

## Section A. Nomenclature Topics

### Part III. First Law of Thermodynamics

#### Chapter 8. Law of Energy Conservation in Thermodynamics

### LECTURE 9. NOTHING DISAPPEARS

#### § 1.10. The first law of thermodynamics

The **first law of thermodynamics (first beginning)** in the general view represents by itself the **law of conservation and conversion of energy** [113, pp. 24-29], [79, pp. 405-410].

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Let us give a few formulations of the first law.

1. All kinds (sorts, types) of energy are able mutually to convert (transform) in strictly equal to each other quantities (amounts), i.e. (that is) energy does not appear from nothing and does not disappear to nowhere, but transfers from one kind (sort, type) into another instead. The **thermal equivalent of heat**

$$J = \frac{L}{Q} = 4.1868 \text{ J/cal,}$$

if work is measured in Joules, and heat in calories. If work and heat are measured in the same units, then

$$J = 1.$$

The value which is inverse to the thermal equivalent of heat is called the **mechanical equivalent of heat**

$$A = \frac{1}{J} = \frac{Q}{L}.$$

2. It is impossible to create such a periodically acting machine, with the help of which it would be possible to get a useful (helpful) work without spending external energy (from the surroundings, outside), i.e. (that is), drawing (getting, deriving, sourcing) energy out of (from) nowhere. Such a contraption (device, machine, apparatus) is called a **perpetual motion machine** ([COB, p. 216] Latin: *Perpetuum Mobile I*) (**eternal engine**) of the first kind [79, pp. 409, 410], creation, building, and work of which, in accordance with the law of conservation of energy, is impossible.

3. The internal energy of a completely isolated system is the constant value. The proof of this formulation will be given bellow.

Let us write down the equation of the first law of thermodynamics. For this reason let us assume, that some amount of heat  $Q$  is flown into (taken in) the body. This heat will be spent upon the change of the internal energy of  $\Delta U$  and for performing (carrying out, doing, execution) the work of  $L$ . Then, for  $m$  kg of the body's mass the equation of the equivalency will be [113, p. 25, (2.16)]

$$Q = \Delta U + L, \quad (2.16)$$

where  $Q = mq$ ;  $\Delta U = m\Delta u$ ;  $L = ml$ .

For one kg of mass  $m = 1$  the relation of (2.16) will have the view of

$$q = \Delta u + l, \quad (2.16a)$$

where  $q$ ;  $\Delta u$ ;  $l$  – **specific amounts of heat, internal energy change, and work.**

For an **infinitesimally small process** [113, p. 25, (2.17)]

$$dq = du + dl. \quad (2.17)$$

The relation of (2.17) represents by itself the mathematical notation of the equation of the first law of thermodynamics. Following this equation, ***the heat taken in by the body is spent upon the change in internal energy and for doing the work.***



$$\delta l \qquad \delta q .$$

\* \* \* \* \*

**Josiah Willard Gibbs – enthalpy**

[113, p. 26, (2.20)]

$$i = u + pv . \qquad (2.20)$$

\* \* \* \* \*

[113, p. 27, (2.21)]

$$di = du + pdv + vdp . \qquad (2.21)$$

\* \* \* \* \*

*du* form (2.21)

$$du = di - pdv - vdp . \qquad (2.21a)$$

(2.21a) into (2.17) and taking into account (2.18) [113, p. 27, (2.22)]

$$dq = di - pdv - vdp + pdv = di - vdp , \qquad (2.22)$$

where

$$-vdp = dl_0 - \mathbf{available\ work} .$$

Integrating (2.22)

$$q_{1-2} = i_2 - i_1 - \int_{p_1}^{p_2} vdp .$$

\* \* \* \* \*

For available work see fig. 2.5

\* \* \* \* \*

Fig. 2.5

**Filling up – positive work**

$$l_1 = p_1 v_1.$$

\* \* \* \* \*

**Work of expansion (2.19)**

$$l = \int_{v_1}^{v_2} p dv.$$

\* \* \* \* \*

**Pushing out – negative work**

$$l_2 = p_2 v_2.$$

\* \* \* \* \*

**Available work**

$$l_0 = l_1 + l - l_2 = p_1 v_1 + \int_{v_1}^{v_2} p dv - p_2 v_2 = l + l_1 - l_2 = l - (l_2 - l_1),$$

$$l_0 = l - (p_2 v_2 - p_1 v_1).$$

From here [113, p. 28, (2.23)]

$$l = l_0 - p_1 v_1 + p_2 v_2. \tag{2.23}$$

Substituting (2.23) into (2.16a)

$$q = u_2 - u_1 + l_0 - p_1 v_1 + p_2 v_2 = (u_2 + p_2 v_2) - (u_1 + p_1 v_1) + l_0 = i_2 - i_1 + l_0.$$

From here [113, p. 28, (2.24)]

$$dq = di + dl_0. \quad (2.24)$$

The obtained equation coincides with the equation of (2.22). This equation represents by itself the **second mathematical form of notation of the equation of the first law of thermodynamics**.

If  $p = \text{const}$  (**isobaric processes**), then (2.22) will have the view of

$$dq = di.$$

$$q_{1-2} = i_2 - i_1.$$

Thus, the *physical sense of enthalpy is that in isobaric processes the change of enthalpy equals the amount of heat, absorbed or given out by a system*.

**Adiabatic processes,**

$$dq = 0.$$

The equation of (2.22) will be

$$dl_0 = -di,$$

or

$$l_0 = i_1 - i_2.$$

Since enthalpy is a function of the independent parameters of state (state variables), then for its complete differential at the independent variables of  $v, p$ ;  $v, T$ ;  $p, T$  there are correct (true) equations of:

$$di = \left( \frac{\partial i}{\partial p} \right)_v dp + \left( \frac{\partial i}{\partial v} \right)_p dv; \quad (a)$$

$$di = \left( \frac{\partial i}{\partial T} \right)_v dT + \left( \frac{\partial i}{\partial v} \right)_T dv; \quad (b)$$

$$di = \left( \frac{\partial i}{\partial T} \right)_p dT + \left( \frac{\partial i}{\partial p} \right)_T dp. \quad (c)$$

Enthalpy of an ideal gas, as well as internal energy, is a function of temperature only and does not depend upon volume and pressure, because there is absence (there is no presence) of the forces of the interaction between molecules [113, pp. 24-29].

$$i = u(T) + pv = u(T) + RT.$$