



FIRST AND SECOND LAWS OF THERMODYNAMICS

[Content]

- Enthalpy and the caloric equation of state
- Wording and equation of the first law of thermodynamics
- The first law of thermodynamics for the working medium flow

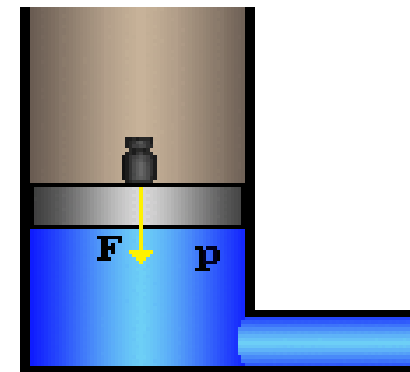
[Enthalpy]

- total energy of an expanded system, including working medium and the environment

$$H = U + p \cdot V, \text{ J}$$

- specific enthalpy

$$h = u + p \cdot v, \text{ J/kg}$$



Caloric equation of the system state

for equilibrium state:

$$h = f(p, T),$$

where h – specific enthalpy

Wording of the first law of thermodynamics

- Perpetual motion machine of the first kind is impossible.

First law of thermodynamics

The first law of thermodynamics is the quantitative expression of the law of conservation and transformation of energy for the goals of thermodynamics.

- The notion of energy is inseparably linked with the matter motion: energy is a physical measure of the matter motion, and the law of conservation and transformation of energy expresses the fact of indestructibility of the material world motion.
- Based on the law of conservation and transformation of energy can be determined the precise quantitative relationships between different forms of energy.

Wording of the first law of thermodynamics

- Energy of an **isolated system** is a constant value

$$E_1 = E_2 = \text{const}$$

- heat Q delivered to the thermodynamic system is used to change the system energy ($E_2 - E_1$) and do the work L :

$$Q = E_2 - E_1 + L, \text{ J}$$

$$q = e_2 - e_1 + l, \text{ J/kg}$$

where $(e_2 - e_1)$ – specific energy change, J/kg

Wording of the first law of thermodynamics

- **Perpetual motion machine of the first kind is impossible.**
- Previously, it was found that total energy of the fixed thermodynamic system equals its internal energy U .
- Based on this, in expression $Q = E_2 - E_1 + L$ we replace energy change $(E_2 - E_1)$ with internal energy change $(U_2 - U_1)$, and work L with expansion (compression) work L_v .

Equation of the first law of thermodynamics

- Based on this, analytical expression of the first law of thermodynamics for m kg is written as:

$$Q = U_2 - U_1 + L,$$

- i.e., heat Q delivered to the system is used to change the internal energy ($U_2 - U_1$) and do the expansion (compression) work. For 1 kg of substance the first law of thermodynamics can be written as:

$$q = u_2 - u_1 + l \quad l = \int p dv \quad q = u_2 - u_1 + \int p dv$$

In the differential form:

$$dq = du + p dv$$



SECOND LAW OF THERMODYNAMICS

Content

- Wording of the second law of thermodynamics
- Entropy
- Thermodynamic identity

Wording of the second law of thermodynamics

“Heat cannot by itself pass from a colder to a hotter body, i.e., without compensation”

Clausius (1850)

“Not all of the heat received from heat source can be converted into work, but only a certain part of it. Another part of it must inevitably go into the heat sink”.

Thomson (1851)

“Perpetual motion machine of the second kind is impossible”


Ostwald (1892)

Wording of the second law of thermodynamics

1. In an engine running on a cycle it is not possible to convert all the quantity of heat, received from the heat source, into work.
2. Heat flow is always directed toward the lower temperature.

Statistical formulation of the second law of thermodynamics

- A closed system of many particles is spontaneously converted from a more ordered into a less ordered state (or from a less probable to a more probable).

