Average Life of Active Molecules and Oscillatory-Type Models of Monomolecular Reactions

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To construct oscillation-type models of monomolecular reactions the average lives of excited oscillating molecules were calculated in terms of the oscillation-inducing energy and true harmonic oscillations. The results show that Sleiter's Quantum Theory overrates the effect of the ducts on the decomposition rates. Elimination of the excess contribution opens a way to calculate the lives of oscillating excited molecules at the threshold of a monomolecular reaction and to estimate their upper and lower life limits.

Flame Propagation in Oxygen-Hydrogen Mixtures Within Ignition Limits

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A study of oxygen-hydrogen flames was made at different temperatures and pressures within the ignition limits. It was found that kinetics of flame propagation can be calculated by use of the well known equation for the chemical reaction rate constants. Calculations with the aid of electronic computers show that use of appropriately chosen reaction rate constants results in highly accurate data to describe the reaction at the conditions employed. Consequently, accuracy of the data calculated for the reaction, $H + O_2 + M \rightarrow HO_2 + M$, is greatly influenced by the choice of the rate constant values. A comparison of the calculated and empirical data shows that at temperatures of 600–800°K highly accurate results are obtained using values as small as 10^{-33} cm^6/mol^2 $\times$ sec.

A Method to Determine Excitation Energy of Molecular Ions

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A novel method is described to determine excitation energy of molecular ions. This is based on measuring the magnitudes of the momentum imparted to molecules by impacting electrons. Validity of the new method is supported by theoretical and experimental data.

Mechanism and Kinetics of Addition of Hydrogen Iodide to Common Carbon—Carbon Bonds of Hydrocarbons Dissolved in Organic Solvents: Addition of Hydrogen Iodide to Dimethyl Ester of Acetylene Dicarboxylic Acid in Toluene, Chlorobenzene, and *n*-Hexane Solutions

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The rate of addition of hydrogen iodide to dimethyl ester of acetylene dicarboxylic acid (ADE) in toluene, chlorobenzene, and n-hexane solutions can be calculated by the following kinetic equation:

$$-\frac{d(\mathrm{HI})}{dt} = k_2(\mathrm{ADE})(\mathrm{HI})$$

The maximum temperature points on the temperature-rate constant (k_2) curves for toluene and chlorobenzene are 30° and 13.5°, respectively. With n-hexane as the solvent, the rate of HI addition ($E = +2.8$ kcal/mol) changes only slightly at temperatures of 0° to 30°.

The slow-down of the HI addition reaction in presence of iodine is due to catalytic addition of the iodine to the acetylene dicarboxylic ester. The anomalies of the temperature-rate curves are attributed to formation and subsequent decomposition of the complex formed by interaction of HI with the carbomethoxy group of the ester.

Mechanism of Formation of Hydrogen Peroxide in 0.4 *M* Aqueous Solution of Sulfuric Acid by High-Dosage Radiolysis

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Radiolysis of 0.4 *M* aqueous solution of sulfuric acid was investigated with and without added oxygen in the reaction system, using electronic pulses of 5×10^{-6} sec duration and a dosage rate of 3×10^{23} ev/ml $\times$ sec. The results show that at this dosage rate the yields of hydrogen peroxide, $G(H_2O_2)$, and of the per-acids, $G(H_2S_2O_8 + H_2SO_5)$, are substantially greater than at smaller dosage rates. The yields of hydrogen, $G(H_2)$, also increase when the solutions are saturated with argon gas. Addition of small amounts of KBr to the oxygen-containing solutions markedly decrease the H_2O_2 yields.

In the main, the results obtained are attributed to the increasing influence of recombination of the H and OH radicals in the solutions.

Using the experimental data, the relative reac-