ESO201A

Lecture#33

(Class Lecture)

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The Thermodynamic Temperature Scale

It was pointed out earlier that the zeroth law of thermodynamics establishes the basis for the measurement of temperature, but an empirical temperature scale must be defined in terms of the thermometric property of a specific substance and thermometer, such as the ideal-gas temperature scale using the constant-volume gas thermometer. A temperature scale that is independent of the nature of the working substance, which is called an absolute or thermodynamic temperature scale, would be most desirable. We also know from the second proposition of Carnot that the efficiency of a Carnot cycle is independent of the working substance and depends only on the temperatures of high and low-temperature reservoirs, that is, T_H and T_L. The Carnot engine provides the basis for the thermodynamic temperature scale.

A Carnot engine absorbing Q_H amount of heat from a reservoir at a higher temperature T_H and rejecting Q_H amount of heat to a reservoir at a lower temperature T_L has an efficiency of η_{RE} that is independent of the nature of the working substance. The thermal efficiency of such an engine is given by

$$\eta_{RE} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \qquad (1)$$

The thermal efficiency depends only on the two temperatures of the reservoirs,

$$\eta_{RE} = \phi(T_H, T_L) \qquad (2)$$

where $\phi(T_H, T_L)$ is an unknown function of the two temperatures.

From eqs. (1) and (2),

$$\frac{Q_L}{Q_H} = 1 - \eta_{RE}$$

$$\text{or} \quad \frac{Q_H}{Q_L} = \frac{1}{1 - \phi(T_H, T_L)} = f(T_H, T_L) \qquad (3)$$

Let us apply eq. (3) to the three Carnot engines operating between the three reservoirs shown in Fig. 1, where $T_1 > T_3 > T_2$. For engine RE_A,

$$\frac{Q_1}{Q_2} = f(T_1, T_2) \qquad (4)$$

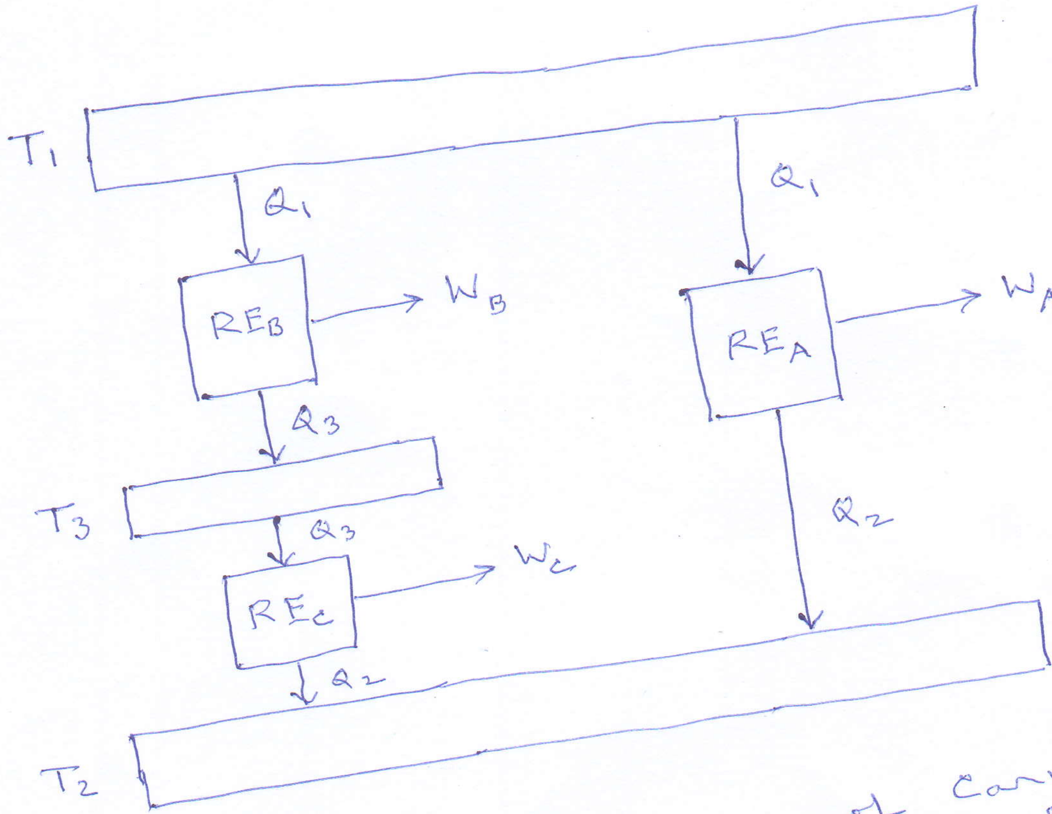

Fig. 1 Schematic diagram of Carnot engines used to demonstrate the thermodynamic temperature scale

