

with fresh samples of the catalyst, the thermo-EMF distribution is governed by the normal principles. On the other hand, the distribution on the aged samples is asymmetric in character. An equation is derived to calculate the thermo-EMF distributions and a correlation established between the distribution parameters and catalytic activity of the samples.

### The Overlap Integral Method in Determining of Various Forms of Chemisorption on Metals: Dissociative Chemisorption

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The heats of hydrogen chemisorption on metals during the first transition period were calculated by the overlap integral method. In line with the experimental data, the calculations show that the heats decrease with the on-stream time. The calculated information predicts that at equilibrium conditions the bonding distance, M—H, decreases with the in-service time. The concept regarding the major role of the *d*-orbitals in the formation of the M—H bond was confirmed.

### Hydrogenation of Olefins in the Presence of Complex Organometallic Catalysts

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Hydrogenation of cyclohexene and of heptene-1 was studied in the presence of organometallic catalysts, comprising mixtures of triethylaluminum with one of the following transition metal-containing compounds:  $(C_5H_7)_2TiCl_2$ ;  $VO(C_5H_7O_2)_2$ ;  $Cr(C_5H_7O_2)_3$ ;  $Mn(C_5H_7O_2)_2$ ;  $Fe(C_5H_7O_2)_3$ ;  $Co(C_5H_7O_2)_2$ ;  $Ni(C_5H_7O_2)_2$ .

In terms of the transition metal components of the catalysts with the Al/Me ratio of 10, catalytic activity of the preparations in hydrogenation of cyclohexene and of heptene-1 decreases in the following orders:  $Co > Ni > Fe > Cr$  and  $Co > Ni > Fe > Cr \geq Ti > Mn > V$ , respectively.

Hydrogenation of heptene-1 is complicated by the concurrent isomerization of the reactant, involving the double bond shift.

### Reactions of $\alpha$ -Oxides: The Mechanism and Kinetics of a Base-Catalyzed Reaction of Ethylene Oxide with Alcohols

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The reactions of ethylene oxide with alcohols of different acid strengths are of the first order with

respect to both the oxide and the alcoholate; however, in terms of the alcohol concentration, kinetics of these reactions are complex. Here, with the weakly-acidic alcohols, the concentration -*v*s- rate constant curves pass through a minimum; on the other hand, with strongly-acidic alcohols, the correlation is linear in character. A clear-cut relationship was established between the acidity and reactivity of the alcohols.

The results of this study are interpreted as showing that the reaction passes through a transition stage, and that during this stage the alcoholate attacks carbon atoms of the ethylene oxide, while the free alcohol molecules attack oxygen atoms of the oxide.

### The Mechanism and Kinetics of Catalytic Interaction of Isocyanates with Alcohols in the Presence of Organotin Compounds: The Reagent-Catalyst Complexes as the Reaction Intermediates

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The results of *n*-chlorophenylisocyanate reaction with methyl alcohol dissolved in *n*-heptane show that in the presence of added dibutylallyllaurinate of tin, the active intermediate is the complex formed by interaction of the catalyst with an alcohol. This conclusion is supported by the observation that the reaction rates are proportional to concentrations of the activated complex. The equilibrium constants and the true interaction rates of the catalyst-alcohol complex with the isocyanate were determined at temperatures of 25°, 35°, and 45° with the aid of the kinetic data. The thermodynamic parameters were calculated for each stage of the reaction.

### Catalytic Activity of Polychelates in the Liquid Phase Oxidation of Hydrocarbons

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Certain kinetic relationships were established in oxidation of isopropylbenzene and ethylbenzene in the liquid phase in the presence of a catalyst on a polymeric chelate carrier. The results show that catalytic decomposition of the hydroperoxide is the fundamental source of the free radicals produced in the reactions studied. Based on the kinetic data obtained, a multi-stage reaction