JOURNAL OF CATALYSIS 4, 312 (1965)

BOOK REVIEW

On Physical Adsorption. By SYDNEY ROSS and JAMES P. OLIVIER, with Foreword by J. H. DEBOER. Interscience (Wiley), New York, 1964. xxvi + 401 pp. Illus. Price $15.

The development of the Brunauer-Emmett-Teller (BET) method of determining surface areas (1935–1940) and the subsequent extensions and variations for elucidating pore distributions were important milestones in catalytic research. The researcher could for the first time determine surface areas reliably and define pore geometry. G. D. Halsey, Jr., and others as early as 1945 challenged the basic concepts of the BET model for physical adsorption. The usual smooth isotherms resulted from surfaces with a wide distribution of adsorptive energies; for uniform surfaces stepwise isotherms should be obtained. About 10 years ago, stepwise isotherms for argon and krypton were reported on graphitized carbon blacks.

"On Physical Adsorption" is concerned primarily with the effect of heterogeneity on the first adsorbed layer, and carries the work of J. H. de Boer, T. L. Hill, and G. D. Halsey, Jr. to a logical conclusion. The work of Professor Ross and co-workers at Rensselaer Polytechnic Institute over the last decade is summarized.

Chapter I introduces general concepts of mobile and localized adsorbed layers, and shows that the equation for adsorption isotherms may be expressed by a term K, independent of surface coverage, times a second term that is a function of coverage. Experimental methods for determining adsorption isotherms and heats of adsorption are given in Chapter II, and the third chapter defines the different heats of adsorption.

With Chapter IV the development of the theme of the book begins in earnest. Complications of the adsorption process by heterogeneity are introduced, and the authors demonstrate that useful analytic determinations of the distribution of adsorptive potentials can not be obtained. Therefore, the distribution of adsorptive potentials is approximated by a Gaussian function, and model isotherms are computed (and tabulated for mobile adsorbed layers in an appendix) for a wide range of adsorption and distribution parameters. The experimental isotherm is matched to one of the calculated curves. From the parameters of the model isotherms, experimental isotherms varying from conventional to stepwise types can be predicted accurately at several temperatures, and heat of adsorption data can be calculated precisely. Also the monolayer capacity, usually slightly larger than V_m or point B values, is obtained, and reasonable values for kinetic-molecular behavior of the adsorbate can be calculated. For all of the data considered, the mobile-, rather than the localized-layer model provided a more consistent interpretation. The Gaussian distribution hypothesis is not adequate for all adsorbents; however, these exceptions can usually be resolved as a composite of two Gaussian distributions.

The authors are fully cognizant of the limitations and hazards of curve matching, especially for adsorption data where the shape of the isotherm and its changes with temperature contain only limited information of diagnostic value. The present approach derives about as much information as can be obtained from the isotherm and its temperature dependence. Independent methods for determining the nature of the adsorbed molecule are needed.

The methods of Ross and Olivier are more useful in characterizing surfaces for physical processes, such as wetting and floatation, than for characterizing catalysts. Most catalysts are prepared in ways that produce heterogeneous surfaces, and stepwise isotherms at coverages less than a monolayer are uncommon. For catalysts the BET equations will usually give essentially the same area as the present methods.

R. B. ANDERSON

Department of Chemistry,
The Queen's University of Belfast,
Northern Ireland