# GENERALIZING THE MEANING OF "HEAT"

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Abstract—The concept of "heat" has a strict meaning in thermodynamics which is less general than the use of the concept in this journal. The author concludes that the usage in this journal is correct and that if any changes are to be made, they should be made in the structure of thermodynamics.

#### INTRODUCTION

FROM time to time the editors and reviewers of this publication must consider whether a particular paper of merit should be accepted and published or whether, though technically correct, it should be rejected because it falls outside the scope of the Journal. Since the Journal, by its title, is devoted to the fields of heat and mass transfer, the decisions depend very much upon the definitions of the words "heat" and "mass transfer". There seems to be very little doubt over what is meant by "mass transfer" and there is not much that needs to be said on that topic, but the concept of "heat" gives some heattransfer authors trouble because "heat" has a strict definition in thermodynamics. In this paper I wish to show that the definitions of "heat" as often used in this Journal, conflict with the strict thermodynamic interpretation and that if any changes are to be made, they ought to be made in the structure of thermodynamics to accommodate the broader usages which are required in this Journal.

There are, of course, many papers published in the Journal which clearly meet the traditional ideas of what constitutes heat transfer. These ideas were laid down by the pioneering works of Newton, who recognized that heat flux could be put proportional to temperature difference, by the observations of Lomonosov, and (almost simultaneously) by Rumford, who recognized the role of temperature difference in producing

density differences and thereby free convection. They are also based on the work of Cleghorn, who formalized the caloric theory. Later Carnot, Mayer, Joule and finally Clausius, demonstrated conclusively that the caloric theory was inconsistent with a mechanical theory of heat (as it was called) and by all logical tests it was clear that the caloric theory had to be abandoned.

Our ideas about "heat" have been conditioned by the caloric theorists who visualized it as a massless fluid. Essentially all technical publications in this century give official acknowledgement to the death of the caloric theory and the rise of the mechanical theory, but there is an underground movement which seems to keep the caloric view alive. Today, in reading papers in this Journal. I am struck by the fact that some of them may be understood quite well on the basis of caloric theory. A few years ago, Dr. George Tunell, a geologist at UCLA, reviewed about fifty elementary and advanced textbooks of physics and found in each the vestiges of the caloric theory in such expressions as the "heat in a body" or "heat in the kinetic energy of the particles". These lapses into outmoded concepts would not cause much difficulty if there were only the first principle of thermodynamics to consider, for energy fluxes may be partitioned into many categories without introducing inconsistencies. All that is necessary is to define a set of mutually exclusive categories and to remain consistent with these definitions.

However, the second principle of thermodynamics has historically been developed from a particular definition of heat and this definition must be followed strictly if the classical type derivations are to produce an unambiguous definition for entropy. This is why unwitting perpetuation of the caloric theory in introductory texts in physics has created such unhappiness for instructors in classical thermodynamics.

It is the author's view that the time is approaching either to enlarge the definition of the word "heat" or perhaps to replace it with another more general concept. It is not that the word and concept are wrong. Even the caloric fluid concept is right for some problems. But just as the caloric fluid concept has to be replaced by a broader and more general view, so it seems now that the concept of "heat" needs to be broadened so that consistency may be retained when problems of "heat transmission" are intermixed with other applications in thermodynamics. Probably a new name needs to be found—but whatever name is adopted, the important issue is how to define the broader concept and still retain a consistency when different fields are brought together.

A study of textbooks in thermodynamics, heat and mass transfer over the last 25 years reveals an unmistakable trend towards the incorporation of statistical and quantum mechanical considerations along with the classical views of thermodynamics. There are various reasons for this trend, the principal one being the importance of newly developed practical devices whose design can only be understood with the aid of quantum and statistical thermodynamics.

For example, how should we regard the "heating" of a ceramic as it moderates a neutron flux? Is a laser beam merely a source of "heat"? When a spectroscopist irradiates an Li F crystal with a particular frequency of radiation, how is the flux to be regarded?

