# Chapter 19

## The Definition of Temperature and the Efficiency of Heat Engines

*Why the various definitions of temperature are the same; The elegance of classical thermodynamics; The derivation of the maximum efficiency of a heat engine; The importance of functions of state*

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### 1. Didn't We Do This at School?

One of the iconic equations of physics is the maximum possible efficiency of a heat engine,

$$\eta = \frac{W}{Q_{in}} \leq \frac{\Phi_{in} - \Phi_{out}}{\Phi_{in}} \tag{1}$$

where $Q_{in}$ is the heat energy supplied to the engine at absolute temperature $\Phi_{in}$, $W$ is the work obtained from the engine, and $\Phi_{out}$ is the absolute temperature of the cold sink where waste heat is discarded. This could hardly be a more practical matter, born as it was out of the nineteenth century development of steam power. Every day, power stations around the world discard to the environment most of the energy they use. Typically only a quarter to a half of the input energy, whether from fossil fuels or from a nuclear reactor, is sent out from the power station as electrical power. Equ.(1) tells us that, try as we might, there will always be a strict limit to the fraction of heat which can be converted to electricity (or any other form of work). Moreover, this absolute limit is determined only by the two temperatures between which the heat engine operates. Why?

The brief answer, of course, is "the second law of thermodynamics". Allow me to indulge in heuristics a little. Heat is a form of energy contaminated by chaos (entropy). Work, or electric current, is a purified form of energy of low entropy. To distil the purified energy from the chaotic form, you must expect to loose some quantity in order to gain in quality. Heat is beer, whereas electricity is whiskey. So heat engines will not be 100% efficient. But how is equ.(1) derived? We shall see that one possible answer is that it follows trivially from a definition of temperature based on heat engines (the Kelvin scale).

However we are generally introduced to thermodynamics via the perfect gas laws, which provide an alternative definition of temperature. So how do we know that these two definitions are consistent? Moreover, there is yet another way of introducing temperature, in the relationship between entropy and heat, $dQ_{rev} = TdS$. In statistical thermodynamics the derivative form of this is used to define temperature, $\frac{1}{T} = \frac{\partial S}{\partial U}$. So why is this definition also consistent with the other two definitions?

These questions can all be addressed perfectly satisfactorily within the confines of classical thermodynamics without any recourse to statistical thermodynamics. It is possible that classical thermodynamics is rather going out of fashion these days. Admittedly statistical thermodynamics provides a framework of greater generality and range of applicability than its classical progenitor, so a concentration on statistical thermodynamics in undergraduate courses is perfectly understandable given the limited time available. However, classical thermodynamics is a wonderfully elegant

and self contained subject in its own right. And it has the advantage of appeal directly to the intuitive idea of temperature which is hardly conveyed by being told that temperature is the Lagrange multiplier corresponding to the constraint of conserved energy. Understanding is, of course, considerably enhanced by appreciation of both points of view. This chapter is a reminder of the classical approach.

## 2. Carnot's Theorem

As noted by Pippard (1966), it would make an interesting study in the history of science to explain how Carnot (1824) came to so many correct conclusions based on the entirely erroneous caloric theory of heat. One such striking success is Carnot's theorem which states,

(A) *No engine operating between two given heat reservoirs can be more efficient than a reversible engine operating between the same two reservoirs.*

The original version stipulated a particular reversible engine, now called a Carnot engine (of which more later), but we loose nothing by expressing the theorem more generally. To prove Carnot's theorem we must first be given some more basic axiom or law, which we know will be equivalent to the second law of thermodynamics. We choose to start with the second law expressed in Clausius (1850) form,

(B) *No process is possible whose sole result is the transfer of heat from a colder to a hotter body.*

The starting point therefore requires only a provisional idea of temperature as a ranking label such that $T_1 > T_2$ implies the first body is hotter than the second. Any monotonically increasing function of $T$ would do just as well. That (A) follows from (B) is easily established. It helps to think of the energy flows diagrammatically. Firstly the reversible engine, with $T_1 > T_2$,

