

2 Thermodynamics

2.1 Fundamental laws

The first law of thermodynamics is a statement of the principle of conservation of energy. For a system of constant mass the first law may be stated thus:

The amount of work done on or by a system is equal to the amount of energy transferred to or from the system.

In other words energy cannot be created or destroyed during a process, although it may change from one form of energy to another.

The second law of thermodynamics is more abstract, but may be formulated thus:

Heat cannot, of itself, pass from a colder to a hotter body.

This means that energy exists at various temperature levels and is available for use only if it can move from a higher to a lower level.

2.2 Ideal gases

An ideal gas is one that follows the perfect gas equation without deviation.

Boyle's law states that, if the temperature is held constant, the product of pressure and volume will be constant; or, in other words, the absolute pressure of a gas changes in inverse proportion to the volume

$$p_1 V_1 = p_2 V_2$$

If the volume is halved, the pressure is doubled.

A telescopic gas-holder is a constant pressure con-

tainer. The volume of the gas-holder varies with changes in gas temperature or quantity.

The cylinder in figure 1:8 contains gas molecules. When the piston is pushed down, the gas is forced to occupy a smaller space. The gas exerts more force on each square centimetre it touches and gas pressure increases. If the cylinder holds one cubic metre of air at an effective pressure of 1 bar, it has an absolute pressure of 2 bar. If the gas is compressed to half its original volume, with the temperature constant, the new absolute pressure of the gas will be 4 bar.

Charles' law states that the volume of a gas changes in direct proportion to changes in absolute temperature.

$$V_1/T_1 = V_2/T_2 \text{ or } \Delta V = V_1/T_1 \cdot \Delta T$$

Example: If 10 cubic metres of an ideal gas is heated from +15°C to +44°C at constant pressure, what is the new volume?

The absolute temperature $T_1 = 15 + 273 = 288 \text{ K}$

The absolute temperature $T_2 = 44 + 273 = 317 \text{ K}$

Applying Charles' law

$$10/288 = V_2/317$$

Answer:

$$V_2 = 10 \cdot 317/288 = 11 \text{ cubic metres.}$$

If the gas had instead been cooled from +15°C to -14°C the new volume would have been:

$$T_1 = 15 + 273 = 288 \text{ K}$$

$$T_2 = -14 + 273 = 259 \text{ K}$$

$$10/288 = V_2/259$$

$$V_2 = 10 \cdot 259/288 = 9 \text{ cubic metres.}$$

Pressure, volume and temperature are thus gas variables. When one of these is changed, at least one other variable is influenced.

Another way to describe the relationship between pressure, volume and temperature is to say that $p \cdot V/T$ always has the same value for a given quantity of a gas.

Example: 5 cubic metres of air is compressed from atmospheric pressure to an effective pressure of 7 bar. The intake temperature is +20°C and the discharge temperature is +120°C.

What is the volume at the discharge flange?

$$p_1 = 1 \text{ bar (absolute)}$$

$$p_2 = 7 + 1 = 8 \text{ bar (absolute)}$$

$$T_1 = 20 + 273 = 293 \text{ K}$$

$$T_2 = 120 + 273 = 393 \text{ K}$$

$$p_1 \cdot V_1/T_1 = p_2 \cdot V_2/T_2$$

$$1 \cdot 5/293 = 8 \cdot V_2/393$$

Answer:

$$V_2 = 1 \cdot 5 \cdot 393/(293 \cdot 8) = 0.84 \text{ cubic metres.}$$

Amontons' law states that the pressure of a gas, at constant volume, varies directly with the absolute temperature:

$$p_2/p_1 = T_2/T_1 \text{ or}$$

$$p_1/T_1 = p_2/T_2 = \text{constant}$$

Dalton's law states that the total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases. The partial pressure is the pressure each gas would exert if it alone occupied the volume of the mixture at the actual temperature.

$$p_{\text{tot}} = p_1 + p_2 + p_3 + \dots + p_n$$

As long as the constituent gases do not chemically react with each other, they act quite individually without regard to each other's presence.

Dalton's law applies during the compression of any gas mixture.

