The Discovery of Entropy and its Significance

"Through an ingenious argument whose steps we cannot follow here, Clausius concludes that the equivalence value of an isothermal conversion of work into heat is equal to *Q/T*, where Q is the heat and T is the temperature." (lecture, p. 20)

Question: How exactly did Clausius arrive at Q/T for the equivalence value of a transformation of work into heat Q at absolute temperature T?

Here is a summary of the steps of Clausius's exceptionally complex reasoning (mostly to be found in his 1854 paper):

1. "The value of a transformation from work into heat must be proportional to the quantity of heat produced; and besides that it can only depend on the temperature." So the equivalence value must be of the form $Qf(T)$, where $f(T)$ is some function of the absolute temperature T.

2. For the reverse transformation, from heat into work, the equivalence value will be $-Qf(T)$.

3. Similarly, for the **fall** of heat Q from temperature T_1 to temperature T_2, the equivalence value must be of the form $QF(T_1, T_2)$, where $F(T_1, T_2)$ is some other function of the two temperatures.

4. For the reverse (the **rise** of heat Q from temperature T_2 to temperature T_1, the equivalence value will be: $QF(T_2, T_1) = -QF(T_1, T_2)$.

5. For Clausius's six-point reversible Carnot cycle (see Lecture Handout, p. 4), the conversion of heat Q_1 into work at temperature T_A and the fall of heat Q from temperature T_B to temperature T_C must be equal in magnitude but opposite in sign: $-Q_1f(T_A) + QF(T_B, T_C) = 0$.

6. Suppose the original six-point Carnot cycle is modified in three ways: (1) the conversion between heat and work occurs now at some new temperature T_D rather than at T_A, (2) it now involves a quantity of heat Q_2 rather than Q_1, and (3) the whole cycle is now run in reverse (so that work is converted into heat Q_2 at temperature T_D, and heat Q rises from temperature T_C to temperature T_B). For the whole modified cycle, we now have: $Q_2f(T_D) + QF(T_C, T_B) = 0$.

7. Adding together the equations from steps 5 and 6, and applying the equation from step 4, yields: $Q_2f(T_D) + QF(T_C, T_B) - Q_1f(T_A) + QF(T_B, T_C) = Q_2f(T_D) - Q_1f(T_A) = 0$.

8. If we now run both six-point cycles (the original cycle and the modified reverse cycle) **together** as **one process**, then the **fall** of heat Q from temperature T_B to temperature T_C and the **rise** of heat Q from temperature T_C to temperature T_B precisely *cancel* each other, leaving only the **conversion** of heat Q_1 into work at temperature T_A and the **conversion** of work into heat Q_2 at temperature T_D. These are transformations of the *same* kind; and together they form a standard 4-point reversible Carnot cycle, either overall **turning heat into work** (standard Carnot engine) if T_A is higher than T_D, or overall **turning work into heat** (reverse Carnot engine) if T_D is higher than T_A.

9. "These two transformations of the *same* kind, however, may be so divided and combined as again to appear as transformations of *different* kinds." Suppose T_D is greater than T_A; then we have a reverse Carnot engine (overall converting work into heat), and it follows that, of the two quantities of heat, $Q_2 > Q_1$. We may therefore divide the quantity of heat Q_2 into two parts, Q_1 and $Q_2 - Q_1$. The first part Q_1 can then be interpreted as **rising** from temperature T_A to temperature T_D, while the second part $Q_2 - Q_1$ is interpreted as being **generated from work** at temperature T_D.

10. Thus, when run together, simplified, and reinterpreted in this way, the two six-point cycles (from steps 5 and 6 above), each of which represents a *double process* (including both a **conversion** between heat and work and a **fall** or **rise** of heat), also describe a double process (except that only two, not three, temperatures are involved). For *this* double process it follows that: $(Q_2 - Q_1) f(T_D) + Q_1 F(T_A, T_D) = 0$.

11. But in step 7 we found that $Q_2 f(T_D) - Q_1 f(T_A) = 0$. We can combine this equation with the equation from step 10 to eliminate Q_2: $Q_1 f(T_A) - Q_1 f(T_D) + Q_1 F(T_A, T_D) = 0$, or $Q_1[f(T_A) - f(T_D)] + Q_1 F(T_A, T_D) = 0$.

12. Dividing this last equation by Q_1 yields $F(T_A, T_D) = f(T_D) - f(T_A)$. In other words, "the function F of two temperatures which applies to the second kind of transformation is reduced, in a general manner, to the function f of one temperature which apples to the second kind."

13. At this point, for reasons of convenience, Clausius defines θ as the reciprocal of f ($f = 1/\theta$); so that θ, like f, is some as yet unknown function of the absolute temperature T.