**Figure 1        A Reversible Heat Engine**



$$\eta^R = \frac{W^R}{Q_1^R}$$
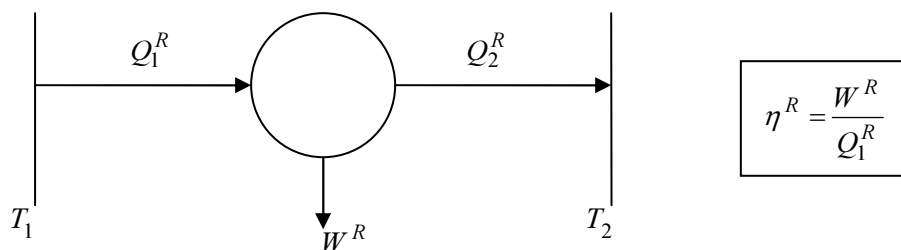
Now consider another heat engine operating between the same reservoir temperatures and distinguished from the above reversible engine by the omission of the $^R$ superscripts,

**Figure 2        Any Heat Engine**



$$\eta = \frac{W}{Q_1}$$
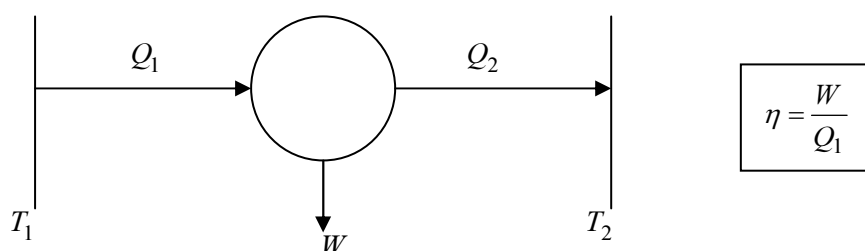
Now we can run the reversible engine backwards and arrange its size to be such that the magnitude of the work (which will now be done **on** the engine) is equal to that output by the second engine, $W^R = W$. This composite engine does no net work and looks like this,

**Figure 3          The Compound Heat Engine**



$$\boxed{W = \eta Q_1 = \eta^R Q_1^R}$$
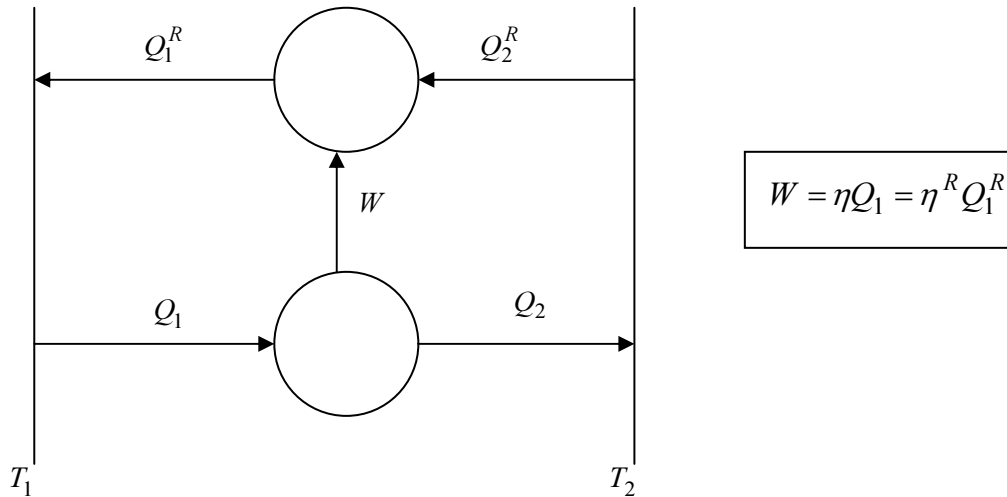
This device is now transferring a net amount of heat $Q_1 - Q_1^R = Q_2 - Q_2^R$ from the hotter to the colder reservoir with no other effect. According to (B) these quantities must be positive, so the heat really *is* flowing from hot to cold, not the other way around. So we have,

$$Q_1 - Q_1^R = Q_1 - \frac{\eta}{\eta^R} Q_1 \geq 0 \qquad (2)$$

and hence, $$\eta^R \geq \eta \qquad (3)$$

which is just Carnot's theorem, (A). QED.