When wet air is compressed, the compressor handles both the air and the water-vapour. Air, being a mixture of nitrogen, oxygen, argon, etc., has a total pressure equal to the sum of the partial pressures of each component. However, because of the negligible variations in the composition of dry air it may be considered as a single gas. After compression, partial pressures are used to determine moisture condensation in inter- and aftercoolers. When the dewpoint temperature of any component is reached, the space occupied is said to be saturated with that component.

The atmospheric pressure is the sum of the partial pressure of dry air and the partial pressure of the water-vapour. Suppose a quantity of atmospheric air at +20°C is saturated with water-vapour. In this state the air contains all the moisture it can hold at this temperature. Any added water-vapour would condense. If the total atmospheric pressure is 1.013 bar, the pressure exerted by air alone must be the difference between 1.013 bar and the water-vapour saturation pressure at +20°C. Table 2:17 shows that the saturation pressure of water is 23.37 millibar at +20°C. So the absolute partial pressure of the dry air is $1.013 - 0.023 = 0.990 \text{ bar}$. Partially saturated air contains less than the maximum amount of water-vapour that can be held. The moisture content is often expressed as relative vapour pressure. If the atmospheric air at +20°C has a relative vapour pressure of 65 per cent it holds only 0.65 as much water as it could.

The actual vapour pressure is thus $0.65 \cdot 23.37 = 15 \text{ millibar}$. The absolute partial pressure of the dry air is then $1.013 - 0.015 = 0.998 \text{ bar}$.

Amagat's law states that the volume of a mixture of gases is equal to the sum of the partial volumes which the constituent gases would occupy if each existed alone at the total pressure of the mixture.

Avogadro's law states that equal volumes of all gases under the same conditions of pressure and temperature contain the same number of molecules.

Since one mole of any substance, by definition, contains the same number of molecules, the molar volume of all gases should be the same. The number of molecules in one mole is called **Avogadro's number**. $N = 6.022 \cdot 10^{23} \text{ mol}^{-1}$.

Poisson's law states that, for a process without any heat exchange with the surroundings, the relationship between pressure and volume follows the equation:

$$p_1 \cdot V_1^{c_p/c_v} = p_2 \cdot V_2^{c_p/c_v}$$

The ratio of specific heat-capacities c_p/c_v is fairly constant at low pressures.

It is usually designated κ .

$$\kappa = c_p/c_v$$

For mono-atomic gases $\kappa = 1.66$

For di-atomic gases $\kappa = 1.40$ (air)

For tri-atomic gases $\kappa = 1.30$

κ varies with pressure and temperature (2:1).

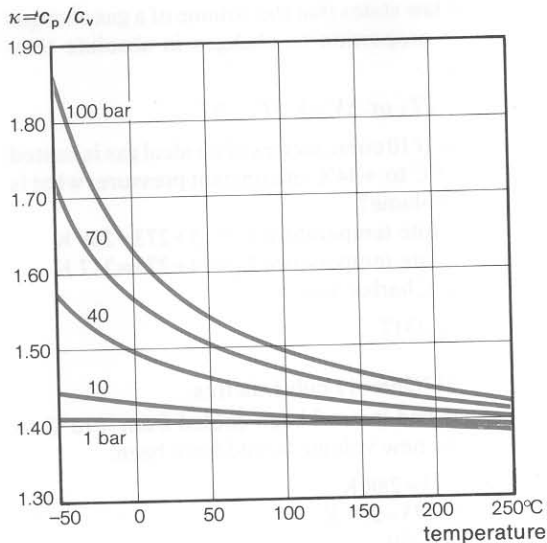


Diagram 2:1 The isentropic exponent for air

2.3 The general gas law

Combining Boyle's law and Charles' law gives

$$p \cdot V/T = \text{constant}$$

The value of the constant depends only on the gas and on the system of units chosen.

Avogadro's law states that an equal number of molecules of any gas will be contained in a given volume at the same temperature and pressure.

The fact that the volume of a mole at some fixed temperature is the same for any gas is very significant when factored into the relationship obtained from Charles' and Boyle's laws.

