other α-keto acids in *Clostridium welchii* has been described.[11] Although the mechanism of coenzyme binding and function in the heart system requires further study, the evidence supports the hypothesis that both PAMPO and PALPO play significant roles in enzymatic transamination.

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[11] A. Meister, H. A. Sober and S. V. Tice, *J. Biol. Chem.*, **189**, 577 (1951).

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BOOK REVIEWS

Principles of Chemical Thermodynamics. First Edition. By MARTIN A. PAUL, Ph.D., Professor of Chemistry, Harpur College, State University of New York. McGraw-Hill Book Company, 330 West 42nd Street, New York 18, N. Y. 1951. viii + 740 pp. 16 × 23.5 cm. Price, $7.50.

In the preface the author states: "This book is intended to serve a course in chemical thermodynamics which may accompany or immediately follow the introductory course in physical chemistry, at either the senior undergraduate or the first-year graduate level. The emphasis throughout is on general principles and their origins, with specific applications to a limited number of fields which are primarily the concern of the chemist." Actually a one-year course in physical chemistry would seem to be a prerequisite for the study of this text. This book, in common with other recently published texts in chemical thermodynamics, is fairly satisfactory in the presentation of those applications considered by Lewis and Randall, but is entirely unsatisfactory in the discussion of the fundamentals of thermodynamics. The author gives for the most part correct equations and presents some of the mathematical methods employed in thermodynamics, although the derivation of thermodynamic relations, particularly the problem of change in independent variables, should be discussed more fully. The main trouble with the text is a dearth of precise definitions, lack of logic, and vagueness in interpretation. There is a noticeable tendency toward the long and sometimes ambiguous discussion that is apt to confuse the student.

One general criticism is that the author does not distinguish between the process and the change in state. He does not seem to have defined the concept of the change in state of a system. He writes far too few changes in state and those that he does give are not sufficiently defined.

After a long chapter on temperature and its measurement, the author introduces the first law by a discussion of the mechanics of conservation and non-conservative systems. This is an unfortunate starting point since the term work is used in thermodynamics in a different sense from that in which it is used in mechanics. Quantity of heat is correctly defined (p. 55). However, the author employs the ambiguous terms work done on or by the system and heat received by the system, which may lead to confusion. Apparently the author does not define the concept of the boundary, the location of which is frequently of paramount importance in discussing work and heat. The first law is announced as the conservation of energy, and then the equation $\Delta U = Q - W$ appears during a discussion of the internal energy of a system. This would seem to be the wrong order of presentation. If it is the author's intention to define work and heat first, then he should state the first law in terms of these quantities and proceed to prove the existence of the energy function.

The next two chapters deal with the thermal behavior of simple systems and with thermochemistry. The author discusses open systems (pp. 75–78) apparently without the realization of all of the implications of Eq. (3–12). Equation (3–15) is incorrect since the substance i has energy which it carries across the boundary of the system. The same error does not occur in the treatment of partial molal enthalpy. The writing of a change in state would have made the error obvious. Equations (3–16) and (4–36) would hardly be called Gibbs–Duhem equations. Early in the chapter on the application of the first law, the author introduces a second law equation. This is a dangerous pitfall for the student and one into which the author falls. In the chapter on thermochemistry a different convention regarding the sign of quantity of heat is used. Under the paragraph heading "Heat of a Chemical Reaction" (p. 132) we find the typically vague statements: "The heat of a chemical reaction is defined in general as the quantity of heat evolved when a given quantity of the reaction takes place, as represented by its chemical equation. For example, the combustion of methanol is represented by the thermochemical equation

$$CH_3OH(l) + \frac{3}{2}O_2(g) = 2H_2O(l) + CO_2(g)$$

$$Q_{25°C} = 173.64 \text{ kcal.}"$$

The change of ΔH (of a chemical change in state at constant pressure and temperature) with temperature is not discussed for the case that a change in aggregation-state of a reactant or product occurs.

