The peroxide radical concentrations were determined at various fixed reaction initiation rates. These experimental values agree closely with the values calculated for various known initiation rates, using an appropriate recombination rate constant.

Kinetics of Pinacoline Interaction with Ethyl Magnesium Bromide

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A thermographic method was developed to determine the interaction kinetics of pinacoline with ethyl magnesium bromide. The rate constants for the reaction were determined in diethyl ether at 20.5°. The pseudo-molecular rate constant is a linear function of ethyl magnesium bromide solutions of 0.17 to 0.40 mol/l concentrations.

Reduction with Ammonia of Uranous and Uranic Oxides

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The kinetics of reduction of uranium (-ous; -ic) oxides by ammonia were studied at temperatures of 500°–650° and P_{NH_3} pressures of 25 to 600 mm Hg, using one sample of each oxide. The apparent activation energy, E, was determined to be 50.5 ± 4.5 kcal/mol. At constant reaction temperatures, the relationship between P_{NH_3} and the reaction rate, v, is, $v = kP^n_{NH_3}$, where n is 0.35 and 0.42. The ideas as to the possible reaction limiting stage are supported by the experimental data. The phase transformations occurring during reduction of U_3O_8 with NH_3 at the stated temperatures, may be represented by the following reaction scheme:

$$U_3O_8 \rightarrow U_3O_{8-x_{max}} \rightarrow U_4O_9 \rightarrow UO_{2+x_{max}} \rightarrow UO_{2+x}$$

Oxidation of Alkyl Radicals in γ-Transitions of Amorphous Substances

By V. G. Neekolsky, J. J. Chkhe'eedzé, and N. Ya. Booben
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Thermoluminescence and EPR spectra of several amorphous organic compounds were studied in irradiation at 77°K with fast electrons. On reheating of the irradiated samples, the stabilized alkyl radicals react with the oxygen dissolved in the amorphous substances. In reactions of this type, the rate of oxidation sharply increases at the γ-transition temperature. The results obtained help to explain the shape of the thermal fluorescence curves for the irradiated amorphous substances and, at the same time, demonstrate that in the radiolysis the alkyl radicals serve as the ion stabilization centers.

Effect of Nuclear Radiation on Catalytic Properties of Nickel Oxide

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The permanent defects due to irradiation of NiO (containing 2.5 mol % of Li_2O) increase its catalytic activity and electroconductivity. The transitory defects produced during irradiation at temperatures of 300°–400° have no effect on the catalytic activity; but at a room temperature the temporary defects increase electroconductivity of NiO.

The permanent defects also decrease the activation energy in catalytic oxidation of CO with oxygen.

To maximize the changes in electroconductivity and catalytic activity, the reaction must be carried out at the lowest possible temperature, using catalysts with a very small conductivity characteristic.

Interactions of Oxygen and Ethylene with Atomic Hydrogen Adsorbed on Silica Gel Surface

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Recombination of the atomic hydrogen initially produced on a silica gel surface by radiolysis of its hydroxyl groups and reactions of the hydrogen atoms at low temperatures (−170° to −100°) with oxygen and ethylene were investigated by an EPR method. The results indicate increased reactivity and thermal stability for the hydrogen atoms adsorbed on the silica gel surface.

Kinetics of Chromatographic Reactions Over Non-Homogeneous Surfaces

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Equations are derived for the chemical reaction kinetics in chromatographic systems, using a statistical theory of adsorption and catalysis as the basis. Some of the qualitative and quantitative characteristics of these reactions are described. The correlations to determine kinetic constants are derived. These are based on experimental data at small surface coverages.

