

oxygen groups. However, in the case of  $\text{Cr}_2\text{O}_3$ , 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 promoted and unpromoted molten iron catalysts (used in the  $\text{CO}-\text{H}_2$  synthesis). Also give calculated activation energy values for the diffusion-controlled 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. Mendeleev 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. YAGODOVSKII  
*M. V. Lomonosov State University  
in Moscow, 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 catalysts was studied by abstracting it from benzene solutions and in vapor phase hydrogenation o

benzene doped with this compound. Concurrently, the changes in catalytic activity were observed for a number of supported nickel catalysts. The results show that identical amounts of carbon bisulfide sulfur are chemisorbed by a unit of the nickel surface of the catalysts studied.

Thiophene poisons nickel five times as much as carbon bisulfide. Adsorption from solutions results in blockage of the entire metal surface. In the hydrogenation process, consumption of carbon bisulfide is not affected by preadsorbed thiophene. Poisoning of the catalysts—in any degree—by thiophene or by carbon bisulfide does not alter the energy of activation in hydrogenation of benzene.

#### Oxygen-Initiated Heterogeneous Catalytic Olefin Condensation Reactions in Presence of Hydrogen: Conversion of Ethylene

By YA. T. EIDOOS, N. I. YERSHOV, V. R. YEROOKEENA, AND N. S. ANDREIYEV  
N. D. ZELEENSKII Institute of Organic Chemistry of the Academy of Sciences of U.S.S.R.

Summarize the results of a study to condense ethylene in presence of hydrogen over a clay-supported cobalt catalyst, using small amounts of oxygen as the initiator.

#### Effect of Added Lithium and Gallium on Catalytic Properties of Zinc Oxide in Homomolecular Isotopic Oxygen Exchange Reaction

By V. I. GORGORAKY, L. A. KASATKEENA, AND V. YU. LEVEEN  
D. I. Mendeleev Institute of Chemical Technology in Moscow

A study of the homomolecular isotopic oxygen exchange,  $^{16}\text{O}_2 + ^{18}\text{O}_2 = 2^{16}\text{O}^{18}\text{O}$ , was carried out at 425°–550°C and oxygen pressures of 5–200 mm Hg over ZnO—alone and with various amounts of admixed lithium and gallium. The results indicate that for the systems investigated the sorption of molecular oxygen and its subsequent dissociation into atoms are the limiting steps of the exchange reaction.

List comparative physical and catalytic properties of the exploratory catalysts. Propose a mechanism to explain the modifying effects due to the additives used in the study.

#### Catalytic Activity of Copper Polyphthalocyanines in Decomposition of Hydrogen Peroxide

By S. Z. ROGEENSKII, A. A. BERLEEN, E. S. DOKOOKEENA, M. M. SAKHAROV, AND L. G. CHERKASEEN  
Institute of Chemical Physics of the Academy of Sciences of U.S.S.R.

The monomer and a number of polymers of copper phthalocyanine differing in electrophysical properties were investigated as catalysts in decomposition of aqueous solutions hydrogen peroxide at temperatures of 20° to 52°C. The polymer with the greatest electroconductivity at a room temperature and the smallest electroconductance activation energy has the greatest catalytic activity. Conversely, the polymer with the smallest electroconductivity and the greatest activation energy values is the least active catalyst. At the conditions of this study, the monomer shows practically no catalytic activity. These results show that catalytic activity of copper polyphthalocyanines in decomposition of  $\text{H}_2\text{O}_2$  is correlative with their electrophysical properties.

#### Interaction of Hydrogen with Oxygen Over Vaporized Palladium Films

By Z. CNOR, V. PONIEZ, AND S. CHERNY  
Prague Institute of Physical Chemistry of the Academy of Sciences of Czechoslovakian S.S.R.

The conditions for interaction of hydrogen with oxygen over palladium were determined from measured volumetric and electrical resistance properties of vaporized palladium films. A careful note was made of the differences in performance of nickel and palladium in the oxygen-hydrogen interaction process and of the relative ability of the transition metals at both ends of the Periodic System to sorb various gases.

#### Effect of Promoters in Hydrogenolysis of Xylite

By N. A. VASIUNEENA, A. A. BALANDEEN, AND YU. MAMOTOV  
N. D. ZELEENSKII Institute of Organic Chemistry

CaO, BaO, and NaOH were investigated as promoters in hydrogenolysis of xylite over nickel catalyst at 200°–245° and constant hydrogen pressure of 200 atm. At the conditions studied, due to thorough mixing of the three-phase reaction system, Cannizzaro's reaction was absent and consequent possible decrease of the system pH was avoided.

The promoting action of CaO and BaO is due to their chemical properties and not to the alkalinity produced in the hydrogenolysis. Addition of either of these compounds causes three- to four-fold increase in the rupture of xylite C—C bond, leading to the formation of glycerine and ethylene glycol. Compared to these two oxides, NaOH is an appreciably weaker catalytic promoter of the subject reaction.