position of molecular complexes and usefulness of Transition State Theory in calculating the reaction rate.

Empirical Determination of Mechanism of Interaction of "Hot" Atoms and Hydrocarbon Molecules

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Based on kinetic calculations, different experiments are outlined to determine reaction kinetics of "hot" atoms with hydrocarbon molecules. As a result, valuable information is obtained regarding the mechanism of individual collisions. The experiments involving heterogeneous reactions yield the greatest amount of information of this type—particularly so, when employing inert moderators with atomic weights appreciably smaller than those of the hot atoms. In the latter case, experimental determinations of reaction rates between "hot" atoms and the surface—as a function of the inert gas layer thickness, serve to re-establish the functional dependence of energetics of these reactions.

Mechanism and Kinetics of Interruption of Chain Oxidation Reactions

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Chain oxidation reactions can be interrupted by aliphatic nitrate radicals, with resulting addition of the alkyl radicals. The effectiveness of interruption depends on availability of alkyl radicals in a reaction due to competition for them by the nitrate radicals and oxygen. At a temperature of 60° the ratios of the rate constants of the two competing reactions are 26 ± 3 for ethyl benzene and 1.4 ± 0.2 for diphenyl benzene.

The nitrate radicals are very convenient "counters" of the radicals present at the inception of radical polymerization reactions. For this reason, the nitrate radicals are useful quantitative indicators in determining the rates to initiate the reactions of ths type and in studying the "cage" effect in liquid phase reactions of radicals.

Kinetics of Thermal Decomposition of Methane

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Analytical methods were developed to solve kinetic equations for isothermal decomposition of methane and to evaluate its optimum conversion to acetylene at different reaction temperatures. Numerical solutions of the equations are presented when processing at different isoenthalpic conditions. The reaction time for the maximum yields of acetylene (70–80%) is shown to be 10^{-4}–10^{-3} sec.

The rate of heat abstraction to quench the acetylene and other reaction products exceeds 2,000 kcal/sec per mole of methane charge.

Low Temperature Halogenation of Simplest Olefins in Solid Phase

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Using suitable melting point curves, thermographic studies were made of low temperature chlorination and bromination of ethylene, propylene, and isobutylene—as solid nomogeneous mixtures at the reaction conditions. For equimolecular mixtures of these hydrocarbons at temperatures below −180°C, the reactions are practically instantaneous and occur near the melting points of the olefins studied. Isobutylene is rapidly halogenated at a temperature of −196°C, during condensation of gaseous reaction mixtures. It appears that exothermal formation of molecular complexes—with accompanying transfer of electrical charge—represents the initial stage of reactions of this type.

A qualitative comparison of relative reactivities of olefins with halides is presented in a tabulated form. The courses of these reactons in solid, liquid, and gaseous states are compared qualitatively.

Based on the results of this study and the published data, presence of negative temperature coefficient is hypothesized for the reactions in liquid phase.

Alteration of Physico-Chemical Properties of Solids by Additives: Thermal Decomposition of Silver Oxalate

By Yu. A. Zakharov, G. G. Sav'yel'yev, V. K. Jooravl'yov, V. V. Boldir'yev

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The effect of addition of Cd^{++}, Hg^{++}, and Pb^{++} on some of the properties of silver oxalate was studied in the light of some of the properties of these ions. The results show that at similar conditions these ionic additives alter to a quantitatively different degree the electrical properties and thermal stablity of $Ag_2C_2O_4$. Thermal decomposition of silver oxalate is increasingly retarded by the additives in the following order: $Cd^{++} < Hg^{++} < Pb^{++}$.

Compared to Cd^{++}, Pb^{++} increases the loss of dielectric properties of silver oxalate to a lesser degree and alters its ionic conductivity to a greater degree. The most probable reason for the quantitatively different effects of these additives is their increasingly stronger ionic bonding ($Cd^{++} \rightarrow Hg^{++} \rightarrow Pb^{++}$) with the charge-compensating cationic vacancies.

Principles of Formation of High Melting Point Compounds of Desired Catalytic Properties

By G. V. Samsonov

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Catalytic properties of the transition series metals and of their alloys and reaction products with non-metals (boron, carbon, nitrogen, and silicon) were examined from the standpoint of relative degree of fill up of the atomic d-electron shells of these metals and the fillage of the d-shells on forming alloys and compounds by combination with the electron-donating non-metallic elements.

The discussion also points out the role of different types of atomic chemical bonds due to combination of alloys and compounds with the non-metallic elements, and the role of isolated structural complexes which are formed by the nonmetallic atoms within crystalline lattices. The factors responsible for low catalytic activity of non-metallic compounds are cited.

Effect of Adsorbed Oxygen on Changes in Zinc Oxide Conductivity with Temperature

By Yu. P. Soloneetzeen

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The results of simultaneous measurements of conductivity of zinc oxide and of oxygen gas pressure in a system at constant volume and at 20°–200° show that the anomalous decrease in conductivity of the oxide is accompanied by partial desorption of the oxygen. This phenomenon may be due to transition of the chemisorbed oxygen to a more highly charged state and to a simultaneous shift of the adsorption equilibrium toward desorption. The abnormally weak effect on the conductivity due to the oxygen adsorbed at temperatures of over 200°C is attributed to a gradual consumption of the system oxygen in oxidizing organic impurities.

EPR Studies of Structure of Active Centers of Chromium Oxide Catalysts for Polymerization of Ethylene

By V. A. Aleksandrov, V. B. Kazansky,
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A structural model is proposed for active centers in chromium oxide on silica gel catalysts for use in extensive polymerization of ethylene. The active centers are the Cr^{+5} ions stabilized on the carrier surface. It is suggested that the Cr^{+5} ions partially displace the Si atoms of the silica oxide tetrahedra in the surface layer of silica gel. As a result, the tetrahedra are deformed, causing anisotropy of *g*-factor of the EPR signals. The parameters of the signals, which were calculated on the basis of the model proposed, are in good agreement with the experimental results. The model also serves to explain the changes in the EPR signals due to poisoning of the catalysts by alkalies.

Electron Work Functions of Titanium Dioxide and of Its Solid Solutions in Chemisorption and Catalysis

By I. S. Sazonova, N. P. Keiyer

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The work functions of TiO_2 and of its solid solutions in WO_3 and Fe_2O_3 were determined in vacuum. Changes in the work function values were determined in chemisorbing gases of the electron-donor and electron-acceptor types, in oxidizing carbon monoxide, and in decomposing isopropyl alcohol. Based on the experimental results, feasible mechanisms are considered for the chemisorption and catalysis reactions over the catalysts studied.

Reactions of α-Oxides: Acid- and Auto-Catalyses in Reactions of Ethylene Oxide with Amines

By N. N. L'yeb'yed'yev, M. M. Smeernova

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This study of reaction kinetics of ethylene oxide with aniline and cyclohexylamine solvents demonstrates that these reactions are autocatalyzed by the aminoalcohol and that they are accelerated by water and alcohols in proportion to their relative acidity.

Diverse catalytic effects of many acids, such as phenol and perchloric acid, are shown to be func-