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INTENSIVE AND EXTENSIVE PROPERTIES

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INTENSIVE AND EXTENSIVE PROPERTIES

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May 1969

Abstract

A pair of simple and primitive concepts, extensive and intensive, has often been improperly introduced and interpreted. The abuse of these concepts leads to the core of a serious deficiency in fundamental thermodynamics.

In all physical sciences and in particular in all technical problems we are interested either in the behavior of an object or in the characteristic qualities of a material. When we design a caustic-chlorine plant we want to know how many kilograms of mercury must be invested; but for the valuation of the product we want to know the impurities it contains, as for instance how many grams sodium chloride per kilogram sodium hydroxide.

1. Definition

For these reasons, the classification of properties as extensive or intensive has been accepted in thermodynamics and actually in the whole field of physical sciences. The names have been introduced by Tolman (1) in 1917. Lewis and Randall (2) expressed his definition in an inimitably simple and elegant way:

"Most of the properties which we measure quantitatively may be divided into two classes. If we consider two identical systems, let us say two kilogram weights of brass or two exactly similar balloons of hydrogen, the volume, or the internal energy, or the mass of the two is double that of each one. Such properties are called extensive.

On the other hand, the temperature of the two identical objects is the same as that of either one, and this is also true of the pressure and the density. Properties of this type are called intensive."

Up to this point the whole matter is so plain that one hesitates to talk about it. It is one of the strange accidents in the history of science, that this matter is at the core of an incredible confusion in the thermodynamics of our days.

2. Significance and Various Definitions

One of the more primitive mistakes rests on the belief that the classification extensive-intensive is basic for the development of thermodynamics. It is not. The square root of the volume clearly is neither extensive nor intensive; yet it is a well-defined property and all thermodynamic knowledge could be expressed if we replace the volume by the new variable. It would be awkward, cumbersome and inefficient. But science could live with it. It is obviously wrong to say that only extensive and intensive variables exist. It is true that for good reasons of convenience we introduce only extensive and intensive quantities.

A frequent error shows up in the statement that extensive and intensive properties are homogeneous functions of first and zero order, respectively, of the amounts (or masses) of the components. It is obvious that this statement leaves out such properties as surface area, length of boundary lines, electric charge or magnetization. All these variables are extensive but they are independent of the amounts of the components.

The omission has deep roots in the history of thermodynamics. Even today these "unusual" variables are often introduced as an afterthought, though Gibbs, Helmholtz, and others had discussed them extensively. The general scope of thermodynamics has very often not been taken seriously. Often the main body of thermodynamics has been developed with work represented exclusively by the volume-pressure term. The other kinds of work, and in particular the non-mechanical terms, have then been patched on. Zemanski (3) realized the danger of this bad habit but his good example has not converted many of the later authors.

The patching-on method impairs the understanding of thermodynamics as the general basis of physical sciences. It is easy, then, to forget "unusual" properties in the definition of "extensive" ones. Earlier or later the result is confusion.

"Extensive" is a purely formal term. Interaction or non-interaction between parts of an object is alien to the idea and cannot be discussed in connection with it. High-browed words such as "subsystems" have only decorative value.

3. Preemption and its Consequences

The distinction of extensive and intensive properties was of course clear to Gibbs when he discussed the phase rule. But he did not coin any specific terms. Planck (4) did; he chose the words "external" and "internal" variables. Apparently Tolman did not know Planck's definition; probably he would have simply adopted Planck's terms if he had known them.

Obviously he also did not know that the terms "extensive" and "intensive" had been preempted by Helm (5) long before. This is not really surprising since Helm was generally forgotten by 1917. But the consequences of this accident have been disastrous.

Helm appears to be the first to feel that work and the two factors of every work term require a systematic discussion. He did not succeed in presenting a general characterization of these variables but gave a list of what we call today generalized coordinates and generalized forces. On the basis of this list he selected the name "extensities" for generalized coordinates and "intensities" for generalized forces. This was a perfectly legitimate procedure since at that time nobody had used these terms otherwise.

For some time, acquaintance with Helm's ideas must have been widely spread, perhaps through the influence of his friend Wilhelm Ostwald. In any case, Ehrenfest (6) knew the terms and felt strongly that they needed a systematic and consistent discussion. Somehow they survived in the subconscious of thermodynamics.

Under the influence of G. N. Lewis, general interest was directed to consistent and efficient methods of application rather than to fundamental questions. Helm's problem and ideas were forgotten. It would be difficult to put the finger on the spot where Helm's "extensities" and "intensities" have been confused the first time with Tolman's extensive and intensive quantities. In any case, in the last twenty years this confusion has become more and more frequent.

Contributed to the confusion has the fact that most coordinates happen to be extensive. But not all are. The negligence of an identification can be shown in various examples. In a galvanic cell the charge is unquestionably a coordinate, the voltage a force. If we switch two cells parallel the charge doubles, so it is indeed extensive. But if we arrange the two cells in series, the charge becomes intensive and the voltage extensive. Stress and strain of a rod show a similar situation. It depends therefore on the specific problem whether a property is extensive or intensive. The distinction is certainly not fundamental.

But the characterization of a property as a coordinate or force is indeed fundamental. Without these concepts we cannot define work and thermodynamics simply would not exist. Whether a property can be a coordinate in one problem and not in some other one, is an unsolved question, though I do not believe in such a possibility. It is certain that a

generalized force never can lose its quality as such; this follows from its definition (7).

Until recently, the literature did not contain a single statement explicitly explaining what we meant by coordinates and forces. The misleading characterization of coordinates as extensive, and of forces as intensive was therefore an alluring means to patch over this deficiency.

Thus the abuse of a simple pair of concepts leads to the root of the confusion of thermodynamics in our days. In this situation we cannot expect a student to understand thermodynamics. It is time for a change.

The present work has been done under the auspices of the Atomic Energy Commission.

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