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- A large black left square bracket is on the left side of the slide. A large yellow right square bracket is on the right side. A horizontal line with a yellow-to-white gradient runs across the slide, starting from the left bracket and ending at the right bracket.
- The second law of thermodynamics is a consequence of the irreversibility of thermal processes.

Entropy

$$ds = dq/T, \quad \text{J}/(\text{kg}\cdot\text{K})$$

Clausius (1850)

ds is a total differential

S is a function of the system state and is unambiguously determined by any two thermodynamic parameters:

$$s = s_1(p, v)$$

$$s = s_2(p, T)$$

$$s = s_3(v, T)$$

$$s = s_4(p, h)$$

etc.

Entropy

$$ds = dq/T, \quad \text{J}/(\text{kg}\cdot\text{K})$$

Clausius (1850)

ds is a total differential

s is a function of the system state and is unambiguously determined by any two thermal or caloric parameters:

$$s = s_1(p, v)$$

$$s = s_2(p, T)$$

$$s = s_3(v, T)$$

$$s = s_4(p, h)$$

etc.

Entropy

Entropy S for mass m of gas equals:

$$S = m \cdot s, \text{ J/K}$$

As zero entropy for gas is taken on a value $s_0 = 0$ at temperature $T = 0 \text{ }^\circ\text{C}$.

Caloric parameters of state

Caloric parameters u , h , s unambiguously describe any state of a thermodynamic system.

Caloric u , h , s and thermal p , v , T parameters possess unambiguous correspondence.

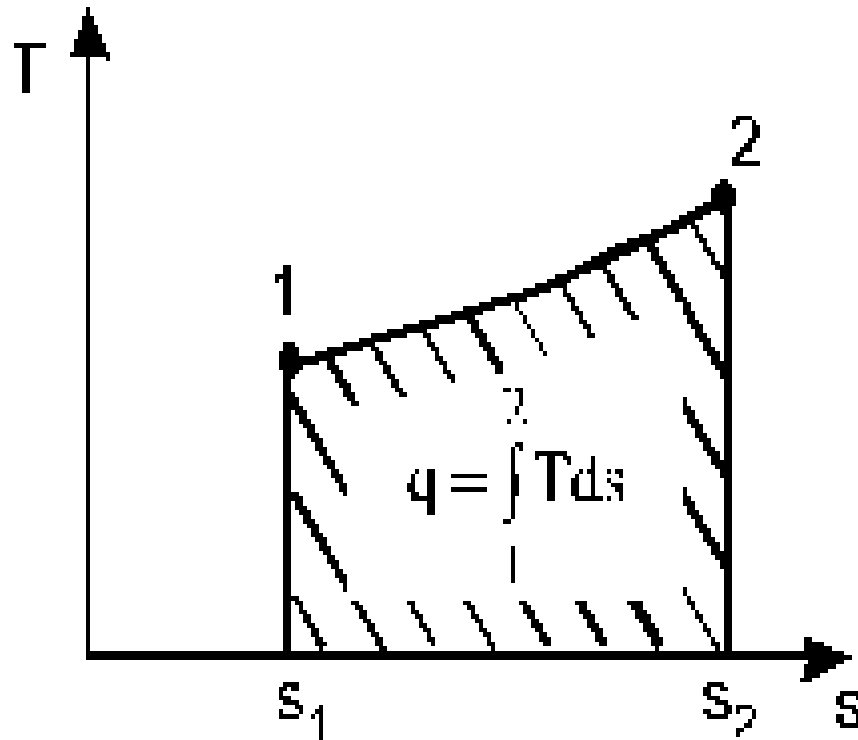
Thermodynamic identity

or basic equation of thermodynamics

$$Tds = du + pdv$$

is obtained from $dq = du + pdv$ and $dq = Tds$

Ts-diagram



$$q = \int_{s_1}^{s_2} T ds$$



THERMODYNAMICS

IDEAL GAS PROCESSES

Content

- Thermodynamic processes research method
- Ideal gas
- Polytropic process
- Analysis of the basic ideal gas processes

THERMODYNAMIC PROCESSES RESEARCH METHOD

The main goal of the study of thermodynamic processes is to find:

- the finite state parameters, achieved by the process;
- work done;
- heat, transferred during the process.