The author does not use a Carnot cycle to derive the second law equation but a cycle consisting of two isothermals and two isometrics, with an ideal gas as the working fluid. In the derivation he makes use of the relation proved in an earlier chapter from a second law equation that the constant volume heat capacity of an ideal gas is independent of the pressure! From the discussion under "Maximum Work and Thermodynamic Reversibility" (pp. 192–199) the student is apt to draw the incorrect conclusion that a maximum work function exists, although the author does not actually state this. The derivations of the Clausius inequalities are not satisfactory. In the discussion of the conditions of equilibrium in an isolated system the author follows the German treatment rather than the more general methods of Gibbs. Thus his Eq. (5–39), $(\Delta S)_{U,V} \leqq 0$, contains the unnecessary subscript V.

A chapter on the thermodynamic behavior of simple systems is followed by a long one on solutions (including gaseous solutions) and heterogeneous mixtures. The treatment of gas mixtures is not rigorous and the student may well draw the incorrect conclusion that the equation (p. 325) for the fugacity coefficient of a gas in a mixture can be derived from Dalton's law (p. 310) or Amagat's law (p. 311). The discussion of liquid solutions would be improved if the relation of the activity to the choice of standard state and of activity coefficient to the choice of reference state were treated in greater detail. This portion of the text contains some excellent tables on the computation of activity coefficients and the effect of the choice of the reference state on the numerical values of activity coefficients.

In the chapter on chemical equilibrium the author introduces the ideal gas assumption too early in the argument in some of the examples discussed and he does not consider the effect of pressure on the activity of a condensed phase. This leads to some peculiar misconceptions. Thus he states that his Eq. (8-1-8) for the effect of temperature on the dissociation pressure of $CaCO_3$ "bears a close relationship to the Clausius-Clapeyron equation for the vapor pressure of a pure liquid or solid." If care had been taken especially in regard to the change in state under consideration the question of when the standard heat content increase $\Delta H^\circ(T)$ and when the heat of the reaction $\Delta H(p,T)$ for the azeotropic change in state is to be used would be settled.

In the last two chapters galvanic cells and the statistical molecular theory of thermodynamics are considered. The discussion of transference cells with a liquid junction would be clarified if the change in state accompanying the passage of one faraday of electricity through the cell were written instead of discussed, and the author's error in regard to Loeb's measurement of membrane potentials (p. 564) would presumably not have occurred had the change in state been written. The inclusion of the quantum numbers zero in Eq. (10–92) is evidently an oversight.

Mathematical technique is briefly considered in an appendix.

A large number of problems, many from the recent literature, is given at the end of each chapter.

From a consideration of the above criticisms and others not mentioned we can only conclude that this is not a satisfactory text for a course on chemical thermodynamics.

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Thermodynamics of Irreversible Processes. By S. R. DE GROOT, Professor of Theoretical Physics in the University of Utrecht. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y., 1951. xvi + 242 pp. 16 × 23 cm. Price, $4.00.

This book is the first and as yet the only text dealing with a recent development of major importance, namely, the general and systematic application of thermodynamics to irreversible processes in the neighborhood of equilibrium. This development was made possible by a principle discovered by Lars Onsager, and now known as the *Onsager reciprocal relations;* or more simply as the *Onsager relation.* Although Onsager's discovery appeared in 1931 in the *Physical Review*, its exploitation did not begin until 1941, and has moreover to date been carried out entirely in Continental Europe; in this country it has not yet received the attention it deserves. Thus we are fortunate in that Professor de Groot chose to write his important book in English.

Attempts to extend thermodynamics beyond the domain of equilibrium, into that of rate and transport, go back to the early days of the subject. The first attempt was the theory of thermoelectricity initiated by Wm. Thomson in 1854. The next one of note was the theory of the galvanic cell with liquid junction introduced by Helmholtz in 1877. A third important one was the theory of the Soret effect advanced by Eastman in 1926. These three authors and their successors obtained equations in agreement with experiment, but only by dint of a procedure which is open to objections. This procedure, a bed of Procrustes designed to force the application of equilibrium methods to non-equilibrium situations, is called by de Groot *pseudo-thermostatics*, a term suggested by the designation, now quite familiar, as *thermostatics*, of that part of thermodynamics which deals exclusively with equilibrium. Pseudo-thermostatics consists in mentally splitting the irreversible phenomenon investigated into two parts, of which one is admittedly irreversible and is neglected, whereas the other is treated as if reversible. This procedure is not only very artificial, but leads to inconsistency in that the irreversible part of one phenomenon is in some cases the pseudo-reversible part of another. Thus in Helmholtz's liquid junction theory diffusion is neglected as irreversible, whereas in Eastman's theory of the Soret effect diffusion is just the pseudo-reversible part. We may add that in 1927 De Donder introduced a theory of chemical affinity, which, although apparently not subject to these difficulties, yet showed no way to overcome them. The Onsager relation however not only resolves the difficulties of pseudo-thermostatics, but also unifies the whole field by furnishing a standard treatment for all irreversible phenomena in the neighborhood of equilibrium.