Note that the key requirement in the above derivation is reversibility, which often seems a rather slippery concept in thermodynamics. Here it could not be more concrete. It literally means a heat engine which can be run backwards, in other words as a refrigerator, with the same values of $Q_1, Q_2, W$ being applicable, but in the reverse direction.

### 3. The Kelvin Scale of Temperature

It follows immediately from Carnot's Theorem, (A), that all reversible heat engines operating between the same reservoirs must have the same efficiency. So their efficiency is a function of $T_1, T_2$ only, so we can write,

$$1 - \eta^R = \frac{Q_2^R}{Q_1^R} = f\left(T_1, T_2\right) \qquad (4)$$

where $f$ is a universal function independent of any details of the engine, requiring only its reversibility. But we can also consider a reversible engine operating between temperature $T_2$ and some still lower temperature, $T_3 < T_2$, so that,

$$1 - \widetilde{\eta}^R = \frac{Q_3^R}{Q_2^R} = f(T_2, T_3) \qquad (5)$$

Note that the efficiency, $\widetilde{\eta}^R$, between the second pair of temperatures will generally be different from that between the first pair of temperatures, $\eta^R$. However, we can now consider the above two engines as a composite engine operating between the temperatures $T_1$ and $T_3$. This gives,

$$1 - \widetilde{\widetilde{\eta}}^R = \frac{Q_3^R}{Q_1^R} = f(T_1, T_3) \qquad (6)$$

The product of (4) and (5) equals (6) so that,

$$f(T_1, T_3) \equiv f(T_1, T_2) f(T_2, T_3) \qquad (7)$$

This is an identity, true for all values of its arguments. The dependence of the RHS on $T_2$ must therefore cancel, since there is no $T_2$ dependence on the LHS. This establishes that the function must be of the form,

$$f(T_1, T_2) \equiv \frac{\Phi(T_2)}{\Phi(T_1)} \equiv \frac{\Phi_2}{\Phi_1} = \frac{Q_2^R}{Q_1^R} \qquad (8)$$

So we can use $\Phi$ as our measure of temperature, rather than our initial ranking temperature $T$. This is Kelvin's absolute temperature. In words it is defined via,

(C) *The ratio of the Kelvin temperatures of two reservoirs is equal to the ratio of the amounts of heat exchanged at those reservoirs by a reversible heat engine operating between them.*

The efficiency of such a reversible heat engine, which we now know is the maximum possible efficiency, is found from (4), which, with (8), gives us equ.(1). QED. So we see that the famous formula for the maximum efficiency of a heat engine is actually a trivial consequence of the absolute Kelvin scale of temperature. But that begs the question: is the Kelvin scale defined by (8) equal to the perfect gas scale? Is it equal to the temperature appearing in the relationship $dQ_{rev} = TdS$?

**4. Perfect Gases**

At school it is common to learn three gas laws,

(D) Boyle's Law: *If temperature is held constant then the product of pressure and volume is constant, $PV = \text{constant}$.*

(E) Charles's Law: *If pressure is held constant then the volume is proportional to the absolute temperature, $V \propto T$.*

(F) The Pressure Law (or Gay-Lussac's Law): *If volume is held constant then the pressure is proportional to the absolute temperature, $P \propto T$.*

From these the equation of state for a perfect gas follows, $PV = RT$ where $R$ is some constant and equals the usual gas constant if expressed per mole. The problem with this is that it is not clear that we have any right to expect the temperature $T$ to be the same as the Kelvin temperature, $\Phi$, defined as in §3 and (C). The approach taken in most developments of classical thermodynamics is therefore not to employ Charles's

Law or the Pressure Law, since these involve changing temperature, but instead to define a perfect gas as follows,

(G) *A perfect gas is a gas obeying Boyle's Law and Joule's Law.*

where the latter is,

(H) Joule's Law: *The internal energy of a fixed mass of perfect gas is independent of pressure and volume, depending only upon temperature.*

After defining the absolute Kelvin temperature, $\Phi$, the classical approach shows that (G) and (H) suffice to prove that the equation of state is $PV = R\Phi$ (from which Charles's Law and the Pressure Law immediately follow). This shows that the Kelvin temperature is equivalent to the perfect gas scale. It is actually Joule's Law which is the key ingredient in deriving the equation of state and the manner of doing this requires the introduction of entropy. The argument requires a subtle but crucial property of entropy, not shared by heat or work, the nature of which is described in §6 and §7.

