

Between 40° and 70°C, the decomposition is unimolecular:

$$k_{\text{specific}} = 1.5 \times 10^8 \exp -(13200/RT) \text{ sec}^{-1}\text{m}^2.$$

Between 90° and 110°C, the biomolecular mechanism takes over:

$$k_{\text{specific}} = 3.6 \times 10^{10} \exp -(24600/RT) \text{ liters/mole-sec-m}^2.$$

Data on products and changes of catalytic activity with time are given. The authors also compared data obtained by the inhibitor technique with those obtained by the direct decomposition of the hydroperoxide.

#### Modification of the Iron Catalyst for Ammonia Synthesis by Certain Metals

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The authors have studied the activities and work functions of industrial type GK catalysts for the ammonia synthesis. Various concentrations of Cu, Ni, and Co were introduced, and these caused changes in activity which could be correlated with changes in the work function. Addition of cobalt (0-4%) does not alter either the  $\Delta\phi$  or the  $\log k_{\text{specific}}$ , but Ni and Cu increase the  $\Delta\phi$  and decrease the  $k_{\text{specific}}$ .

#### Integrated Study of the Porosity of Catalysts. I. Some Questions on the Present Status of the Sorption Technique

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Analysis of the capillary condensation technique showed that its accuracy in determining the porosity of solids can be improved if one knows the shape of the pores; the latter can be found by electron microscopy. The author also analyzed the methods for selecting (for calculations) one branch of the capillary condensation hysteresis curve, as well as the selection of adsorbates. He shows that much better results are obtained by using the desorption data.

#### The Effect of Adsorption of Metal Vapor on the Conductivity of Zinc Oxide Films

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Vapors of Na, Zn, and In were adsorbed on thin zinc oxide films, and the conductivity of the latter was then measured. The kinetics of ZnO conductivity under the influence of metal vapors were studied, and it was shown that all metals act as donors on the ZnO surface. Their behavior is extremely complex. The thin ZnO film technique permits detection of very small concentrations (less than  $10^7$ - $10^8$  atoms/cm<sup>3</sup>) of metal atoms. By a probe technique the authors have measured the evaporation of these nonstoichiometric Na atoms from the ZnO surface, and have determined the heats of vaporization.

#### Supported Chromium Oxide Catalysts for Polymerization of Ethylene. The Reason for Stabilization of Hexavalent Chromium

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Spectral analysis of these catalysts shows that deposition of chromium trioxide on silica gel or an aluminum silicate with a low aluminum content leads to formation of bichromate ions on the surface, but that chromate ions are formed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It is this formation of salts of chromic acids that stabilizes the hexavalent chromium upon the deposition of chromium trioxide on supports.

#### Effect of the Preparative Technique on the Porosity and Strength of Catalysts and Supports. I. Silica Gels of Uniform Porosity

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The authors have studied the porosity and strength of silica gels of uniform porosity as functions of the moisture content of the paste used as the starting material, the activation treatment and the calcining temperature. It was found that at lower moisture contents in the paste, the volume and radius of the pores decreases. The increase in strength accompanying this phenomenon is due to the increased number of contacts between individual globules, with no reduction in strength

of the contacts themselves. The hydrothermal activation treatment substantially increases the strength of the interglobular contacts. The increase in strength accompanying the calcining is largely due to strengthening of individual contacts.

### Control of Reaction Temperature by Introduction of a Cold Stream as a Means of Producing Optimal Condition for an Exothermic Reaction

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The problem of optimal temperature for a catalytic process in which the cold stream is introduced at a uniform rate was solved by the Pontryagin maximum principle. This gave the conditions necessary for the optimality of the temperature, as well as the boundary conditions for the quantity and feed rate of the cold stream and the maximum process temperature. The results are applied to the case of the reversible exothermic oxidation of  $\text{SO}_2$  with continuous feed of cold air, where the theoretically-optimum conditions were determined.

#### NOTES

### The Calculations of the Orienting Effect of Substituents in the Addition of Atomic Hydrogen to Substituted Benzenes (MO-LCAO approximation)

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The simple MO-LCAO approximation was used to evaluate the orienting effect of substituents on the addition of atomic hydrogen to various substituted benzenes; the effect of superconjugation of the  $\text{CH}_2$  group with the  $\pi$ -system of the ring is discussed.

### The Role of Additives in Radiolysis

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The author formulates the quantum-mechanical condition under which it is possible to localize excitation in molecules of the main substance near the impurity particles. It is shown that most

of the radiolysis of the main substance will take place near the impurities.

### Kinetics of Decomposition of Copper Benzoates

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The authors have studied the kinetics of the thermal decomposition of copper benzoates, toluates, as well as *o*- and *p*- chlorobenzoates. This is a first-order reaction;

$$k_{\text{toluates}} > k_{\text{benzoate}}; k_{p\text{-toluate}} < k_{m\text{-toluate}}; \\ < k_{o\text{-toluate}}; k_{o\text{-chlorobenzoate}} \gg k_{p\text{-chlorobenzoate}}$$

Magnesium oxide promotes the rate of decomposition of copper *o*-toluate to cresol and the starting acid.

### Catalysis of Ammonium Nitrate Radiolysis by Semiconducting Oxides

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The authors have studied the effect of mechanical admixtures of  $\text{ThO}_2$ ,  $\text{ZnO}$ ,  $\text{NiO} + \text{ZnO}$ , doped  $\text{Li}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  on the X-ray induced radiolysis of  $\text{NH}_4\text{NO}_3$  *in vacuo*. It was shown that the activity of these oxides correlates with their  $\Delta\phi$  (where  $\phi$  = electron work function), and that oxides with the lowest  $\phi$  are the best catalysts. As far as oxide concentration is concerned, the greatest effect was obtained at a relatively low concentration.

### Participation of Channel Black in the Chain Termination in Polyethylene Oxidation

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The authors have studied the oxidation of high-pressure polyethylene in the presence of the antioxidant 2, 4, 6 tri-*tert*-butylphenol, as well as an antioxidant of moderate activity (phenyl- $\beta$ -naphthylamine), and channel black. Channel black decreases the rate of oxidation in all cases where the  $\text{RO}_2^*$  concentration is high (whether in the absence of the antioxidant, or whether in the presence of the weak antioxidant, or subcritical concentrations of the moderate-activity compound). This phenomenon is probably due