Now consider the second carnot engine RE_B and third carnot engine RE_C. Since the heat Q_3 rejected by the second carnot engine RE_B is absorbed by the third carnot engine RE_C, both engines working together are equivalent to the first carnot engine RE_A. Thus, engine RE_B absorbs the same heat Q_1 from the reservoir at T_1 that engine RE_A absorbs. So, for engine RE_B,

$$\frac{Q_1}{Q_3} = f(T_1, T_3) \tag{5}$$

Engine RE_A rejects heat Q_2 to the low-temperature reservoir, so engine RE_C also must also reject Q_2 to the low-temperature reservoir. Thus, for engine RE_C,

$$\frac{Q_3}{Q_2} = f(T_3, T_2) \tag{6}$$

Since $$\frac{Q_1}{Q_2} = \frac{Q_1/Q_3}{Q_2/Q_3},$$

we have the result that

$$f(T_1, T_2) = \frac{f(T_1, T_3)}{f(T_2, T_3)} \qquad (7)$$

Now, the temperature T_3 is arbitrarily chosen; and since it does not appear in the L.H.S. of eq. (7), T_3 must, therefore, drop out of the ratio on the R.H.S. Thus,

$$\frac{Q_1}{Q_2} = \frac{\psi(T_1)}{\psi(T_2)} \qquad (8)$$

where ψ is another unknown function of one temperature.

The ratio on the R.H.S. is defined as the ratio of two thermodynamic temperatures and is denoted by T_1/T_2. We have, therefore, finally,

$$\boxed{\frac{Q_1}{Q_2} = \frac{T_1}{T_2}} \qquad (9)$$

Thus, two temperatures on the thermodynamic scale are to each other as the magnitudes of the heats absorbed and rejected, respectively, by a Carnot engine operating between reservoirs at these temperatures.

It is seen that the thermodynamic temperature scale is independent of the specific characteristics of any particular substance. Thus, the Carnot engine supplies the universality that is lacking in the ideal-gas temperature scale. Finally, the thermodynamic temperatures are called "absolute" temperatures, because they are independent of any material.

Equation (8) is the fundamental relationship based on the second law of thermodynamics and the Carnot cycle. All that is necessary of the arbitrary function ψ is that ψ be a function of the thermodynamic temperature. Any function will do. In 1848, Kelvin was forced to choose a linear function of temperature in eq. (9), because all the scientific and engineering data had been obtained from the mercury-in-glass thermometer, which is essentially linear over its useful range.

To complete the definition of the thermodynamic scale, we proceed to assign the aribrary value of 273.16 K to the temperature of the triple point of water as explained in the early part of this course. Thus,

$$\boxed{T_{TP} = 273.16\ K}$$

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

$$\frac{Q}{Q_{TP}} = \frac{T}{T_{TP}} \tag{10}$$

$$\text{or} \quad T = 273.16 \frac{Q}{Q_{TP}}$$

We also know that the ideal-gas temperature T is defined as

$$T = 273.16 \left(\frac{p}{p_{TP}} \right) \qquad (11)$$

Comparing eqs. (10) and (11) it is seen that, in the thermodynamic scale, Q plays the role of a "thermometric property" for a Carnot cycle, just as pressure is the thermometric property for a constant-volume gas thermometer.

Absolute Zero and Carnot Efficiency

It follows from eq. (10),

$$T = 273.16 \frac{Q}{Q_{TP}}$$

that the smaller the value of Q, the lower the corresponding T. The smallest possible 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.

It should be noted that the definition of absolute zero holds for all substances and is, therefore, independent of the specific properties of any arbitrarily chosen substance. Furthermore, the definition is in terms of purely macroscopic concepts. No reference is made to atoms or molecules.

A Carnot engine is absorbing heat Q_H from a hotter reservoir at T_H and rejecting heat Q_L to a cooler reservoir at T_L has an efficiency

$$\eta_{RE} = 1 - \frac{Q_L}{Q_H}$$

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

we have

$$\boxed{\eta_{RE} = 1 - \frac{T_L}{T_H}} \qquad (12)$$

For a Carnot engine to have an efficiency of 100%, it is clear that T_L must be zero. Only when the lower reservoir is at absolute zero will all heat be converted to work. Since nature does not provide us with a reservoir at absolute zero, a heat engine with 100% efficiency is a practical impossibility.

