
Heat and Laws of Thermodynamics

1 Heat

Heat is a form of energy exchange between systems. It is the spontaneous energy exchange between systems, without any external agency and solely due to temperature differences between them. When two bodies at different temperatures are brought in contact with each other, it is common experience that the hotter body's temperature tends to decrease and that of colder body increase. Earlier people thought this to be due to exchange of a fluid called caloric between the two objects. It was the quantity of caloric in a body which was thought to be the direct measure of temperature. In this sense heat was thought to be something contained in a body in a fixed quantity. This theory explained many attributes of heat, (in fact if no work is done, it is really true that heat behaves as an indestructible conserved quantity), but it were the experiments of Joule, Kelvin and earlier Count Rumford, which proved that heat is just a form of energy exchange, and not a conserved quantity in itself. Since we can provide energy to a system by other means (doing work on it) we can produce as much heat as we want from a body (by converting work into heat). This is what Count Rumford observed while boring the canons for Bavarian king. Joule showed that same amount of work always produced same amount of heat, no matter how the work is done, or the materials involved. This established firmly that heat is a form of energy. In strict thermodynamical terms, the way we have been treating the subject, Joule's experiments showed that same change in the state of a system can be brought about by work as is by heat.

2 Internal Energy

Joule's experiments basically showed that same amount of work "under adiabatic" conditions always produces same changes in the state of the system. Or in other word, If you put the system in adiabatic walls i.e., it is not affected by the temperature of things outside the walls, work done to bring the system from state a to state b is independent of the path when done in adiabatic conditions. The work need not be quasi-static either.

This suggests existence of a new state function with dimensions of energy. If we always have to supply same amount of energy in the form of work, in adiabatic conditions, in going from state a to an arbitrary state b, we could assign this value of work to the state itself. This new state function is called "Internal Energy" U . Since the starting state a was also arbitrarily chosen, we can not assign absolute value to Internal energy. We only measure differences in internal energy.

Hence internal energy is defined by

$$\Delta U = U(2) - U(1) = W_{Adiabatic}$$

where ΔU represents the change in internal energy in going from state 1 to state 2 and $W_{Adiabatic}$ is the work required to go from state 1 to state 2. In a sense system is like a spring with capacity to hold energy in the form of internal energy.

3 1st Law

But if we remove adiabatic walls then it is found that the work done on a system in taking it from a to b is not always same, but depends on at what temperature the surroundings are. To restore the usefulness of internal energy function, and encouraged by the understanding of heat as a form of energy, the difference of work needed to take the system from a to b in adiabatic and non-adiabatic conditions is attributed to transfer of heat into or out of the system. And one writes,

$$\Delta U = W + Q \quad (1)$$

Where Q is heat. Equation (1) is called first law of thermodynamics. This law is nothing but an expression of energy conservation. It says that, if heat is taken into account, the work done on the system is equal to change in its internal energy.

Notice that internal energy can be measured by doing work on the system in adiabatic conditions. Similarly work is a mechanical concept which can be measured. On the other hand heat is basically defined by first law. Hence it is not obvious and usually not easy to verify this law. Our belief in this law comes from when we apply this law combined with other equations for different systems and get verifiable results. A stronger reason to believe in it is probably our current understanding of forces which govern the microscopic behavior of atoms comprising the system. They are electromagnetic forces which are conservative. Hence if all macroscopic thermodynamic processes have their origin in microscopic phenomena, the energy must be conserved, In fact heat is understood to be the energy transfer due to "random" motion of atoms, hence it's spontaneous nature.

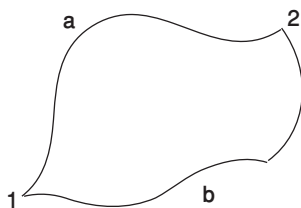
It is important to note that the differentiation of energy given to the system into heat and work depends on the way we define our system (where we draw boundaries). For example, consider a water tank with a high resistance electric heater immersed in it. If we consider only water to be our system with boundaries at the surface of the heating resistor, we have a process of heating at our hand because the energy transfer into the system takes place solely due to temperature differences with the surroundings and does so spontaneously. On the other hand if we take the resistor as part of the system then we have a process of work at hand, where we do work on the resistor to run current through it. Hence it is the boundary of the system where we must decide if the energy is being transferred in an organized way by an external agency (a work source) or spontaneously due to temperature difference. (As a rule of thumb, to decide if some process is work or not, we must be able to describe it with the help of falling weights.)

