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Evaluation of Thermodynamic Functions of Activated Complexes Using Empirical Kinetic Equations

By G. S. Golodietz and V. A. Roiter

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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

L. Ya. Karpov Physico-Chemical Institute

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