Decomposition of Dicyanodiamide in Aqueous Alkaline Media

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A study of kinetics of decomposition of dicyanodiamide in aqueous solutions of potassium hydroxide was carried out at various temperatures and pH values. An equation was developed to relate the decomposition rate constant to the reaction temperature. The study demonstrates that at the conditions investigated decomposition of dicyanodiamide proceeds via a parallel-series route. The approximate values of the decomposition rate constants were determined for each parallel course as functions of pH and temperature —but neglecting the effect of the amide concentration in the reaction mixture. The equations to relate these constants to the pH and temperature of the system are also presented.

Kinetics of Hydrazine Oxidation by Nitrous Acid

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Scientific Institution—Not Shown

A study of kinetics of hydrazine reaction with nitrous acid at temperatures of 9°–40° was carried out in solutions of nitric and hydrochloric acids. The reaction is of the first order with respect to the reactants and the H^+ ions, the reaction rate increasing with increasing ionic strength of the solutions.

The reaction mechanism proposed assumes interaction of the $N_2H_5^+$ and NO^+ ions as the rate-determining step.

Formation of Radicals in Radiolysis of Organic Solids: EPR Spectra and Yields of Radicals in Radiolysis of Some Organosilicon Compounds

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The yields, G_R, of the radicals formed in a fast electron radiolysis of certain organosilicon compounds at temperatures of —130° to —180° were determined by an EPR technique. The results show that with saturated- and aromatics-substituted tetramethylsilane, the yields, G_R, of $(4 - 5)(10^{-2})$ and $(0.2 - 0.6)(10^{-2})$ ev, respectively, do not differ from the G_R values of other hydrocarbons of analogous strucure. With the compounds of general formula, $(CH_3)_3Si(CH_2)_nCH{=}CH_2$ (where $n = 0$, 1, or 2), the radiative yields G_R, are approximately (1×10^{-2}) ev, or roughly 4 times smaller than those with the hydrocarbons having only one double bond. Analyses of the EPR spectra lead to the conclusion that insertion of one atom of silicon into an aliphatic chain does not alter noticeably the radiolysis mechanism.

Interaction of Atomic Oxygen Generated in the Gaseous Phase with Solid Hydrocarbons: Reaction of Atomic Oxygen with Solid Ethylene at Temperatures of 65°–69°K

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An analytical method developed is described to determine small amounts of oxygen in various substances, using a chromatograph of capillary type and a mass-spectrometer, type MX-1302, arranged in series. The analytical data show that at temperatures of 65°–69°K the principal products of interaction of atomic oxygen with solid ethylene are ethylene oxide and acetaldehyde. At the temperatures, above, the product distribution remains practically unchanged regardless of the degree of conversion.

A General Principle Governing Catalytic Activity of Metals

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A correlation was established between catalytic properties of metals (activity, reaction order, etc.) in different reactions and the volumetric thermodynamic parameter, the heat of formation of a metal oxide in the highest state of oxidation per gram-atom of the metal.

Effect of Properties of a Salt Cation on Kinetics of Formation of Pheophytinates in Ethanol Solutions

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Based on the experimentally-determined kinetic data of formation of pheophytinates, Ph, of Fe^{+2}, Ca^{+2}, Ni^{+2}, Pd^{+2}, and Ag^+ in absolute ethanol —via the reaction, $H_2(Ph) + MX_2 \rightarrow M(Ph) + 2HX$, a relationship was established between individual kinetic variables of the process (the rate constants and the activation energies and entropies) and: composition, X, of the anionic solutions, concentration, MX_2, of the salts used, and the nature of the central ion, M. The reaction was found to be of the first order with respect to both the pheophytins and the salts. A brief discussion of the correlations based on the results of this study is included.

Relationship Between Electronic Structure of Cobalt–Nickel Catalysts and Their Catalytic Properties

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The experimentally-determined data of catalytic properties of cobalt-nickel alloys show that specific catalytic activities, electron work functions, and numbers of the unpaired *d*-electrons change with changes in the chemical composition of these alloys.

Kinetics of Benzene Hydrogenation Over a Nickel Catalyst: Reactions in the Kinetic Region

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A review of the literature on hydrogenation of benzene reveals contradictory results. Possible reasons for the contradictions were examined. The hydrogenation kinetics were determined experimentally in a recycle-continuous unit at widely-different operating conditions. The results show that the reaction order changes with operating temperature due to changes in the adsorption equilibria. Analysis of the information obtained by substitution of pertinent experimental data into the kinetic equations for the feasible reaction mechanisms, resulted in selection of the most satisfactory scheme of the reaction course. The calculations to select the optimum scheme were carried with the aid of linear programming methods and electronic computers.

Catalytic Properties of NiO in Homomolecular Oxygen Exchange Reactions

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The homomolecular isotopic oxygen exchange reaction, $O_2^{18} + O_2^{18} = 2O^{16}O^{18}$, was investigated over "pure" NiO and over the NiO containing admixed Li and In at temperatures of 25° and 275°–400° and oxygen pressures of 10–160 mm Hg. The results show that at the temperatures studied NiO is catalytically active and that the additives used materially alter its catalytic properties. The initial rate of the exchange reaction is significantly greater at a room temperature than at the elevated temperatures.

Kinetics of Cyclohexane Dehydrogenation Over Chromic Oxide in a Non-Gradient System

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The results of a study of kinetics of cyclohexane dehydrogenation over chromic oxide in a recycle-continuous unit show that the reaction is of the first order and that its activation energy is 41.5 kcal/mol. The results obtained are discussed on the basis of a two-step scheme proposed for the process.

Effect of System pH on Kinetics of Hydrogenation Reactions Over a Palladium Catalyst

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The information supplied by the $Pd/BaSO_4$ (5% Pd) "charge" curves at pH of 1.2 and 13.0, leads to the conclusion that energy of the Pd—H bond increases with increasing pH of the reaction system. Compared to Pd-black, the catalyst studied contains a greater amount of adsorbed hydrogen and a smaller amount of dissolved hydrogen.

The rates of hydrogenation of hexene-1 and of cyclohexene reactants, which alter but little the catalyst potential, are at the maximum in an acidic media, the hydrogenation being realized via the weakly-bonded hydrogen.

In hydrogenation of phenylacetylene and nitrobenzene, which strongly displace the catalyst potential, the system pH has no effect on the reaction rates.

Homomolecular and Isotopic Oxygen Exchange on Gadolinium Oxide

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Catalytic activity of gadolinium oxide in isotopic and homomolecular oxygen exchange