examined.

Kinetic Parameters of Dehydrogenation of Tetralin and Ethyl and Isopropyl Alcohols and of Dehydration of the Alcohols Over Erbium Oxide.

A. A. TOLSTOP'YATOVA, A. A. BALANDEEN, AND YUI TZEE TZ'YUAN

N. D. Z'yeleensky Institute of Organic Chemistry of the Academy of Sciences of USSR

The results are presented covering an investigation of kinetics of dehydrogenation of tetralin and of dehydrogenation *and* dehydration of ethyl and isopropyl alcohols—over an erbium oxide catalyst. The relative coefficients of adsorption of the products, true activation energies, and bond energies of the C, H and O atoms interacting with atoms of the catalyst were determined for each reaction. The thermodynamic functions: ΔF, ΔH, and ΔS, were calculated in adsorptive displacement of tetralin and isopropyl ether by the respective reaction products.

Hydrogenolysis of Ethane Over Nickel Catalysts in Continuous Flow Systems

A. A. BALANDEEN, T. A. SLOVOKHOTOVA, A. F. SHOLEEN, AND L. A. OOGOLTZEVA

Department of Chemistry, M. V. Lomonosov State University of the City of Moscow

The results of hydrogenolysis of ethane over nickel catalysts at temperatures of 290°–310° show that pretreating a Ni/kieselguhr catalyst with nitrogen at 290°–310° to displace the surface hydrogen lowers activation energy to 19 kcal/mole. Al_2O_3 and Cr_2O_3 carriers decrease activity of nickel catalysts.

Effect of Anodic and Cathodic Polarization of Catalysts on Their Activity in Ammonia Synthesis

L. M. DMEETREEYENKO, S. S. LACHEENOV, AND R. F. SEEV'YAKOVA

State University for Nitrogen Industry

In ammonia synthesis processes, cathodic polarization of catalysts increases initial yields of ammonia; on the other hand, anodic polarization decreases the yields. The more active a catalyst the smaller the initial effect due to cathodic polarization; the opposite is true of the anodic polarization. The catalysts are deactivated by extended cathodic polarization periods and activated by the anodic.

In ammonia synthesis over iron catalysts, promoting action of additives is attributed to acceleration of the onset of the acceptor stages in the electrochemical mechanism of the process. It