For now we take a different approach. By virtue of Boyle's Law we are entitled to use $PV = RT$ as the definition of a gas scale of temperature, $T$. Our task is to show that this equals the Kelvin temperature, $T \equiv \Phi$ - which is just another way of saying that equ.(1) for the efficiency of a reversible heat engine is also true if the Kelvin temperature, $\Phi$, is replaced by the perfect gas temperature, $T$. This can be done in a straightforward manner by considering an engine based on the Carnot cycle. This is the development followed in many texts (especially engineering texts). It suffers from the flaw that it also requires knowledge of how gases behave in adiabatic conditions, specifically that $PV^\gamma$ is constant, where $\gamma = C_P / C_V$, the ratio of the specific heats at constant pressure and constant volume. This relation can also be derived from Boyle's Law, the algebra of which is simple but whose veracity requires the same "subtle but crucial property of entropy" alluded to above. Ultimately, therefore, a fully cogent derivation of $T \equiv \Phi$ requires the entropy route discussed in §6 and §7. However the derivation via the Carnot cycle is also instructive and is considered first.

**5. The Carnot Cycle Route to $T \equiv \Phi$**

A particular reversible heat engine, using a single working fluid – a perfect gas – takes that fluid around a Carnot cycle. The Carnot cycle consists of four steps, illustrated on the pressure-volume plot of Figure 4, and defined below,

(i) The gas is allowed to expand reversibly whilst in contact with the reservoir at the higher temperature, $T_1$, thus ensuring isothermal conditions. The gas does work and it absorbs heat $Q_1$ from the reservoir;

(ii) The gas is allowed to expand reversibly and adiabatically. The gas does work but exchanges no heat and hence its temperature falls to $T_2$;

(iii) The gas is compressed reversibly whilst in contact with the reservoir at the lower temperature, $T_2$, thus ensuring isothermal conditions. Work is done *on* the gas and it rejects heat $Q_2$ to the reservoir;

(iv) The gas is compressed reversibly and adiabatically. Work is done *on* the gas but it exchanges no heat and its temperature increases back to $T_1$.

Note that these temperatures are specified in the gas scale so that we may assume $PV = RT$.