Coming back to first law, we can write it in differential form as,

$$dU = dW + dQ$$

Here dU is an exact differential of a function while dW and dQ are not differentials of any functions. They are just infinitesimal small quantities. This is because work and heat are not state functions. Such infinitesimals are called inexact differentials. The integral of an inexact differential between two states depends on the path taken, i.e.,

$$\int_{1a}^2 dQ \neq \int_{1b}^2 dQ$$



Similarly for work. This is basically mathematical description of Joule's experiment with heat and work.

However their sum is an exact differential i.e., dU . Its integral is path independent and only depends on the initial and final states.

Note that for an isolated system, $W = 0$, $Q = 0$ and therefore, $\Delta U = 0$.

That is the internal energy of an isolated system does not change in any process. If you build a fairly isolated room with (a presidential bunker) a time bomb inside. When the bomb will explode, you will notice a lot of change in your room, but rest assured that at least internal energy has not change for the room.

4 2nd Law

2nd law deals with irreversible processes and all real processes in nature are irreversible. Although from microscopic perspective, there is no irreversibility in laws of physics but at macroscopic level things seem to move in a particular direction. A glass falls and breaks, if the glass were to spontaneously get together in one piece. It will not violate any of the laws of physics, but it never happens in nature. If you leave a cylinder of gas open in a corner of a room, the gas will soon fill up the whole room. But it never happens that the gas by itself goes back to cylinder, though it is not against any law of physics. Except of course, the 2nd law of thermodynamics. The 2nd law of thermodynamics quantifies this irreversibility of nature through a new state quantity called Entropy. The most obvious irreversible process in thermodynamics is the heat flow. Heat always flow in one direction from hot to cold. Quite understandably, the 2nd law was first stated in terms of heat flow and entropy is also defined in terms of heat. But 2nd law is not limited to heat. And the definition of entropy is general enough to cover any process.

Now one can state the 2nd law as,

” There is a new state function called entropy, which is defined by its differential,

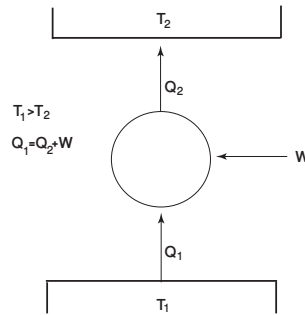
$$ds = \frac{dQ_{rev}}{T}$$

Where dQ is the heat given to the system in a reversible process. Further, Entropy for an isolated system never decrease in any process, rather it increases for all irreversible processes until it reaches a maximum.

This introduction of entropy is rather abstract. One may wonder who thought of defining this quantity in this particular fashion. It is highly instructive to go through the development of entropy concept starting from some more understandable definition of 2nd law. But as a matter of fact all these statements are equivalent and can be derived from each other.

5 Clausius statement

” No process is possible whose sole result is to transfer heat from a cold to a hot body.” This statement says that one cannot reverse the natural order of heat flow unless some external work is provided to the system.



caption Clausius statement: Work must be provided to transfer heat from cold to hot body.

6 Kelvin statement

In order to describe Kelvin’s statement of 2nd law, we first have to define what a heat engine is. A heat engine is a system going through cycles, which takes in heat from a heat source and converts part of it into work which is performed on surroundings. By a cycle we mean a process which brings the system to its original state when the process is completed. Efficiency of a heat engine is defined as

$$\eta = \frac{W}{Q}, \quad (2)$$

where W is the work done by the engine and Q is the heat taken in by the engine.

Now Kelvin’s statement of 2nd law is

” No engine working in a cycle can take heat from one source and convert it completely into work.”

What this statement says is that a heat engine working in cycles, must reject part of the heat taken in by the engine to another reservoir which is at a colder temperature. Or in other words, the efficiency of the heat engine can not be equal to 1. Notice that it does not say exactly how less the efficiency must be than 1. At this point it may be arbitrarily close to 1. But it is a remarkable fact, that this statement is enough to exactly fix the efficiencies of the engines in terms of temperatures of the reservoirs from which the engine takes in and rejects heat as will be shown below.

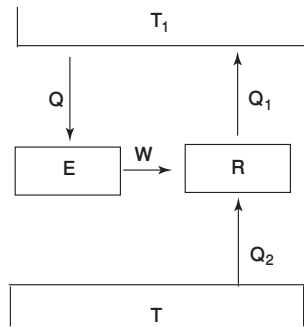
Using the first law, we can write efficiency of an engine as

$$\eta = 1 - \frac{Q_2 - Q_1}{Q_1} \quad \text{as } W = Q_2 - Q_1 \quad (3)$$

or

$$\eta = 1 - \frac{Q_2}{Q_1} \quad (4)$$

The above two statements of 2nd law are actually equivalent. We will show that truth of Clausius statement implies the truth of Kelvin's statement.



