BOOKS

On Physical Adsorption, Sydney Ross and James P. Olivier, John Wiley, New York (1964). 291 pages plus 100 pages of numerical tables, $15.00.

In many chemical engineering circles, especially academic ones, there is a feeling that thermodynamics is essentially a dead science, useful to be sure, and perhaps even essential for the practice of chemical engineering, but nevertheless old, complete, devoid of exciting frontiers. This unfortunate and completely erroneous view can easily be refuted by pointing to the growing literature on how molecular concepts, coupled with thermodynamic reasoning, can lead to highly useful results for the description and interpretation of equilibrium phenomena. A splendid example of this growing literature is presented by this fine monograph on the molecular thermodynamics of physical adsorption.

This book will appeal to research oriented chemical engineers, because unlike so many publications of contemporary physical chemists, it deals with real rather than highly idealized situations, and because it develops its theme with simple, familiar thermodynamic tools without the frustrating mathematical complexity so common in works on pure statistical mechanics. Fortunately, the authors have succeeded in providing a happy synthesis between the modern theory of intermolecular forces and the phenomenological description of the adsorption isotherm based on classical Gibbsian thermodynamics.

This book is concerned only with the physical adsorption of gases on solids up to monolayer coverage; chemisorption, multilayer adsorption, and adsorption of or on liquids are not covered. The book is intended for research workers who are concerned with solid surfaces, and it therefore includes a comprehensive chapter on various types of experimental apparatus for measuring gas-solid equilibria and heats of adsorption. This chapter points out advantages and disadvantages of various experimental techniques and should be especially helpful to anyone who is about to embark on adsorption measurements for the first time.

The central thesis of this monograph is based on the idea that an adsorbed molecule is part of a mobile adsorbed layer on the solid surface and is subject to two separable forces: a (vertical) force, acting between the molecule and

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mass transfer calculations than the practical diffusion coefficient form.

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NOTATION

C = total molar concentration
C_i = concentration of species i
$\mathcal{D}_{ij}$ = binary diffusion coefficient
D_{ij} = multicomponent diffusion coefficient
$[D]$ = multicomponent diffusion coefficient matrix with elements D_{ij}
$[k]$ = multicomponent mass transfer coefficient matrix
k_i = binary mass transfer coefficients
$\ulcorner k_i \lrcorner$ = diagonal matrix whose elements are k_i
n = one less than the number of components
$[t]$ = modal matrix of $[D]$
(u) = column vector defined by $\beta(y)$
$\ulcorner u \lrcorner$ = diagonal matrix with elements of (u)
y_i = mole fraction of component i
(y) = column vector with elements y_i
$\ulcorner y \lrcorner$ = diagonal matrix with elements of y_i
α_{ij} = $1/\mathcal{D}_{ij}$
(α_{n+1}) = column vector with elements $\alpha_{i,n+1}$
$\ulcorner \alpha_{n+1} \lrcorner$ = diagonal matrix with elements $\alpha_{i,n+1}$
β_{ij} = defined by Equation (5)
$[\beta]$ = matrix whose elements are β_{ij}
$\underline{\theta}_i$ = molar flux of species i with respect to molar average velocity, a three vector
(θ) = column vector with elements θ
$\ulcorner \underline{\theta} \lrcorner$ = diagonal matrix with elements $\underline{\theta}_i$
∇ = gradient operator

Subscripts

i, j, k = indices

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the surface, and a (horizontal) force, acting between the molecule and other adsorbed molecules in the immediate vicinity. The first of these forces depends upon the potential energy function between the surface and a single gas molecule, whereas the second can be characterized by a two-dimensional equation of state for the adsorbed layer. For an idealized homogeneous adsorbent, the characteristic potential energy between the surface and a single gaseous molecule is uniform over the surface, but for a real, heterogeneous adsorbent the potential energy is not the same for all parts of the surface since some sites are more active than others. To characterize the heterogeneity of the solid surface, the authors use a Gaussian distribution function $\Phi(U_o)$ for the characteristic adsorption potential energy U_o. For the equation of state of the adsorbed layer they use a two-dimensional analogue of the van der Waals equation which, through the Gibbs adsorption isotherm, may be integrated to give a fractional coverage θ at equilibrium pressure P having the form $\psi(P, U_o)$. It is then shown that the experimentally obtained adsorption isotherm, up to monolayer coverage, has the general form

$$\theta = \int \Phi\,(U_o)\;\Psi\,(P, U_o)\;dU_o.$$

Perhaps the most important contribution of the book is concerned with a discussion of this integral equation. The equation has four temperature-independent molecular parameters having clear physical significance. The function Φ involves the mean characteristic potential energy of adsorption and its (Gaussian) variance, and the function ψ involves the two van der Waals constants α and β which are two-dimensional analogues of the familiar a and b in the van der Waals equation for nonideal gases. For this particular model numerical integrations are presented in tabular form at the end of the book; the calculated isotherms are matched with experimental results to yield the desired molecular parameters. This type of data reduction enables interpretation of adsorption data along rational molecular lines. According to this simple but reasonable model the variance of the adsorption energy is independent of the adsorbate but depends only on the heterogeneity of the adsorbent, and the van der Waals constants depend only on the nature of the adsorbate, being independent of the adsorbent. Only the mean characteristic potential energy of adsorption is a function of the adsorbent-adsorbate pair. Molecular parameters are presented for various gases and solids, and it is reasonable to expect that at least some of these may be correlated in terms of more readily available macroscopic properties.

In addition to a detailed analysis of the heterogeneous solid-mobile gas model, the authors devote a chapter to a lucid discussion of the various heats of adsorption and their interrelation, and another chapter to a generous treatment of intermolecular potentials between solids and adsorbed gases. The latter, unfortunately, does not include any mention of the effect of nonadditivity which, as Sinanoglu and Pitzer have shown, is by no means negligible.

Dr. Ross, Professor of Colloid Science at Rensselaer Polytechnic Institute, and his former student and associate, Dr. Olivier, have performed a valuable service to the chemical profession in summarizing the present state of monolayer physical adsorption, a subject to which Professor Ross and his co-workers have contributed much original material. As pointed out in the foreword by Professor de Boer, the complex subject of the physical adsorption of gases on solids, which has for so long been known only empirically, is now at last beginning to stand on a sound theoretical foundation, one on which future research workers may build with confidence. This well-written monograph will serve admirably to introduce interested chemical engineers to one of the fascinating frontiers of current research in molecular thermodynamics.

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Process Systems Analysis and Control, Donald R. Coughanowr and Lowell B. Koppel, McGraw-Hill Book Company, Inc., New York (1965), 491 pages, $15.50.

Although it has become apparent in recent years that one of the major areas of application of control systems is the chemical and petroleum industries, there has been a decided lack of textbooks written for the chemical engineer and the chemist that deal with this type of analysis. The current book is therefore welcome as an attempt to familiarize the chemical engineer with available process control techniques from both an analytical and a simulation point of view.

The first half of the book is devoted to linear-systems analysis of such topics as open- and closed-loop systems, root

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