Equality of Ideal-Gas and Thermodynamic Temperatures

We now demonstrate that the ideal-gas temperature scale discussed earlier is, in fact, identical to the thermodynamic temperature scale, which was defined in the discussion of the carnot cycle and the second law. Our objective can be achieved by using an ideal gas as the working fluid for a carnot-cycle heat engine and analyzing the four processes that make up the cycle. The four state points, 1, 2, 3, and 4, and the four processes are shown in Fig. 2. For convenience, let us consider a unit mass of gas inside the cylinder. Now for each of the four processes, the reversible work done at the moving boundary is given by

$$\delta w = P\,dv \tag{1}$$

Similarly, for each process the gas behaviour is, from the ideal-gas relation,

$$P v = RT \tag{2}$$

where R is the gas constant.

Since for an ideal gas,

$$u = f(T) \text{ only}$$

$$c_{v_0} = \frac{du}{dT} \tag{3}$$

$$\text{or} \quad du = c_{v_0}\, dT$$

The subscript, '0', indicates ideal gas.

Assuming no changes in kinetic and potential energies, the first law is,

$$\delta q = du + \delta w \tag{4}$$

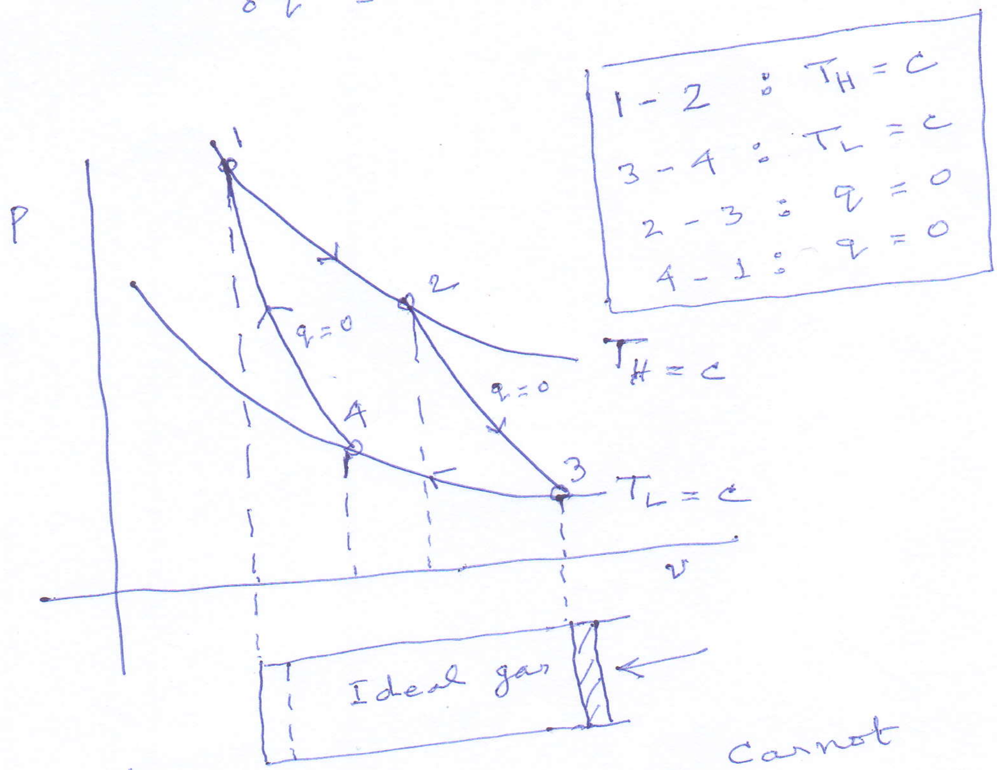

Fig. 2 The ideal-gas Carnot cycle

Substituting eqs. (1), (2), (3) into eq. (4),

$$\delta q = c_{v_0}\, dT + \frac{RT}{v}\, dv \tag{5}$$

The shape of the two isothermal processes shown in Fig. 2 is known, since pv = const. in each case. The process 1 - 2 is an expansion at T_H, such that $v_2 > v_1$. Similarly, the process 3 - 4 is a compression at a lower temperature, T_L, and $v_4 < v_3$.

