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SOME COMMENTS ON THE SECOND AND THIRD LAWS OF THERMODYNAMICS

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I. The Second Law of Thermodynamics

In many discussions on the second law of thermodynamics whose purpose it is to acquaint the student with its physical content, the student is presented with two statements identified as the physical expression of the second law. One is termed Kelvin's principle and the other, Clausius' postulate.

Kelvin's principle states: In a cycle of processes it is impossible to transfer heat from a heat reservoir and convert it all into work without at the same time transferring a certain amount of heat from a hotter to a colder body.

Clausius' postulate states: It is impossible that, at the end of a cycle of changes, heat has been transferred from a colder to a hotter body without at the same time converting a certain amount of work into heat.

Any system or device which can be imagined that violates these two principles is termed a perpetual motion machine of the second kind, and the second law is thus a statement of the incapability of constructing such devices.

Along with the above, one often reads that if violations of the Kelvin principle are allowed, there could be constructed, for example, a ship capable of utilizing the energy stored in the oceans as the sole source of power for running the ship.

The purpose of this article is to point out that the Kelvin principle (and also the Clausius postulate) may be made to appear easily violable to the student and thus its force mitigated.

We begin by first considering the following set-up of two engines, E-1 and E-2, operating between two reservoirs, one a hot reservoir at temperature T_h, and the other a cold reservoir at temperature T_c. E-1 operates cyclically to remove heat (q_{c1}) from the cold reservoir by utilizing an amount of work (W_1), while rejecting heat (q_{h1}) into the hot reservoir. Simultaneously E-2 abstracts heat (q_{h2}) from the hot reservoir and converts some of it into work (W_2), while rejecting heat (q_{c2}) into the cold reservoir, all done reversibly and in accordance with the first law of thermodynamics (see Fig. 1-a).

Assume now that E-2 has a higher thermal efficiency than E-1, i.e., $W_2/q_{h2} > W_1/q_{h1}$. Further specify that the situation is so adjusted that $q_{h2} = q_{h1} = q$. Thus $W_2 > W_1$ (and from the first law, $q_{c1} > q_{c2}$). Also since $q_{h2} = q_{h1}$, the situation is one which is entirely equivalent to the absence of the hot reservoir altogether, as E-2 abstracts precisely the amount of heat E-1 rejects. This equivalent representation is shown in Fig. 1-b.

Finally since $W_2 > W_1$, E-2 can be used to run E-1 with the production of an amount of useful work

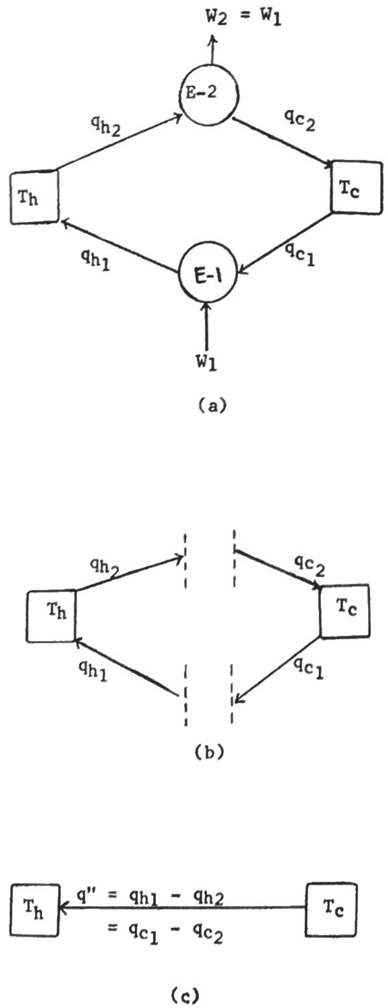

Fig. 1. A Device for Violating Kelvin's Principle.

$W' = W_2 - W_1$, per cycle with no effect other than the cooling of the cold reservoir, i.e., the reservoir in effect loses heat $q' = q_{c1} - q_{c2}$ per cycle. This is represented by the drawing of Fig. 1-c.

It is precisely this set-up which represents a ship (the

E-1 and E-2 system) operating by just abstracting heat from the ocean (the reservoir at T_c), to run itself.