It is important to emphasize that the *name* of the concept is not at issue. Indeed, the name may vary from language to language. What is at

issue is the *concept* and the relations among concepts which derive from or produce the heat concept. This is not a new problem. When it was decided to change the name of the quantity defined by H = E + PV from "total heat" to "enthalpy", the same issue was involved. A change of name was necessary to emphasize a change in underlying appreciation of the significance of the function.

# THE HEAT CONCEPT IN THERMODYNAMICS IS CONSTRAINED BY THE DEFINITION OF A SYSTEM

It is useful to examine the logical structure of part of thermodynamics because whatever is done with the concept of heat must not introduce inconsistencies in the parent subject. A study of a large number of textbooks reveals that one of the first steps in the development of thermodynamics is the definition of the concept of a "system".

It is interesting to note that engineers and physicists seem to use the concept of a system in rather different fashion. By and large engineering thermodynamicists seem to take a view that no one knows what a system is until it has been carefully defined. On the other hand, most physicists seem to think that "system" does not need definition. It will be convenient to call the conventional engineering approach (endorsed by some physicists as well) the "C" approach or classical treatment. In the "C" view, a system is defined by defining a volume in physical space. The words "heat" and "work" are given meaning only in relation to the boundaries of this system. Kestin [1], for example, (p. 177) makes it very explicit that a shift in the boundaries can change the meaning of these concepts in a particular application. According to the "C" view, there is no meaning to be attached to the words "heat" and "work" unless a surface (boundary) in three dimensional physical space has been defined. The meaning of heat is then defined by reference to what would happen to a calorimeter brought up to that surface.

In contrast, to judge from publications in

journals devoted to modern physics, quantum physicists use the word "system" in a broader sense. Their approach will be called the "Q" treatment. In the "Q" view, the system is regarded as any one of the following:

- (a) A region of space (i.e. the "C" system).
- (b) A subset of particles mixed with other particles.
- (c) A subset of possible states of a "C" system.

A few examples will serve to illustrate the "Q" usage:

- 1. A magnetic spin system—the basis for the concept of negative absolute temperature.
- 2. A system of vibrational spin states—the basis for the disequilibrium behind the shock wave in a diatomic gas at high speeds.
- 3. A system of radiation in a non-absorbing gas.
- 4. A system of phonons in a solid—the basis for investigations into the nature of heat conduction in solids.
- 5. A system of electrons in a plasma—which often displays a temperature different from the ions with which the electrons are mixed.
- 6. A system of neutrons being "thermalized" in an absorbing medium.
- 7. A system of reacting molecules mixed with inert molecules.

It has been suggested privately by Kestin that these cases would all be described as "subsystems" of the "C" system, and to this suggestion I would agree. But it should be noted that these subsystems partake of energy exchanges, have equations of state and, in particular, are candidates for analysis by methods used in heat transfer. For example, I have seen digital computer programs which may be used for either neutron absorption or photon absorption and thus use a single algorithm to treat problems of heat transfer by radiation or the thermalization of neutrons.

Systems of negative absolute temperature have been described and well summarized by Abragam [2]. For such systems it is easier to

understand their behavior by using the parameter  $\beta = 1/kT$  than to use the normal measure of absolute temperature. In terms of the parameter,  $\beta$ , Abragam shows that the general rule for thermal energy transfer (heat?) is that if systems of different  $\beta$  are allowed to interact, energy will flow from the system of low  $\beta$  to the one of high  $\beta$ . (High T to low T). It has been shown [2] that it makes no difference if a system of spin states at negative absolute temperature is allowed to interact with a system at positive absolute temperature or another system at negative absolute temperature. The rule for the direction in which the energy will flow (expressed in terms of  $\beta$ , not T) is the same and, except for the problem of defining the system as a "Q" system and not a "C" system, it would seem quite proper to call the interaction "heat". This behavior is derived in reference [3] where it was suggested that since the parameter  $\beta$ plays such a fundamental role it ought to have a name and the name "temper" was proposed.

