

### I. Ionization of 1,1-Diphenyl Ethylene in Aqueous Sulfuric Acid

By K. S. KAZANSKII AND S. G. ENTELIS

A study of ionization of 1,1-diphenyl ethylene in an  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  system was made by a spectrophotometric method. The concentrations of the  $\text{H}_2\text{SO}_4$  used were 66 to 80%.

It was shown that the ionization is of a complex nature: the diphenyl-ethyl cation is in equilibrium with two conjugated bases, namely, 1,1-diphenyl ethylene and methyl diphenyl carbinol. The equilibrium constants,  $K_1$  and  $K_2$ , for both processes were determined at temperatures of 5°, 20° and 40° and the heats of ionization in either direction were found to be as follows:  $\Delta H_1 = 8.1 \pm 1.4$  kcal/mole and  $\Delta H_2 = -5.3 \pm 1$  kcal/mole.

The authors give reasons for the belief that the new ionization process, as exemplified by the study described herein, might also be applicable to other aryl olefins.

### Kinetics of Thermal Decomposition of Pyroxylin

By G. B. MANELIS, U. I. RUBZTOV, L. P. SMYRNOV, AND F. I. DOBOVITZKII

Study was made of the kinetics of thermal decomposition of pyroxylin gunpowder. The composition of the gaseous products and the heat of thermal decomposition were determined at temperatures of 140°-165°C, both at normal pressure and in vacuum, by measuring heat liberated, the amount of gas formed, and the change in weight of the liquid phase.

It is shown that thermal decomposition of pyroxylin gunpowder consists of primary, secondary, and catalytic reactions; also, that the auto-acceleration of thermal decomposition of pyroxylin gunpowder is caused by the formation of gaseous and condensed products.

### Calorimetric Study of Reactions of Atomic Hydrogen with Solid Olefins at a Temperature of 77°K

By U. P. LOMANOV, A. N. PONAMARYOV, AND V. L. TALROSE

A method has been worked out which permits simultaneous measurement of the rate of consumption of atomic hydrogen and of the rate of heat liberation (up to  $10^{-4}$  cal/sec) in the reaction layer during the interaction at a temperature of 77°K of hydrogen atoms from the gaseous phase with solid hydrocarbons. Using this method, a study was made of the mechanisms for reaction of atomic hydrogen with solid propylene and iso-

butylene and of recombination of hydrogen atoms in the corresponding alkane layers.

On the basis of the data for reactions of hydrogen atoms with alkyl radicals, an evaluation is presented of the relative role of some of the reactions in the processes of this type.

### Recombination of Radicals in Solid Organic Substances. I. Investigation of Defreezing Techniques

By V. K. YERMOLAYEV, U. N. MOLIN, AND N. J. BOOBEN

Using the EPR method, an investigation was made to determine the temperature range in which recombination of radicals occurs during defreezing of various organic substances exposed to fast electrons. It was established that for crystalline substances rapid recombination occurs, as a rule, just before their fusion temperature; on the other hand, for amorphous substances this takes place at their vitrification temperature. With cyclopentane and cyclohexane, the radicals recombine at their polymorphic transition points. For isolated substances it is possible to establish several regions of radical recombination. In the majority of cases, recombination of radicals is, apparently, dependent upon auto-diffusion, which originates in the neighborhood of temperatures of fusion, vitrification, and polymorphic transition points.

### The Spectra of Pure Nickel Oxide and of Nickel Oxide-Containing Adsorbed Gases

By K. KLEEYER

The spectra of variously prepared samples of pure nickel oxide and of the oxide containing adsorbed gases were photographed in the wavelength range of 3,300-11,000 Å. The spectra were found to agree well with the crystal field theory, provided the value of  $Dq$  is taken to be equal to 850  $\text{cm}^{-1}$ . Adsorption of oxygen produces a change in the spectrum because of accompanying formation of  $\text{Ni}^{3+}$  ions. Adsorption of carbon monoxide and of hydrogen results in a different change of the spectrum, which might be explained by the assumption that the  $\text{Ni}^{2+}$  ions on the surface are reduced to  $\text{Ni}^+$ .

### A Theory of the Effect of Photoadsorption Upon Semi-Conductors

By F. F. VOLKENSHEIN AND I. V. KARPYENKO

With the electronic theory of chemisorption as the basis, there are derived the criteria for positive and negative photoadsorption effects (the