To prove this we suppose that Kelvin's statement is not true. Then we can consider a combined system as shown in the figure. The engine E takes heat Q from a hot reservoir at temperature T_1 and converts it completely into work. Now this work can be used to run a refrigerator which takes heat Q_2 from a cold reservoir and transfers heat Q_1 to the hot reservoir at T_1 . Now if we consider both E and R to be one system, then the net result is transfer of Q_2 from a cold to a hot body. Which means Clausius' statement is not true. Therefore, if Clausius' statement is true, Kelvin's statement must also be true.

7 Carnot's Engine

Carnot's engine is a system which performs reversible cycles, taking in heat only from one reservoir at one temperature and rejecting part of it to only one, colder, reservoir at one temperature.

The cyclic process of Carnot's engine, called a Carnot's cycle, consists of the following steps.

1. Isothermal expansion at temperature T_1 , absorbing heat Q_1 from the hot reservoir.
2. Adiabatic expansion taking temperature from T_1 to a lower temperature T_2 .
3. Isothermal Compression at temperature T_2 , rejecting heat Q_2 to the colder reservoir.
4. Adiabatic compression which brings the temperature back to T_1 and the system to its original state.

The work performed by Carnot's engine is equal to the area enclosed by the above four curves. See fig (??)

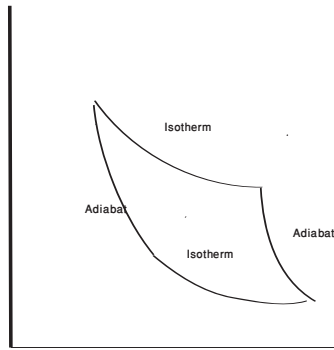


Figure 1: Carnot Cycle

8 Carnot's Theorem

Carnot's Theorem states that the efficiency of a Carnot's engine working between two temperatures T_1 and T_2 is greater than any irreversible engine working between those two same temperatures.

To prove Carnot's theorem, suppose that a Carnot's engine is working between reservoirs at temperatures T_1 and T_2 and another engine is also working between same temperatures. The heats taken in and works performed by the two engines are shown in figure ??.

Now suppose that the efficiency of the other engine which is called "E" is better than Carnot's engine i.e.,

$$\eta_E > \eta_C. \quad (5)$$

Where η_E and η_C are efficiencies of the hypothetical engine and the Carnot's engine respectively. Eq (5) implies

$$\frac{W_E}{Q_{E1}} > \frac{W_C}{Q_{C1}}. \quad (6)$$

Now we can always adjust the cycle of Carnot's engine (by bringing the adiabats closer or farther from each other) so that we have

$$W_C = W_E. \quad (7)$$

Now since Carnot's engine is reversible, we can run it backwards. With the arrangement we already made (??), the work required to run it backwards can be provided by the engine E . Now the Carnot's engine is working as a refrigerator, transferring heat from lower temperature T_2 to higher temperature T_1 . Using (??) in (??), we get

$$Q_{C1} > Q_{E1}, \quad (8)$$

which shows that the combined effect of the two engines is the transfer of heat (by a positive amount $Q_{C1} - Q_{E1}$) from a low temperature reservoir to a high temperature reservoir. But this is impossible according to Clausius' statement. Therefore our assumption that $\eta_E > \eta_C$ must be wrong i.e., we must have