14. Clausius now enunciates the *theorem of the equivalence of transformations*: *If two transformations which, without necessitating any other permanent change, can mutually replace one another, be called equivalent, then the generation of the quantity of heat Q of the temperature T from work has the equivalence value Q/θ, and the passage of the quantity of heat Q from temperature T_1 to temperature T_2 has the equivalence value $Q(1/\theta_2 - 1/\theta_1)$, wherein θ is a function of the temperature T, independent of the nature of the process by which the transformation is effected.* The question remains: **What is the dependence of θ on T?**

15. Since all **rises** or **falls** of heat can thus be reinterpreted as **pairs of conversions** of heat into and out of work, it follows that the total equivalence value N of all the transformations in a cyclical process will be: $N = Q_1/\theta_1 + Q_2/\theta_2 + Q_3/\theta_3 + \ldots = \Sigma Q/\theta$. In the most general case, where infinitesimal quantities of heat dQ are transformed into and out of work at a continuous range of temperatures, $N = \int dQ/\theta$. If the cyclical process is reversible, then $N = \int dQ/\theta = 0$. If this were not the case, one could use the process to lift heat from a lower to a higher temperature **without employing any work**, contrary to Clausius's **second fundamental principle**, *that heat can never of itself pass from a colder body to a warmer body.* Thus $\int dQ/\theta = 0$ is an analytical expression, for all reversible cyclical processes, of Clausius' second fundamental principle.

16. Next, on the assumption that the conditions of a body are defined by its temperature T and volume V, let us express dQ as $dQ = (dQ/dT)dT + (dQ/dV)dV$, where dT and dV are incremental changes to the body's temperature and volume due to work done on the body or by the body. Then, for reversible cyclical processes, $\int dQ/\theta = \int (1/\theta)(dQ/dT)dT + (1/\theta)(dQ/dV)dV = 0$, and the quantity $(1/\theta)(dQ/dT)dT + (1/\theta)(dQ/dV)dV$ must be a **complete differential,** from which it follows that $d/dT[(1/\theta)(dQ/dV)] = d/dV[(1/\theta)(dQ/dT)]$.

17. From the last result we obtain: $(1/\theta)d/dT(dQ/dV) - (dQ/dV)(d\theta/dT)/\theta^2 = (1/\theta)(d/dV)(dQ/dT)$ or $(dQ/dV)(d\theta/dT) = \theta[d/dT(dQ/dV) - d/dV(dQ/dT)]$.

18. Earlier in the paper, Clausius had shown that, when heat Q in a body is made to do exterior work W (and is thus "converted into work"), Q = AW, where A is "the equivalent of heat for the unit of work." Also, the work done during a simultaneous increase of temperature dT and volume dV is dW = PdV (since the change in temperature contributes to the work by only changing the volume), where P is the pressure (which can be expressed as a function of V alone). From this (by a rather involved argument) Clausius had concluded that $d/dT(dQ/dV) - d/dV(dQ/dT) = A(dP/dT)$. Applying this to the equation in step 16 gives: $(dQ/dV)(d\theta/dT) = A\theta(dP/dT)$.

19. Clausius now proceeds to evaluate **the dependence of θ on T**, invoking "an accessory assumption" to the effect that *a permanent gas, when it expands at a constant temperature, absorbs only so much heat as is consumed by the exterior work thereby performed.* The exterior work done when a gas expands by volume dV under pressure P is dW = PdV, and the quantity of heat absorbed thereby is (dQ/dV)dV. But since Q = AW, dQ = AdW = APdV. Therefore dQ/dV = AP.

20. Substituting this last result into the equation from step 17 gives $AP(d\theta/dT) = AT(dP/d\theta)$, or $(d\theta/dT)/T = (dP/d\theta)/P$.

21. Clausius now invokes the combined gas law, which states that PV = kT or P = kT/V. Substituting that value of P into the equation from step 19 gives $d\theta/\theta = dT/T$. By integration this means $\theta = TK$, where K is some constant that we might as well set equal to 1. **It follows that θ is nothing other than the absolute temperature T!**

22. Clausius's conclusion is that (a) the equivalence value of every conversion of work into heat Q at absolute temperature T is Q/T; (b) the equivalence value of every conversion of heat Q into work at absolute temperature T is -Q/T; and (c) the equivalence value of every fall of heat Q from temperature T_1 to temperature T_2 is $Q\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$. It was on this basis that, eleven years later, in his paper of 1865,

Clausius gave the name **entropy** to the quantity $\Delta S = \int \dfrac{dQ}{T}$. In this equation, ΔS is the total change in the entropy of a body that, over some period of time, absorbs or releases incremental quantities of heat dQ at absolute temperatures T. As we have seen, for reversible cyclical processes ΔS = 0. For all other processes (and for every **actual** process in the real world, in which at least some **uncompensated falls of heat** are unavoidable) $\Delta S = \int \dfrac{dQ}{T} > 0.$ And that inequality is a precise statement of what is now known as the **Second Law of Thermodynamic.**

Q.E.D.