

Section A. Nomenclature Topics

Part III. First Law of Thermodynamics

Chapter 10. Heat Capacities

LECTURE 11. HEAT CAPACITY

§ 1.12. Heat capacity

The amount of heat which is necessary to be taken in into a body or withdrawn from it in order to change its temperature in 1 °C is called **heat capacity** [113, pp. 32-36] [79, p. 357]. Heat capacity is calculated by the formula [113, p. 33, (2.37)]

$$C = \frac{dQ}{dT} \text{ [J/K]}. \quad (2.37)$$

Dependently on the quantitative unit of a substance, into which the heat is taken in, there distinguished (differentiated): **mass specific heat capacity** c_x [J/(kg·K)]; **volumetric specific heat capacity** c'_x [J/(m³·K)]; **mole specific heat capacity** c_μ [J/(mol·K)].

The **specific heat capacity**, or simply the **specific heat** (to put it briefly [79, p. 357]), c_x is equal to the ratio of the heat capacity of a uniform body to its mass of m

$$c_x = \frac{C}{m} \text{ [J/(kg·K)]}.$$

Thus, *mass specific heat – this is the heat capacity of a unit mass of a substance (1 kg).*

The ratio of the heat capacity of a body to its volume at the **normal physical conditions** ($p_0 = 101325 \text{ Pa}$, $t_0 = 0^\circ\text{C}$) is called the **volumetric specific heat capacity** c'_x

$$c'_x = \frac{C}{V} = \frac{mc_x}{V} = c_x \rho \text{ [J/(m}^3\cdot\text{K)]}.$$

Thus, **volumetric specific heat** – *this is the heat capacity of a substance in the amount, that occupies at the normal physical conditions the unit volume (1 m^3).*

It is convenient in some cases to apply such a quantity of a unit amount of a substance that equals the molecular weight of μ of this substance. In such a case there used the **mole or molar specific heat capacity** c_μ

$$c_\mu = \frac{C}{n} = \frac{mc_x}{\frac{m}{\mu}} = \mu c_x \text{ [J/(mol}\cdot\text{K)]}.$$

where $n = \frac{m}{\mu}$ – the **number of moles [mol]**; $\mu = m_\mu N_A$ – the **molecular mass [kg/mol]**; where m_μ – the **mass of a molecule [kg/molecule]**; N_A – **Avogadro's number [molecules/mole]**, $N_A = 6.02 \cdot 10^{23}$ molecules/mole [79, p. 381].

Heat capacity depends upon a process character. In thermodynamics the **heat capacities at constant volume** c_v and **constant pressure** c_p , determined by the formulas of [113, p. 33, (2.38)]

$$c_v = \frac{dq_v}{dT}; \quad (2.38)$$

$$c_p = \frac{dq_p}{dT}; \quad (2.39)$$

have a great significance.

These capacities are found in the view of the ratio of the quantity of the heat, transferred in a process at the constant volume or pressure, to the body's temperature change.

From the first law of thermodynamics (2.25)

$$dq = du + pdv, \quad (2.25)$$

$$l = \int_{v_1}^{v_2} dl = \int_{v_1}^{v_2} p dv, \quad (2.19)$$

we get [114, p. 67, (B)]

$$q_{1-2} = u_2 - u_1 + l. \quad (2.25b)$$

Since, for any process of an ideal gas

$$u_2 - u_1 = c_v(T_2 - T_1),$$

and for isobaric process

$$l = p \int_{v_1}^{v_2} dv = p(v_2 - v_1), \quad pv = RT, \quad pv_2 - pv_1 = RT_2 - RT_1 = R(T_2 - T_1), \quad (2.19a)$$

$$l = R(T_2 - T_1), \quad (2.19b)$$

the equation of (2.25b) can be represented in the following view:

$$q_{1-2} = c_v(T_2 - T_1) + R(T_2 - T_1)$$

or [114, p. 68, (r)]

$$q_{1-2} = (c_v + R)(T_2 - T_1). \quad (a)$$

Also, being guided by [114, p. 41, (5.5)]

$$q_{1-2} = c(T_2 - T_1),$$

derived from the definition [114, p. 39, (5.1)]

$$c = \frac{Q_{1-2}}{m(T_2 - T_1)};$$

for isobaric process [114, p. 65, (7.9)]