If v_m is the volume of one mole of gas at the reference temperature and pressure, then for one mole of any gas

$$(p/T)_{\text{ref}} \cdot v_m = \bar{R}$$

$$\bar{R} = 8314 \text{ J/(kmol} \cdot \text{K)}$$

This special value of \bar{R} is independent of the gas, since v_m is the same for all gases. The constant \bar{R} is termed **the universal gas constant** and for any gas that obeys Charles' and Boyle's laws

$$p \cdot v_m = \bar{R} \cdot T$$

For engineering work, it is usually desirable to convert the molar specific volume to more convenient units of volume per unit mass. This is equivalent to converting the unit of mass from mole to kilograms. As stated in the description of a mole, the number of mass units in a mole is numerically equal to the molar mass of the gas, regardless of the system of units. Therefore it follows that

$$p \cdot V = m \cdot R \cdot T$$

or if we introduce the specific volume

$$v = V/m \quad \text{m}^3/\text{kg}$$

$$p \cdot v = R \cdot T$$

$$\text{with } R = \bar{R}/M$$

where p is the absolute pressure in Pa

V is the volume in m^3

m is the mass of the gas in kg

\bar{R} is the universal gas constant in $\text{J/(kmol} \cdot \text{K)}$

T is the absolute temperature in K

R is the gas constant in $\text{J/(kg} \cdot \text{K)}$

M is the molar mass in kg/kmol

Example: For air with $M=28.96$ kg/kmol the gas constant is

$$R = 8314/28.96 = 287.1 \text{ J/(kg} \cdot \text{K)}$$

If the gas pressure instead is expressed in bar, the general gas law reads:

$$10^5 \cdot p \cdot V = m \cdot R \cdot T \quad \text{or} \quad 10^5 \cdot p \cdot v = R \cdot T.$$

2.4 Real gases

2.4.1 Critical conditions

There is one temperature above which a gas will not liquefy with pressure increase, no matter how great. This is the critical temperature. The pressure required to condense a gas at the critical temperature is the critical pressure.

For air $t_{cr} = -140.63^\circ\text{C}$ and $p_{cr} = 37.66$ bar absolute. For other gases see table 24:1.

For mixtures of gases that do not combine chemically, the critical constants are equal to the sum of the critical constants of the individual gases in the mixture, multiplied by their respective volume fraction.

2.4.2 Compressibility factor

At high pressures and temperatures, as well as in regions near the critical point where the gas condenses to the liquid phase, variations from the ideal p - V - T relationship occur. There exist numerous equations of state that compensate for the deviation from perfect gas behaviour. However, a simpler method is to use the compressibility factor, $Z = p \cdot v / (R \cdot T)$.

The compressibility factor is determined experimentally and plotted as function of pressure for lines of constant temperature.

But instead of using such diagrams for each gas it has been found that by replacing the actual pressure and temperature by ratios of these values to the pressure and temperature at the critical point, the compressibility curves for practically all gases fall together with but small divergence (2:3, p 36).

These ratios are called reduced quantities,

$$p_R = p/p_{cr} \quad \text{and} \quad T_R = T/T_{cr}$$

where p_{cr} and T_{cr} are the critical values for the gas. Diagram 2:3 shows the compressibility factor in generalized form.

The volume after polytropic compression of a real gas is:

$$V_2 = V_1 \cdot (p_1/p_2)^{1/n} \cdot Z_2/Z_1$$

The work spent on polytropic compression of a real gas is:

$$W = p_1 \cdot V_1 \cdot n / (n-1) \cdot [(p_2/p_1)^{(n-1)/n} - 1] \cdot (Z_1 + Z_2) / (2 \cdot Z_1)$$