Thermodynamic studies are based on the first and second laws of thermodynamics, allowing to obtain the calculated ratios for specific processes.

THERMODYNAMIC PROCESSES RESEARCH METHOD

To calculate the reversible processes required:

- thermal equation of state $f(p, v, T) = 0$
- state functions u, h, s , etc.

or

- Dependences of heat capacity c_p or c_v on parameters state

When calculating the irreversible processes, finite parameters can be determined by replacing irreversible transition from state 0 to state 1 with reversible one.

[Notion of ideal gas]

Notion of ideal gas is a scientific abstraction, which is a limiting case of real gases diluted:

- no interaction forces between molecules;
- molecular size is much smaller than intermolecular distances.

Ideal gas equation

✓ *Clapeyron* (1834)

■ $pv=RT$

where R – gas constant, $J/(kg \cdot K)$

✓ for mass m

■ $pV=mRT$

where V - volume, occupied by gas, m^3

✓ for one kmol

■ $pV_{\mu} = R_{\mu} T$

where V_{μ} – molar volume, $m^3/kmol$

$R_{\mu} = 8314,4$ – molar gas constant, $J/(kmol \cdot K)$

Molar gas constant

$$R_{\mu} = \frac{p_0 V_{\mu 0}}{T_0} = \frac{1,0133 \cdot 10^5 \cdot 22,4}{273,15} = 8314 \quad J/(kmol \cdot K)$$

Knowing R_{μ} , can be found a gas constant R for any gas, using the value of its molecular mass μ :

$$R = \frac{R_{\mu}}{\mu}$$

The molar mass μ kg/kmol for some gases have the following values: nitrogen – 28, ammonia – 17, argon – 40, hydrogen – 2, air – 29, oxygen – 32, carbon oxide – 28, carbon dioxide – 44.

Heat capacity, enthalpy and entropy of ideal gases

- The dependence of heat capacity of ideal gas on the parameters can be determined based on the general ratios. In addition, for ideal gas:

$$\left(\frac{du}{dv}\right)_T = 0 \quad \text{and} \quad \left(\frac{dh}{dp}\right)_T = 0$$

- whereby, heat capacities c_p and c_v of ideal gas depend on temperature only

$$c_p, c_v = f(T)$$

Mayer equation

$$c_p - c_v = R$$

Polytropic process

The process, characterized by a constant value of heat capacity c_n , is called **polytropic**.

General thermodynamic equation for any processes can be obtained from the equations:

- First law of thermodynamics $dq = c_v dT + p dv$
- Clapeyron $p v = RT$
- Mayer $c_v = c_p + R$

Solving these equations, we obtain:

$$n = \frac{c_p - c_n}{c_v - c_n} \quad n \frac{dv}{v} + \frac{dp}{p} = 0$$

where n – polytropic index

Polytropic process equation

- After integration we obtain **the equation of polytropic process**

$$pv^n = \text{const}$$

- Using the ideal gas equation $pv = RT$, we obtain:

$$Tv^{n-1} = \text{const} \quad Tp^{\frac{1-n}{n}} = \text{const}$$

- The expression for **heat capacity of a polytropic process**

$$c_n = c_v \frac{n-k}{n-1} = c_v - R(n-1)$$

- where $k = \frac{c_p}{c_v}$ – Poisson ratio

Change of internal energy and enthalpy in the polytropic processes of ideal gas

$$\Delta u = u_2 - u_1 = c_v (T_2 - T_1)$$

$$\Delta h = h_2 - h_1 = c_p (T_2 - T_1)$$

Polytropic process heat

$$q = c_n (T_2 - T_1)$$

$$q = c_v \frac{n - k}{n - 1} (T_2 - T_1)$$

Specific work of polytropic process expansion

$$\ell = \int p dv = \frac{R}{n-1} (T_1 - T_2)$$

Factor out T_1 and replace RT_1 with $p_1 v_1$

$$\ell = \frac{p_1 v_1}{n-1} \left(1 - \frac{T_2}{T_1}\right)$$

or

$$\ell = \frac{p_1 v_1}{n-1} \left(1 - \frac{p_2}{p_1} \cdot \frac{n-1}{n}\right)$$