**Figure 4        The Carnot Cycle (Schematic Only)**
Clockwise = Engine ($Q_1 > Q_2 > 0$); Anticlockwise = Refrigerator ($Q_1 < Q_2 < 0$)
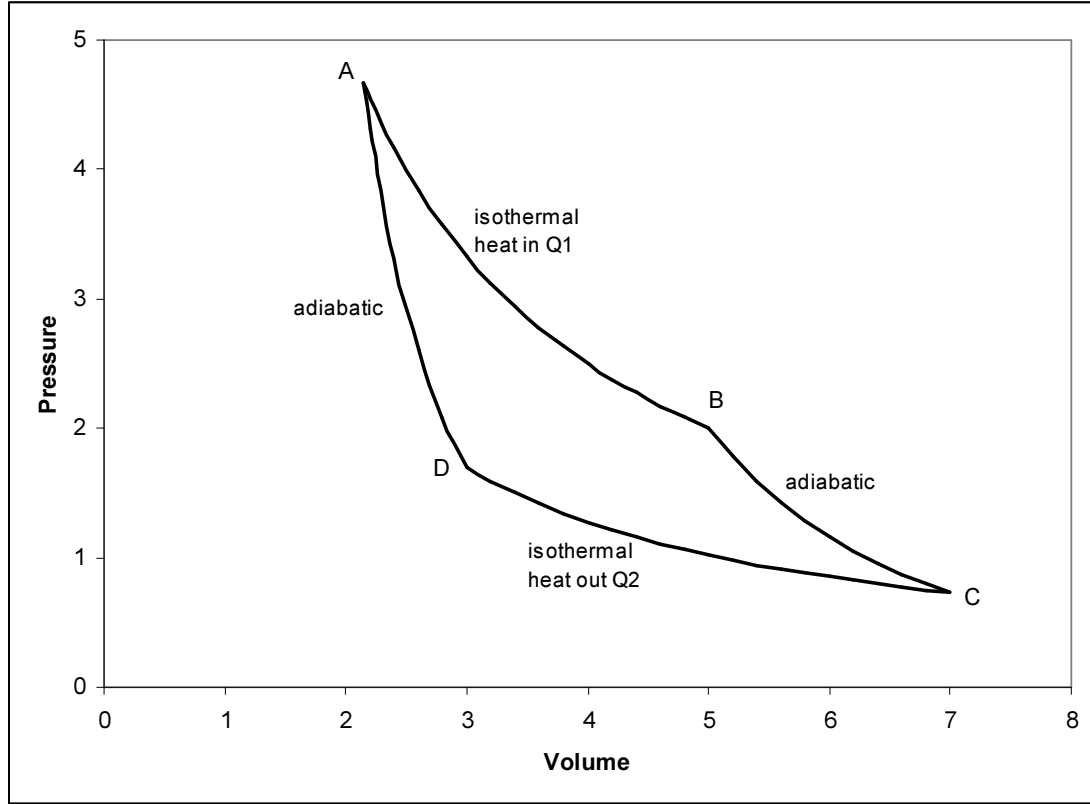


From equ.(8) all we need in order to find the Kelvin temperature is to evaluate the heat exchanges, $Q_1$ and $Q_2$. These heat exchanges occur only during isothermal conditions for which Joule's Law tells us that the internal energy is constant. Consequently these heat exchanges balance with the work done by the gas during these steps. Being reversible, the work done is the integral of $PdV$. Hence,

$$Q_1 = \int_A^B PdV = \int_A^B \frac{RT_1}{V} dV = RT_1 \log\frac{V_B}{V_A} \tag{9}$$

$$-Q_2 = \int_C^D PdV = \int_C^D \frac{RT_2}{V} dV = RT_2 \log\frac{V_D}{V_C} \tag{10}$$

So equ.(8) gives the ratio of Kelvin temperatures as,

$$\frac{\Phi_2}{\Phi_1} = \frac{Q_2}{Q_1} = -\frac{T_2}{T_1} \cdot \frac{\log(V_D/V_C)}{\log(V_B/V_A)} = \frac{T_2}{T_1} \cdot \frac{\log(V_C/V_D)}{\log(V_B/V_A)} \tag{11}$$

That the ratio of the log terms is unity follows from the adiabatic relation $PV^\gamma =$ constant which gives,

$$P_B V_B^\gamma = P_C V_C^\gamma \qquad \text{and} \qquad P_D V_D^\gamma = P_A V_A^\gamma \tag{12}$$

Hence,

$$\frac{P_D}{P_C} \cdot \frac{V_D^{\gamma}}{V_C^{\gamma}} = \frac{P_A}{P_B} \cdot \frac{V_A^{\gamma}}{V_B^{\gamma}} \tag{13}$$

But Boyle's Law gives,

$$\frac{P_A}{P_B} = \frac{V_B}{V_A} \qquad \text{and} \qquad \frac{P_D}{P_C} = \frac{V_C}{V_D} \tag{14}$$

Hence,

$$\frac{V_D}{V_C} = \frac{V_A}{V_B} \tag{15}$$

So finally, from (11),

$$\frac{\Phi_2}{\Phi_1} = \frac{Q_2}{Q_1} = \frac{T_2}{T_1} \qquad \text{QED.} \tag{16}$$

**6. The Entropy Route to $T \equiv \Phi$**

Now we come to the nub of the matter: how is the adiabatic gas equation, $PV^{\gamma} = $ constant, established, and how is the perfect gas equation of state $PV = R\Phi$ established directly in terms of the Kelvin temperature? Recall that the derivation of $PV = R\Phi$ by showing that $\Phi \equiv T$ in §5 was flawed because the adiabatic relation was assumed without proof. This logical hole can be plugged by some rather elegant mathematics, as will now be shown. The reader might like to try to discover the key hidden assumption which lies at the heart of the following mathematics before it is revealed in §7.