$$\eta_C > \eta_E. \quad (9)$$

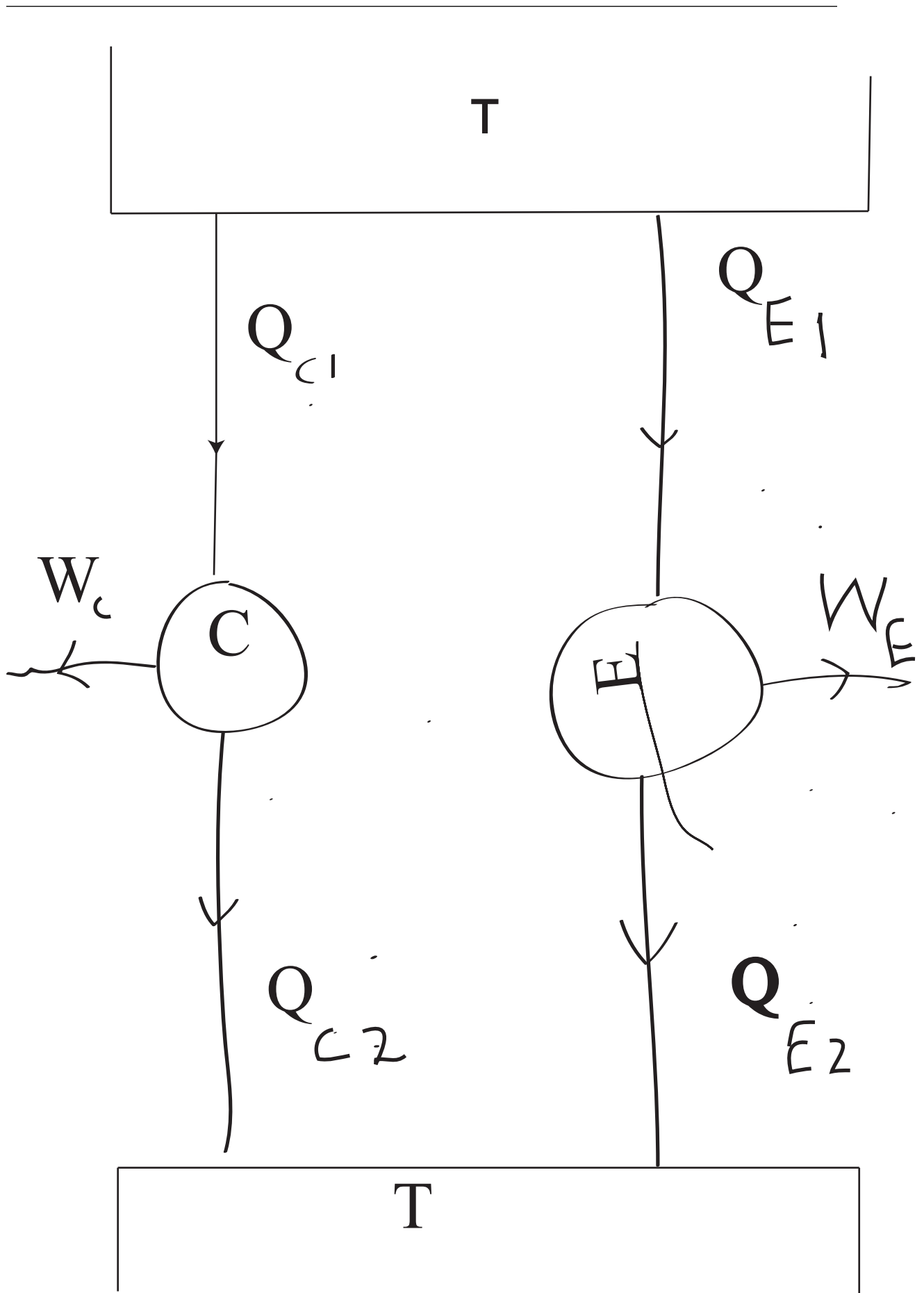


Figure 2: Two engines for proving Carnot's theorem

This proves the result that Carnot's engine is more efficient than any irreversible engine.

Notice that the only property of the Carnot's engine which we used was its reversibility. A direct corollary of this result is that all reversible engines, working between same temperatures have same efficiency. Suppose that the second engine E is also reversible. In that case, we could run that engine backwards and use the work performed by Carnot's engine to power it. In that case we will have the result

$$\eta_E > \eta_C \quad (10)$$

Combining (??) and (??) we get the result that all reversible engines working between two temperatures have same efficiency.

Now this corollary gives another, perhaps more important for us, corollary. As we have proven that the efficiency of any reversible engine is same, it must be that it does not depend on the material the engines is made of (gas box, magnet, electric dipole), or the processes through which it works. Therefore, the efficiency can at most depend on the two temperatures the engine is working between and nothing else i.e.,

$$\eta_C = h(T_1, T_2) \quad (11)$$

Now we will fix this functional form.