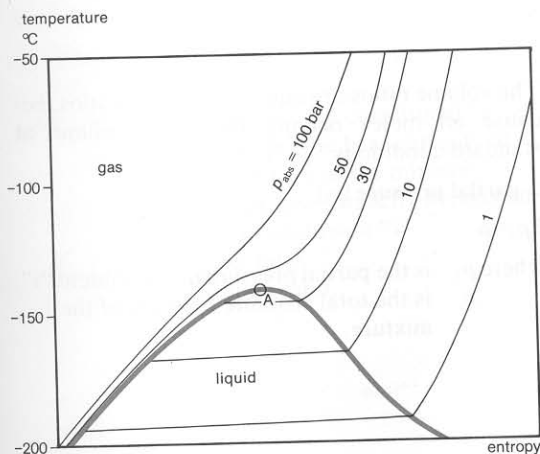


Diagram 2:2 Temperature-entropy diagram for air. "A" is the critical point

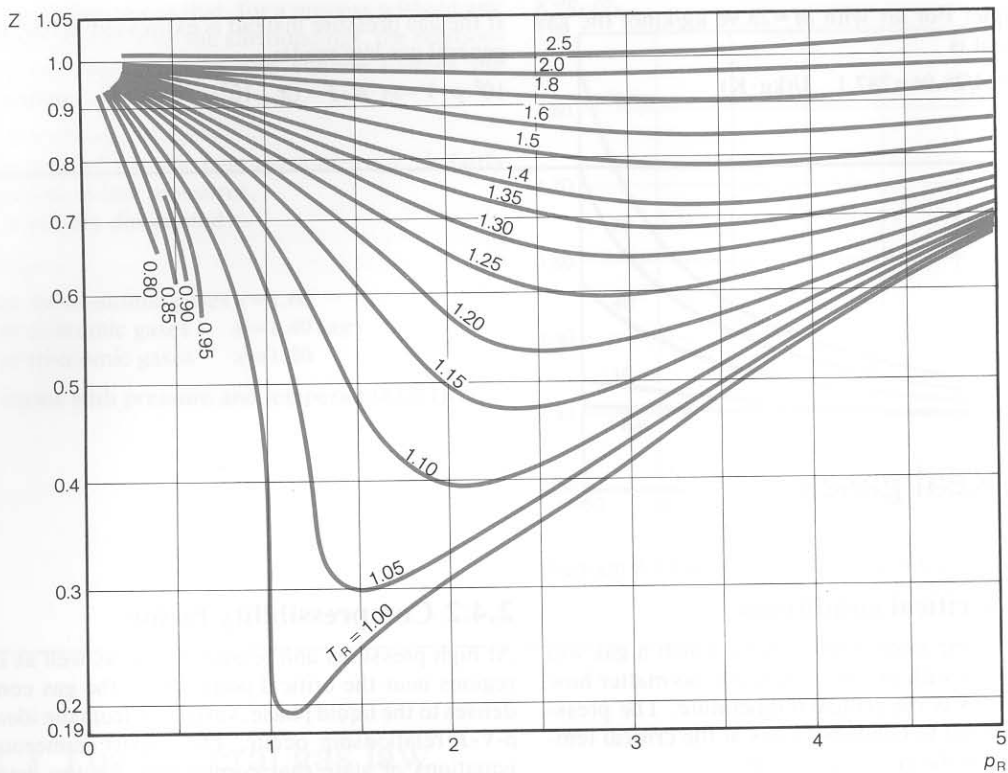


Diagram 2:3 The generalized compressibility factor
Note that the compressibility factor scale is distorted to increase readability

2.5 Properties of gas mixtures

The composition of a gas mixture is given in one of the following ways:

□ mass ratio (x)

$$x_i = m_i / m \quad \Sigma x_i = 1$$

where x_i is the mass ratio

m_i is the mass of constituent "i"
 m is the total mass of the mixture.

□ volume ratio (y)

$$y_i = V_i / V \quad \Sigma y_i = 1$$

where y_i is the volume ratio

V_i is the partial volume of the constituent "i"
 V is the total volume of the mixture.

The volume ratios are equal to the mole ratios, because all moles occupy the same volume at standard conditions.

□ partial pressure (p_i)

$$\Sigma p_i = p$$

where p_i is the partial pressure of constituent "i"
 p is the total absolute pressure of the mixture.