Introduce a quantity called entropy, defined through its increment, $dS = dQ/\Phi$. (Those versed in these matters and tempted to cry foul should not do so before reading §7, where all will be confessed). The first law of thermodynamics, the conservation of energy, can therefore be written,

$$dU = dQ + dW = \Phi dS - PdV \tag{17}$$

where $U$ is the internal energy and $W$ is the work done *on* the gas. Now define the Helmholtz free energy via,

$$F = U - \Phi S \tag{18}$$

Taking the derivative of (18) and using (17) gives,

$$dF = -Sd\Phi - PdV \tag{19}$$

If we consider a change at constant volume then (19) gives,

$$\left. \frac{\partial F}{\partial \Phi} \right)_V = -S \tag{20}$$

where the subscript denotes the quantity which is held constant. Similarly, considering a change at constant temperature gives,

$$\left. \frac{\partial F}{\partial V} \right)_\Phi = -P \tag{21}$$

Now taking the derivative of (20) with respect to volume at constant temperature gives,

$$\left.\frac{\partial}{\partial V}\right)_\Phi \left.\frac{\partial F}{\partial \Phi}\right)_V = -\left.\frac{\partial S}{\partial V}\right)_\Phi \tag{22}$$

Similarly, taking the derivative of (21) with respect to temperature at constant volume gives,

$$\left.\frac{\partial}{\partial \Phi}\right)_V \left.\frac{\partial F}{\partial V}\right)_\Phi = -\left.\frac{\partial P}{\partial \Phi}\right)_V \tag{23}$$

However the order of differentiation does not matter, i.e., the derivatives commute,

$$\left.\frac{\partial}{\partial V}\right)_\Phi \left.\frac{\partial F}{\partial \Phi}\right)_V \equiv \left.\frac{\partial}{\partial \Phi}\right)_V \left.\frac{\partial F}{\partial V}\right)_\Phi \tag{24}$$

Consequently, equating (22) and (23) gives,

$$\left.\frac{\partial S}{\partial V}\right)_\Phi = \left.\frac{\partial P}{\partial \Phi}\right)_V \tag{25}$$

This is one of four similar differential relations between the quantities $S, P, V, \Phi$ called the Maxwell Relations. A great tranche of similar differential relations can be derived by including the internal energy, $U$, the Helmholtz free energy, $F$, the enthalpy, $H = U + PV$, and the Gibbs fee energy, $G = F + PV$ along with $S, P, V, \Phi$. I recall as an undergraduate being slowly driven bonkers by these relations, though they are essentially algebraically trivial, as seen above.

We are now a short step away from deriving the equation of state, $PV = R\Phi$. The first law, (17) gives us,

$$\left.\frac{\partial U}{\partial V}\right)_\Phi = \Phi \left.\frac{\partial S}{\partial V}\right)_\Phi - P \tag{26}$$

Using (25) this becomes, $\qquad \left.\frac{\partial U}{\partial V}\right)_\Phi = \Phi \left.\frac{\partial P}{\partial \Phi}\right)_V - P \tag{27}$

But, by Joule's Law, this must be zero because the internal energy does not depend upon volume if the temperature is held constant. Hence,

$$\left.\frac{\partial P}{\partial \Phi}\right)_V = \frac{P}{\Phi} \tag{28}$$

Integration of (28) gives,

$$\log P = \log \Phi + a(V) \tag{29}$$

which is equivalent to, $\qquad P \cdot b(V) = \Phi \tag{30}$

where $a$ and $b$ are arbitrary functions of volume. But Boyle's Law tells us that $PV$ is constant at constant temperature, so that $b(V) \propto V$. Hence there is some constant $R$ such that,

$$PV = R\Phi \qquad\qquad \text{QED} \tag{31}$$

Hence the equivalence $\Phi \equiv T$ is established, and note that this has been done without needing to assume the adiabatic relation $PV^\gamma = $ constant. This is fortunate since the

constancy of $PV^\gamma$ assumes the constancy of $\gamma$ which is only an empirical approximation, not precise theory. On the other hand, $\Phi \equiv T$ is precise, within the idealisations involved (e.g., prefect gases).

