ently, belongs to the chain-radical class of reactions.

High-Dosage Radiolysis of Neutral Solutions of Nitrate Salts

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Radiolysis of neutral aqueous solutions of $NaNO_3$ was investigated at various solution concentrations and x-ray dosage rates. The NO_2^- ion yields were determined by irradiation of solutions containing nitrite and hydrogen peroxide. With dilute- and medium-strength solutions, increasing the x-ray dosage rates also increases the values of $G(NO_2^-)$ and $G(H_2O_2)$. For $1\,M$ solutions of $NaNO_3$, the values of $G(NO_2^-)$ are independent of the dosage rates. A mechanism is proposed to explain the radiolytic reduction of the nitrate ions. The distinguishing feature of the postulated mechanism is competition between the reverse oxidation of the NO_2^- ions by the OH radicals and the recombination of the radicals.

In irradiation of relatively dilute $NaNO_3$ solutions by powerful pulsed beams, recombination of the hydrogen atoms, originating from various tracks, plays an important role.

Determination of Absolute Rate Constants of Free Radical Reactions: Addition of Trichloro-Bromo-Methane to Cyclohexane and to Heptene-1

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A new method is proposed to investigate the non-stationery kinetics of chain reactions. This method involves measuring the non-adiabatic temperature rise following complete or partial cessation of the photochemical initiation. Using this method, the following rate constants (as $1/\text{mol} \times \sec$) were obtained: $CCl_3^{\cdot}$ + cyclohexane, 773 (at $25°$); $CCl_3^{\cdot}$ + Heptene-1, $2.30 \times 10^9 \exp(-7000/RT)$; $C_7H_{14}CCl_3^{\cdot}$ + CCl_3Br, $2.48 \times 10^9 \exp(-8500/RT)$; $CCl_3^{\cdot}$ + $CCl_3^{\cdot}$, 1×10^8; $C_7H_{14}CCl_3^{\cdot}$ + $C_7H_{14}CCl_3^{\cdot}$, 1.0×10^6. A comparison with published data shows that the constants of addition of $CH_3^{\cdot}$ and $CCl_3^{\cdot}$ radicals to cyclohexene, heptene, vinyl acetate, anthracene, and styrene increase in the order mentioned. The absolute values of the constants for these radicals differ but little.

Synthetic Zeolites as Ion Exchangers: Study of Kinetics of Ionic Exchange

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The results of a study of kinetics of ionic exchange processes are summarized for various systems of synthetic zeolites and solutions of LiCl, NH_4Cl, NH_4NO_3, $CaCl_2$, $MgCl_2$, and $PC(NO_3)_2$. For the solution concentrations of 0.1 to $1.0\,N$, external diffusion processes control the ion exchange rates. Agglomeration of the original particles into larger aggregates does not substantially decrease the exchange rates.

Effect of Reaction Temperatures on the Rates of Addition of Atomic Hydrogen to Some Solid Unsaturated Hydrocarbons

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A method is described to measure the rates of consumption of atomic hydrogen (being produced in the gaseous phase) by certain solid unsaturated hydrocarbons. For the adsorbed-hydrogen layers at $63°$ to $160°K$, the adsorption rates are temperature-dependent. Effective activation energies were determined in hydrogenation of a number of unsaturated hydrocarbons. For some of these compounds, the relatively minor differences in the heterogeneous hydrogenation rates are accompanied by significant differences in the effective activation energy values.

Effect of Additives and Conditions of Preparation of Zinc Oxide on Its Performance in Isotopic Oxygen Exchange Reactions

By V. J. GORGORAKEY, L. A. KASATKEENA, AND V. YU. LEVEEN

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A study was made of the effects of Li, Ga, and In additives in ZnO catalyst and of the catalyst preparation conditions upon the kinetics of isotopic oxygen exchange. Increasing calcination temperature of pure ZnO from $850°$ to $1200°$, increases the exchange rate to some extent. Li added to ZnO in amounts of 0.5–0.75 atom % at $850°$ increases the rate of isotopic oxygen exchange with the ZnO catalyst so that it exceeds

the homomolecular exchange rate. Addition of Ga and In to ZnO at 850° decreases the isotopic exchange rates. However, raising the calcination temperature of Ga-containing (0.5 at. %) ZnO catalyst from 850° to 1200°, also increases the isotopic oxygen exchange rate until it approximates that of pure ZnO. Except for the cases of Li addition to the carrier in amounts of 0.5 to 0.75 at. %, the rates of homomolecular exchange either equal or exceed by several-fold those of the isotopic exchange with ZnO.

A Mechanism of Radical Adsorption on Semiconductors and Phenomena of Radical Desorption from Hot Reactor Walls

By I. A. M'YASNEEKOV, E. V. BOL'SHOON, AND E. E. GOOTMAN

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This article summarizes the results of investigation of electroconductivity of ZnO films and of the electroconduction kinetics in the chemisorption-desorption of alkyl radicals. The kinetic correlations which are based on the experimental results of photolysis and pyrolysis of ketones are compared with those derived by assuming a radical adsorption-desorption mechanism.

As a result of this investigation, a new variant of the method to determine relative concentrations of radicals is proposed. This is based upon measuring in presence of adsorbed radicals the initial rates of electroconductivity changes at various test-points in semiconductors. A novel phenomenon uncovered is that of desorption of the radicals—initially in the reaction zone—from the reactor walls of quartz or glass.

Basic Concepts of the Mechanism of Activated Complex Formation from the Viewpoint of Electronic Theory of Catalysis on Semiconductors

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This study represents an attempt to calculate the chemical reaction rates on catalytic semiconductor surfaces by applying Eyring's fundamental concepts of the theory of activated complexes. Basic equations are derived to cover the reaction kinetics. These account for the possibility that some of the reactants, products, and activated complexes are chemisorption-bonded to a semiconductor surface, with accompanying attraction of the free electrons and holes of the semiconduc-

tor. The subject equations were derived by assuming that the reaction system is in electronic equilibrium.

Kinetics and Reactivity of Aromatic Compounds in Halogenation Over Metal Halides: Halogenation of Benzene Over Chlorides of Aluminum, Tin, and Titanium

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The kinetics and activation energy were determined for chlorination of benzene in presence of various solutions of Al_2Cl_3, $SnCl_4$ and $TiCl_4$. These catalysts differ significantly from the ferric chloride with respect to the effects of the solvent media with the reaction order relative to the catalyst. The effect of the media polarity on activity of these catalysts is in line with the anticipated changes in the activation energy; yet, activity of the catalysts increases with increasing activation energy values. Various solvation processes are believed to be the principal factors responsible for these results.

Investigation of Mechanism of Oxidation of Lower Hydrocarbons Using a Competing Reaction Technique

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Using a competing reaction technique, the authors demonstrate that oxidation of lower hydrocarbons on silver is by interaction of the oxygen and hydrocarbon molecules chemisorbed on the catalyst surface. The order of chemisorption and oxidation of these hydrocarbons over the silver catalyst is as follows: $Iso\text{-}C_4H_8 > C_3H_6 > C_2H_4 > C_3H_8$. Various possible reasons are given to explain the relationship between the properties and structures of the hydrocarbons studied.

Kinetics of Cumene Cracking Over Spherical Aluminosilicate Catalysts

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The kinetics of cumene cracking were studied at a temperature of 450° over several spherical aluminosilicate catalysts. The catalyst samples used were calcined at temperatures of 75° to