Specific technical work

Work of 1 kg of gas in a continuous flow is linked with expansion work by the following dependence

$$l_{tech} = l + p_1 v_1 - p_2 v_2$$

For ideal gas $pv = RT$, then

$$l_{tech} = l - R(T_2 - T_1)$$

Substituting the value l , we write

$$l_{tech} = \frac{n}{n-1} R(T_1 - T_2)$$

$$l_{tech} = n l$$

Special cases of polytropic process

- $n=0$ – isobaric process
- $n=1$ – isothermal process
- $n=\infty$ – isochoric process
- $n=k$ – adiabatic process

Analysis of the basic ideal gas processes

Processes in pv-diagram, Ts-diagram

- isobaric process
- isothermal process
- isochoric process
- adiabatic process

Analysis of the basic ideal gas processes

Parameters ratio

- isobaric process
- isothermal process
- isochoric process
- adiabatic process

Analysis of the basic ideal gas processes

The change in internal energy, enthalpy, and entropy

- isobaric process
- isothermal process
- isochoric process
- adiabatic process

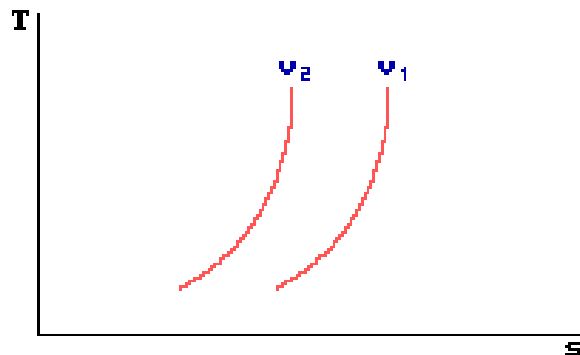
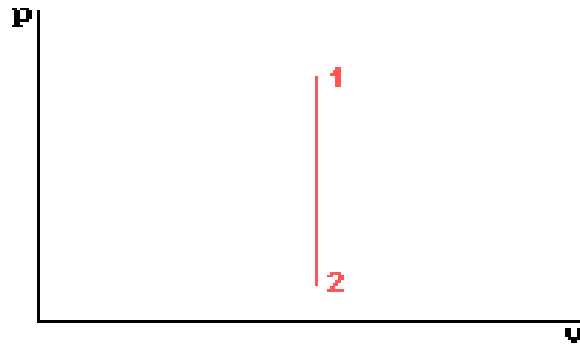
Analysis of the basic ideal gas processes

Heat and work

- isobaric process
- isothermal process
- isochoric process
- adiabatic process

ISOCHORIC PROCESS

- In the isochoric process, specific volume v remains constant, but pressure and temperature of the working medium change.



$$v_1 > v_2$$

Isochores in Ts-coordinates are logarithmic curves. The smaller the value of specific volume v , the more to the left will pass an isochore, i.e., the smaller the entropy value will be at a predetermined temperature T .

As for ideal gas $h = c_p T$, then h - s -diagram will bear a complete similarity to T - s -diagram.

