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Temperature—Conversion Rate Correlation in Radiolysis of Hydrocarbons

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The decomposition rates of various hydrocarbons by radiolysis were studied at various reaction temperatures. Present detailed results of thermocracking a straight-run gas oil in a nuclear reactor.

The results obtained show the fundamental effects of the reaction temperature upon the direction and rate of these reactions. This information is of both theoretical and practical interest.

The Role of Reactor Surface in Oxidation of Methane

By P. M. STADNEEK AND V. I. GOMONAI The Oojgorod State University, Department of Physical Chemistry

List the results of oxidation of methane at 700°-800°C in a quartz reactor, using a quenching technique.

Plating the reactor surface with copper, brass, or platinum demonstrates that quartz selectively directs the reaction toward predominant formation of formaldehyde, which, as a component of the reaction mixture, promotes the chain oxidation process. Present a scheme for a heterogeneous-homogeneous catalytic process of oxidation of methane over quartz.

Oxidation-Reduction Reactions of Acceptors in Organic Solvents Due to Ionizing Irradiation: Conversion of Copper Compounds Dissolved in Acetone

By M. RODER, N. A. BAKH, AND L. T. BOOGAYENKO M. V. Lomonosov State University in Moscow, Department of Chemistry

In absence of oxygen, x-ray irradiation of acetone solutions of CuCl_2 and Cu_2Cl_2 results in the reduction of Cu^{II} to Cu^{I} . Here, the limiting yield of Cu^{I} is 17.3 \pm 0.5 ions/100 ev. Oxidation of Cu^{I} does not occur. In presence of oxygen, Cu^I is oxidized to Cu^{II} in high yields.

Mechanism and Kinetics of Iodizing Aniline in Aqueous Iodine Solutions

By F. M. VAINSHTEIN, E. I. TOMEELENKO,

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The kinetics of iodizing aniline by aqueous iodine solutions was investigated in the solution pH range of 1.5 to 9.7. The reaction follows the acceptor-donor mechanism, with the base serving as the proton acceptor and not as a component of an iodizing complex.

In absence of the added buffer solutions, some of the aniline molecules serve as the proton acceptors. (In this case, the energy of activation is 7.5 kcals/mole). In presence of a carbonate salt, the CO_s^{2-} ion is the acceptor; in aqueous HCl solutions, the water molecules perform this function.

In aniline iodization, the kinetic effect due to the isotopes is independent of the solution pH and nature of the proton acceptor. However, the effect decreases with a decrease in the iodine anion concentration and with an increase in the dioxane content.

In water-dioxane solutions, the rate of aniline iodization decreases as a complex function of increasing concentration of dioxane in the reaction mixture.

Investigation of Interaction of Oxygen with NiO, Fe_2O_3 and Cr_2O_3 with the Aid of Spectral Absorption in Infra-Red Region

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The interaction of samples of finely divided NiO, Fe₂O₃, and Cr₂O₈ when heated in vacuum and in oxygen atmosphere was studied by means of spectral analyses in the infra-red region. After interacting with oxygen these oxides develop absorption bands of the order of 1,150-820 cm⁻¹. Their presence could be explained by the formation on the oxide surfaces of double-bond metal-

oxygen groups. However, in the case of Cr_2O_3 , absorption of foreign molecules may produce structural changes and destruction of these groups.

Kinetics of Reactions Involving Participation of a Solid Phase: Carbiding Molten Iron Catalysts by Carbon Monoxide

By A. YA. ROZOVSKII, M. M. BEERIUKOVITCH, A. A. IVANOV, YU. B. KAGAN, AND A. N. BASHKEEROV The Institute for Petrochemical Synthesis of the Academy of Sciences of U.S.S.R.

Propose a method to calculate kinetics of the extra-kinetic-region reactions which involve participation of a solid phase. Using this method, present calculated values of specific reaction rates and activation energies in CO-carbiding of prownoted and unpromoted molten iron catalysts (used in the CO—H₂ synthesis). Also give calculated activation energy values for the diffusioncontrolled region of this reaction.

The calculated data indicate that interstitial migration of carbon is the limiting step in the reaction.

Chemiluminescence in Slow Chemical Reactions: Effect of Chemical Composition of a Reaction System on Intensity of Chemiluminescence

By R. F. VASEELIEV, A. A. VEECHOOTEENSKII, O. N. KARPOOKHEEN, AND V. YA. SHLIAPEENTOKH The Institute of Chemical Physics of the Academy of Sciences of U.S.S.R.

A kinetic mechanism is proposed to explain the effect of composition of radicals upon intensity of chemiluminescence. Subsequent verification of the proposed mechanism substantiates accuracy of the correlations based on experimental data.

Possible utilization of the chemiluminescence measurements is considered to evaluate the relative and absolute rate constants of the reactions between radicals and molecules.

Homomolecular Exchange of Oxygen Over Oxides of Metals of the Fourth Period: Catalytic Activity and Bond Energy of the Oxide Oxygen

By G. K. BORIESKOV, A. P. DZEESIAK, AND L. A. KASATKEENA The Institute of Catalysis of the Siberian Division of the Academy of Sciences of U.S.S.R., D. I. Mendeleyev Chemico-Technological Institute in Moscow

In terms of isotopic exchange with molecular oxygen, catalytic activity is, in the main, defined by the bond energy of the oxygen in the surface layer of the oxides. No simple correlation has been found between the electron work function and catalytic activity.

Catalytic activity of these oxides is correlatable with respect to the isotopic exchange and hydrogen oxidation reactions. Thus, the homomolecular oxygen exchange rates can conveniently serve as the indices of reactivity of the oxide oxygen in the surface layer.

Effect of Covalent Bonding Upon Kinetics of Hydrogenation of Polycyclic Hydrocarbons

By I. V. KALETCHEETZ, A. S. NAKHMANOVITCH, AND V. M. KAZANTZEVA The Institute for Petro- and Coal-Chemical Synthesis of the Siberian Division of the Academy of Sciences of U.S.S.R.

The reaction rate constants were determined in hydrogenation of aromatic hydrocarbons (benzene, diphenyl, tetracene, anthracene, naphthalene, phenanthrene, benzophenanthrene, coronene) over a platinum catalyst. The results show that the rate of hydrogen addition to the hydrocarbons of the SAME type-linear, angular, or centered-depends upon the number and type (single, double, or triple) of the covalent bonds. These results are explainable in terms of peculiarities of geometric orientation of the bonds at the catalyst surface. The rate of hydrogenation also depends upon the nature of solvent used, since it is affected to a varying degree by the products formed. In addition, the rate is a function of the ratio of an adsorbed substance to the hydrogen.

Kinetic Data as a Basis for a Mechanism of Hydrogen Redistribution in Cyclohexene and Cyclohexadiene-1,3 Over a Palladium Catalyst

By V. M. GRIAZNOV AND V. D. YACODOVSKII M. V. Lomonosov State University in Mocsow, Chemistry Department

Present evidence to support the concept that redistribution of hydrogen in cyclohexene and in cyclohexadiene results from the combination of distinct stages in dehydrogenation and hydrogenation of hydrocarbon feeds.

Demonstrate that the concept of direct hydrogen transfer among the three cyclohexene molecules is not supported by the experimental data

Poisoning of Nickel Catalysts by Carbon Bisulfide

By G. D. LIUBARSKII AND L. B. AVDEYEVA L. V. Karpov Physico-Chemical Institute

Absorption of carbon bisulfide by nickel cat alysts was studied by abstracting it from benzen solutions and in vapor phase hydrogenation o