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Use of the Cage Model in Calculating Rates of Bimolecular Reactions in Condensed Phases

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This article proposes a simple method for calculating rates of bimolecular reactions in condensed phases, assuming the existence of two elementary reaction stages: site migrations occurring with a frequency k_m, and cage reactions occurring with a frequency k_i. The kinetic equation so derived affords a good description of the available data on radical recombinations in solids and liquids. In particular, it explains the nature of those segments of the kinetic curves which lie near the origin and which exhibit very high initial rates. The nature of constants k_m and k_i, as well as the possibilities of their determination by experiment, are discussed.

Processes Preceding the Appearance of the Flame and the Ignition of Hydrocarbons as Functions of Their Structure. 1. Delayed Appearance of Cold Flame and Ignition as Functions of Temperature and Pressure

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The authors have studied the delays in the ignition and in the appearance of a cold flame as functions of the temperature and pressure achieved during compression of stoichiometric mixtures of air and various hydrocarbons (*n*-hexane, 1-hexene, cyclohexane, cyclohexene, isooctane, diisobutylene, and a 60:40 mixture of isooctane and *n*-heptane). They have found sharp differences in the nature of the preflame processes and of the delays in ignition occurring in saturated and unsaturated as well as cyclic and acyclic hydrocarbons. Within each of the structural groups, the authors have found a good correlation between its ignition delay temperature relationship and its behavior in internal combustion engines. In particular, the authors have noted the effect of temperature on a tendency toward detonation.

Mass-Spectrometric Studies of Kinetics of Fast High-Temperature Reactions. II. Pyrolysis of Ethyl Formate

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The authors have studied the pyrolysis of ethyl formate at 551–716°C and 12–55 mm Hg by a new technique. The length of the reaction zone was 4 cm. Microsamples of the reaction mixture were withdrawn from that zone via a vacuum line (this immediately "quenched" the sample), and led into the input system of a mass spectrometer.

The degree of conversion of the ethyl formate and the reaction time were determined by the use of an "internal standard." Within the range investigated, ethyl formate decomposes to ethylene and formic acid. The reaction is unimolecular. An equation describing the reaction constant was also obtained.

Kinetics of Polymerization of Ethylene over the $(C_2H_5)_2TiCl_2$-$Al(C_2H_5)_2Cl$ Catalyst Dissolved in Ethyl Chloride

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The authors have studied the kinetics of polymerization of ethylene over the (soluble) catalyst $(C_2H_5)_2TiCl_2 - Al(C_2H_5)_2Cl$, dissolved in ethyl chloride. The reaction temperatures ranged from 10° to 40°C, and the pressures, up to 3000 mm Hg. The polymerization rate is virtually constant over a certain period whose length depends on the temperature, pressure, and catalyst concentration. The rate decreases if the concentration of either of the compounds comprising the catalyst is increased. The apparent activation energy, E_{app}, is 15.3 kcal/mole.

Effect of Solvents on the Rate of Radical Formation in the Thermal Decomposition of azo-bis-Isobutyronitrile

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The authors have measured the rates of initiation of chain reactions in thermal decomposition of azo-bis-isobutyronitrile in media comprising mixtures of methyl ethyl ketone with benzene, nitrobenzene, or water at 40–70°C. In methyl ethyl ketone, the activation energy for removal of a radical from the cage, E_e, is 1.9 kcal/mole. Addition of nitrobenzene does not affect E_e, but that of benzene decreases it and that of water increases it.

Catalytic Activity of Alkali Metal Ions in Oxidative Dissolution of Diamonds

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The authors have studied the oxidative dissolution of diamonds in superheated steam and in carbon dioxide at 870–880° over alkali metal carbonates or hydroxides. Li^+, Na^+, K^+, Rb^+, and Cs^+ promote this oxidation in superheated steam and suppress it in CO_2. The highest activity is exhibited by K^+, and the lowest by Li^+ and Na^+; the activities of Rb^+ and Cs^+ are lower than that of K^+, but much higher than those of Li^+ and Na^+. It appears that the activity of these ions is induced by the formation of an intermediate alkoxide-resembling complex.

Kinetics of Biphotonic Reactions. The System Carbazole-Ethanol

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The authors have studied the kinetics of biphotonic reactions in which the second photon is absorbed when the molecule is a triplet. They have shown that in the system carbazole-ethanol at 77°K, there are considerable deviations from the I^2 relationship at low (~3%) degrees of filling of the triplet level. Data obtained on discontinuous illumination are well correlated by a theoretically derived equation containing a factor describing this deviation.

Temperatures and Rates of Reduction of PbO_2, Pb_3O_4, and PbO by Hydrogen and Carbon Monoxide

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A method allowing direct measurement of sample temperature while also measuring the reaction rate was used to study the reduction of lead oxides with gases. The reduction has no induction period. Its rate decreases from the very beginning, even though the sample temperature rises quite high during the initial period of the reaction. The authors have studied the effect of addition of oxygen on the reduction, and have shown that in some cases the reduction process starts inside the solid sample.

Catalysis Occurring during Thermal Decomposition of Silver Oxide

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Direct quantitative measurements of liberated O_2 and CO_2 proved that silver oxide decomposes above 280°C. The reaction has a long induction period. Metallic dusts of silver or nickel deposited on the surface are very active catalysts of this reaction.

Effect of Additives on the Thermal Decomposition of Ammonium Perchlorate

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The authors have studied the effects of particle size and specific surface on the catalytic activity of NiO or CuO in the low-temperature (thermally induced) decomposition of NH_4ClO_4. Specific surface has a strong effect on the activity, while variation of particle size from 100 to 300 μ has virtually no effect. Oxides of copper, nickel, chromium, cobalt, etc., catalyze processes occurring during gas-phase decomposition of NH_4ClO_4. It appears that these oxides not only catalyze the decomposition in the solid but also substantially affect the gas-phase processes.