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Thermodynamics and Technology

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Frank Lloyd Wright used to say about San Francisco that only a city as beautiful as this could survive what we were doing to it.

We can say something similar about thermodynamics. Indeed, its beauty as a clear, strict doctrine and its value in creating overwhelming technological advances have not been destroyed by mistakes, misunderstandings and confusion, by the numerous errors you can find if you have studied thermodynamics more than fifty years.

Some of these errors are fairly harmless, as, for instance, the idea that the reversible cycle is an indispensable tool in thermodynamic derivations; this idea, like some other misconceptions, is a relic from the ancient times of thermodynamics. Other errors are more serious, such as the statement that any not extensive property is intensive. But the most important defect has been the absence of a clean and straightforward introduction of the basic concepts. For a long time, the beautiful thermodynamic building has stood on shaky grounds.

1. Basic Concepts

Numerous students of thermodynamics always have had the indistinct feeling that something was wrong. Most have been afraid or ashamed to confess that their understanding was not quite complete. A single scientist in the whole history of thermodynamics, Ehrenfest[1], had the courage to state frankly: "I have not been able either to find a completely satisfactory definition of these concepts in the literature or to formulate it myself."

"These concepts" go nowadays under the names of "generalized coordinates" and "generalized forces." The names are fairly new (they have been taken over from analytical mechanics apparently by Zemansky[2]); the ideas are old (Helm[3]).

There is something very strange about these terms: Nobody has defined them or stated in plain English what he means by them. Textbooks present a table of the kind of Table 1. If any of the authors felt that there was a defect, he certainly did not say so. Ehrenfest was the only exception in more than a century of thermodynamic development.

This is an unsatisfactory situation for anybody who wants to know what he is talking about. Actually it is still more shocking if we consider the consequences. There is no doubt that the differential of work must be introduced as

$$f_i \, dx_i \tag{1}$$

for any generalized coordinate x_i and the appropriate ("conjugate") force f_i. The work terms are an indispensable requisite for stating the first law. Thus the energy principle is expressed in terms that have no explicitly stated meaning.

Table 1. Generalized Coordinates and Forces

Process	Coordinate x_i	Force f_i
Mechanical	path	(ordinary) force
	area	surface tension
	volume	pressure
	strain	stress
Electrical	charge	electromotive force
Magnetic	magnetization	field strength
Chemical	number of moles	chemical potential

The penetrating mind of G. N. Lewis noticed this situation. He said[4]: "... an unfriendly critic might claim, with some reason, that the law of conservation of energy is true because we make it true, by assuming the existence of forms of energy for which there is no other justification than the desire to retain energy as a conservative quantity." But neither Lewis nor anybody else followed up this comment. Actually it expresses just the lack of definition of the work factors; if the meaning of "generalized coordinates" and "forces" can be explained, future "forms of energy" are straight given by the work expression (1) and no arbitrariness remains.

We have to ask, therefore, what the coordinates and forces are. What is the reason for their distinction from all other properties or variables? The answer will be immediately clear if we spend a few minutes on a seemingly remote, abstract consideration of the purpose of natural science and of technology.

2. Science and Technology

It is trivial of course to state that the purpose of science is the description of the world and what happens in it, and that the goal of technology is to change the world according to our pleasure. Yet it will be useful to look into how it is done.

At once we realize that it requires splitting the world into parts which we can arbitrarily isolate from their environments; we call them objects. The first problem of science is the description of objects, piece by piece. The second problem is then the description of interaction between objects, in the simplest case between two objects which are otherwise isolated.

The interesting point in this discussion is its general scope. It provides a framework into which the collision of two billiard balls fits as well as the interaction of the car battery with the battery charger or the neutralization of spilled acid by sodium carbonate.

There is an important characteristic in the interaction between two objects. Let us consider a very simple example. The length x' of a spiral spring hanging down from the ceiling is a property which we can arbitrarily change by extending or compressing the spring. We can also vary the height x'' of a weight over the floor. As soon as we establish interaction between the two objects, i.e., as soon as we fasten the weight to the lower end of the spring, the quantities x' and x'' cannot both be arbitrarily varied. They still can change: The spring can expand or contract, but the height of the weight diminishes or increases correspondingly. The quantities of two objects, which before had nothing to do with each other, are now subject to a condition of interaction

$$\delta x' + \delta x'' = 0 \; . \qquad (2)$$

I have to apologize for the circumstantial discussion of a simple matter. The reason is that this example contains the essential elements of any interaction. In the interaction of a storage cell and a capacitor the quantities x' and x'' are the electric charges; connection of the poles establishes the same condition (2). The reaction between sulfuric acid and sodium hydroxide requires an interaction condition similar to (2) for the amount of hydrogen (or any other element) in the reaction mixture. If we establish interaction in a situation leading to a nuclear reaction, a condition similar to (2) applies to the sum of masses and energy content.

