Lecture Notes Dated: Oct 19 - 20, 2012

Identity of Thermodynamic Temperature Scale with the Perfect Gas Scale

Suppose that the interval between the freezing and the boiling points of water is divided into 100 equal parts on thermodynamic temperature scale,i.e., $T_{steam}=T_{ice}+100$

Then eq. (87) can be written as

$$\frac{Q_{steam}}{Q_{ice}}=\frac{T_{steam}}{T_{ice}}=\frac{T_{ice}+100}{T_{ice}} \qquad (88)$$

The thermodynamic scale is thus completely defined and fixed. Now we will see its identity with the perfect gas. For a Carnot engine using a perfect gas as the working substance, we know from eq. (34) (here *θ's* are used instead of *T's*, because *T's* are already in use for absolute scale)

$$\frac{Q_1}{Q_2}=\frac{\theta_1}{\theta_2} \qquad (89)$$

where θ_1 and θ_2 are the temperature measured on the perfect gas scale. Eq. (87) combined with (89) yields

$$\frac{T_1}{T_2}=\frac{\theta_1}{\theta_2} \qquad (90)$$

i.e., the ratios of any two temperatures on the thermodynamic scale and the perfect gas scale are equal. Thus the absolute zero of the thermodynamic scale coincides with the zero of the perfect gas thermometer, for if $T_2 = 0$, $\theta_2 = 0$. Further from eq. (88) and (90) since the interval between the ice point and steam point is 100 on both scale, i.e.,

$$T_{steam}-T_{ice}=100$$

and

$$\theta_{steam}-\theta_{ice}=100$$

Hence, on the efficiency of Carnot engine on perfect gas scale is

$$\eta=1-\frac{\theta_{ice}}{\theta_{steam}}=\frac{\theta_{steam}-\theta_{ice}}{\theta_{steam}}=\frac{100}{\theta_{steam}}$$

and on absolute scale is

$$\eta=1-\frac{T_{ice}}{T_{steam}}=\frac{T_{steam}-T_{ice}}{T_{steam}}=\frac{100}{T_{steam}}$$

Since the efficiencies are the same,

$$\frac{100}{\theta_{steam}}=\frac{100}{T_{steam}}$$

thus,

$$\theta_{steam}=T_{steam}$$

i.e., the absolute temperature of the boiling point of water is the same, whether measured on the perfect gas scale or on the thermodynamic scale of temperature. In a similar manner it can be shown that any other temperature will have the same value on the two scales, i.e.,

$$\theta=T \qquad (91)$$

Thus, ***the thermodynamic temperature is, therefore, numerically equal to the perfect gas temperature*** and, in the proper range, may be measured with a gas thermometer.

Absolute Zero

To complete the definition of the thermodynamic scale, we assign the arbitrary value of 273.16 ^{o}K to the temperature of the triple point of water T_{TP}. Thus

$$T_{TP} = 273.16^{o}\,K$$

For a Carnot engine operating between reservoirs at the temperatures T and T_{TP}, we have

$$\frac{Q}{Q_{TP}} = \frac{T}{T_{TP}}$$

or,

$$T = 273.16^{o}\,K\,\frac{Q}{Q_{TP}} \tag{92}$$

that the smaller the value of Q, the lower the corresponding T. The smallest possible value of Q is zero, and the corresponding T is absolute zero. Thus, *if a system undergoes a reversible isothermal process without transfer of heat, the temperature at which this process takes place is called* ***absolute zero***. In other words, at absolute zero, an isotherm and an adiabatic are identical.

A Carnot engine absorbing heat Q_H from a heat reservoir at T_H and rejecting heat Q_L to a sink at T_L. Since,

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

Then it has an efficiency

$$\eta = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

For a Carnot engine to have an efficiency unity, it is clear that T_L must be zero. When the sink is at absolute zero, all the heat from source Q_H will be converted into work by the Carnot engine, which is against the second law. ***A heat engine with 100% efficiency is thus practically impossible***.

The T_L cannot be less than zero, i.e., negative, for if it were so, Q_L would be negative which implies that the engine would be drawing heat both from the source and the sink. However, this contradicts the second law of thermodynamics. Therefore, we may conclude that thermodynamic temperature of ***absolute zero or negative cannot be achieved by any mechanical means***. That is, ***impossibility of attaining the absolute zero*** is implied by second law of thermodynamics.

The Third Law of Thermodynamics

To achieve progressively lower temperatures become more and more difficult. Essentially, it is a fact that lower the temperature, less useful the heat is. This means that to attain absolute zero, an infinite number of adiabatic demagnetisation operation will be needed. This observation is contained in the third law of thermodynamics:

It is impossible to attain the absolute zero by a finite number of operations.

Just like the second law, the third law has a number of equivalent statements. In the light of the first and second laws we can calculate entropy difference only, i.e., we cannot find the absolute value of entropy. This aspect is contained in the third law, which deals with the entropy of a system as its temperature tends to absolute zero.

It was discovered experimentally by Nernst. He observed that the net change in entropy of a system is very small, when there is change from one low temperature equilibrium state to another. For example, we may change liquid helium into solid helium by applying pressure or convert separate samples of sodium and chlorine at, say $4^{o}K$ into sodium chloride at the same temperature. This means that near absolute zero all systems are highly ordered and the entropy of all states (of every substances) is the same; in fact extremely small or essentially zero. Thus we may also state the third law of thermodynamics as follows:

The entropies of all systems and the entropy changes in all reversible isothermal process tend to zero as temperature approaches absolute zero.

Mathematically, we may write

$$\lim_{T\to 0} S \to 0 \qquad (93)$$

and,

$$\lim_{T\to 0} \Delta S \to 0 \qquad (94)$$

Impossibility of Attaining the Absolute Zero

Now we show that impossibility of attaining the absolute zero is equivalent to entropy tending to zero as $T\to 0$. Let us assume the contrary, so that we can operate a Carnot engine between two reservoirs, one maintained at absolute zero and the other at some finite temperature T, as in figure 18.

Figure 18 *T-S diagram of Carnot cycle operating between absolute zero and a finite temperature.*

For a cyclic process, we recall that

$$\Delta S = \oint \frac{\delta Q}{T} = 0$$

But we can write, $\Delta S = \Delta S_{12} + \Delta S_{23} + \Delta S_{34} + \Delta S_{41}$

with, $\Delta S_{12} = \frac{Q}{T}$

where Q is heat absorbed at temperature T. For an adiabatic process,

$$\Delta S_{23} = \Delta S_{41} = 0$$

and by the third law $\Delta S_{34} = 0$

Hence, $dS = \oint \frac{\delta Q}{T} = \Delta S_{12} \neq 0$

But this contradicts the second law of thermodynamics. This inconsistency demands that we cannot operate a Carnot engine using a single reservoir, i.e., ***it is not possible to attain absolute zero***.