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BOOK REVIEWS

Introduction to the Principles of Heterogeneous Catalysis. By J. M. THOMAS AND W. J. THOMAS. Academic Press, London and New York, 1967. 544 pp., 166 fig. Price $21.50.

One can hardly imagine a subject more difficult to write a book on than heterogeneous catalysis. Its literature presents an almost babylonic confusion of tongues because the theoretical models applied to rationalize the experimental results are widely different. If therefore a new book is presented that sets out to describe the material according to a unifying treatment there is considerable reason to become interested.

If, moreover, it is even tried to do this for such widely divergent but equally complex topics as the fundamental study of surface reaction mechanisms on the one hand and catalytic reactor design on the other hand and this all in the scope of 544 pages the reader becomes fascinated at the boldness of the attempt. The question is then: Will he also be fascinated by the result?

My answer is that the outcome of the work by Thomas and Thomas is a highly valuable book, a book that even may become a focal point for further developments in the quest for improved theoretical insight and for the furthering of industrial investigations. From the very outset I would therefore recommend it warmly. It brings an amazing amount of information and it succeeds in doing this while remaining very readable. Interestingly enough this is achieved by using two types of approach. One is used in the description of the chemical aspects of catalysis where a lively account is given of the various types of models used. The other is applied in the chemical engineering treatments where a strictly logical treatment is followed that starts from a small number of simple models to proceed subsequently to more intricate situations.

But does the book in fact succeed in its unifying treatment? I do not believe this to be the case. There is a beautiful coherence in Chapters 2, 4, 7, and 9, concerned primarily with reaction kinetics in connection with transport phenomena. However, this is not the case for the chemistry of heterogeneous catalysis as exposed in Chapters 5, 6, and 8; they may perhaps have been conceived originally as originating from an unifying concept but this approach ultimately leads to confusion. Perhaps this is unavoidable at the present moment and I would not hold it against the book: even when it fails in its object it still remains interesting. But it becomes very clear that either no such unifying treatment is feasible or that one should start from a quite different starting point than used by the authors.

We shall now follow the book in more detail. After a short introduction (Chapter I), Chapter II discusses "Adsorption, energetics, isotherms and rates." The discussion is adequate although I prefer the original Fowler-Guggenheim theoretical treatment for localized and nonlocalized adsorption equilibria. Indeed, this theory is introduced later on but at the wrong moment, that is, to develop the absolute rate theory of Eyring and Laidler. Of course, it is also relevant there but its fundamental importance is situated in the theory of equilibria. It is reintroduced later on in Chapter III to discuss the results of LEED-measurements but at this crucial point Kastelein's addition to it, showing that repulsive interaction leads to sublattice ordening and therefore to discontinuities in the isotherm remains unmentioned. The emphasis placed on the Keier-Roginski experiment to show the heterogeneity of real surfaces seems somewhat misplaced: a better approach was suggested earlier by Eley. Finally, the results discussed in Chapter III under the title "Information from Heats of Adsorption and Entropy of Adsorption" would have fitted better in Chapter II.

Apart from this point Chapter III "Experimental Aspects of Adsorption and Allied Phenomena on Catalyst Surface" is excellent, a remarkable achievement in the limited scope allotted to it. It presents a well-chosen selection of the various important experimental methods.

Chapter IV, "The Significance of Pore Structure and Surface Area in Heterogeneous Catalysis" has already been praised as very valuable. It starts with a description of catalyst textures from measurements of surface areas, pore volumes, and pore-size distribution to finally arrive at capillary shapes from hysteresis loops where de Boer's work is the guiding factor. The model thus established is used for further calculations on the influence of material and finally also heat transport.

Chapter V, "The Role of Lattice Imperfections

in Heterogeneous Catalysis" sets out to formulate the unifying concept in the further discussion of the chemistry of catalysis. It starts with a description of dislocations (edge and screw), of point defects (Schottky, Frenkel, nonstoichiometric and impurity types) and a discussion of the band model and the space charge layer, in the latter case with only passing mention of surface states. We are then confronted with specific examples and the results are disastrous. We are first led to believe, following Sosnovsky that dislocations are of fundamental importance for catalysis, to be informed later on that after all there exists grave doubt whether dislocations were actually present in Sosnovsky's samples (Sanders).

Disgusted we leave dislocations and turn to point defects following Schwab's theory on CO oxidation over doped NiO. The well-known Schwab-Parravano discrepancy is mentioned and also the work of Selwood, with the final result that we do not know any more whether there is any connection between catalytic activity and semiconductivity. At this moment Wolkenstein's theory is called to the rescue but is quickly dropped again without sufficient attention being given to its rather interesting way of introducing a somewhat naive type of surface state. We then arrive at the Cossee-Arlman theory of the Ziegler-Natta polymerization. There is no warning that this extremely valuable addition to our theoretical knowledge actually involves a complete rejection of the basic concepts of the chapter; instead of starting from lattice imperfections and band models it starts from localized imperfections due to the presence of a surface and handles the situation as if it were a transition metal complex with due regard to the complexity of the chemical bonding model. Then follows Haber and Stone's theory for the photodesorption of O_2 from NiO that possesses similar characteristics as the Cossee-Arlman theory but applies the older crystal field chemical bond approximation. (Parenthetically, Jongepier's experimental results are in variance with those of Haber and Stone in that he ascribes the desorption to a heating of the catalyst instead of to a *d-d* excitation).

Summing up, a remarkable interesting chapter but showing conclusively that its title is misleading.

