terminology reexamined

Physical versus Chemical Change

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Most elementary chemistry texts, generally in the first few pages, present a short discussion of "physical" and "chemical" change. Often this includes a definition that reads something like: Physical changes are those that involve a change in state or form of a substance but do not produce a new substance; chemical changes are those that result in a new chemical entity. Examples of physical processes or changes are given as: boiling, melting, and other phase changes; breaking one piece of material into two; thermal expansion; solution; deformation; etc. Most texts also say something about physical properties, an incomplete list of which would include: size, shape, state, melting point, temperature, color, density, taste, smell, ductility, viscosity, hardness, thermal conductivity, electrical conductivity, etc.

The present note argues that the distinctions drawn between "physical" and "chemical" are neither warranted nor wise. This position plus the prevalent attitude that trying to define a distinction is more a pastime for idle moments than a matter of deep significance leads to the conclusion that such distinctions should find no place in first-year textbooks.

The phase changes of water provide a favorite illustration of physical change. Thus: "Water boils; in this change no new substance is formed, but water changes from the liquid state to the gaseous state." "Steam is still water and may be condensed to the common liquid." "In freezing water to ice, only the physical aspects of the matter are changed. It is still water." Let us examine this and some of the other illustrations more closely. Through first hand experience, everybody knows that, in fact, ice is *not* water; to maintain otherwise smacks of double talk. In effect, in a discipline where experiment is paramount, the novice is being asked to distrust and discard his own experimental results and to place his faith in authority. Some texts develop the idea of a phase change as "physical" change by stressing the identity of the "chemical composition" in the different phases. But this is either the beginning of an unproductive circular argument or it forces the introduction of terms that at this stage have little meaning. Even from a more sophisticated point of view, it is not clear why phase changes are non-chemical. A detailed description of the processes—i.e., the mechanism of phase changes—is surely best given

Intensive and Extensive Properties

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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.

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 a serious confusion in the thermodynamics of our days.

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.

Physical Versus Chemical Change
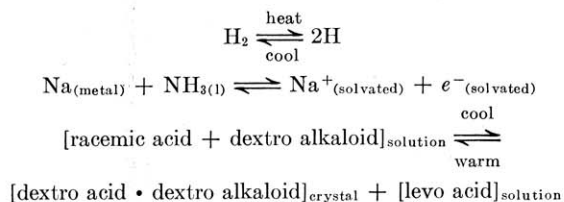
in terms of changes in intermolecular "chemical" bonding. Polymorphism, for example, can be treated logically by specifying the changes in intermolecular or interionic bonding. Some may hold that the intermolecular (as against the intramolecular) nature of these changes provides the basis for classification as "physical." In the first place, it would seem that this kind of distinction is pointless. In the second place, even accepting this differentiation, some phase changes would still emerge as "chemical" (e.g., graphite to diamond; gaseous P_4 to black polymeric P_n), since they involve what is unreservedly "chemical," namely, the covalent bond.

Solution, or its converse, crystallization from solution, is often presented as an example of physical change. Here too, only by asking for blind faith can the text expect a novice to accept the statement that a piece of sugar is the "same" before and after it dissolves in water. The evidence of the student's repeated, first-hand observations (i.e., experiment) strongly suggests that this is not true. Actually, the student's reasonable conclusion has much to commend it, since a detailed picture for dissolution or for crystallization will inevitably involve changes in "chemical" bonding between submicroscopic particles. Where ions are involved, additional processes of ionization, ion aggregation, and ion dissociation—all "chemical" processes in good standing —come into consideration.