Onsager was led to his discovery by a statistical-mechanical analysis of certain aspects of irreversibility which were previously known empirically, as for instance the symmetry of the matrix of the nine heat conduction coefficients for anisotropic crystals. The Onsager relation itself however involves only macroscopic parameters, and may therefore be regarded as a *thermodynamic* principle justified by the agreement between its deductive consequences and experiment. At any finite "distance" from equilibrium the Onsager relation is an approximation, but it approaches exactness as equilibrium is approached; thus as a limiting law it is exact in the thermodynamic sense. Since it is also extremely general, and has resulted in a vast extension of the scope of thermodynamics, one may feel impelled to ask whether the Onsager relation ought not to be regarded as "the fourth law of thermodynamics."

De Groot's book has eleven chapters. In Chapter I some general features of the thermodynamics of irreversibility are discussed, the Onsager relation and the associated "phenomenological equations" connecting the thermodynamic flows and forces are stated, and these flows and forces themselves are defined. Chapter II presents a statistical-mechanical deduction of the Onsager relation. Before summarizing the further chapters it will be helpful to note that by a *discontinuous system* de Groot means a system consisting of two homogeneous parts separated by a capillary or membrane through which in general both heat and matter can flow (a steady state being a situation in which the material flow is zero), and that by a *continuous system* he means a system which is likewise subject in general to both heat and material flows, but in which the intensive state varies continuously from point to point. Chapter III treats the discontinuous system of one component. Chapter IV deals with heat conduction (in the absence of material flow), electrical conduction and relaxation phenomena. Chapter V treats the discontinuous system of any number of components in the absence of chemical reactions. Chapter VI treats the discontinuous system of any number of components among which a single chemical reaction occurs. Chapter VII deals with the continuous system of any number of components among which a single chemical reaction occurs. Chapter VIII deals with thermoelectric, thermomagnetic and galvanomagnetic effects. Chapter IX deals with chemical reactions—including ionic ones—in closed and in open systems, with electrokinetic phenomena, and with the interaction between a chemical reaction and a relaxation phenomenon; most chemists will probably be astonished, as was this reviewer, to learn that some of the fundamental laws of electrokinetics, *e.g.*, the Saxén relationships, are now deducible *thermodynamically*. Chapter X gives an account of Prigogine's beautiful theory of stationary states of various orders, a theory in which equilibrium appears as the stationary state of the zeroth order, and which leads to an interesting generalization of Le Chatelier's principle. Chapter XI finally is devoted to a further discussion of the fundamental matters introduced in Chapters I and II. References to the literature are complete and are handled in an adroit fashion. The index is fairly good. The text is marred throughout by misprints which it is to be hoped will be removed in a second edition.

By way of criticism there are five matters which the present reviewer feels may be worth pointing out, because this might perhaps smooth the way for some of the future readers the book so eminently deserves.

The coefficients L_{ik} involved in the Onsager relation are functions of the parameters $A_1^\circ, \ldots A_n^\circ$ characterizing the *equilibrium* state derived from a given non-equilibrium state by adiabatic isolation. It would increase the clarity of the exposition on p. 6 if this were pointed out.

The fundamental equation $\Delta' S = \Sigma J_i X_i$, introduced on p. 7, is an exact consequence of the definitions of flow and force. It is therefore misleading to deduce it, as is done in the text, from the approximate equation I.3. The latter equation moreover would look a good deal less mysterious if the author would tell us on the spot that it follows from Taylor's expansion in conjunction with the condition that at equilibrium the entropy is a maximum.

In the course of the deduction in paragraph 9, the operator Δ seems to change its meaning. At the beginning it definitely denotes departure of a quantity from its equilibrium value, and at the end it seems to denote the difference between the two values of a quantity in the two regions respectively of the discontinuous system under discussion.

