comparative data show that the hydrogen atoms which are split off in the initial reaction step from the CH_3 group and from the phenyl ring have different reactivities. Basically, the hydrogen atoms from phenyl groups enter into addition reactions, forming radicals of cyclohexadiene-type; whereas those from the CH_3 group—due to their greater kinetic energy content—are primarily consumed in the secondary reactions of atomic hydrogen split-off from toluene molecules.

Kinetics of Heterogeneous Catalytic Reactions in Chromatographic Pulsed Flow Units at Conditions of Ideal Linear Chromatography

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The authors analyze from a theoretical standpoint the kinetics of heterogeneous catalytic reactions of different orders. The reactions are assumed to be carried out in pulsed flow units at the conditions of ideal linear chromatography. The equations derived to evaluate the rate constants and activation energies of the first order reactions are used in processing the experimental data on dehydrogenation of cyclohexane to benzene over a number of catalysts. The effect of various types of pulsed feed on conversion is also shown.

Kinetics of Liquid Phase Hydrochlorination of Acetylene in Presence of Cuprous Chloride

By R. M. FLEED, N. F. ALEKSEIYEVA, T. G. KHMELEVSKAYA, AND N. A. GAIDAI

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The kinetics of hydrochlorination of acetylene in liquid phase at 40°–98° was studied, using $CuCl—MeCl—HCl—H_2O$ and $CuCl—HCl—H_2O$ as the contact solvents. The reaction rate constants bear linear relationship to activity of the catalyzing ions. The conditions to select contact solvents of optimum composition are described.

Chemiluminescence in Slow Chemical Reactions: Investigation of Kinetics of Accumulation of Hydroperoxide in Catalytic Oxidation of Ethyl Benzene by a Chemiluminescence Technique

By I. V. ZAKHAROV AND V. YA. SHLIAPEENTOKH

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This study of the chemiluminescence-controlling factors during initial stages of oxidation of ethyl benzene in a catalytic solution of cobalt acetate in glacial acetic acid shows that the change in chemiluminescence intensity with reaction time is directly tied to the kinetics of hydroperoxide accumulation. A chemiluminescence technique is proposed to determine the hydroperoxide decomposition rate constants in the course of the oxidation process. The rates of oxidation and concentrations of hydroperoxide at steady state conditions were also determined by use of this technique.

Mechanism and Kinetic Principles of Dimerization of 1,1-Diphenylethylene in Aqueous Sulfuric Acid

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A spectrographic study of kinetics of dimerization of 1,1-diphenylethylene in aqueous (64–68%) sulfuric acid was carried out at temperatures of 5°, 20° and 40°. In terms of decreasing carbonium ion concentration, the rate of the second order reaction decreases with increasing concentration of the acid. At the conditions studied, the reaction temperature has practically no effect upon the rate.

To explain observed regularities of the process, production of the dimer is assumed to occur by two parallel routes: (1) interaction of 1,1-diphenylethylene with carbonium ions and (2) interaction of carbonium ions with diphenylmethylcarbinol, which is produced from the olefin in presence of aqueous sulfuric acid. The values of activation energies and reaction rate constants for the two processes are listed.

The conclusions presented satisfactorily agree with the earlier-published (1) principles of ionization of 1,1-diphenylethylene.

Liquid Phase Dehydrogenation of Isopropyl Alcohol

By S. L. KEEPERMAN, N. V. NEEKOLAYEVA AND I. P. DAVIDOVA

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A study of the mechanism and kinetics of liquid phase dehydrogenation of isopropyl alcohol was carried out over a skeletal nickel catalyst. The reaction which in the initial stage is of zero order, approaches a near-zero order at the subsequent steady state conditions—although at a much slower rate.

The data on reaction kinetics, catalytic activity and comparative para-ortho rates of hydrogen conversion indicate that the rate of acetone desorption is the limiting step of the process.

The study of the reaction kinetics was based on the concepts applicable to two-stage reactions over nonhomogeneous catalytic surfaces.

Mechanism and Kinetics of Catalytic Hydrogenation in Liquid Phase: Some of the Principles of Hydrogenation of Unsaturated Hydrocarbons Over a Skeletal Nickel Catalyst

By A. B. Fasman and D. V. Sokolskii
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Reaction kinetics of catalytic hydrogenation of hexene-1 and of *trans*-piperylene were studied to determine the effects of the following operating variables: intensity of mixing; nature of solvent; temperature; concentration of the unsaturated hydrocarbons and of the catalyst in the reaction mixture. At identical reaction temperatures and mixing intensities and different concentrations of the catalyst and olefin in the reaction zone, the maximum specific hydrogenation rate remains constant. The maximum catalytic activity occurs at surface coverages of 33 to 50% by the reacting hydrocarbon. The factors hindering hydrogen transport to the catalyst improve its selectivity.

Kinetics of Dehydrogenation of Cyclohexadiene-1,3 Over Platinum Films at a Wide Range of Reaction Temperatures

By V. D. Yagodovskii, V. M. Griaznov, and E. A. Savel'yeva
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In dehydrogenation of cyclohexadiene-1,3 over dense platinum films, the experimentally-determined value of activation energy sharply increases at reaction temperatures in the 200°–500° range. The activation energy shows a similar increase in value when thermal pretreatment of Pt films is followed by operation at 500°–600°. These results are possibly due to thermodynamic near-equilibrium state of the active portion of catalyst surface.

Conversion Reactions of Ethylene Over an Aluminosilicate Catalyst

By S. V. Markevitch
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The effects of reaction temperature and of thermal pretreatment of catalyst in vacuum and in oxygen atmosphere upon conversion of ethylene were determined using a commercial-grade aluminosilicate bead catalyst. The results show that rupture of the C—C and C—H bonds occurs at 350°–450°. The yields of ethane, propane, propylene, butanes, butylenes, and butadiene were calculated from the results of mass spectrographic analyses. A scheme of possible reaction routes is presented to explain formation of the end-products from the primary surface complexes.

Application of Law of Maximum to Determine Optimum Conditions for Exothermal Reactions

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A method to select optimum operating temperatures by application of the "Law of Maximum" is described for the rate of reaction-limited chemical processes, using liquids with ideal displacement characteristics. An analysis of the generalized scheme is presented to obtain optimum temperatures. A relationship is shown between the "Principle of Maximum" and the variational and the dynamic programming methods of calculation.