The interaction conditions may become more complicated than (2), particularly when more than two objects participate. But the essential point of interaction is the establishing of conditions such as (2) between otherwise independent variables.

An object can interact with respect to more than one property. An electrochemical cell, for instance, in which water is split into oxygen and hydrogen, can interact with a capacitor regarding the electric charge and at the same time share a given constant volume with another object so that the volumes of the two objects are subject to condition (2).

Thus we may build up for any object a set of properties x such that we can arbitrarily change any of them (by interaction with another object) while all other properties x are kept constant. Obviously there are many properties that cannot be included in the set of the x's . For instance, we cannot have the electric conductivity in such a set since we cannot establish interaction with another object such that only the conductivity is affected and no other property of the set.

We conclude that the properties x are indeed a class distinct from all other properties and call them generalized coordinates. Table 1 gives examples, but our discussion leads to more than the open-ended enumeration of examples. We conclude that the generalized coordinates of any object are a set of properties each of which can be changed by interaction with another object while all other coordinates are kept constant.

The gratifying feature of this discussion is its cogency. The introduction of generalized coordinates is not just one way we may choose to describe the physical world, it is the only way we have.

At the same time the generalized coordinates are precisely the properties in which we are technically interested. If we want to change the state of any object, we can do so by letting it interact with an other object (a tool, for instance) in respect to a coordinate. Thus the coordinates give us the key to technical work as well as to scientific description.

3. Prediction

The description of the interaction of two or more objects implies the prediction that the same objects under equal conditions will react in the same way. Two concepts have been developed as tools for prediction, generalized force and entropy.

The problem is simple for the interaction of two objects regarding the coordinates x' and x'' . In each of the examples discussed one of three things may happen as soon as we establish interaction (fasten the weight to the spring or close the electric circuit and so on). The three possible happenings are represented by

$$\begin{aligned} &(a) \quad \delta x' > 0 \text{ , therefore } \delta x'' < 0 \text{ ,} \\ &(b) \quad \delta x' < 0 \text{ , therefore } \delta x'' > 0 \text{ ,} \\ &(c) \quad \delta x' = 0 \text{ , therefore } \delta x'' = 0 \text{ (equilibrium).} \end{aligned} \tag{3}$$

Since the changes $\delta x'$ and $\delta x''$ are subject to condition (2), no other changes (such as positive values of both $\delta x'$ and $\delta x''$) can occur.

We decide by observation which of the three cases is occuring. Whenever it happens that observation leads to a decision between three cases similar to (3), we express the result by means of a new quantity. If x in (3) is a length or height, the new quantity is the (mechanical) force; if x is an electric charge, the new quantity is the voltage or the electromotive force; if x is a volume, the new quantity is the pressure. Thus we find for each generalized coordinate x_i a conjugate <u>generalized force</u> f_i .

We measure a generalized force in the same manner as any other quantity, namely, by comparison of two quantities of the same kind. We compare gravitational forces acting on two objects by putting them on the pans of a balance. The coordinates x' and x'' are the heights of the pans. In the case (a) the force of the left object is smaller, in the case (b) greater. In the case (c), equilibrium, the forces are equal. In order to complete the method of measuring gravitational forces, we have only to fix a conventional standard (by means of a piece of platinum-iridium kept in Paris) and set up a method of dividing and multiplying the standard.

The same procedure can be established for every one of the generalized forces in Table 1. In a potentiometer we compare a voltage with the electromotive force of a standard element, in a manometer the pressure of a gas with that exerted by a mercury column, and we measure chemical potentials by observing the transfer of solvent from one solution to another kept in the same vacuum chamber. Numerous such methods have been found and may still be found. The principle is always the same: Comparison of two objects by observing the interaction and establishing a conventional standard which allows us to characterize by a number the force exerted by any object. The characteristic distinction of generalized forces from other quantities (including coordinates) is the fact that in order to measure forces we have to establish equilibrium. This condition applies only to one other quantity, the temperature, which has some qualities in common with forces though it generally is not called a force.