It is obvious certainly to the teacher that the fallacy lies in assuming that one reversible Carnot engine with one working substance is more efficient than another such engine with a different working substance, both operating between the same two temperatures. But this is not necessarily so with the student. The assumption at first glance appears to be rather plausible. It is precisely on this point that the author feels the inadequacy of the Kelvin (and also the Clausius statement) *as far as the student is concerned.*

In point of fact the statement of the second law in terms of entropy production seems the more incisive here, i.e., in an isolated system the total entropy change is $\Delta S \geqslant 0$. As a corollary to the above statement, we may say that *any device which operates cyclically to convert heat into work must do so under the restriction that the entropy of the universe must not be made to decrease.* The device described above is easily and decisively shown to violate this statement of the second law.

The analysis is as follows: Since the operation is a cyclic one, no effect will be found in the engines themselves. Any effects must be found in the surroundings (i.e., the reservoir at T_c). We have seen that the only effect of this device has been the loss of an amount of heat $q' = q_{c1} = q_{c2}$ by the reservoir (i.e., surroundings). Since this is a loss of heat, the only effect of this device is to produce a decrease in the entropy of the universe. Such a device must, by virtue of the second law, be incapable of existence.

A similar argument can be applied to the Clausius postulate.

Here we merely adjust our device such that the work (W_1) utilized by E-1 is precisely that amount of work (W_2) produced by E-2. Since E-2 is the more efficient apparatus $q_{h2} < q_{h1}$. This situation is represented by Fig. 2-a. However, since $W_2 = W_1$, the net effect is precisely that which would have occurred in the absence of the engines themselves (recall that the engines are still operating in a cycle). This situation is depicted by Fig. 2-b. Thus since $q_{h1} > q_{h2}$ and by the first law $q_{h1} - q_{c1} = q_{h2} - q_{c2}$, we obtain the result that a net amount of heat $q'' = q_{c1} - q_{c2} = q_{h1} - q_{h2}$ is rejected by the cold reservoir and is just equal to the net amount of heat (non-zero) taken up by the hot reservoir. Thus the total net effect is that an amount of heat q'', has been transferred from a cold to a hot reservoir without the expenditure of work, as is represented by Fig. 2-c. It is obvious that we again have a decrease in the entropy of the universe contrary to the second law.

II. The Third Law of Thermodynamics

The statement of the third law is often presented in the following form: The absolute zero of temperature is unattainable by a finite number of operations no matter how idealized. The erroneous conclusion, sometimes inferred by the student, from the above statement is that it also implies the performance of an infinite amount of

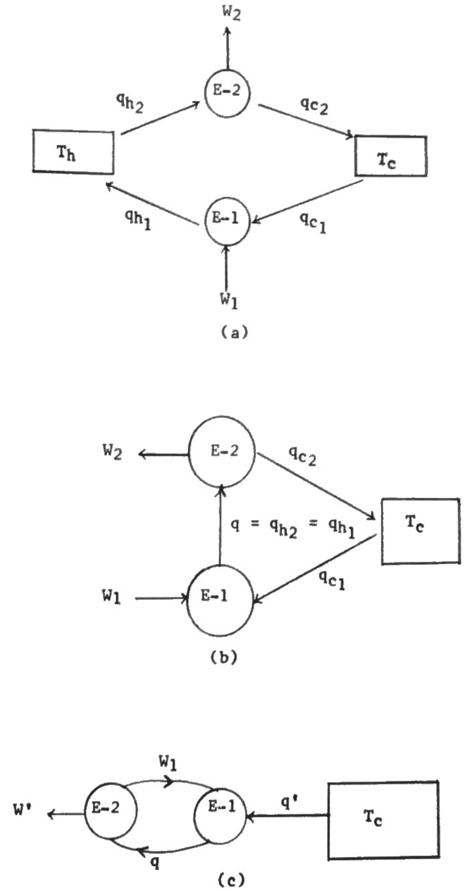

Fig. 2. A Device for Violating Clausius' Postulate.

work as necessary to the attainment of absolute zero and thus is responsible for its unattainability.