Infrared Spectra of Ethylene and of Some Aliphatic Alcohols Adsorbed on Titanium Dioxide

By YU. M. TSHCHEKHOCHEEKHEEN, V. N. FEELEEMONOV, N. P. KEYER, AND A. N. T'YERENEEN

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The infrared spectra of CH_3OH, CH_3OD, C_2H_5OH, n-C_3H_7OH, iso-C_3H_7OH, and C_2H_4 were obtained by adsorption at 20°–300° on TiO_2—alone and with admixed WO_3. The spectra of these compounds in the adsorbed state are clearly similar. The possibility of formation of two types of ethers on the TiO_2 surface is discussed. These ethers are regarded as the intermediates in the alcohol dehydration reactions.

Investigation of Homomolecular Oxygen Exchange Over ZnO at Low Temperatures

By V. J. GORGORAKEY, G. K. BOR'YESKOV, L. A. KASATKEENA, AND V. D. SOKOLOVSKY

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The homomolecular isotopic oxygen exchange, $^{16}O_2 + {}^{18}O_2 \rightarrow 2{}^{16}O{}^{18}O$, was studied at temperatures of 25°, −63°, and −194° over a ZnO, which was first calcined in air at 850° and then rapidly cooled to the reaction temperatures, above.

At the reaction temperatures of −63° and −164°, the isotopic oxygen exchange rates approximate that at 425°. In this temperature range, the catalyst is stable in activity. The apparent activation energy of this reaction is 0.18 kcal/mol. This was calculated from the exchange rates at −63° and −194°. The exchange rate with ZnO at 25° is initially many times greater than at 425° to 500°. But in oxygen atmosphere at 25°, the catalyst rapidly (5–6 hrs) loses its activity.

Activity of ZnO, deactivated by contact with air at elevated temperatures, can be restored by contacting with vaporized zinc.

A Mechanism of C_5-Dehydrocyclization

By A. L. LEEBERMAN

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The proposed mechanisms for dehydrocyclization of pentane and for the reverse reaction of hydrogenolysis of the C_5 ring are based on the assumed participation of atoms, of the catalyst in a transition state at the active surface, the geometry of the transition state, and the concept of cyclical electron transfer within the transitory system.

Kinetics of Catalytic Oxidation of Propylene into Acrolein—in Presence of Steam

By YA. B. GOROKHOVATSKY AND E. N. POPOVA

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The kinetics of oxidation of propylene over a copper catalyst with unlimited diffusion characteristic were investigated at temperatures of 380°–420° in presence of large amounts of steam. The kinetic equations, as proposed below for the conversion of propylene into acrolein and carbon dioxide, are valid at the following concentrations (vol. %) of the components in the reaction mixture: H_2O, 3–60; O_2, 3–15; C_3H_6, 16–60; C_3H_4O, 0.25–1.25.

$$W_1 = k_1 \frac{C_{O_2}{}^{0.8} \times C_{C_3H_6}}{1 + b' C_{acrol}} \cdot \frac{(1 + C_{H_2O})^{0.5}}{1 + b_1 C_{H_2O}}$$

$$W_2 = k_2 \frac{C_{O_2} \times C_{C_3H_6}}{1 + b'' C_{acrol}} \cdot \frac{1}{1 + b_2 C_{H_2O}}$$

The heats of activation to form acrolein and CO_2 were determined.

The action mechanism of steam at the reaction conditions is explained. The improvement in selectivity of the copper catalyst in presence of steam is believed to be due to the inhibiting action of steam to prevent complete oxidation of the product acrolein.

Catalyzed Reactions of Acetylene in Vapor Phase: Kinetics and Mechanism of Vapor Phase Synthesis of Vinyl Acetate Over Various Metal Acetate Catalysts

By I. B. VASIL'YEVA, A. J. GELBSHTEIN, I. N. TOLSTEEKOVA, AND DAO VAN T'YONG

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The study of kinetics of vapor phase synthesis of vinyl acetate from acetylene and acetic acid was carried out, using Zn, Cd, Hg, and Bi acetates on activated carbon as the catalysts. Activity of other metal (Be, Mg, Ca, Ba, Fe, Co, Ni) acetates as catalysts for the reaction was also evaluated. The schemes proposed describe the acetylene-acetic acid reaction mechanisms over