The reader may think the above mathematics is a little too slick, possibly concealing some slight of hand. We do seem to have got something for nothing. The whole derivation follows from what appears to be merely a definition, namely $dS = dQ / \Phi$, which seems innocuous enough. Let us use some more of this slick mathematics before revealing the key ingredient which makes it valid. We shall now derive the adiabatic relation $PV^\gamma = $ constant.

Firstly we establish a result known as the reciprocity theorem. Consider three variables $x, y, z$ related by some constraint $F(x, y, z) = 0$. What we have in mind is a set of three variables chosen from $P, V, \Phi, S, U, H, F$. These are related by the equation of state (which, for this purpose, can be any relationship, not necessarily that for a perfect gas). The constraint equation means that we can consider any one of $x, y, z$ to be a function of the other two. Hence we have, for example,

$$dx = \frac{\partial x}{\partial y}\bigg)_z dy + \frac{\partial x}{\partial z}\bigg)_y dz \qquad (32)$$

and,
$$dz = \frac{\partial z}{\partial y}\bigg)_x dy + \frac{\partial z}{\partial x}\bigg)_y dx \qquad (33)$$

Substituting (33) into (32) gives,

$$dx = \frac{\partial x}{\partial y}\bigg)_z dy + \frac{\partial x}{\partial z}\bigg)_y \left[ \frac{\partial z}{\partial y}\bigg)_x dy + \frac{\partial z}{\partial x}\bigg)_y dx \right] \qquad (34)$$

This must be true for arbitrary (infinitesimal) $dx$ and $dy$, so in particular we can choose $dy = 0$ which gives us the identity,

$$\frac{\partial x}{\partial z}\bigg)_y = \frac{1}{\dfrac{\partial z}{\partial x}\bigg)_y} \qquad (35)$$

which is known as the reciprocal theorem, as is hardly surprising. On the other hand, choosing $dx = 0$ in (34) gives the less obvious result,

$$\frac{\partial x}{\partial y}\bigg)_z \equiv -\frac{\partial x}{\partial z}\bigg)_y \frac{\partial z}{\partial y}\bigg)_x \qquad (36)$$

Or, using (35), in more symmetrical form,

$$\frac{\partial x}{\partial y}\bigg)_z \frac{\partial y}{\partial z}\bigg)_x \frac{\partial z}{\partial x}\bigg)_y \equiv -1 \qquad (37)$$

Equs.(36) or (37) are known as the reciprocity theorem. We can use this to find a relationship between the compressibility ratio and the ratio of specific heats. The specific heats at constant volume and constant temperature are given by,

$$C_V = \frac{\delta Q_V}{\delta \Phi} = \Phi \frac{\partial S}{\partial \Phi}\bigg)_V \quad \text{and} \quad C_P = \frac{\delta Q_P}{\delta \Phi} = \Phi \frac{\partial S}{\partial \Phi}\bigg)_P \tag{38}$$

The ratio of these specific heats is denoted $\gamma = C_P / C_V$. The isothermal and adiabatic compressibilities are given by,

$$\beta_\Phi = -\frac{1}{V} \cdot \frac{\partial V}{\partial P}\bigg)_\Phi \quad \text{and} \quad \beta_S = -\frac{1}{V} \cdot \frac{\partial V}{\partial P}\bigg)_S \tag{39}$$