The **mean molar mass** of the mixture is given by:

$$M = \sum (y_i \cdot M_i) \quad \text{or} \\ M = 1 / \sum (x_i / M_i) \quad \text{or} \\ M = \sum (p_i \cdot M_i / p)$$

where M is the mean molar mass of the mixture
 M_i is the molar mass of constituent "i"
 p is the total absolute pressure of the mixture
 p_i is the partial pressure of constituent "i"
 x_i is the mass ratio
 y_i is the volume ratio.

The **mean gas constant** of the mixture is given by:

$$R = 8314 / M \quad \text{or} \\ R = \sum x_i \cdot R_i \quad \text{or} \\ R = 1 / \sum (y_i / R_i)$$

where M is the mean molar mass of the mixture
 R is the mean gas constant of the mixture
 R_i is the gas constant of constituent "i"
 x_i is the mass ratio
 y_i is the volume ratio.

The **mean dynamic viscosity** in the temperature range -50° to $+25^\circ\text{C}$ and for effective pressures up to 10 bar is given by:

$$\eta = (\eta_1 \cdot y_1 \cdot M_1^{1/2} + \eta_2 \cdot y_2 \cdot M_2^{1/2} + \dots \eta_i \cdot y_i \cdot M_i^{1/2}) / (y_1 \cdot M_1^{1/2} + y_2 \cdot M_2^{1/2} + \dots y_i \cdot M_i^{1/2})$$

where η is the mean dynamic viscosity
 η_i is the dynamic viscosity of constituent "i"
 y_i is the volume ratio of constituent "i"
 M_i is the molar mass of constituent "i".

The **mean specific heat-capacity at constant pressure** is given by:

$$c_p = \sum (x_i \cdot c_{pi}) \quad \text{or} \\ c_p = 1 / M \cdot \sum (y_i \cdot M_i \cdot c_{pi})$$

where M_i is the molar mass of constituent "i"
 c_p is the mean specific heat-capacity at constant pressure of the mixture
 c_{pi} is the specific heat-capacity at constant pressure of constituent "i"
 x_i is the mass ratio
 y_i is the volume ratio.

The **mean specific heat-capacity at constant volume** is given by:

$$c_v = c_p - 8.314 / M \quad (\text{ideal gas})$$

where c_v is the mean specific heat-capacity at constant volume of the mixture
 c_p is the mean specific heat-capacity at constant pressure of the mixture.

The **mean isentropic exponent** is given by:

$$\kappa = c_p / c_v \quad (\text{ideal gas})$$

Example: Determine the gas constant and the isentropic exponent of a gas mixture with the composition:

methane (CH_4)	81.9 per cent by volume
ethane (C_2H_6)	8.1
propane (C_3H_8)	5.3
nitrogen (N_2)	4.7
	100.0 per cent (2:4)

Answer:

The mean gas constant of the mixture is:

$$R = 8314 / 19.24 = 432.1 \quad \text{J/(kg} \cdot \text{K)}$$

Table 2:4

Constituent	Molar mass M_i	Specific heat-capacity c_{pi} kJ/(kg·K)	Volume ratio y_i	$y_i \cdot M_i$	$y_i \cdot M_i \cdot c_{pi}$
CH_4	16.04	2.207	0.819	13.14	29.00
C_2H_6	30.07	1.715	0.081	2.44	4.18
C_3H_8	44.09	1.627	0.053	2.34	3.81
N_2	28.02	1.039	0.047	1.32	1.37
—	—	—	1.000	$M = 19.24$	$M \cdot c_p = 38.36$

The mean specific heat-capacity at constant pressure is:

$$c_p = 38.36 / 19.24 = 1.995 \quad \text{kJ/(kg} \cdot \text{K)}$$

The mean specific heat-capacity at constant volume is:

$$c_v = 1.994 - 8.314 / 19.24 = 1.562 \quad \text{kJ/(kg} \cdot \text{K)}$$

The isentropic exponent is:

$$\kappa = 1.994 / 1.562 \\ \kappa = 1.28$$

2.6 Thermodynamic processes

2.6.1 The isobaric process

This takes place under constant pressure. To change the volume from state 1 to state 2, heat must be removed. The temperature change is proportional to the volume ratio.

$$T_2 - T_1 = T_1 \cdot (V_2/V_1 - 1)$$

The amount of heat to be removed is:

$$q_{12} = c_p \cdot m \cdot (T_1 - T_2) \quad \text{J}$$

where c_p is the specific heat capacity at constant pressure in J/(kg · K)

m is the mass in kg

T is the absolute temperature in K.