ISOCHORIC PROCESS

Using the equation of ideal gas state $pv = RT$, we obtain the process equation

$$\frac{p_2}{p_1} = \frac{T_2}{T_1}$$

Polytropic index of isochoric process:

$$n = \frac{c_p - c_v}{c_v - c_v} = \pm\infty$$

Process specific heat:

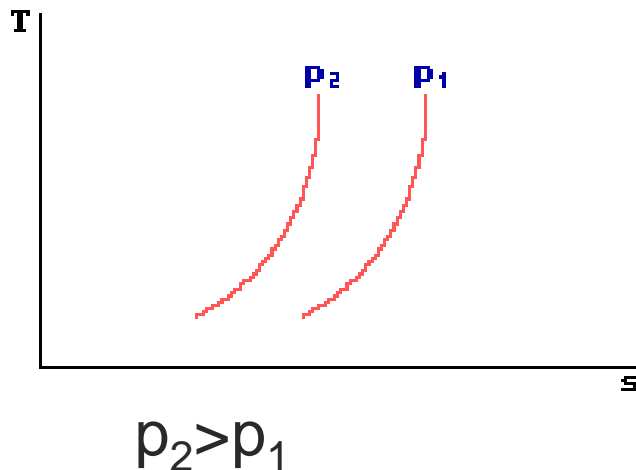
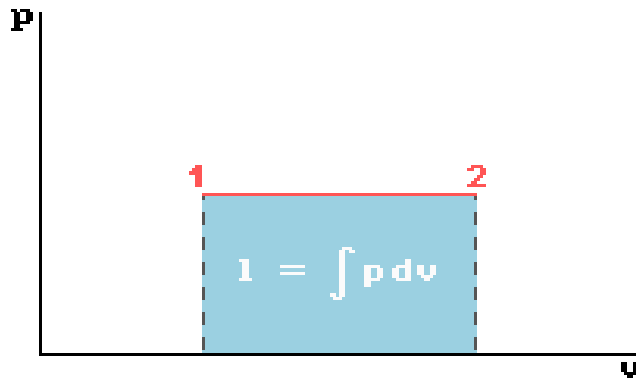
$$q_v = u_2 - u_1 + \int p dv = u_2 - u_1 = c_v (T_2 - T_1)$$

Specific work of volume change:

$$dl_v = p dv = 0 \qquad \ell_v = 0$$

ISOBARIC PROCESS

In the isobaric process, pressure p remains constant, but volume and temperature of the working medium change.



Isobars, like isochores, are logarithmic curves.

As $c_p > c_v$, then $\Delta s_p > \Delta s_v$, so isobars become flatter than isochores.

Higher pressure isobars are located to the left of the lower pressure isobars.

ISOBARIC PROCESS

- Using the equation of ideal gas state $pv = RT$, we obtain the process equation

$$\frac{v_2}{v_1} = \frac{T_2}{T_1}$$

- Polytropic index of isobaric process:

$$n = 0$$

- Process specific heat:

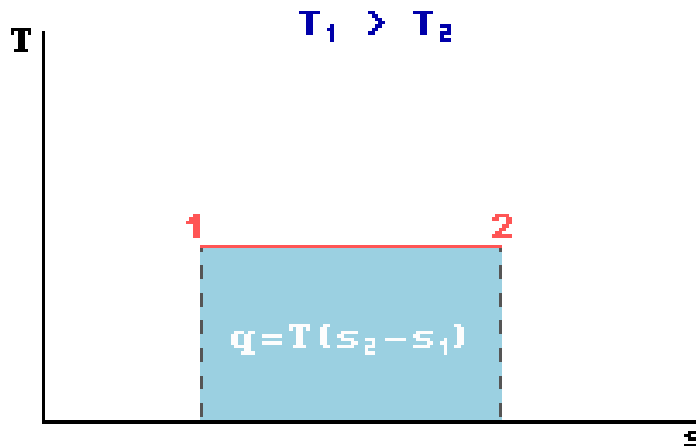
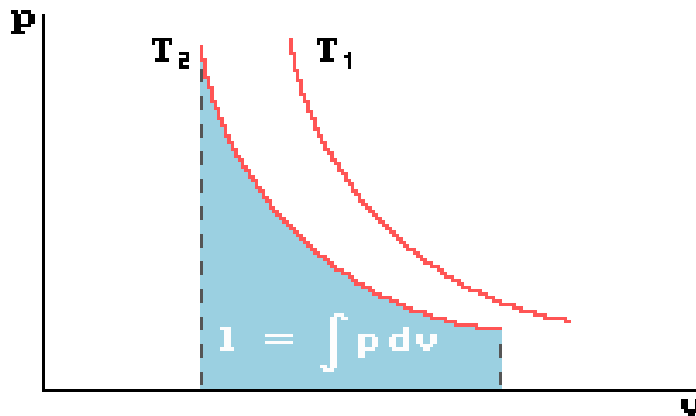
$$q_p = h_2 - h_1 - \int v dp = h_2 - h_1 = c_p (T_2 - T_1)$$

