Book Reviews

A Different Approach to Thermodynamics, W. F. Luder, Reinhold, New York (1967). 162 pages, \$2.95.

This reviewer was unable to find the "different approach" indicated in the title. The treatment is essentially the classical one made in an elementary manner so that it can be easily grasped by a beginner. This is all to the good but it does not substantiate the claim to a novel approach.

The author takes previous writers on thermodynamics to task for careless use of words but he proceeds to commit a few such errors himself. For example he states that a "thermodynamic calculation permits a chemist to predict whether a chemical reaction *will take place.*" This is a loose use of words. It only predicts what *could take place* if certain conditions existed. Hydrogen and oxygen will not react at room temperature if brought together even though thermodynamics says they should.

He makes a great point of the misuse of the word *process* and its relation to *change*. A *change* refers to the two states involved, to take a simple case, and *process* refers to the manner by which the change is brought about. Then he repeatedly uses the term *spontaneous change*. Since *spontaneous* clearly refers to a manner, the *change* here refers to a process. I fail to see the distinction he is trying to make. Incidentally, Webster says that a process is "a change undergone by a substance, as a change in P, V or T."

It is stated that the expressions Δw and Δq are "semantic absurdities," because w and q, not being properties, cannot have changes. The reviewer examined twenty well-known books on thermodynamics and in only one did he find any use of Δw and Δq. One gets the impression in several places in the book that the author has belabored the question of semantics and has only compounded confusion.

The author is not above making rather loose statements himself. One would be inclined to overlook these had not the author been so outspoken in pointing out the carelessness of others. I will cite just a few examples. He stresses the fact that the energy of a system is its capacity to do work. Consider a large body of water at ambient temperature. It possesses a large store of energy but has no capacity for work. In fact this is the very essence of the second law. He gives an example based on the product PV which is called "pressure-volume energy." Consider an isothermal expansion of an ideal gas from state 1 to state 2. Work is done but $P_2V_2 = P_1V_1$, so the work didn't come from a change in any energy. It obviously comes from heat flowing in from the surroundings.

On page 10 one finds the equation

$$E \text{ (energy)} = E_T + A$$

E_T is "thermal energy" (a rather loose terminology) and A is "nonthermal" energy. Later (p. 49) A is identified as the Helmholtz free energy or maximum isothermal work of a work-producing system. From this he concludes that TS is "isothermally unavailable internal energy of the system." Let's see where this leads us. Since

$$E = A + TS$$

one concludes from the above that E, the total energy of a system, is made up of two parts, A which is available to do work and TS which is unavailable. For an isothermal change, one can write

$$\Delta E = \Delta A + T\Delta S$$

Now suppose ΔS is negative as it is for some chemical reactions, then $\Delta A > \Delta E$. In other words, the work done is *greater than* the total energy change. How can this be if some of the energy is "unavailable"? The answer is simple: $T\Delta S$ is simply the reversible heat flow from the surroundings. It is not a part of the energy of the system.

On p. 17 we find that for an ideal gas, $C_v = 3/2\ R$ and $C_p = 5/2\ R$. This is a very loose statement, because in the first place it makes no distinction between monatomic, diatomic, and molecules of higher complexity. Furthermore, it implies that C_v and C_p are constants. Both are functions of the temperature even for ideal gases unless the author has some unique definition of an ideal gas. The common definition of an ideal gas is concerned with the intermolecular forces and has nothing to do with the way energy is taken up within a molecule, which is what C_v and C_p are concerned with.

One could give other examples but space does not permit. The main purpose in pointing these out is to show that the author is not above making the same kind of loose statements that he deplores in previous writers on the subject. If the "different approach" is to correct such "semantic absurdities" it hasn't succeeded very well.

I do not mean by these criticisms to imply that the whole book is poorly written. Far from it. It has many good points and, on the whole, it presents the beginning student with a simple and lucid (with some exceptions) treatment that he will appreciate.

One further point must be made. Chapter 4, "Solutions of Electrolytes," deals with phenomena almost entirely outside the realm of thermodynamics. It treats such things as transference numbers, colligative properties, conductance, and the Arrhenius theory and its refinements by Debye, Hückel, Onsager, and others. The excuse for presenting this material was that it is background information for the last chapter on electrochemical cells. However, the fact is that practically none of the material of Chapter 4 is used in Chapter 5 and actually is quite unnecessary for understanding Chapter 5.

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