Mathematical Modeling of Platforming for Purposes of Process Optimization. II.

Yu. M. Zhorov, G. M. Panchenkov,
Yu. A. Tirakyan, S. P. Zeltser,
and F. R. Fradkin
The Gubkin Institute of the Petrochemical and Gas Industries, Moscow

Mathematical modeling of platforming is used as an example in discussing the various stages at which such a mathematical description of a complex process can be used for purposes of optimization. In its differential form, the platforming model is invariant with respect to reactor dimensions. The optimal operating modes of the platforming process, obtained by a search for the extremum points of the model, are described.

Lifetimes of Atoms and Molecules Adsorbed on Solids. I. A Lifetime Measuring Technique Based on the Time Required for Passage of Molecules through a Long Channel

E. B. Gordon and A. N. Ponomarev
Branch of the Institute of Chemical Physics, Academy of Sciences, USSR

The authors suggest (and develop to the point of presenting calculation formulas and graphs) a technique for determining the lifetime of molecules of a gas adsorbed on a solid surface. This technique is based on measuring the time required for passage of a packet of molecules through a long channel. This technique may also be used for experimental determination of the probability of absorption of such molecules upon collision with a wall.

NOTES

Kinetics of Alkaline Hydrolysis of *tert*-Butyl Perbenzoate

V. L. Antonovskiy, M. M. Buzlanova,
and Z. S. Frolova
The Novo Kuybyshev Branch of the Research Institute for Synthetic Alcohols and Organic Products

The alkaline hydrolysis of peresters was studied on the example of *tert*-butyl perbenzoate in aqueous methanol. The hydrolysis is quantitative and irreversible: *tert*-$C_4H_9—OOC(O)C_6H_5 + OH^- \rightarrow$ *tert*-$C_4H_9OOH + C_6H_5C(O)O^-$. The rate of consumption of the perester is governed by the equation, $\nu = Kk[H_2O][OH][C_6H_5C(O)OOC_2H_9]$. In water at 20°C, Kk is 0.31 liter^2-mole^{-2}-min^{-1}. The activation energy for the alkaline hydrolysis involves formation of a ring complex consisting of (1 mole each) the perester, water, and the hydroxyl group.

The Rate Constants for the Elementary Reactions of Chain Propagation and Termination in the Liquid Phase Oxidation of Methyl Ethyl Ketone

G. E. Zaikov, A. A. Vichutinskiy,
and Z. K. Mayzus
Institute of Chemical Physics, Academy of Sciences, USSR

The rate constants for chain propagation (k_2) and termination (k_6) in liquid-phase oxidation of methyl ethyl ketone are

$$k_2 = (1.26 \pm 0.08) \times 10^5 \times \exp(-8400 \pm 500/RT) \text{ liters}\cdot\text{mole}^{-1}\cdot\text{sec}^{-7};$$
$$k_6 = (2.02 \pm 0.21) \times 10^7 \times \exp(-1600 \pm 800/RT) \text{ liters}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}.$$

The values of $\Delta H‡$, $\Delta S‡$, and $\Delta F‡$ for both reactions are also given.

Radiation-Induced Polymerization of Isobutylene in Liquid and Glassy States

R. I. Miluytinskaya and Kh. S. Bagdasaryan
The Karpov Institute of Physical Chemistry

The initiation yield ($G_{\text{init.}}$) of carefully purified isobutylene is 0.5 at 195°C; the mean length P of the resulting polymeric chain is 10^4 molecules. This shows that 15% of the secondary electrons recombine with the parent ion in less than 10^{-7} sec; these electrons travel no less than 200 Å. The isobutylene polymerization in methylcyclohexane solution (1.4:1) and in a glassy state at 77°K exhibit $G_{\text{init.}} = 2.3$ and $P = 10^2$. The presence of aromatic amines in the glass leads to a lower yield of the polymer and a lower molecular weight, as well as to formation of cation radicals of these amines. Processes occurring in the presence of amines are discussed.

Rate Constants for Elementary Reactions of Polymerization of Tetrafluoroethylene

E. I. Nosov
Institute of Chemical Physics, Academy of Sciences, USSR

The kinetics of the initial unsteady state were used to determine the rate constants for the elementary reactions of tetrafluoroethylene polymerization in aqueous solutions. Equations for free radical lifetimes and their steady-state concentrations are derived. The rate constants for chain termination are extremely small.