In some texts, recovery of the unchanged solute when solvent is removed is offered as evidence that "the solution process does not produce a different substance" and hence is a "physical process." More generally, "Physical changes are those changes which do not permanently alter the material and which allow the material to be recovered unchanged by restoring the original conditions." So far as recovery from solution is concerned, what is observed is the macroscopic end result of a series of submicroscopic steps, none of which can be defended as "physical." Thus, why the appearance of unchanged material on "restoring the original conditions" is diagnostic of a "physical" process is not clear. Reversibility turns out to be a precarious and unsatisfactory criterion for the absence of chemical change, for were this criterion to be applied, the following changes would have to be classed as "physical"

$$H_2 \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} 2H$$

$$Na_{(metal)} + NH_{3(l)} \rightleftharpoons Na^+_{(solvated)} + e^-_{(solvated)}$$

$$[\text{racemic acid} + \text{dextro alkaloid}]_{solution} \underset{\text{warm}}{\overset{\text{cool}}{\rightleftharpoons}}$$

$$[\text{dextro acid} \cdot \text{dextro alkaloid}]_{crystal} + [\text{levo acid}]_{solution}$$

Breaking a solid into two pieces is a traditionally reliable example of a "purely physical" change. Yet, as soon as the events at the rupture point are examined closely, one realizes that either covalent bonds are broken or that intermolecular forces (i.e., chemical bonds) are overcome. Thus, even disregarding the high chemical reactivity of a new "clean" surface, fragmentation is by no means devoid of "chemistry." Speculation on the process taking place at the contact point when one piece of solid touches another would probably lead into some interesting areas of chemistry. It is true that the amount of material undergoing "chemical change" on fracture or contact is so small as to make little difference macroscopically or thermodynamically. But to base a distinction on the percentage of the material affected is not satisfying. When fragmentation is repeated and specific surface goes up, the extent of change is no longer negligible and a recognized branch of chemistry emerges. In this connection, the distinction between physical adsorption (a "physical process") and chemical adsorption or chemisorption is not sharp; it is made more for convenience than because of any fundamental difference. Similar considerations apply to the "physical" process of liquid subdivision as in emulsification or in fog formation from bulk liquid.

The deformation of a solid by drawing or forging (and the related physical properties of ductility, elasticity, malleability, hardness and brittleness) are given as familiar "physical changes." But in the last analysis, these macroscopic changes must be described in terms of changes in "chemical" bonding. To classify the macroscopic aspect of a phenomenon as "physical" and the submicroscopic aspect of the same phenomenon as "chemical" is again not particularly appealing.

Placing taste and odor under "physical properties" is inappropriate. Working hypotheses of these imperfectly understood processes involve preliminary solution of the substances followed by interactions between the molecules and receptor sites that are just as "chemical" as the Michaelis-Menten interactions between substrate and enzyme. Fascinating and probably very lengthy chapters on the detailed chemistry of taste and smell are yet to be written.

Fluorescence, or perhaps more often, the more familiar phosphorescence, is sometimes given as an example of a "physical" process. This brings up the whole area of the interactions of radiation and matter. To classify the production and the behavior of the photochemically excited state as "physical" will be supported by some and decried by others. Most chemists, in a sensible way, would avoid the question as barren. Although not presented in the early sections of texts, the "physical" or "chemical" nature of the processes leading to, and away from, the transition state comes to mind as a similar kind of concern. Another would be labeling conformational changes as "physical" or "chemical."

Perhaps a logical, appealing and useful distinction between "physical" and "chemical" processes will be (or possibly already has been) formulated. If so, the definitions would probably involve concepts of model systems, submicroscopic particles, interatomic bonds, intermolecular bonds, etc., whose understanding and appreciation call for more than a few introductory pages in a general chemistry text. Since the distinction is not really meaningful to the beginner—in fact, as now presented it is frequently indefensible and confusing— and since the way in which such an empty distinction helps the author in his exposition of chemistry is not obvious, why not forget the traditional distinction and leave it out altogether?

Intensive and Extensive Properties

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.

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 subconscience 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 mistake has become more and more frequent.

The fact that most coordinates happen to be extensive contributed to the confusion. 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 energy; thus, 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) and the ensuing fact that the measurement of a force requires the establishment of an equilibrium.

Until recently, the literature did not contain a single statement explicitly explaining what we meant by coordinates and forces. The misguiding characterization of coordinates as extensive, and of forces as intensive, concealed this gap. Clarification of the fundamental terms is an indispensable condition for the understanding of thermodynamics.

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