- Specific work of volume change:

$$d\ell_p = p dv \quad \ell_p = p(v_2 - v_1) = R(T_2 - T_1)$$

ISOTHERMAL PROCESS

In the isothermal process, temperature remains constant, but pressure and specific volume of the working medium change.



Isotherm in p - v -coordinates is an equilateral hyperbola. In p - v -diagram isotherm is an equilateral hyperbole, but in T - s -diagram – a horizontal line.

ISOTHERMAL PROCESS

- Using the equation of ideal gas state $pv = RT$, we obtain the process equation

$$\frac{p_2}{p_1} = \frac{v_2}{v_1}$$

- Process polytropic index:

$$n = 1$$

- Process heat capacity $c_t = \pm\infty$

- Change in internal energy and enthalpy equals:

$$\Delta u_t = \Delta h = 0$$

- In the isothermal process of ideal gas its internal energy and enthalpy remain constant.

ISOTHERMAL PROCESS

- To calculate the amount of heat delivered, use the first law of thermodynamics

$$dq = du + pdv$$

- As $du = 0$ $q = \ell = \int pdv$

- Replace p with RT/v and obtain after integration

$$q = \ell = RT \ln \frac{v_2}{v_1} = RT \ln \frac{p_1}{p_2}$$

- For the isothermal process the expansion work equals the technical work.

This follows because the isotherm in pv -coordinates is an equilateral hyperbola.

ADIABATIC PROCESS

- In the adiabatic process, heat is not delivered to or rejected from the working medium.
- For the reversible adiabatic processes, entropy remains a constant value $s = \text{const}$, since $dq = Tds = 0$.
- At the adiabatic expansion or compression, temperature, pressure, and volume of gas change.
- Heat capacity of the adiabatic process $c_s = 0$, since $dq = cdT = 0$

ADIABATIC PROCESS

- Polytropic index:

$$n = \frac{c_p}{c_v} = k$$

where k – adiabatic index or Poisson ratio

- All ratios given are obtained by replacing the polytropic index n with the adiabatic index k

- Equation of adiabatic process: $p v^k = \text{const}$

- whereof $T v^{k-1} = \text{const}$ $T p^{\frac{1-k}{k}} = \text{const}$

ADIABATIC PROCESS

- Specific work of expansion (compression):

$$\ell = \frac{R}{k-1} (T_1 - T_2) \quad \ell = \frac{p_1 v_1}{k-1} \left(1 - \frac{p_2}{p_1} \cdot \frac{k-1}{k} \right)$$

- Specific technical work:

$$\ell_{tech} = \frac{k}{k-1} R (T_1 - T_2)$$

- or $\ell_{tech} = k\ell$

- All ratios given hold only for **monatomic ideal gases**, since their heat capacities c_v and c_p don't depend on temperature.
- **For di- and polyatomic gases** $c_v, c_p = f(T)$ and, consequently, the adiabatic index $k = f(T)$ also depends on temperature.

Behavior of the adiabatic process in pv- and Ts-diagrams

Show that in pv-diagram adiabatic is of the form of a hyperbole, which is steeper than an isotherm.

