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THE SO-CALLED ZEROTH LAW OF THERMODYNAMICS

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Abstract

The "zeroth law of thermodynamics" is neither a law nor a statement of facts. It is a guideline for checking our description of nature. As such it applies actually to any and every observed quantity. There is no reason to single out temperature as a special case. The discussion of the "zeroth law" elucidates the difference between the axiomatic and the epistemological method.

1. History

Apparently it was Maxwell[1] who first made the definition of temperature dependent on the condition: "Bodies whose temperatures are equal to that of the same body have themselves equal temperatures."

Maxwell commented:

> "This law is not a truism, but expresses the fact that if a piece of iron when plunged into a vessel of water is in thermal equilibrium with the water, and if the same piece of iron, without altering its temperature, is transferred to a vessel of oil, and is found to be also in thermal equilibrium with the oil, then if the oil and water were put into the same vessel they would themselves be in thermal equilibrium, and the same would be true of any other three substances.
>
> This law, therefore, expresses much more than Euclid's axiom that 'Things which are equal to the same thing are equal to one another,' and is the foundation of the whole science of thermometry."

Poincaré[2] introduced temperature in the following manner:

> "By definition, two objects are at equal temperatures or in temperature equilibrium if they show no change of volume when brought together (mis en présence).
>
> This definition requires that two objects A and B, which separately are in temperature equilibrium with a third object C, are also in temperature equilibrium with each other. This is confirmed by experience."

[1] J. C. Maxwell, Theory of Heat, Longmans, Green: London 1872, p. 32.

[2] H. Poincaré, Thermodynamique, Gauthiers-Villars, Paris. The quotation has been translated by the author from the 2nd ed. (1908).

The looseness of the first of these two paragraphs is of no concern for the following. The second paragraph was discussed by Lorentz[3], who mentions "very serious difficulties" in connection with it, apparently in regard to a derivation from molecular theory.

The condition for the temperature definition was taken over by Carathéodory[4] and Born[5]. Since then it has been generally accepted. Fowler and Guggenheim[6] coined the name "zeroth law of thermodynamics."

2. Generalization

It is strange that none of hundreds of authors of thermodynamic books and papers has noticed that the same condition should be postulated for the introduction of mechanical force, voltage or any generalized force. Moreover, if we disregard equilibrium and keep only equality in the definition, the same condition must be prescribed not only for generalized forces but for any and every quantity in the whole realm of physical science. This is easily demonstrated: Every quantity in science is defined by the prescription of a measuring procedure which consists in the comparison of a property p_A of object A with the property p_B of B. The result of the measurement is then either $p_A > p_B$, or $p_A < p_B$, or $p_A = p_B$. This is true for the measurement of a length or an electrostatic capacity or a light intensity or a pressure or anything else. In order to exclude possible contradictions one has to postulate a "zeroth law" before defining length or pressure just as well as for temperature.

[3]H. A. Lorentz, Bull. Soc. Franc. de Phys. 1905, 35; Collected Papers, vol. 7, p. 290 (1934).

[4]C. Carathéodory, Math. Ann. 67, 355 (1909).

[5]M. Born, Physik. z. 22, 218, 249, 282 (1921).

[6]R. M. Fowler and E. A. Guggenheim, Statistical Thermodynamics, MacMillan, New York (1939); p. 56.

One has to go even further and require transitivity; i.e., one must also require that

$$T_A > T_B \text{ and } T_B > T_C \text{ implies } T_A > T_C \ .$$

3. Axiomatics and Physical Science

If we build up thermodynamics as an autonomous, closed logical system, the "zeroth law" may be indispensable. The question is, therefore, whether such a construction of a branch of physical science is appropriate. Every theoretical representation of our experience involves necessarily some idealization. The calorimeter that we actually use is more or less different from the ideal calorimeter whose properties are used in calculating the heat of reaction from our measurements. The adequateness of the idea of a calorimeter rests on the fact that it gives the desired information (though perhaps within a large error margin), and that its accuracy can be improved if the error is too great.

According to Maxwell, Poincaré, or any axiomatic system the position of the temperature is quite different from our habitual idealized concepts.

If we postulate the "zeroth law" and find in an example that it is not satisfied, we must discard the concept of temperature. Suppose that we have ascertained the thermal equilibria between A and C, and separately between B and C, and that we find that B on contact with A is warmer than A. Do we really discard the concept of temperature? This would be the last idea to enter our mind. What we really do is to represent our observations by means of a new type of interaction, which we had not described before.

We may find, for instance, that A emits some kind of radiation for which C happens to be transparent while B absorbs it. The radiation may be emission of neutrons, or phosphorence, or some other kind.

Or, we may come across the example that C is a glass container, B a graphite crucible, and A uranium enriched in U^{235}. The graphite moderates and reflects the neutrons produced and thus accelerates the production rate, so that no thermal equilibrium exists between A and B.

A more trivial example would be represented by the selection A = zeolite (molecular sieves), B = water, C = mesitylene. The molecular sieves adsorb water but not mesitylene. The heat of adsorption flows on contact from the zeolite into the bulk of the water, so that there is no thermal equilibrium.

4. Epistemological Critique

At this point somebody undoubtedly will explain to us that it is understood in the zeroth law that the objects must be protected from all other interactions except thermal contact, for instance by appropriate membranes. It is a characteristic fact that this idea has not been expressed explicitly by any of the numerous authors who have repeated the zeroth law. The reason is simply that it cannot be properly expressed. Even if one did specify all known kinds of interaction, there is always the possibility of interactions unknown today. The general exclusion of "all other interactions," however, is vague and prescribes the exploration of unknown country when it should describe the trail (The same defect is well known in patent practice).

What we actually do when we come across a violation of the zeroth law is not to drop the concept of temperature but to look for a new kind of interaction. Thus the zeroth law cannot ever be shown to be invalid: It cannot be refuted. As Popper[7] has clearly demonstrated, the characteristic quality of a statement in physical science is that it can be refuted, perhaps by the next observation.

This result leads to the question whether an axiomatic system can adequately represent a branch of physical science. Actually it is too rigid, too ponderous. The appropriate method for the presentation of physical sciences is the epistemological method[8]: We analyze our actual procedure, find the general and inevitably necessary features, and assemble them in a natural and unbiased system.

The "zeroth law of thermodynamics" elucidates the difference between the axiomatic and the epistemological method. It is neither a law nor a statement of fact but a guideline for checking our description of nature.

[7] K. R. Popper, Die Logik der Forschung (Julius Springer, Vienna 1935). Conjectures and Refutations (Basic Books, New York, 1963).

[8] O. Redlich, Revs. Modern Phys. 40, 556 (1968).

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