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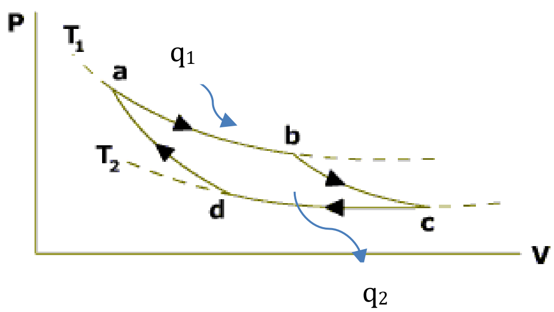
Lecture 12 The 2nd Law of Thermodynamics

(Sec.3.6 of Hess – 2nd Law of Thermodynamics)

[For classical equation editor: ($dq = 0$)]

- ***Claim*:** In a Carnot cycle, $q_2 / q_1 = T_2 / T_1$.



Proof:

Applying the first law of thermodynamics ($dq=c_v dT+pd\alpha$) to the isothermal processes a => b and c => d leads to

$$q_1 = \int_a^b p d\alpha = \int_a^b \frac{RT_1}{\alpha} d\alpha = RT_1 ln \frac{\alpha_b}{\alpha_a} \qquad (12.1)$$

$$q_2 = -\int_c^d p d\alpha = -\int_c^d \frac{RT_2}{\alpha} d\alpha = RT_2 ln \frac{\alpha_c}{\alpha_d} \qquad (12.2)$$

Equations (12.1) and (12.2) gives

$$\frac{q_2}{q_1} = \frac{RT_2 ln(\alpha_c/\alpha_d)}{RT_1 ln(\alpha_b/\alpha_a)} = \left(\frac{T_2}{T_1}\right) \frac{ln(\alpha_c/\alpha_d)}{ln(\alpha_b/\alpha_a)}.$$

Therefore, in order to have $q_2/ q_1 = T_2/ T_1$, it requires

$$\frac{\alpha_c}{\alpha_d} = \frac{\alpha_b}{\alpha_a}. \qquad (12.3)$$

Applying the equation of state,

$$p\alpha=RT$$

to the initial and final states of the isothermal processes *a* => *b* and *d* => *a* and the Poisson's equation,

$$p\alpha^{\gamma} = \text{constant}$$

to the adiabatic processes *b* => *c* and *d* => *a* gives

$$p_a\alpha_a = p_b\alpha_b = RT_1 \qquad (1)$$

$$p_b\alpha_b^{\gamma} = p_c\alpha_c^{\gamma} \qquad (2)$$

$$p_c\alpha_c = p_d\alpha_d = RT_2 \qquad (3)$$

$$p_d\alpha_d^{\gamma} = p_a\alpha_a^{\gamma}. \qquad (4)$$

Eq. (3) gives

$$\frac{\alpha_c}{\alpha_d} = \frac{p_d}{p_c} \qquad (5)$$

Eqs. (2) and (4) gives

$$P_c = P_b(\alpha_b^{\gamma}/\alpha_c^{\gamma})$$

$$P_d = P_a(\alpha_a^{\gamma}/\alpha_d^{\gamma})$$

Substituting p_c and p_d into (5) yields

$$\frac{\alpha_c}{\alpha_d} = \left(\frac{p_a}{p_b}\right)\left(\frac{\alpha_a^{\gamma}\alpha_c^{\gamma}}{\alpha_b^{\gamma}\alpha_d^{\gamma}}\right). \qquad (7)$$

Eq. (1) gives

$$p_a/p_b = \alpha_b/\alpha_a \tag{7}$$

Substituting (7) into (6) leads to

$$\frac{\alpha_c}{\alpha_d} = \frac{\alpha_b}{\alpha_a}, \tag{12.3}$$

which proves $q_2/q_1 = T_2/T_1$.

➢ *The Second Law of Thermodynamics*

The above claim leads to the 2nd Law of Thermodynamics, which concerns about the maximum fraction of a quantity of heat that can be converted into useful work.

From the expression of the efficiency of heat engine:

$$\eta = 1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

Therefore, in order to have a 100% efficiency ($\eta = 1$), T_2 must be zero ($T_2 = 0\ K$). Is it possible? The answer is "no".

The 2nd law of thermodynamics (Kelvin-Planck statement):

It is impossible to construct an engine which operates in a cycle and which produces no other effect than the extraction of heat from a heat reservoir and the performance of an equivalent amount of work.

Alternative statement:

Heat cannot of itself (i.e., without the performance of work by some external agency) pass from a cold to a warm body.