Int. J. Heat Mass Transfer. Vol. 5, pp. 793–794. Pergamon Press 1962. Printed in Great Britain.

BOOK REVIEW

Diffusion and Heat Flow in Liquids: H. J. V. TYRRELL (University of Sheffield), Butterworths, London, 1961, 329 pp. 65*s*.

EVER since the appearance, in 1951, of the book *Thermodynamics of Irreversible Processes* by S. R. De Groot, there has been a growing interest in coupled irreversible phenomena. There has been an abundancy, nay, a surplus, of pamphlets and papers purporting to "derive" and elucidate the Onsager rule and a concomitant shortage of comparisons between analysis and experiment. This book, published a decade after the appearance of the De Groot volume will be most welcomed by those who raise the question, "of what value has this theoretical structure turned out to be?" Professor Tyrrell has collected a very large amount of experimental information and has discussed the insights to be gained from the new irreversible thermodynamics in the interpretation of the experiments. For this collection of data, discussion of competing theories and critical description of experimental techniques we should all be thankful.

The first two chapters consider the manner in which descriptions of heat conduction and diffusion have evolved, first as separate phenomena and then as coupled flows. The basic equations for balances of energy, matter, entropy and mechanical forces are derived with many helpful explanations.

In Chapter 3 the author considers the phenomenological approach to mass and thermal diffusion, contrasting the nomenclature and symbols of different authors.

Chapter 4 considers the derivation of basic equations describing coupled fluxes of matter and energy in matter and energy in continuous systems.

Chapter 5 reviews experimental methods for studying isothermal diffusion processes. This chapter is impressive (129 references are given).

Chapter 6 reviews the hydrodynamic and kinetic theories available for predicting diffusion coefficients.

Chapter 7 reviews the data available from experiments and makes extensive comparisons between observed and computed diffusive coefficients.

Chapter 8 considers experimental methods for studying thermal diffusion.

Chapters 9 and 10 compare experiment and theory in thermal diffusion.

Chapter 11 considers experimental methods and theoretical predictions for thermal conductivity in liquids.

This reviewer believes that the diffusion of energy and matter cannot be understood until an unambiguous meaning has been given to the "heat" as it is used in this book and other contributions to irreversible thermodynamics. In 1923 G. N. Lewis and Merle Randall wrote, "There are two terms, 'heat' and 'work', that have played an important part in the development of thermodynamics, but their use has often brought an element of vagueness into a science which is capable of the greatest precision." Wherever these words are employed in coupled flows, as in the present case, a certain vagueness ensues which mars the presentation.

The first place where the difficulty arises is in Chapter 2, where the correct equation

$$\mathrm{d}s = \frac{\mathrm{d}q}{T} + \sum_{k} \frac{(F_k - \langle F_k \rangle)}{T}\,\mathrm{d}X_k \tag{1}$$

is not used but rather

$$\mathrm{d}s = \frac{\mathrm{d}q}{T} + \frac{\mathrm{d}q'}{T} \tag{2}$$

is presented with the statement that $\mathrm{d}q'$ was called by Clausius the "uncompensated heat". Clausius did not use this terminology—he called it the "uncompensated transformation". The equation (1) above is correct if we mean by the symbols:

$\mathrm{d}s$,	change in entropy of a closed system;
$\mathrm{d}q$,	heat transfer as indicated by a calorimeter;
F_k,	force applied to system as measured by reference to contiguous devices;
$\langle F_k \rangle$,	force which system would exert in equilibrium process (as inferred from equation of state);
T,	temperature;
X_k,	generalized displacement.

The symbol $\mathrm{d}q$ is unambiguous in this context; it represents what is measured in a calorimeter.

When the extension to open systems is made the "flow of heat" is introduced as one of the "fluxes". The author uses the symbol J_q and identifies this flux with Fourier's law (and therefore with calorimetry) on page 12. For a closed system the author writes

$$\mathrm{d}U = \mathrm{d}q - P\mathrm{d}V \tag{3}$$

which is obtained from

$$\mathrm{d}U = \mathrm{d}q - \mathrm{d}W. \tag{4}$$

However, whenever $P\mathrm{d}V = \mathrm{d}W$ it must follow that $\mathrm{d}q = T\mathrm{d}s$. (i.e. that $P = \langle P \rangle$). It is not proper to define $\mathrm{d}q$ by writing

$$\mathrm{d}q = \mathrm{d}U + P\mathrm{d}V \tag{5}$$

unless one restricts attention to circumstances for which $\mathrm{d}W = P\mathrm{d}V$.

As this reviewer has shown elsewhere,* at a boundary

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* *Thermostatics and Thermodynamics* (D. Van Nostrand, 1961) page 606.

across which matter flows by a diffusive process, $PdV \neq dW$. In view of equation (4) above, whenever dW is ambiguous, so will dq be ambiguous. One cannot construct a "leaky" calorimeter and determine dq. An impervious calorimeter will not permit mass flux to continue whilst the "heat" flux is measured. On page 15 the author considers this ambiguity but dismisses it (and the objections previously raised by Denbigh). The authors definition of what he calls "total heat flow" is

$$dq = \left[\left(\frac{\partial H}{\partial T}\right)_{T,\,m} - V\right] dP + \left(\frac{\partial H}{\partial T}\right)_{P,\,m} dT + \sum_j (h_j - h)\, dm_j. \qquad (6)$$

In a reversible process, in the absence of mass transfer, the first of two terms represent the heat flux to the resultant closed system. Equation (6) comes from subtracting a term $h\,dm$ from equation (5), i.e. from writing

$$dq = dU + PdV - h\,dm. \qquad (7)$$

It is clear from equation (7) that even in reversible processes, dq has a different meaning from dq in equation (5). The dq in equation (6) for example is not equal to Tds, for comparing equation (7) with (8)

$$T\,ds = dU + PdV - \sum_i \mu_i\, dm_i \qquad (8)$$

we see that

$$dq = Tds + \sum_i (\mu_i - h)\, dm_i. \qquad (9)$$

Even in a reversible process quantity $dq \neq T\,ds$ for an open system, if dq is defined by equation (6).

The "new" dq is not directly measurable. It is, in the reviewer's opinion, an unnecessary concept. It does not simplify matters to introduce a quantity Q^* called by De Groot "heat of transfer" but, as the author says, page 16, "They are not, however, the heats absorbed from the surroundings when unit quantity of the diffusing molecule is removed and replaced by other species, but the total heat energy (using the term heat in the more comprehensive manner proposed earlier) transported with the diffusing molecule." Perhaps the best course would be to reintroduce the word "caloric" (as proposed by Dr. R. S. Silver) to cover this new concept.

Despite the reservations about the use of the word "heat", this reviewer does not hesitate to commend the book to all who are interested in combined energy and mass transfer. It will doubtless be a primary reference for many years to come.

MYRON TRIBUS

Symbols not defined in text

dW,	differential of work;
H,	enthalpy;
h,	specific enthalpy;
h_j,	partial enthalpy;
m,	mass:
$_i$,	chemical potential of i-th species;
P,	pressure;
U,	internal energy;
V,	volume.