## Chemiluminescence in Slow Chemical Reactions. I. Regularity of Chemiluminescence in Catalytic Oxidation of Ethyl Benzene

*By* I. V. Zakharov and V. A. Shliapeentokh

*Moscow Physico-Chemical Institute.*
*Institute of Chemical Physics of the*
*Academy of Sciences of U.S.S.R.*

Oxidation of ethyl benzene catalyzed by cobalt acetate is accompanied by chemiluminescence of intensity which is proportional to the reaction rate. Both the intensity of chemiluminescence and the rate of oxidation vary with the temperature and concentrations of the catalyst and of the hydrocarbon.

A kinetic mechanism is proposed to explain basic regularity of chemiluminescence.

## Effect of Reaction Components in Polymerization of Ethylene on the EPR Spectra of Chromoaluminosilicate Catalysts

*By* V. B. Kazanskii and Yu. I. Pecherskaya

*Institute of Chemical Physics of the*
*Academy of Sciences of U.S.S.R.*

The change in the narrow line signal of the EPR spectra of a chromoaluminosilicate catalyst in polymerization of ethylene is due to adsorption of water, ethylene, heptane, and cyclohexane on the $Cr^{+5}$ ions. Studies of the EPR spectra of the catalyst enriched with $Cr^{53}$ isotope support the conclusion that the shape of the narrow line is affected by the $Cr^{+5}$ ions.

## Isotopic Exchange Between Molecular Oxygen and Carbon Dioxide Over Manganese Dioxide

*By* L. A. Kasatkeena and G. V. Antosheen

*D. I. Mendeleyev Chemico-Technological*
*Institute in Moscow*

A study of isotopic exchange (a) between molecular oxygen and carbon dioxide over manganese dioxide, (b) between these two gases and the oxygen from $MnO_2$, and (c) in the reaction, $C^{16}O_2 + C^{18}O_2 = 2C^{16}O^{18}O$, leads to the following conclusions:

1. The rate of isotopic oxygen exchange in the oxygen-carbon dioxide system is many times smaller than in the $C^{16}O_2$—$C^{18}O_2$ system *and* is roughly equal to the exchange rate with the oxygen from $MnO_2$;
2. Isotopic oxygen exchange in an $O_2$—$CO_2$ system is believed to occur via the exchange with the oxygen from $MnO_2$ and that the exchange of molecular oxygen is the limiting step in the reaction.

## Non-Equilibrium Kinetics in Ammonia Synthesis

*By* M. I. Tiomkeen, N. M. Morozov,
and E. N. Shapateena

*L. Yu. Karpov Physico-Chemical Institute*

A study of the ammonia synthesis kinetics over a doubly-promoted iron catalyst was carried out in a recycle-continuous unit at atmospheric and sub-atmospheric pressures to obtain widely varying concentrations of $NH_3$ in the reaction products. At near-equilibrium concentrations of ammonia, the reaction rates are expressed by Equation (1). At ammonia concentrations well below the corresponding equilibrium values, Equation (7) gives the reaction rates. For the catalyst employed in this study $m = m' = 0.5$.

The results obtained are interpreted to mean that the limiting step concept applies only to near-equilibrium reaction conditions. Consequently, Horiuti and Takesawa's stoichiometric values for the limiting stage of ammonia synthesis are ill-founded.

## Soluble Unsaturated Hydrocarbon—Metal Salt Complexes and Their Function in Catalytic Reactions. III. Soluble $\pi$-Complexes of Acetylene and Mercury

*By* O. N. Tiomkeena, R. M. Fleed, and
A. I. Malakhov

*M. V. Lomonosov Institute*
*of Fine Chemical Technology*

The thermodynamics of acetylene-mercury sulfate complex formation in $H_2SO_4$ solutions was investigated at hydration-promoting conditions using a potentiometric analytical technique. The formation of $\pi$-complex, $HgC_2H_2^{2+}$, occurs at the optimum levels of catalytic activity, corresponding to the $H_2SO_4$ concentrations of 1.5–3.0 mol/l. The hydration process is realized via the $\pi$-complex formation and conversion steps. In presence of $HgI^{2+}$ in the solution, conversion of the $\pi$-complex to acetaldehyde is the limiting step of the process.

## Kinetics of Dimerization of Styrene in Aqueous Solution of Sulfuric Acid. I. Ionization of Styrene in $H_2SO_4$–$H_2O$ System

*By* S. G. Entielees, K. S. Kazanskii
and G. A. Kagan

*The Institute of Chemical Physics of*
*the Academy of Sciences of U.S.S.R.*

A spectrographic study to correlate process variables in ionization of styrene in aqueous sul-