Another interesting form of "heat transfer" is the approach to equilibrium of a diatomic gas behind a shock wave. The subsystem of vibrational states retains the original temperature for a brief interval and then, depending upon the frequency of the collision process, "relaxes" to come to equilibrium with the translational and vibrational states. This process, too, could be called "heat transfer" except that clearly it is not conduction, convection or radiation.

The case of a plasma is interesting because it represents a system with two temperatures, both of which can be measured. In an ordinary fluorescent tube, for example, a thermometer can be used to measure the temperature of the ions. A measurement of the noise in the electrical circuit (which has associated with a voltage equal to kT) indicates the electron temperature.

Bahadori and Soo, in this Journal, [4] have in fact considered thermal phenomena in a plasma and discuss the transport phenomena in terms of the two temperatures, one for the electrons and the other for the ions and atoms. These phenomena are "real" in the sense that the concepts may be related quite directly to measureable quantities. The "heat" and "temperature" not only are measurable but they may also be combined to satisfy the equation  $dS = k\beta dQ = dQ/T$ .

Of course, once the lid is raised on Pandora's box, all sorts of things escape. Once it is considered acceptable to denote as "heat" the above interactions, then the following case presents itself and cannot be argued away. Consider a mixture of oxygen and hydrogen in stoichiometric proportions diluted with nitrogen. We may regard the system (in the "Q" sense) as made of O<sub>2</sub> and H<sub>2</sub> and by considering the possible states of the system, the approach to equilibrium, etc., assign energies, temperatures, entropies to these states. It seems quite logical to regard the exchange of energy between the high temperature H<sub>2</sub>O molecules and the system composed of nitrogen molecules as "heat". Indeed, in this Journal, such reactions constitute "heat sources" in a stream.\* It seems that the concept that reacting gases "heat" the inert gases is inherent in most treatments of combustion in flowing streams and I have no doubt, whatsoever, that most students tend to think this way regardless of how hard thermodynamics teachers try to teach them otherwise. Of course, if we were to tell students it is legitimate to so regard the process, all the beautifully designed procedures for keeping them from getting confused about the definition of entropy would have to be given up.

Consider, for example, the paper by Libby [5] which appeared in Volume 9, No. 10 of this Journal. This paper was concerned with the state of affairs at the boundary between a laminar flow and a porous wall with fluid injected into the flow. Libby is obviously aware of the constraint on the heat concept—he simply does

not use the word "heat" anywhere in the article! Instead the unambiguous phrase "energy flux" is employed. On the other hand, Gollnick [6] when considering the same type of problem uses the following words (the parentheses around "heat" is the author's choice, not mine): "It is now argued that though the thermal diffusion induced energy (heat) flux may be small when the overall flux level is high...".

Gollnick then goes on to write:

$$\dot{q} = -k_w \left(\frac{\dot{q}T}{\partial y}\right)_w + (\rho v)_w \left(RT \frac{k_T}{c_1}\right)_w$$

to indicate that "the heat flux to the wall is the sum of the usual Fourier conduction contribution and that due to thermal diffusion". It should be noted that there is no operational way in which the term  $k_w$  can be measured. It represents the thermal conductivity of the gas mixture at the wall while diffusion is taking place parallel to the "heat flux". There is no calorimeter which can be inserted at a plane in space which would simultaneously measure q and not interfere with the diffusional process. The "heat" is not what is meant classically. But the concept is necessary.

### LET'S CHANGE THERMODYNAMICS

It is the writer's contention that these violations of the spirit of classical thermodynamics are correct and justified. Rather than view such treatments as though they were evidence of "sloppy thermodynamics" I propose that we view them as evidences of an inadequacy in the way thermodynamic concepts are developed. The classical approaches do not yield rich enough concepts to provide for the kinds of problems we want to solve.

It is not too difficult to divide energy fluxes into mutually exclusive categories (diffusion thermo, thermo diffusion, heat flux in binary mixing, convective transport, etc.) and still retain consistency with the first law of thermodynamics. The second principle presents the difficulty.