$$q_{1-2} = c_p(T_2 - T_1). \quad (b)$$

Comparing equations of (a) and (b) we will get

$$c_p(T_2 - T_1) = (c_v + R)(T_2 - T_1)$$

or after cancelling for the difference of

$$T_2 - T_1$$

$$c_p = c_v + R.$$

Having rearranged (transformed, shifted) c_v into the left part of the equation, we have [114, p. 68, (7.11)], which is equivalent to the equation of (2.42)

$$c_p - c_v = R. \quad (2.42)$$

One of the more complicated methods (ways) of derivation of the equation of (2.42) is as follows. The apparatus of thermodynamics differential equations allows finding a series of (few) important relations for heat capacities including the (2.42) [110, pp. 101-103].

Differentiating the relation of (2.20)

$$i = u + pv \quad (2.20)$$

with respect to temperature at

$$p = \text{const},$$

we get [110, p. 102, (4-49)]

$$\left(\frac{\partial i}{\partial T}\right)_p = \left(\frac{\partial u}{\partial T}\right)_p + p \left(\frac{\partial v}{\partial T}\right)_p. \quad (4-49)$$

In order to transform (rearrange) from the partial derivative of

$$\left(\frac{\partial u}{\partial T}\right)_p$$

into the derivative of

$$\left(\frac{\partial u}{\partial T}\right)_v,$$

let us apply the equation of [110, p. 102, (4-13)]:

$$\left(\frac{\partial z}{\partial x}\right)_\xi = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_\xi, \quad (4-13)$$

where z – a function of the two variables [110, p. 95]

$$z = f_z(x, y),$$

for which [110, p. 95, (4-3)]

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy; \quad (4-3)$$

and ξ – a certain parameter of state (state variable) which is constant.

Then, in the given case:

$$z = u, \quad x = T, \quad y = v, \quad \xi = p.$$

Having substituted them into the relation of (4-13) we get [110, p. 102, (4-50)]:

$$\left(\frac{\partial u}{\partial T}\right)_p = \left(\frac{\partial u}{\partial T}\right)_v + \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p. \quad (4-50)$$

Using the relations of [110, p. 99, (4-25)]:

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p, \quad (4-25)$$

and [110, p. 102], [113, p. 34, (2.41)]:

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v,$$

we get [110, p. 102, (4-51)]:

$$\left(\frac{\partial u}{\partial T}\right)_p = \left(\frac{\partial u}{\partial T}\right)_v + \left[T \left(\frac{\partial p}{\partial T}\right)_v - p \right] \left(\frac{\partial v}{\partial T}\right)_p = c_v + T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p - p \left(\frac{\partial v}{\partial T}\right)_p. \quad (4-51)$$

Substituting the (4-51) into the relation of (4-49), and applying the relation of [110, p. 102]:

$$c_p = \left(\frac{\partial i}{\partial T}\right)_p;$$

which is got from the equation of the first law of thermodynamics in the view of [113, p. 27, (2.22), 34]

$$dq = di - vdp \quad (2.22)$$

in a process at a constant pressure

$$dp = 0$$

where we will get [113, p. 34, (2.43)]

$$dq = di, \quad (2.43)$$

then substituting (2.43) into (2.39), we get

$$c_p = \frac{dq_p}{dT} = \left(\frac{di}{dT}\right)_p; \quad (2.39a)$$

we find:

$$c_p = c_v + T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p - p \left(\frac{\partial v}{\partial T}\right)_p + p \left(\frac{\partial v}{\partial T}\right)_p = c_v + T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p.$$

And finally, we have [110, p. 102, (4-52)]

$$c_p - c_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p. \quad (4-52)$$

This important equation, that binds the values of the heat capacities of c_p and c_v between themselves, with the help of the equation of [110, p. 97, (4-12a)]

$$\left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_p \left(\frac{\partial v}{\partial p} \right)_T = -1 \quad (4-12a)$$