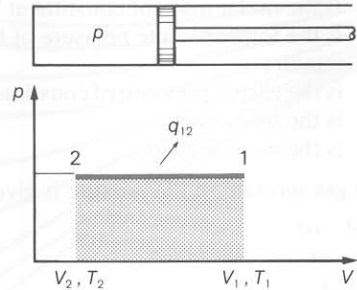


Diagram 2:5 The isobar

2.6.2 The isochoric process

This takes place under constant volume. To raise the pressure from state 1 to state 2, heat must be added. The temperature change is proportional to the pressure ratio.

$$T_2 - T_1 = T_1 \cdot (p_2/p_1 - 1)$$

The amount of heat to be added is:

$$q_{12} = c_v \cdot m \cdot (T_2 - T_1) \quad \text{J}$$

where c_v is the specific heat-capacity at constant volume in J/(kg · K)

m is the mass in kg

T is the absolute temperature in K.

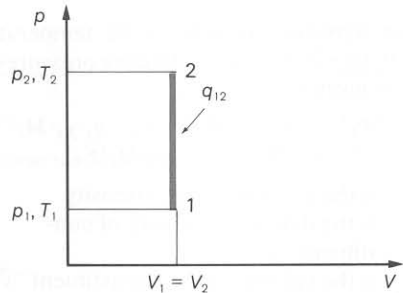


Diagram 2:6 The isochor

2.6.3 The isothermal process

This takes place under constant temperature. To compress the gas from state 1 to state 2, heat must be removed to keep the temperature constant. The pressure change is inversely proportional to the volume ratio.

$$p_2 - p_1 = p_1 \cdot (V_1/V_2 - 1)$$

The amount of heat to be removed is equal to the work of compression

$$q_{12} = p_1 \cdot V_1 \cdot 10^5 \cdot \ln(V_1/V_2) \quad \text{J, or}$$

$$q_{12} = R \cdot T_1 \cdot m \cdot \ln(p_2/p_1) \quad \text{J}$$

where p is the absolute pressure in bar

V is the volume in m³

m is the mass in kg

R is the gas constant in J/(kg · K).

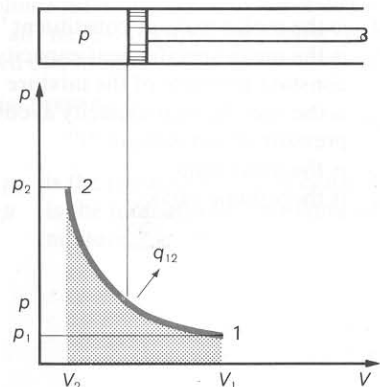


Diagram 2:7 The isotherm

2.6.4 The isentropic process

This takes place without any heat exchange with the surroundings. Such a process follows Poisson's law.

$$p_2/p_1 = (V_1/V_2)^\kappa \quad \text{or}$$

$$p_2/p_1 = (T_2/T_1)^{\kappa/(\kappa-1)}$$

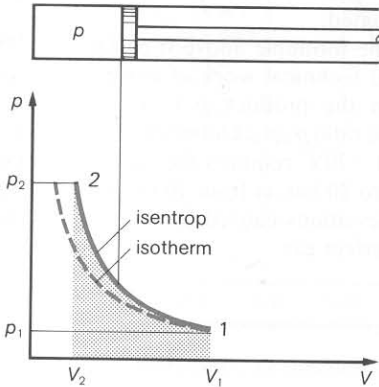


Diagram 2:8 The isentrop

2.6.5 The polytropic process

The isotherm is based on complete heat exchange with the surroundings. The isentrop is based on no heat exchange with the surroundings. In reality all compressor processes will fall between these two. This generalized process is called polytropic. The polytrop follows the law:

$$p \cdot V^n = \text{constant}$$

By giving "n" suitable values the polytrop will include all the four basic processes described above.