An examination of all "C" type developments

<sup>\*</sup> Professor M. W. Zemansky has pointed out to me that the verb "to heat" can be taken to mean "to raise the temperature" and need not necessarily be confused with the noun "heat".

of thermodynamics reveals that the concept of heat is developed as primitive to the entropy concept. This is why thermodynamics teachers have to be so fussy over the definition of "heat". The "C" approach to entropy presumes the "C" definition of "system" of necessity, and with it the "C" definition of "heat".

On the other hand, if the entropy concept were to be taken as primitive and the ideas of thermal energy diffusion taken as derived, there would be no particular reason to guard against a generalized view of the word "heat" and apply it to many processes which do not fit the "C" definition. This procedure seems to describe more or less what many heat-transfer experts now do. That is, they use the "C" definition of "heat" to decide entropy exists, then they broaden the idea of "heat" to cover many other cases. If entropy does not enter any of their problems, this inconsistency causes them no harm. But since year by year engineers and scientists tackle ever more complex systems, it seems worthwhile to eliminate inconsistencies now. (Example: How to keep track of "heat flux" in a thermocouple circuit.)

The only known approach to thermodynamics which gives entropy a life of its own, so to speak, is that based upon information theory. Ordinary statistical mechanics does not do so-indeed. most writers in statistical mechanics presume the prior existence of "C" type thermodynamics and some even go out of the way to warn the reader that this is a necessary order of things [7, 1]. But in the information theory treatment, a rational development of the entropy concept is possible and with it the laws of thermodynamics can be produced in such a way [8, 9, 3, 10, 11] that the concepts of "heat" and "reversible work" become derived and not primitive ideas. In one of his papers on the information theory treatment, Jaynes even refers to a "heat effect of the k-th type" [12]. Such an approach is consistent with what is actually done in the heat-transfer literature. The words "heat" and "thermal flux" may then be applied to any flux of energy which is associated with a temperature difference between two systems. Only a subset of these fluxes will satisfy the equation  $dS = k\beta dQ = dQ/T$ , but this will not cause confustion in thermodynamics (or for thermodynamics students) because the *primitive* ideas of equilibrium energy and entropy (if developed via information theory) would not then depend upon a very special definition for the concept of "heat". It is only when the order of the development is reversed and entropy is based upon heat that we must guard the integrity of the word "heat".

This view of things is inherent in much of what is written in the field of irreversible thermodynamics. For example, the discussion by Prigogine in his 1955 monograph [13] (p. 13) introduces a function which is to be distinguished from the "ordinary heat flow". This function must ultimately be defined from the existence of the entropy function and is not to be considered as definable without reference to entropy.

## CONCLUSION

In no way should these remarks be taken to indicate a sense of urgency on the part of the author. The editors of this Journal have already accepted papers which employ "Q" type systems and "heat fluxes" beyond the strict "C" treatment of thermodynamics. If any changes are to be made, they probably should occur in other journals.

All of the ideas touched on in this paper are, it seems to the author, already incorporated in the writings of many competent physicists. But they are totally at variance with almost every textbook of thermodynamics. Students taking courses simultaneously in quantum mechanics and thermodynamics must be on guard lest they tell the same story to both instructors. One or the other instructor will surely regard the students' views as incompatible with his own beliefs.

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Résumé—Le concept de "chaleur" a un sens strict en thermodynamique qui est moins général que son emploi dans cette revue. L'auteur conclut que l'usage qui en est fait dans cette revue est correct et qui si l'on doit faire quelques changements, ils devraient être effectués dans la structure de la thermodynamique.

Zusammenfassung—Der Begriff "Wärme" hat in der Thermodynamik eine strenge Bedeutung, die weniger allgemein ist als der in dieser Zeitschrift gebrachte Begriff. Der Autor kommt zu dem Schluss, dass die Verwendung, wie sie in dieser Zeitschrift erfolgt, korrekt ist und dass, sollten Änderungen vorgenommen werden, sie in der Struktur der Thermodynamik zu machen sind.

Аннотация—Понятие «теплота» имеет в термодинамике вполне определенный смысл, менее общий, цем значение, используемое в этом журнале. Автор делает вывод, что понятие «теплота» в том значении, в котором оно используется в данном журнале является правильным, а термодинамическое значение требует изменений.