(which also could be obtained from the equation of [113, p. 22, (2.14)])

$$\frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T \left(\frac{\partial T}{\partial v} \right)_v} = -1. \quad (2.14)$$

$$\frac{\left(\frac{\partial V}{\partial T} \right)_p}{m} = - \frac{\left(\frac{\partial V}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v}{m}, \quad -1 = \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_p;$$

can also be represented in the view of [110, p. 102, (4-53)]

$$c_p - c_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p = T \left(\frac{\partial p}{\partial T} \right)_v \left[- \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v \right] = -T \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v^2 \quad (4-53)$$

or [110, p. 102, (4-54)]

$$c_p - c_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p = T \left[- \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p \right] \left(\frac{\partial v}{\partial T} \right)_p = -T \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p^2. \quad (4-54)$$

For an ideal gas [110, p. 102]

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{p}{T} \quad \text{and} \quad \left(\frac{\partial v}{\partial T} \right)_p = \frac{v}{T};$$

thus, we get the equivalent to the (2.42) expressions [110, p. 102]

$$c_p - c_v = -T \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v^2 = -T \left[- \left(\frac{\partial T}{\partial p} \right)_v \left(\frac{\partial v}{\partial T} \right)_p \right] \left(\frac{p}{T} \right)^2 = T \left(\frac{T}{p} \right) \left(\frac{v}{T} \right) \left(\frac{p}{T} \right)^2, \quad (4-53a)$$

$$c_p - c_v = \frac{pv}{T} = R.$$

$$c_p - c_v = -T \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p^2 = -T \left[- \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_p \right] \left(\frac{v}{T} \right)^2 = T \left(\frac{p}{T} \right) \left(\frac{T}{v} \right) \left(\frac{v}{T} \right)^2, \quad (4-54a)$$

$$c_p - c_v = \frac{pv}{T} = R.$$

We would also suggest **one more method of the equation by Mayer derivation**, because of the two reasons:

1. The first way might seem doubtful since the quantity of heat transferred in the process of 1-2 is

$$q_{1,2} = u_2 - u_1 + l_{1,2} \quad (2.25b)$$

but here

$$u_2 - u_1$$

might be interpreted as

$$q_{1,2} = u_2 - u_1$$

for isochoric process. But then, all of sudden, we consider this

$$q_{1,2} = u_2 - u_1 + l_{1,2} \quad (2.25b)$$

to be the isobaric one. Which is wrong (see fig. aaaaa).

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Fig. aaaaa

2. On the other hand, the previous method of the equation by Mayer derivation with the use of calculus might seem too complicated for the first familiarization with the fundamentals of thermodynamics.

Therefore, let us consider the isobaric process of 1-2 (see fig. aaaaa)

$$q_{1,2} = u_2 - u_1 + l_{1,2} \quad (2.25b).$$

And here, indeed,

$$q_{1,2} = c_p (T_2 - T_1) \quad (b)$$

by the definition of the specific heat capacity. On the right side, the work is

$$l_{1,2} = p \int_{v_1}^{v_2} dv = p(v_2 - v_1) = R(T_2 - T_1) \quad (2.19a), (2.19b).$$

But the process of 1-2 is not isochoric, and therefore, there is a difficulty in the logical prescription of

$$u_2 - u_1 = c_v(T_2 - T_1).$$

Now, let us consider the isochoric process of 1*-2 (see fig. aaaaa)

$$q_{1^*,2} = u_2 - u_{1^*} + l_{1^*,2}.$$

Here, indeed,

$$l_{1^*,2} = p \int_{v_2}^{v_2} dv = p(v_2 - v_2) = 0,$$

$$q_{1^*,2} = u_2 - u_{1^*} = c_v(T_2 - T_{1^*}).$$

Though the states of 1 and 1* are different, their temperatures are the same, as they lie (are positioned) on the same isotherm of T_1 . So

$$T_1 = T_{1^*}.$$

And the increment of the internal energy then is also the same for the processes of 1-2 and 1*-2

$$u_2 - u_1 = u_2 - u_{1^*}.$$

It does not depend upon the path of a process at all. Therefore

$$q_{1^*,2} = c_v(T_2 - T_1) = u_2 - u_1.$$

Then

$$q_{1,2} = c_p(T_2 - T_1) = c_v(T_2 - T_1) + R(T_2 - T_1).$$

And finally

$$c_p = c_v + R.$$

Thus

$$c_p - c_v = R. \quad (2.42)$$

In thermodynamics the **ratio of the heat capacities** has a great importance (significance) [113, p. 34, (2.44)]

$$k = \frac{c_p}{c_v}, \quad (2.44)$$

where k – the index of adiabatic curve power; $k \approx 1.67$ – for monatomic (monatomic [79, p. 390]), $k \approx 1.4$ – for diatomic (diatomic [79, p. 381]), $k \approx 1.29$ – for three-atomic gases.