The ratio of these compressibilities is, using both the reciprocity and reciprocal theorems,

$$\frac{\beta_\Phi}{\beta_S} = \frac{\dfrac{\partial V}{\partial P}\big)_\Phi}{\dfrac{\partial V}{\partial P}\big)_S} = \frac{\dfrac{\partial V}{\partial \Phi}\big)_P \dfrac{\partial \Phi}{\partial P}\big)_V}{\dfrac{\partial V}{\partial S}\big)_P \dfrac{\partial S}{\partial P}\big)_V} = \frac{\dfrac{\partial S}{\partial V}\big)_P \dfrac{\partial V}{\partial \Phi}\big)_P}{\dfrac{\partial P}{\partial \Phi}\big)_V \dfrac{\partial S}{\partial P}\big)_V} = \frac{\dfrac{\partial S}{\partial \Phi}\big)_P}{\dfrac{\partial S}{\partial \Phi}\big)_V} = \frac{C_P}{C_V} = \gamma \tag{40}$$

Now we are very close to our goal. Boyle's Law tells us that provided the temperature is held constant then $VdP + PdV = 0$, hence,

$$\frac{\partial V}{\partial P}\bigg)_\Phi = -\frac{V}{P} \tag{41}$$

Substituting from (40) gives,

$$\gamma \cdot \frac{\partial V}{\partial P}\bigg)_S = -\frac{V}{P} \tag{42}$$

Finally, integrating (42) gives $\gamma \log V = -\log P + c(S)$ where $c$ is an arbitrary function of entropy and which is therefore constant under adiabatic conditions. Exponentiating gives, as desired,

$$PV^\gamma = \text{constant} \tag{43}$$

under adiabatic conditions. QED.

## 7. What's the Trick?

Dear reader, you have been conned. Or rather, the key mathematical issue has not yet been exposed. We have apparently worked magic simply by introducing the quantity $dS = dQ/\Phi$. Moreover we have given no clue as what this quantity, entropy, might mean physically. Indeed it truly is not necessary to have a physical interpretation of entropy for the derivations of §6 to be valid. However it **is** necessary for this entropy to posses a certain crucial mathematical property: it must be a function of state. In other words it must have a unique value for any given state of the system. The state of the system may be described, for example, by specifying any two of $P, V, \Phi$, so that entropy must be a function of these variables, e.g., $S(P, \Phi)$. This may seem to be no restriction at all. But it is. It means that we can impose any sequence of changes on the system we like, but provided that $P, V, \Phi$ are the same at the end as at the start, then the entropy will also be the same. This is the subtle but crucial property alluded to previously.

It is by no means obvious that a quantity introduced via $dS = dQ/\Phi$ will have this property. Indeed, it does not. This is not a correct definition of entropy in general. The

relation $dS = dQ/\Phi$ is valid only for reversible changes. As an example of a quantity which is not a function of state, consider heat, $Q$. We have seen in the analysis of the Carnot engine (or any heat engine) that over a complete cycle, so the system returns to its initial state, there will be a net absorption of heat, namely $Q_1 - Q_2$. This is balanced, of course, by a net quantity of work done, $W = Q_1 - Q_2$. But this means that neither heat nor work are functions of state. However, by virtue of the definition of the Kelvin temperature, (8), the entropy **does** return to its initial value because the change in entropy is $\Delta S = \dfrac{Q_1}{\Phi_1} - \dfrac{Q_2}{\Phi_2} = 0$. Had entropy not been a function of state such innocent seeming things as the commutativity of partial derivatives, equ.(24), or the reciprocity relation, equ.(36), would be invalid and the arguments of §6 would fall apart.

From the vantage point of statistical thermodynamics we are not surprised that entropy is a function of state. But the point to be made is that this can be established within classical thermodynamics. Moreover this can be done in a completely general fashion, not reliant on specific examples such as the Carnot cycle. The most satisfying such method is to proceed via yet another statement of the second law, that of Caratheodory,

(I) *In the neighbourhood of any equilibrium state of a system there are states which are inaccessible by an adiabatic process*.

From this it is possible to deduce that there exists a continuous, single-valued function of state with the properties of entropy. This is the logical heart of classical thermodynamics. Caratheodory's original 1909 work is reputed to be opaque, at least to non-mathematicians (I have not read it, I believe there is no English translation). Buchdahl did much to make Caratheodory's approach more comprehensible to physicists in a series of papers from the late 1940s, culminating in Buchdahl (1966). However the interested reader can satisfy his curiosity amply via Pippard (1966) or Adkins (1969).

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