described to determine the limits of applicability of the diffusion-controlling stage.

Two-Stage Combustion of Explosive Mixtures: Ignition Temperature Zones of Heptane-Air Mixtures at Super-Atmospheric Pressures

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The calculations based on the induction period data for the two-stage ignition processes at super-atmospheric pressures show that the effective activation energies, E_{eff}, and the reaction order values, n_{eff}, vary with the ignition temperatures. In two-stage ignition processes at a pressure of 4 atm. and temperature intervals of 240°–310°, 310°–450° and 450°–550°, the respective values of E_{cf} (cf. cold flame) are 36.6; 10.2 and 23.4 kcal/mol. At temperatures in the ignition zone, the values of E_{hf}; n_{hf}, n_{cf}, and Δp_{cf} are negative (hf, hot flame; Δp_{cf}, the maximum increase in pressure in a cold flame process).

A Mechanism of Thermal Decomposition of Ethyl- and Vinyl Iodides and Competition Between Alkyl Halides of the Two Types in the Primary Decomposition Process

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Decompositions of C_2H_5I; C_2H_3I; C_2H_5Br; C_2H_3Br; and C_2H_5Cl in streams of acetone were studied at low pressures and short contact times. Composition analyses of the reaction products show that decomposition of the iodide derivatives is accompanied by a split-off of the iodide atoms and of HI molecules, whereas the decomposition of the other alkyl halides involves the molecular mechanism alone. The activation energy to decompose C_2H_3I is 66.5 kcal/mol. The activation energy of a C—H bond in ethylene—as calculated by assuming that $D(C_2H_3\text{—}I)$ is 66.5 kcal/mol—is in good agreement with the experimental value obtained by an electronic impact method.

Investigation of the Mechanism of Formation of Secondary Products in Cracking of Ethane

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A study of C_2H_6 cracking mechanism at 800°–880° and 90 ± 3 mm Hg was carried out in presence of C^{14} radiotracer added as C_2H_4 (0.45%). The study revealed the basic paths in the formation of various secondary products. At the conditions employed, formation of C_3H_8 and C_4H_{10} occurs by recombination of the methyl and ethyl radicals; on the other hand, the C_3H_6 and C_4H_8 are formed by decomposition of the C_4H_9 radical, a $C_2H_5 + C_2H_4$ addition product. In the final analysis, divinyl was obtained by condensation of the ethylene or from its derivatives.

At temperatures of less than 850°, CH_4—which is formed in the system by other than the usual radical reaction mechanisms—plays an important role in the process.

At the conditions investigated, there was practically no reverse hydrogenation of C_2H_4 to C_2H_6.

Investigation by EPR Methods of the Radicals Frozen Out of Exhaust Gases at 77°K

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Properties of the radicals from the exhaust gases in the neighborhood of the combustion zone were determined by an EPR analytical method. Since concentration of the radicals in the effluent gases is too low for direct analyses, the radicals must be accumulated by freezing out at 77°K. The hydrogen atoms, which are present in the gasified product are stabilizable at 77°K as HO_2 radicals. As a result, sensitivity of the EPR method for atomic hydrogen increases at least 50-fold.

Yet, despite high concentrations of atomic hydrogen in the acetylene combustion products, no HO_2 radicals are found on freezing; instead, the radicals present are peroxides of the RO_2 type. The lower concentration limit of the radicals in an acetylene flame is estimated to be 6×10^{10} l/cm³.

Determination by an EPR Method of Fixed Concentrations of Peroxide Radicals in Oxidation of Cumene

By Ya. S. Lebed'yev, V. F. Tzepalov, and V. Ya. Shl'yapeentokh

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Cumyl peroxide radicals are present in oxidation of cumen over a cobalt stearate catalyst. They are also present when this reaction is initiated by either azo-bis-isobutyronitrol or by dicyclohexyl percarbonate.

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

By E. MAXIM, T. BROWN, AND G. GLANZ
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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