The value of k depends upon the temperature. From (2.44) with taking into consideration the equation by Mayer (2.42), we will get [113, p. 34, (2.45)]

$$k = \frac{c_p}{c_v} = \frac{c_v + R}{c_v} = 1 + \frac{R}{c_v}, \quad (2.45)$$

or for one mole

$$k = 1 + \frac{8.314}{\mu c_v}.$$

Since c_v increases as the temperature of a gas raises, then the value of k decreases, tending to one, but being always more than that.

Knowing the value of k , from (2.45) it is possible to determine the value of the specific heat capacity at a constant volume

$$k = 1 + \frac{R}{c_v}, \quad \frac{R}{c_v} = k - 1, \quad c_v = \frac{R}{k - 1} \text{ [kJ/(kg}\cdot\text{K)]}.$$

Since

$$c_p = k c_v,$$

then

$$c_p = \frac{k}{k - 1} R.$$

As far as heat capacity of an ideal gas depends upon the temperature, and for a real gas upon the pressure as well, then in engineering thermodynamics there divided (distinguished, differentiated) the real (true, actual, factual) and mean heat capacity.

The heat capacity, defined as the ratio of the elementary heat quantity, supplied to (absorbed by) (supplied, absorbed [79, p. 360]) a thermodynamic system, to the infinitesimal temperature difference, is called the real heat capacity

$$C = \frac{dQ}{dT}.$$

Factual heat capacities of real gases can be expressed in the view of the sum of the two components [113, p. 35, (2.46)]

$$C = C_0 + \Delta C, \quad (2.46)$$

where C_0 – the heat capacity of the given gas in the state of rarefaction (at $p \rightarrow 0$ or $v \rightarrow \infty$) which depends only upon the temperature; ΔC – determines the dependence of the heat capacity upon the pressure or specific volume.

The temperature dependence of the heat capacity can approximately be represented in the view of a polynomial expression of the third power with respect to temperature

$$C_0 = a_0 + a_1t + a_2t^2 + a_3t^3,$$

where a_0, a_1, a_2, a_3 – coefficients of the approximation.

In practical calculations at the determination of the heat quantity there usually applied the so called **mean heat capacities**.

The ratio of the heat amount of q_{1-2} , transferred in the process, to the finite temperature difference of $t_2 - t_1$ is called the mean specific heat capacity \bar{c} of the given process in the temperature interval from t_1 up to t_2 [113, p. 35, (2.47)]

$$\bar{c} = \frac{q_{1-2}}{t_2 - t_1}. \quad (2.47)$$

The amount of the heat transferred in the process is being found by the formula [113, p. 35, (2.48)]

$$q_{1-2} = \int_{t_1}^{t_2} c dT, \quad (2.48)$$

where c – the actual specific heat capacity.

The formula of (2.47) with taking into account (2.48) acquires the view of

$$\bar{c} = \frac{\int_{t_1}^{t_2} c dT}{t_2 - t_1}.$$

When heat installations are calculated, one has to deal with some gas mixtures, though in tables there are heat capacities for special ideal gases only. Therefore, one should be able to determine heat capacities of gas mixtures. If a mixture of gases is given by the mass portions, then the specific heat capacity of the mixture is being determined by the formulas (formulae)

$$c_{v_{mix}} = \sum_{i=1}^n g_i c_{v_i} ;$$

$$c_{p_{mix}} = \sum_{i=1}^n g_i c_{p_i} ,$$

where g_i , ($i = 1, 2, \dots, n$) – mass portions of the each gas, composing the gas mixture.

If a mixture of gases is given by the volumetric portions of r_i , ($i = 1, 2, \dots, n$), then the specific volumetric heat capacity of the mixture will be determined by the formulas (formulae)

$$c'_{v_{mix}} = \sum_{i=1}^n r_i c'_{v_i} ;$$

$$c'_{p_{mix}} = \sum_{i=1}^n r_i c'_{p_i} ,$$

where c'_{v_i} , c'_{p_i} – volumetric heat capacities of the each gas [113, pp. 32-36].