In § 17 (Chapter IV) and again in Chapter VII there appear vectors, which are suddenly, without explanation or apology, alleged to be thermodynamic flows, but which do not obey the condition laid down on p. 7 as basic, that any such flow must be the time derivative of a thermodynamic state variable. An apology—it is no more than that—is then made only in Chapter XI (pp. 218–221), near the end of the book. However trivial the point in question may be to experts in irreversible thermodynamics who are conversant with the papers of Casimir, such an order of exposition is bound to be extremely disturbing to any careful reader who is depending upon de Groot's book for his introduction to the subject.

Finally, the usefulness of the treatment of diffusion potentials in § 55 (Chapter VII) would be increased if the deduction were carried to the point of producing at least some of the familiar formulas for the potential drop across a liquid junction.

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Crystal Growth. By H. E. Buckley, D.Sc., Head of the Crystallography Department, The Victoria University of Manchester. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1951. xv + 571 pp. 15 × 22 cm. Price, $9.00.

The title of this book is to be interpreted in the broadest sense as the twelve chapter headings suggest: Solution and solubility, solubility and supersolubility; The artificial preparation of crystals; The Curie theory of crystal growth; The so-called velocities of growth; The diffusion theories; Recent theories of crystal growth; Ideal and real crystals; Miscellaneous types of crystallization; Dissolution phenomena; Crystal habit modification by impurities; Relationship of substances during crystallization; Peculiarities of crystal growth. An appendix lists over fifty well-attested examples of habit modification in the presence of impurities. The three last chapters are in the field of Dr. Buckley's special interest to which he has made many contributions. The scope of the discussion is further increased by a consideration of the growth of crystals from melts and from vapors as well as from water solutions.

The subjects are developed historically and cross-references are made from one chapter to another so that one can perceive the evolution of the great body of information that is covered in the bibliography of more than five hundred titles. The book is not, however, simply a piecemeal review of publications, for an effort is made to summarize contrary views on various phenomena and to evaluate them where that is possible, indicating the trend of current thought. Unfortunately, the apparent complexity of the experimental evidence makes it impossible for the author to conclude much more than that the data form different pieces of the same puzzle. An investigator who became interested in some aspect of the field would not, of course, be able to refer to this book instead of the original literature but he would have a most useful guide and an invaluable array of reference material. Not unexpectedly, the language and the viewpoint are those of the crystallographer rather than the physical chemist; this does not make the reading particularly difficult for the chemist but in view of the amount of detail in some sections of the book, an introduction to crystallographic notation would not be out of place. The orientation of the discussions appears to be toward the practical problem of growing single, perfect crystals and one has the impression that the theories are judged by their success in describing such growth rather than their usefulness in describing how crystals actually grow. This is not offered as an unfavorable comment but chemists would appreciate, in addition, a discussion of nucleation and the factors which affect the size and character of crystals obtained in chemical operations.

Certain of the mechanical features of the book might be improved; for example, an alphabetical listing of references and an index to the plates would assist the reader. The writing itself is not always lucid and some mistakes have crept in, but these are usually minor and apparent and do not detract inordinately from the general success and usefulness of the work. The plates are excellent and the drawings of crystals are very well done.

It seems to this reader that a noteworthy service has been performed by Dr. Buckley in a research field which has attracted the interest of a large number of scientists for seventy-five years or more (about fifty of the papers are before 1900) and which is growing in importance today (two-thirds of the references are later than 1930) with many diverse applications. The bringing together of so much information on the subject is a remarkable feat and the book should stimulate a re-examination of earlier ideas on crystal growth, renewed experimentation with modern tools and a cross-fertilization from various fields of science. Certainly the work is not near completion and the reader will agree with the author when he writes rather sadly near the end of the book, "Evidently the character of the simplest type of crystal growth is far from clearly understood."

Note must finally be taken of a unique feature of the book, one which will warm the hearts of modest men: in spite of his thirty or more publications in the field, Dr. Buckley has listed his own papers with other references at the end of the chapters but has not included his name in the author index.

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BOOKS RECEIVED

March 10, 1952—April 10, 1952

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