It is obvious that the concept of a generalized force is a plain and natural expansion of our naive idea of force; indeed, a tug-of-war is just an example for a measurement according to relations (3). The progress achieved by our discussion is the extension of the naive concept to all possible kinds of forces, not only to the selected examples of Table 1 or any similar list but to any kind that has been observed or will be observed in the future.

Thus the generalized force f'' of the second object measures the effort which the first object has to overcome in order to achieve action

$$f' \geq f'' \tag{4}$$

for a change dx' . If we add up these efforts from an initial state I to a final state F, we obtain the total effort (cf. eqn. 2)

$$w' = \int_I^F f''dx' = -\int_I^F f''dx'' . \tag{5}$$

We call w' the <u>work</u> done on the first object by the second object (the <u>environment</u>).

A special case is a sequence of equilibria, for which we have

$$f' = f'' . \tag{6}$$

In this case, but <u>only in this case</u>, the work

$$w'_{rev} = \int_I^F f'dx' \tag{7}$$

can be expressed by properties of the first object alone. A sequence of equilibria is called a reversible change because even a small alteration of the forces can cause a reversion.

The importance of the concept of work is immediately plausible; it has been very appropriately called "the price we pay" for a change[5]. There is good reason for our circumstantial distinction of w' and w'_{rev} : We can measure the work w' even if the change is irreversible, i.e., if

$$f' < f'' \tag{8}$$

or even if f' does not exist. An important example is given by an electric heating coil, which has no electromotive force f' while the voltage f'' is impressed on it.

Lack of clarity in these matters has caused serious misunderstandings, which in turn have contributed to the impression that thermodynamics is a bunch of tricky rules. The distinction of f' and f'' is essential, for instance, in the interpretation of modern calorimeter design.

As soon as we have listed the forces exhibited by objects in various states (by tables, graphs, or algebraic functions), we are able to <u>predict</u> the result of an interaction between any two of the objects investigated: We have just to see which one exhibits the greater force under the given conditions. Thus the first part of the prediction problem is solved by the invention of the concept of generalized forces and the measurement of these forces.

The problem of prediction is less simple if more than one coordinate is involved. The function introduced for this purpose is the entropy[6].

4. Errors

As soon as we see clearly the distinct peculiarities of generalized coordinates and forces, we realize the mess caused by some widespread errors. The most common and most serious of these mistakes is the confusion of coordinates and forces with extensive and intensive quantities.

These names have been introduced by Tolman[7] and commonly accepted since Lewis and Randall[4] have adopted them. Their distinction is useful because in physical, chemical or technical problems we handle in general only properties belonging to one of two classes: Either we are interested in properties of a material and are not concerned with the amount of the material on hand, or we want to know properties of a total object. An example of the first class, intensive properties, is the sulfur dioxide concentration of the stack gas of a plant; an example of the second class, extensive properties, is the total volume of sulfuric acid produced by a plant in a day. We would hardly introduce properties outside of these two classes. But they exist. The square root or the logarithm of the volume of the daily produced acid is a perfectly good property; yet nobody will introduce it in any calculation.

Thus there are good practical reasons for our distinction of extensive and intensive quantities. But there is nothing miraculous or fundamental in them. And there is not the least connection between these two classes and the coordinates and forces. It is true that several coordinates are extensive; then the conjugate forces must be intensive since work is an extensive quantity. But already the first example in Table 1 does not comply: the gravitational force exerted by a weight is extensive and the height above the ground is intensive.

Some definitions of extensive quantities sound quite grandiose, as for instance the idea that they are homogeneous functions of first degree in the masses. This leaves variables such as the surface area or the electric charge out in the cold.

The confusion of the two classifications is mainly due to an accident: Tolman obviously did not know that the terms he introduced had been preempted for coordinates and forces by Helm[3] (see[8]). Although Helm was more or less forgotten in 1917, his terms somehow survived the new definitions of Tolman without any controversy or clarification.

5. Concluding Remarks

In the whole history of thermodynamics only one author, Ehrenfest, has expressed his desire to know what we mean when we talk of generalized coordinates and forces, the very quantities on which the first law is built. They are also the same quantities which we need in technical problems. By collecting data for generalized forces, entropy and derived quantities such as free energy, we are in a position to make predictions for the mechanical, electrical, chemical reactions that we are concerned with.

If we take the trouble to clarify our concepts and to eradicate the errors that have been accumulated, the haze disappears and we realize that thermodynamics is more than a bunch of incoherent and tricky rules. In the end we may be surprised by the discovery that thermodynamics makes sense.

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