Chapter VI, "Geometric, Electronic and Related Factors in Catalysis," should have been a logical development of the former had this achieved its aims. Now it hangs somewhat in the air. The excessive attention given to the "% *d*-character" is not warranted any more: the theory is completely dead. Pauling's attempt to explain the metal bond presented an interesting semi-empirical chemical bond model. Its application in catalysis never possessed a firm theoretical basis and was more in the line of some guesswork. Even as such it did not work. We should have liked to have heard more from the important concepts introduced by Rooney; they are mentioned briefly but insufficiently. Again, a chapter with interesting information but an uncertain theoretical basis.

Chapter VII, "The Dynamics of Selective and Polyfunctional Catalysis," presents an impressively logical account of the selectivity parameters in single and polyfunctional catalysis. In the former case the work of de Boer and van den Borg is followed, after which Wheeler's theory is introduced to account for diffusion as important in selectivity problems. A similar line is followed in discussing polyfunctional catalysts where the work of Weisz, Prater, and Gunn and Thomas is given; diffusional aspects are shown to be even more important here.

Chapter VIII, "The Mechanism of Some Typical Heterogeneous Reactions," appears to serve the purpose of illustrating the theoretical concepts of Chapters V and VI by the discussion of some important reactions. The choice of the reactions is excellent although one wonders why Ziegler-Natta polymerization is discussed in Chapter V and not here. The examples given are as follows:

The oxidation of CO, a very readable account of the work of Garner, Stone, Winter, and Teichner. It is interesting to see that at that time reaction mechanisms such as on p. 372, e.g., (7)–(10), were indeed considered an "explanation." Nowadays we would not any more be content with CO(ads) and O(ads) without entering into the chemical bond problem of this adsorption.

The oxidation of olefins, following this example suffers from the omission of the important new catalyst systems such as Bi_2O_3—MoO_3, SnO_2—SbO_2, and the theoretical novelty of the introduction of the allyl intermediate.

Hydrogenation is a rather extensive historical treatment of the subject. The absence of a discussion of the work of Kemball and his collaborators and especially the theoretical work of Rooney is noticed with regret.

The Fischer-Tropsch *synthesis* and *NH_3 synthesis* are both adequately covered.

Catalytic cracking is discussed at great length but one notices that there is a figure presenting "some cracking catalysts" that appears to relate to Al_2O_3 hydrates never used as such. The modern zeolite catalysts are not mentioned, neither is there an adequate model of the synthetic SiO_2-Al_2O_3 catalyst.

This chapter ends with *catalysis on electrode reactions* and *oxidation of elemental carbon.*

The final chapter, IX, "Design of Catalytic Reactions," is an extremely valuable account of the basic principles in this field, such as kinetics, mass transfer, and heat transfer. This is followed by actual design calculations for various conditions in packed beds, and a discussion of the stability of the packed bed reactor. The results are then confronted with those of the fluid bed reactor. The chapter terminates in the problem of optimation.

In conclusion, an interesting, very informative sometimes controversial book that is well worth its price. The printing is excellent and there are only a few printing errors.

G. C. A. Schuit

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The Solid–Gas Interface, Volume 2. Edited by E. Alison Flood. Marcel Dekker, Inc., New York, 1967. xvi + 660 pp. Price $27.50.

This is the second and final volume of a book consisting of a compendium of articles dealing with various aspects of adsorption of vapor at solid surfaces. Volume 1 has previously been reviewed in this Journal (8, 397) by Gert Ehrlich.

Volume 2 contains Chapters 17–37 and the author and subject indexes for the entire book. The last chapter is a Commentary by George Halsey on the other chapters, like that of the final chapter in Volume 1.

The variety of topics in Volume 2 is somewhat greater than in Volume 1, which deals largely with the more classic aspects of physical adsorption as studied chiefly by isotherms and calorimetric measurements. Much of Volume 2 is devoted to topics less directly connected with adsorption measurements, including sections on dielectric and magnetic properties of the interface, vapor phase chromatography (both gas–solid and gas–liquid), optical and infrared spectroscopy of adsorbed molecules, X-ray measurements of surface areas, mechanical properties as affected by sorption, surface potentials, surface chemistry of semiconductors, and applications of NMR, EPR, and the Mössbauer effect to studies of the interface. Of a more classical nature are chapters on accommodation coefficients, thermodynamics, and kinetics of adsorption, properties of active carbon, porosity and pore structure, hysteresis, surface and volume flow in porous solids. As in Volume 1 each section is written by an authority (or authorities) in the particular field. The list of authors reads like a who's who of surface chemistry and related fields and is international in scope.

As noted by Ehrlich in his review of Volume 1, there are some omissions in coverage, some duplications in what is said by the various contributors, and a great deal of unevenness in the quality of the treatments by the various authors. Some authors give a very thorough and critical review of their respective topic while others give a more superficial treatment. Such variations are inevitable in a compendium of this nature for in addition to differences in people there is a great deal of variation in the state of knowledge for respective topics. Despite some shortcomings this reviewer feels that taken as a whole the book meets admirably the objective as set forth in the Preface of providing in a single place an overall review of the more important aspects of physical adsorption of vapors at solid surfaces, in order to make available to the investigator in a given area of the field a panoramic view of other aspects of surface chemistry. The need for wide coverage per se precludes coverage in depth. This book is therefore not competitive with monographs in the field or with such publications as Advances in Catalysis. Rather we feel that it supplements the other works by providing a ready reference source. As such it is recommended for the surface chemistry library with the feeling that in some portions at least it will have a useful life of a decade or more.

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