$n=0$ represents the isobar

$n=1$ represents the isotherm

$n=\kappa$ represents the isentrop

$n=\infty$ represents the isochor.

2.6.6 Technical compression work

Diagram 2:9 shows a compressor cylinder with self-acting valves. Air or gas is aspirated from pipe "a", compressed, and discharged to pipe "b". The suction valve opens when the pressure in the cylinder space "c" drops below that in the suction pipe, and the discharge valve opens when the pressure inside the cylinder exceeds that in the discharge pipe. The pV -diagram shows that when the piston moves to the right, air is drawn in at a pressure p_1 until the piston reaches the extreme right hand

position. When the piston returns, the suction valve closes and the air is compressed until it reaches pressure p_2 existing in the discharge pipe. The discharge valve opens and air is delivered at constant pressure until the piston reaches the extreme left position.

If there is a vacuum on the right hand side of the piston the work used may be calculated:

the displacement work delivered by the gas drawn in

$$W_{4-1} = p_1 \cdot V_1$$

the compression work added to the gas

$$W_{1-2} = \int p \cdot dV$$

the work required to move the air against the discharge pressure

$$W_{2-3} = -p_2 \cdot V_2$$

the pressure change

$$W_{3-4} = 0$$

The sum of these four works is called the **technical work of the process**

$$W_t = \int_1^2 p \cdot dV - p_2 \cdot V_2 + p_1 \cdot V_1$$

This work is equal to the area 1-2-3-4 labelled in the figure and can thus also be expressed as an integral of dp .

$$W_t = - \int_1^2 V \cdot dp \quad \text{J}$$

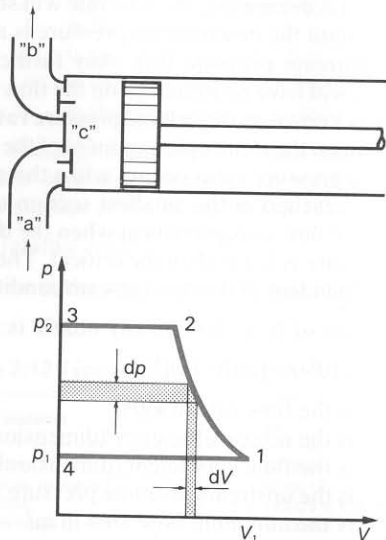


Diagram 2:9 Theoretical compression process (no mechanical losses, no clearance volume)

The technical work remains unchanged if a constant pressure, instead of a vacuum, exists on the right hand side of the piston, as the works of this constant pressure cancel each other out when the piston moves to the right and back again. With double-acting pistons the technical work spent on both sides of the piston has to be added.

The amount of work depends principally on the compression line 1-2.

Isothermal compression gives

$$W_t = -m \cdot R \cdot T_1 \cdot \ln(p_2/p_1)$$

or if the natural logarithm is replaced by Brigg's

$$W_t = -2.303 \cdot m \cdot R \cdot T_1 \cdot \log(p_2/p_1) \quad \text{or}$$

$$W_t = -2.303 \cdot p_1 \cdot V_1 \cdot \log(p_2/p_1)$$

Polytropic compression gives

$$W_t = -p_1 \cdot V_1 \cdot n / (n-1) \cdot [(p_2/p_1)^{(n-1)/n} - 1]$$

The discharge temperature is:

$$T_2 = T_1 \cdot (p_2/p_1)^{(n-1)/n}$$

If n in the equations above is replaced by the isentropic exponent, the isentropic work of compression and the isentropic discharge temperature are obtained.

From the formulae above it can be seen that the required technical work of compression depends only on the product $p \cdot V = m \cdot R \cdot T$ and on the pressure ratio p_2/p_1 . Compression of one kilogram of air at +20°C requires the same amount of work from 1 to 10 bar as from 10 to 100 bar, except for small deviations caused by the fact that the air is not a perfect gas.