

## Kinetics and Catalysis, Vol. IV, Issue 1, pages 24-34 (Jan.-Feb. 1963)

### Free Radical Recombination Processes on Semiconductor Surfaces and Their Role in Luminescence

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The mechanism of luminescence in luminofors was studied as possibly occurring by the radical recombination route under the influence of chemically active gases and by "candor"-luminescence. The intensity of the radical-recombination luminescence was calculated in terms of pressure and the levels of Fermi state. The effect of an outside electric field on the intensity of "candor"-luminescence was determined experimentally. The results qualitatively agree with the theory proposed.

### Possible Explanation of the Compensating Effect in Some Chemical Reactions

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The compensating effect can be rationalized by assuming that (1) the experimentally-determined effective rate of a reaction studied is the sum of the local rates which are independent of each other and (2) the free activation energies follow the Gaussian frequency distribution.

### Decomposition of Molecular Ions Formed in Photoionization of Hydrazine and of Some of Its Alkyl Derivatives

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Summarizes the results of studies of the mass spectra and of the ion formation potentials in photoionization of hydrazine; methyl hydrazine; 1,1-dimethyl hydrazine; and 1-methyl 1-normal butyl hydrazine. Gives calculated values of heats of formation of the ions, ionization potentials of the radicals, and dissociation energies of some of the bonds.

### Formation of Free Radicals in the RH + O<sub>2</sub> System: I. Tetralin, Cyclohexanol, Cyclohexanone

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The mechanism of free radical formation (chain initiation) in an RH + O<sub>2</sub> liquid phase system was studied by use of an inhibition technique. Based on the results for tetralin and cyclohexanol, show that the radicals are formed according to the reaction,  $2RH + O_2 \rightarrow 2R\cdot + H_2O_2$ . List values of the reaction rate constants for tetralin, cyclohexanol and cyclohexanone.

### Determination of Absolute Rates of Chain Initiation and Growth in Anionic Polymerization of Styrene

By H. S. BAGDASARYAN AND  
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The kinetics of chain growth was studied in a single-pass continuous unit by reacting the "live" polymers of styrene with the monomer in a tetrahydrofuran solution. The chain growth rate constant is  $k_p = (1.00 \times 10^6) \cdot \exp(-4,670/RT)$  l/mol-sec.

An analysis of the kinetic data for interaction of sodium diphenyl with styrene shows that conversion of the ion-radicals of styrene into the dianionic dimers is the limiting step in the "live" polymer formation process. The rate constant for this reaction is  $k_2 = (5.6 \times 10^{11}) \cdot \exp(-14,200/RT)$  l/mol-sec. The effects of solvation and interaction of the ions upon the activation energies and entropies of the reactions studied were also examined.

### Mechanisms of Energy Transfer in Luminescence and Chemical Radiation

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Radiolysis and luminescence of three component solutions: toluene, benzoyl peroxide, and