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Evaluation of Thermodynamic Functions of Activated Complexes Using Empirical Kinetic Equations

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Analyze the relationship between the effective activation enthalpy and entropy values calculated from empirical rate constants for single-stage reactions *and* the like thermodynamic constants for activated complexes. The methods proposed are illustrated by calculating the values of S^* for activated complexes in heterogeneous catalytic reactions. Conclude that—regardless of the nature of the kinetics involved—it is generally expedient to express experimentally-obtained data by exponential equations. Show that the values of ΔH_{eff}^* and ΔS_{eff}^*—calculated from the rate constants as derived by means of equations of this type—satisfactorily agree with the differences between the like thermodynamic functions of an activated state and of a certain effective condition which is intermediate to the gaseous and the adsorbed states of the reactants. This intermediate condition of the reactants is defined by the composition of the participating activated complex and the values of the exponents used in the empirical kinetic equation.

Give examples of practical application of these methods; as, for example, the decomposition of ammonia over a promoted iron catalyst and cracking of cumene over an aluminosilicate catalyst.

Determination of Kinetics of Thermal Decomposition of Ethylene by Single-Pulse Percussion Tube Method

By G. I. Kozlov and V. G. Cnorré

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Thermal decompositon of ethylene by a single-pulse percussion tube technique was investigated at 1250°–1850°K, total reacting gas pressure of 4 atm (abs.), and reaction time of about 0.8 millisecond. Ethylene content of the two ethylene-argon mixtures employed in this study was 1 and 5 per cent. The ethylene consumption rates, as determined by use of a first-order kinetic equation, are in good agreement with the rate values calculated from the experimental data at the above temperatures.

The results of this study validate the concept of molecular mechanism proposed for this decomposition reaction in earlier articles.

Oxidation-Reduction Reactions of Acceptors in Organic Solvents Due to Ionizing Radiation. I. Conversions of Chlorides of Iron Dissolved in Acetone

By M. Roder, N. A. Bakh, and L. I. Boogayenko

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The study of the effect of X-rays upon $FeCl_2$ and $FeCl_3$ dissolved in acetone show that Fe^{III} is reduced and Fe^{II} is oxidized as a result of interaction with the short-lived products formed by radiolysis of the solvent. The limiting yields, $G(-Fe^{II})$ and $G(-Fe^{III})$, are 0.82 ± 0.05 and 14.5 ± 0.3 ions/100 ev, respectively. Larger dosages produce a stationary state. Hypothesize that the short-lived products of acetone radiolysis participating in the reduction of Fe^{III} are of a non-radical type.

Effects of Intrinsic Properties of Solvents and Alkali Metals Upon Absolute Rate Constants of Anionic Polymerization of Styrene

By A. I. Niepomnyashchii and H. S. Bagadasariyan

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Report on the effects of the anti-ions of alkali metals (Li, K, Na, Cs) and of solvents (tetrahydrofuran; dimethyl ether of diethylene glycol) upon the kinetics of chain initiation and chain growth in anionic polymerization of styrene—in presence of an alkali metal-diphenyl initiator.

List the experimentally-determined values of the rate constants for the chain growth and for the "live" polymer formation processes.

Report the results of a study to determine the effect of anti-ions and of the solvent upon deactivation of "live" polymers.

Energy Transfer in Sensitized Photolysis of Benzoyl Peroxide Solutions

By I. N. Vaseeliyev and V. A. Krongauz

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Report the results of studies of sensitized photochemical decomposition of benzoyl peroxide solutions in toluene, with and without 2,5-diphenyl oxazole. With the two-component solutions, decomposition of the peroxide is initiated by the light absorbed by the solvent; with the three-component solutions, the peroxide decomposition is due to the light absorbed by the luminophor.

Kinetics of Thermal Decomposition of Sulfates of Magnesium, Zinc, Copper, and Cobalt

By V. V. Petchkovskii, A. G. Zviozdeen, and T. I. Beresniyova

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A comparative study of the kinetics of thermal decomposition of sulfates of magnesium, cobalt, zinc, and copper—alone, and with admixed oxides of chromium, iron, and copper—shows that the added compounds exert almost no effect on the rate of dissociation of the sulfates of copper and cobalt but do increase the decomposition rates of zinc and magnesium sulfates.

The kinetics of thermal decomposition of sulfates is accurately expressed by the Rogeenskii-Todes equation.

In dissociation of sulfates of zinc and copper, the reaction rate constant has two values, corresponding to the initial and intermediate states of decomposition of these salts.

Effect of Pressure on Induction Time in Oxidation of Polypropylene

By V. V. Doodorov

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A study of the effects of oxygen partial pressures and of total system pressures upon induction periods in oxidation of isotactic polypropylene was carried out at 110°–130° and total pressure up to 95 atm (abs.). The results show that toward the end of induction period almost all of the oxygen consumed is in the hydroperoxide radical of the polymer product.

Equations to determine the periods for induction of oxidation and the rates of oxidation were derived from the estimated kinetic constants for the reaction. The values based on these equations are in good agreement with the corresponding experimental data.

The rate of oxidation of polypropylene is proportional to the square root of the oxygen partial pressure. This type of functional relationship is apparently typical of second-order degenerative branching oxidation reactions. Observed dependence of the induction time upon the nitrogen pressure is probably due to a change in the kinetics of oxidation which, in turn, is caused by alterations in the molecular motion within the system.

Effect of Adsorbed Oxygen Upon Thermal Activation-Deactivation of Platinum Black

By Yu. M. Tiureen and L. G. Feokteestov

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Report the results of a study of the effect of adsorbed oxygen upon the catalytic and surface properties of platinum black due to a pretreatment with oxygen-nitrogen mixtures. The adsorbed oxygen alters the temperature of initiation and the rate of recrystallization of platinum black and is one of the factors responsible for the loss of its ability to catalyze decomposition of hydrogen peroxide.

EPR Spectra and Magnetic Susceptibility of Aluminochromate Catalysts

By A. A. Sleenkeen, E. A. Fiodorovskaya, and A. M. Roobeenshtein

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A study of the effect of Cr_2O_3 content (1.5 – 93% by wt) in alumino-chromate gels was carried out at calcination temperatures of 450°, 600° and 1,000°C. The gels produce three distinctly different groups of spectra, corresponding to the following three ranges of Cr_2O_3 content (wt. %): 1.5–14; 20–33; and 60–93. The observed differences in the spectra are due to the differences in the phase compositions of these three groups of gels.

This study also produced some novel information regarding the nature of the narrow line in the EPR spectra of the alumina gels containing small amounts of chromium oxides.