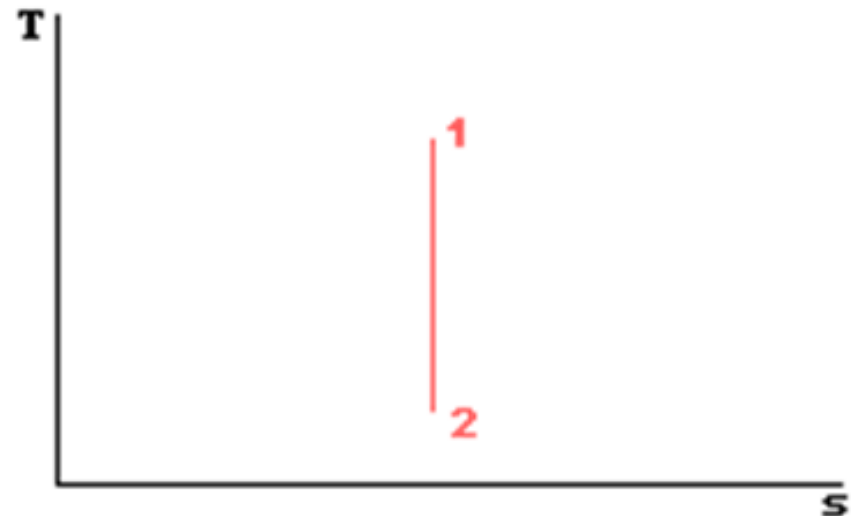
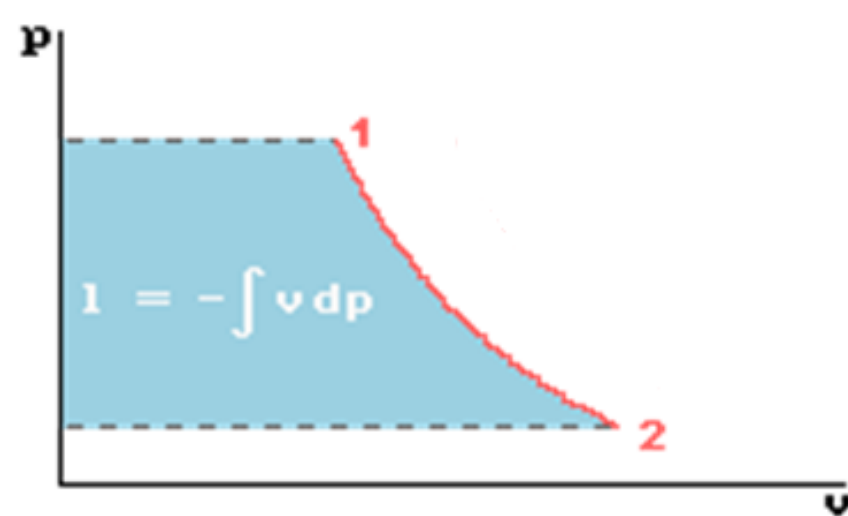
After differentiating the equations of isothermal $pv = \text{const}$ and adiabatic processes $pv^k = \text{const}$, we obtain

$$\left(\frac{\partial p}{\partial v}\right)_t = -\frac{p}{v} \qquad \left(\frac{\partial p}{\partial v}\right)_s = -k \frac{p}{v}$$

i.e., an adiabatic is k times steeper than an isotherm.

In Ts-diagram, a reversible adiabatic is shown as a vertical line.

Behavior of the adiabatic process in pv- and Ts-diagrams





MIXTURES OF IDEAL GASES

[Content]

- Gas mixture design
- Gas mixture laws

BASIC NOTIONS AND DEFINITIONS

- Thermodynamic processes don't usually involve pure gases but gas mixtures
 - air - gas mixture mainly consisting of nitrogen and oxygen;
 - products of combustion in furnaces of steam boilers and internal combustion engines, etc.
- Each gas mixture is subject to the same thermodynamic laws as homogeneous gases
- For gas mixtures go through all equations obtained for pure gases

Mixture of ideal gases

- A mixture consists of several ideal gases, which don't react with one another;
- Some gases, included in the mixture, are called **mixture components**;
- The main goal of calculating gas mixtures is to determine the thermal parameters (pressure and volume) and state functions (internal energy, enthalpy, entropy, etc.)