9 Efficiency of Carnot's Engine

From the expression of efficiency

$$\eta = 1 - \frac{Q_2}{Q_1} \quad (12)$$

and (??), we can write the ratio of heats exchanged by the Carnot's engine as a function of two temperatures only too i.e.,

$$\frac{Q_2}{Q_1} = f(T_2, T_1) \quad (13)$$

Now this function must be universal. Now we imagine that another Carnot's engine is working, between temperature T_2 and T_3 i.e., it takes heat from the cold reservoir of the first engine and rejects heat to an even colder reservoir at temperature T_3 .

$$T_1 > T_2 > T_3. \quad (14)$$

For this engine, we have

$$\frac{Q_3}{Q_2} = f(T_3, T_2) \quad (15)$$

But now we can imagine an engine working directly between T_1 and T_3 . In that case we have

$$\frac{Q_3}{Q_1} = f(T_3, T_1) \quad (16)$$

But

$$\frac{Q_3}{Q_1} = \frac{Q_3}{Q_2} \frac{Q_2}{Q_1} \quad (17)$$

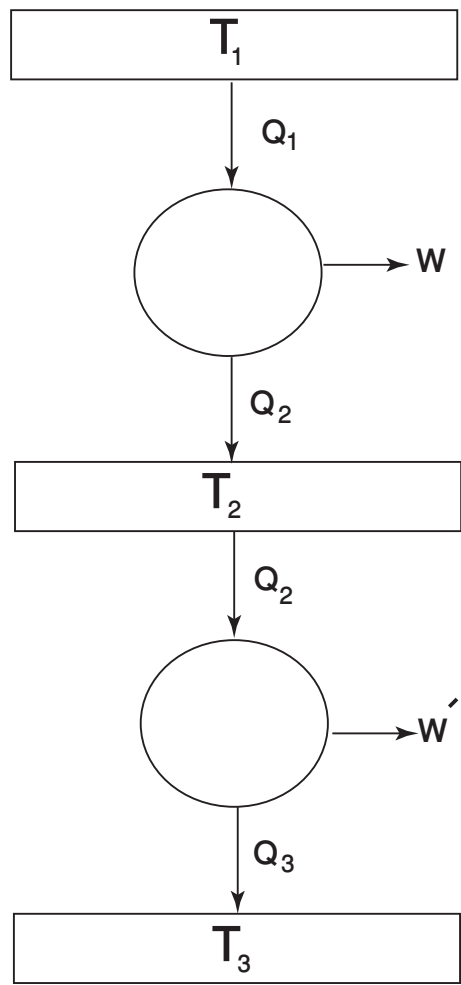


Figure 3: Efficiency of Carnot's Engine and Thermodynamic Temperature

Using above expressions for the ratios of heats in eq (??), we get

$$f(T_3, T_1) = \frac{f(T_3, T_2)}{f(T_1, T_2)} \quad (18)$$

which shows that T_2 must cancel between numerator and denominator as left-hand side depends only on T_3 and T_1 . After we have cancelled it, we are left with some new universal functions of the temperatures

$$f(T_3, T_1) = \frac{T^{th}(T_3)}{T^{th}(T_1)} \quad (19)$$

which finally gives us expression

$$\frac{Q_3}{Q_1} = \frac{T^{th}(T_3)}{T^{th}(T_1)} \quad (20)$$

The function T^{th} is a universal function of our empirical temperature T . As we can always take any monotonic function of the empirical temperature to be a new empirical temperature. We can redefine our temperatures by whatever numerical values we get out of T^{th} . For example, we may have

$$T^{th}(T_1) = T_1^{th}, \quad T^{th}(T_3) = T_3^{th} \quad (21)$$

Then we can write,

$$\frac{Q_3}{Q_1} = \frac{T_3}{T_1} \quad (22)$$

Eq (??) says that in this new temperature scale, the ratio of heats exchanged by a reversible engine is just equal to the ratio of the temperatures of the two reservoirs.

The new temperature scale is called thermodynamic temperature.

“It is defined by eq(??) as the ratio of the temperatures of two bodies is equal to the ratio of heats exchanged by a reversible engine between reservoirs who are at same temperatures as the bodies”

The size of the scale is not determined by above definition, as the temperature is defined only in terms of ratios. Hence we can chose the size as we may like and Kelvin is usually taken. Also notice that it is an absolute scale.

For example, we can take the triple point of water as $273.16K$. Now we put a reservoir at this temperature. Now if we want to measure the temperature of any other body, we put another reservoir, in thermal equilibrium with that body and find out the heats exchanged. The thermodynamic temperature T^{th} of that body will then be given by

$$\frac{Q}{Q_{TP}} = \frac{T^{th}}{T_{TP}^{th} = 273.16K} \quad (23)$$

$$T = 273.16 \frac{Q}{Q_{TP}} K \quad (24)$$

It is a remarkable fact that the temperature appearing in the equation of state of ideal gas is actually thermodynamic temperature.