The following example demonstrates both the erroneous conclusion and its subsequent correction. Consider first an object of constant heat capacity C_v to be cooled by the operation of a refrigerator whose expansion coils are kept exactly at the temperature of the object and whose compressor is kept uniformly at a temperature T_o[1]. We calculate the amount of work necessary to cool the object from an initial temperature T_c to a final temperature T_c'.

Let the temperature of the object and coils be initially T, thus for the extraction of an infinitesimal amount of heat δq, the minimum amount of work required is given by

$$\delta_w = \delta_q \left(\frac{T - T_o}{T}\right) \tag{1}$$

Further this amount of heat is given by

(2)

$$\delta q = C_v \, dT$$

Thus we obtain

(3)

$$\delta w = \frac{C_v}{T} (T - T_o) \, dT$$

Whence the amount of work required to cool the object from T_c to T_c' is given by

(4)

$$W = \int_{T_c}^{T_c'} C_v \left(\frac{T - T_o}{T} \right) dT$$

Upon integration (assuming C_v constant) we thus obtain

(5)

$$W = C_v T_o \ln \frac{T_c}{T_c'} - C_v (T_c - T_c')$$

Hence the work required to cool the object to $T_c' =$ ' K is seen to be infinite.

n the above example, we have neglected the result tnat the heat capacity, C_v, is a function of temperature and in fact approaches zero as the temperature approaches zero. In point of fact we have contradicted the third law by assuming constant heat capacity. This can be seen as follows:

(6)

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_v$$

and by integration

(7)

$$S(T,v) - S(0,v) = \int_0^T \frac{C_v}{T} \, dT$$

The constant of integration, however, would be a function of v only but the third law stipulates that the limiting value S_0 of the entropy be independent of v, thus the existence of such an integration constant is ruled out, and we write

(8)

$$S(T,v) - S_o = \int_0^T \frac{C_v}{T} \, dT$$

Now the third law clearly implies that the entropy increases from O°K to any temperature T must be finite, i.e.,

(9)

$$\int_0^T \frac{C_v(T)}{T} \, dT = \text{Finite}$$

Thus C_v must approach zero with decreasing temperature; if this were not so the integral above would become infinite. This can easily be seen as follows: C_v may be expanded in a power series in the temperature,

$$C_v = \sum_n A_n T^n$$

(10)

$$\int_0^T \frac{C_v}{T} \, dT = \sum_n \int_0^T A_n T^{n-1} \, dT = \sum \frac{A_n T^n}{n} \Bigg|_0^T$$

It is obvious that for this integral to be finite that n must be greater than zero, and hence that $A_o = O$ in $\sum_n A_n T^n$. Thus C_v approaches zero as T approaches zero. Note that the ratio C_v/T does not necessarily remain finite, for example, the case $C_v =$ Constant x $T^{1/2}$ yields a finite entropy but an infinite value of C_v/T at $T = O$. However, all known crystalline substances have heat capacities which yield finite limits of C_v/T. Hence the correct expression for the work required in our example is

(11)

$$W = -T_o \int_{T_c}^{T_c'} \frac{C_v(T)}{T} \, dT + \int_{T_c}^{T_c'} C_v(T) \, dT$$

or the equivalent expression

(12)

$$W = -T_o \int_{T_c}^{T_c'} \left(\frac{\partial S}{\partial T} \right)_v dT + \int_{T_c}^{T_c'} \left(\frac{\partial E}{\partial T} \right)_v dT$$

Upon integration between the limits T_c and $T_c' = 0$ we obtain

(13)

$$W = T_o \left[S(T_c,v) - \lim_{T \to 0} S(T,v) \right] + E(0,v) - E(T_c,v)$$

Also, since by the third law the limiting value of S(T,v) is a constant independent of both T and v, we may assume it to be zero. Hence we have

(14)

$$W = T_o S(T_c,v) + E(O,v) - E(T_c,v)$$

which is seen to be finite. Thus we are forced to conclude that the unattainability of absolute zero is not the result of a requirement of an infinite amount of work. In fact, if this were the case then the third law becomes merely a corollary of the second law.

Literature Cited

1. Wall, Frederick T., *Chemical Thermodynamics*, W. H. Freeman and Company, San Francisco, 1958, p. 100.