Entropy As a Sum of Heat Capacities

ABSTRACT

An attempt is made to explain the meaning of entropy in thermodynamics. A new concept of heat capacity is defined. For it, the temperature change is measured from 0 kelvin. It is supposed that the entropy of a substance is the sum of these heat capacities in the formation of the substance from 0 kelvin to the actual temperature. This conclusion agrees with experimental data.

Keywords: entropy; heat capacity; enthalpy

1. INTRODUCTION

The physical meaning of entropy in thermodynamics is still unknown [1–6]. In this paper, an effort is made to explain what entropy is. It is shown that two types of heat capacity must exist. Another heat capacity is determined which is equal to the ratio of the heat added to a substance to the temperature interval from 0 kelvin to the resulting temperature. The total entropy of a substance is the sum (integral) of these heat capacities.

2. THEORY

The change in entropy is given by this equation:

$$\mathrm{d}S = \frac{\delta q}{T} \tag{1}$$

where δq is the heat introduced into the substance, and T is the absolute temperature. It has the following meaning. One introduces some heat at the temperature $T - \mathrm{d}T$ and the temperature of the substance increases to T (δq and $\mathrm{d}T$ are sufficiently small). One can notice that (1) can be rewritten as

$$\mathrm{d}S = \frac{\delta q}{T - T_0} = \frac{\delta q}{\Delta T} = C_0(T) \tag{2}$$

where $T_0 \to 0$ K. Equation (2) has the following meaning. The change in entropy $\mathrm{d}S$ is the heat capacity of the substance $C_0(T)$ when the heating is calculated in the interval from 0 to T kelvin. This means that 0 K is the reference point, and one takes into account the heat introduced into the substance in the interval from 0 to T that is needed to increase its temperature from $T - \mathrm{d}T$ to T. It differs from the usual heat capacity where the reference point is $T - \mathrm{d}T$.

Therefore, the absolute value of the entropy will be

$$S \approx \sum_i \frac{\delta q_i}{T_i - T_0} = \sum_i C_0(T_i) \tag{3}$$

where T_i = 1, 2, 3, ... K, and δq_i is the quantity of heat needed to increase the temperature from T_{i-1} to T_i. In the continuous case, (3) turns into the well-known formula:

$$S = \int_{T_0}^{T} \frac{C_P(T)\mathrm{d}T}{T - T_0} \tag{4}$$

where C_P is the isobaric heat capacity.

There is the first mean value theorem for definite integrals [7]. If the functions $g(x)$ and $f(x)g(x)$ are integrable functions on [a, b], $f(x)$ is a bounded and a continuous function, and $g(x)$ does not change sign on [a, b], then there exists c in [a, b] such that

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$$\int_a^b f(x)g(x)\mathrm{d}x = f(c)\int_a^b g(x)\mathrm{d}x.$$ (5)

46 Therefore, one can rewrite (4):

47
$$S = \left\langle \frac{1}{T} \right\rangle \int_{T_0}^T C_P(T)\mathrm{d}T = \frac{H}{T_{\mathrm{mean}}}$$ (6)

48 where T_{mean} is the temperature which corresponds to the mean value of the inverse temperature, and
49 H is the enthalpy.
50
51 In [8], the heat is considered for 77 solids needed to raise a substance from absolute zero
52 temperature to standard conditions ($T° = 298.15$ K and atmospheric pressure):

53
$$H° = \int_0^{T°} C_P(T)\mathrm{d}T$$ (7)

54 Here, the superscript ° denotes the standard conditions. It is remarkable that this enthalpy is very
55 nearly proportional to the standard entropy at 298.15 K for a wide variety of solids:

56
$$\frac{S°}{H°} = 0.0066 \ \mathrm{K}^{-1}.$$ (8)

57 Monatomic, diatomic, triatomic, heavy polyatomic ionic solids, and complex covalent solids have data
58 points on or near the best-fit line given by (8). The value 0.0066 K^{-1} corresponds to $T_{\mathrm{mean}} = 151.5$ K $\approx$
59 298/2 K. It is notable that the average function $<1/T>$ has such a simple form. This result agrees with
60 the above definition of entropy, (3); it is plausible to assume that

61
$$S(T) \approx \sum_i \frac{\delta q_i}{0.5T - T_0}.$$ (9)

62
63 Here one can draw an analogy with the Lagrangian and Eulerian specifications of the flow field [9]. In
64 the former, the observer follows an element of fluid as it moves, in the latter, the fluid's motion is
65 observed from a fixed reference point. The traditional heat capacity corresponds to the Lagrangian
66 method, and the heat capacity C_0 corresponds to the Eulerian one (the observer is at 0 K).
67
68 In [10,11] it was inferred that in the description of natural phenomena their development from 0 K
69 must be taken into account. It is not enough to describe the phenomenon at the current moment, it is
70 necessary to include its history from zero kelvin (*i.e.*, its development from 0 K to the current
71 temperature). This leads to new terms in the resulting equations.
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73
74 **3. CONCLUSION**
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76 One can define a different concept of heat capacity for which the temperature change ΔT is counted
77 from zero kelvin: $\Delta T = T - T_0$ where $T_0 \rightarrow 0$ K. Then, the entropy difference $\mathrm{d}S$ is nothing but this heat
78 capacity: $\delta q / \Delta T$.
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81 **REFERENCES**
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