Gas mixture design

- To characterize gas mixture design, the notion of *concentration* is introduced.
- Depending on the measurement units of components, the following kinds of concentration are given:
 - mass concentration **g**;
 - molar concentration **z**;
 - volume concentration **r**.

MASS CONCENTRATION

- Let m denote the mixture mass, and m_1, m_2, m_3 , etc., denote the mass of each component (gas) included in the mixture, then total mixture mass equals

$$m = m_1 + m_2 + m_3 + \dots$$

- Hence, mass concentrations (fractions) of separate components g_1, g_2, g_3 , etc., equal

- or
$$g_1 = \frac{m_1}{m} \quad g_2 = \frac{m_2}{m} \quad g_i = \frac{m_i}{m}$$

$$g_1 + g_2 + g_3 + \dots = 1$$

- i.e., the sum of all mass fractions equals one.

VOLUME CONCENTRATION

- Let v denote the mixture volume, having pressure p and temperature T , and V_1, V_2, V_3 , etc., denote the volume of a separate component (gas) at pressure and temperature of the mixture, then the total mixture volume equals

$$V = V_1 + V_2 + V_3 + \dots,$$

where V_1, V_2, V_3, \dots - partial volumes of mixture components

- Additivity rule for the mixture volume of ideal gases v is due to the fact that each mixture component behaves “independently” with respect to the other gases, since there is no interaction between molecules (mass points) of ideal gas.

VOLUME CONCENTRATION

- Given this issue, volume concentrations (fractions) of the components r_1, r_2, r_3, \dots equal

or

$$r_1 = \frac{V_1}{V} \quad r_2 = \frac{V_2}{V} \quad r_3 = \frac{V_3}{V}$$

$$r_1 + r_2 + r_3 + \dots = 1,$$

- i.e., the sum of all volume fractions equals one.

Relationship between the mass and volume concentrations

$$g_i = \frac{m_i}{m} = \frac{V_i}{V} \cdot \frac{\rho_i}{\rho} = r_i \cdot \frac{\rho_i}{\rho}$$

$$r_i = \frac{V_i}{V}$$

Gas mixture laws

- Dalton law
- Clapeyron equation
- Avogadro law

Partial volumes and partial pressures of gas mixture

- Assume that in the cylinder of constant volume at the pressure p and temperature T is stored gas mixture, e.g., air, consisting of nitrogen and oxygen (neglecting other components).
- In case of removing nitrogen at a constant temperature T from the cylinder, the pressure of oxygen decreases to a value called the *partial oxygen pressure* in the mixture.
- **Partial pressure p_i** – pressure that a gas mixture component has if itself, at the same temperature, fills the whole mixture volume V .

Dalton law

Total mixture pressure p equals the sum of partial pressures of separate gases:

$$p = p_1 + p_2 + \dots + p_n = \sum_{i=1}^n p_i .$$

THERMODYNAMIC STATE FUNCTIONS

- The fact that ideal gas possesses no interaction forces between molecules allows calculating thermodynamic properties and state functions based on the additivity rule, which greatly simplifies the calculations.

Consequently:

- mixture internal energy $u = \sum g_j u_j$;
- mixture enthalpy $h = \sum g_j h_j$

HEAT CAPACITY OF IDEAL GASES MIXTURE

- isochoric heat capacity of mixture $c_v = \sum g_j c_{vj}$
- isobaric heat capacity of mixture $c_p = \sum g_j c_{pj}$

Clapeyron equation

$$p_i V = m_i R_i T$$