

number of CO₂ sources, including decarboxylation of organic matter. Kharaka and coworkers summarize and update their data on the content of organic matter in sedimentary pore-waters and show how these species may influence water chemistry.

The paper by Taguchi *et al.* represents a *tour de force* in the application of analytical techniques. The data reported are almost as overwhelming as the number of authors (8). The remaining papers cover fission-track applications to thermal histories (Naeser), a multipronged field-study using fluid inclusions, clay mineralogy and vitrinite reflectance (Pollastro & Barker), a field study of the Brent Sandstone (Bjorlykke & Brendsdal), a fluid-inclusion, stable isotope and vitrinite-reflectance study in the Guadalupe Mountains (Barker & Halley), a catalogue of possible reactions involving organic acids, carbonic acid and mineral species (Meshri). Wood & Hewett round out the volume with sophisticated mathematical models of fluid flow coupled to thermal mass-transfer.

Overall, this volume is good value for the money. The price of compilations like this seems to climb (what doesn't?), and thus they seem less of a bargain than before. The book does provide an outstanding starting-point for researchers coming into the field and a guide book for graduate courses on diagenesis. The quality of production is good. Most of the work here shows the study of diagenesis to be healthy and progressing rapidly. New concepts are not lacking, but there is certainly not a clear consensus on the manifold problems that the study of diagenesis presents. I recommend the book for those interested in an overview of recent research in chemical aspects of diagenesis.

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Thermodynamic Relations in Open Systems. By George Tunell. Carnegie Institution of Washington Publication 408A, 1977, 69 pages. *Condensed Collections of Thermodynamic Formulas for One Component and Binary Systems of Unit and Variable Mass.* By George Tunell. Carnegie Institution of Washington Publication 408B, 1985, 294 pages, \$15.00 (U.S.).

Classical thermodynamics forms a closed body of knowledge, theoretically complete. However, as any practitioner knows, conceptual and theoretical errors abound in many textbooks on the subject. These two small books correct one of the most persistent errors, introduced, ironically enough, in an obituary for J. Willard Gibbs. In 1905 Sir Joseph Larmor wrote,

incorrectly, that for an open system $dS = dq/T$, where dq is the quantity of heat received by the system, T the absolute temperature and dS the change in entropy of the system. This error propagated widely, as described by Tunell, and resulted in the wide dissemination of incorrect thermodynamic formulae. Although the correct formula, $dS = dq/T + \sum m_i \cdot s_i$, where m_i is the mass of component i and s_i the entropy per unit mass of species i , was published more than 50 years ago, some prestigious texts continue to carry the erroneous formulation. Tunell gives both corrected formulae, and the reasoning and mathematical apparatus necessary to derive them. A feature of the derivation is the use of a minimum number of variables, which leads to some results of unusual appearance. For example, formulae involving two components are not symmetrical in the two components. However, such formulations are to be welcomed, since classical thermodynamics has never been properly reduced to axiomatic form. Tunell's results are of more than theoretical interest, since study of open systems is now much in vogue in connection with ore deposits and metasomatism. One hopes that such collections will prevent further use of incorrect formulae. Tunell points out that the error treated by him may be connected with a view of heat as something that can be transferred isothermally from one body to another, rather than the (correct) view of heat as energy transferred from one body to another owing to a temperature difference. A similar confusion, explicitly pointed out in the text, surrounds the definition of work in an open system. Tunell makes it clear that a suitable operational analysis and mathematical apparatus avoid all difficulties with these definitions. In this connection, it is interesting that thermodynamics texts quoted approvingly in this work tend to be engineering texts, whereas texts on theoretical and chemical thermodynamics tend to fare badly.

These thin volumes make no pretence of being textbooks, and make no attempt to systematically develop classical thermodynamics in a systematic manner. However, they are a model of thermodynamic reasoning, completely general, yet carefully tied to experimental methods. The mathematical methods involving Jacobians are fully explained, and a necessary theorem proved. Tunell makes no concessions for the sake of ease of style or presentation, but there is nothing here that cannot be easily grasped by anyone familiar with advanced calculus. These volumes will be of interest to anyone with a serious interest in thermodynamics, not only as a source of carefully checked formulae, but also as an inspiration to concise, rigorous presentation.

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