The adiabatic process 2 - 3 is an expansion from T_H to T_L, with an increase in specific volume, while the adiabatic process 4 - 1 is a compression from T_L to T_H, with a decrease in specific volume. The area below each process line represents the work for that process.

We now proceed to integrate eq. (5) for each of the four processes that make up the Carnot cycle.

For the isothermal heat addition process 1-2, we have

$$q_H = 0 + RT_H \int_{v_1}^{v_2} \frac{dv}{v}$$

$$\Rightarrow q_H = q_{1-2} = 0 + RT_H \ln \frac{v_2}{v_1}$$

$$\Rightarrow q_H = + RT_H \ln \frac{v_2}{v_1} \qquad (6)$$

For the adiabatic expansion process 2-3 we divide by T to get,

$$q_{2-3} = 0 = \int_{T_H}^{T_L} \frac{c_{v_0}}{T} dT + R \int_{v_2}^{v_3} \frac{dv}{v}$$

$$\Rightarrow 0 = \int_{T_H}^{T_L} \frac{c_{v_0}}{T} dT + R \ln \frac{v_3}{v_2} \qquad (7)$$

For the isothermal heat rejection process 3-4,

$$q_L = -q_{3-4} = -0 - RT_L \int_{v_3}^{v_4} \frac{dv}{v}$$

$$\Rightarrow q_L = -q_{3-4} = -0 - RT_L \ln \frac{v_4}{v_3}$$

$$\Rightarrow q_L = + RT_L \ln \frac{v_3}{v_4} \qquad (8)$$

For the adiabatic compression process 4-1 we divide by T to get

$$0 = \int_{T_L}^{T_H} \frac{c_{v_0}}{T} dT + R \ln \frac{v_1}{v_4} \qquad (9)$$

From eqs. (7) and (9), we get

$$-\int_{T_H}^{T_L} \frac{c_{v_0}}{T} dT = \int_{T_L}^{T_H} \frac{c_{v_0}}{T} dT = R \ln \frac{v_3}{v_2} = -R \ln \frac{v_1}{v_4} = R \ln \frac{v_4}{v_1}$$

Therefore,

$$\frac{v_3}{v_2} = \frac{v_4}{v_1} \qquad (10)$$

$$\text{or} \quad \frac{v_3}{v_4} = \frac{v_2}{v_1}$$

From eqs. (6) and (8) and substituting eq. (10), we find that

$$\frac{q_H}{q_L} = \frac{R T_H \ln \frac{v_2}{v_1}}{R T_L \ln \frac{v_3}{v_4}} = \frac{R T_H \ln \frac{v_2}{v_1}}{R T_L \ln \frac{v_2}{v_1}}$$

$$= \frac{T_H}{T_L} \qquad (11)$$

$$\text{or} \quad \frac{Q_H}{Q_L} = \frac{T_H}{T_L}$$

Equation (11) is the definition of the thermodynamic temperature scale in connection with the second law.

Ideal Versus Real Machines

Following the definition of the thermodynamic temperature scale, it was noted that the thermal efficiency of carnot cycle heat engine is given by

$$\eta_{HE} = 1 - \frac{Q_L}{Q_H} \underset{\text{Carnot}}{=} 1 - \frac{T_L}{T_H} \qquad (12)$$

It also follows that a carnot cycle operating as a refrigerator or heat pump will have a COP expressed as

$$COP_R = \frac{Q_L}{Q_H - Q_L} \underset{\text{Carnot}}{=} \frac{T_L}{T_H - T_L} \qquad (13)$$

$$COP_{HP} = \frac{Q_H}{Q_H - Q_L} \underset{\text{Carnot}}{=} \frac{T_H}{T_H - T_L} \qquad (14)$$

For all three "efficiencies" in eqs. (12), (13), (14), the first equality sign is the definition with the use of the energy equation and thus is always true. The second equality sign is valid only if the cycle is reversible, that is, a Carnot cycle. Any real heat engine, refrigerator or heat pump will be less efficient, such that

$$\eta_{\substack{real, \\ HE}} \text{thermal} = 1 - \frac{Q_L}{Q_H} \leq 1 - \frac{T_L}{T_H}$$

$$COP_{R,\,real} = \frac{Q_L}{Q_H - Q_L} \leq \frac{T_L}{T_H - T_L}$$

$$COP_{HP,\,real} = \frac{Q_H}{Q_H - Q_L} \leq \frac{T_H}{T_H - T_L}$$