ELEMENTS OF MOLECULAR PHYSICS

Molecular Kinetic Theory of Gases

MOLECULAR PHYSICS. Glossary-1

absolute temperature	—	абсолютна температура
absolute zero	—	абсолютний нуль
atom	—	атом
biatomic gas	—	двоатомний газ
density	—	густина
equilibrium state	—	рівноважний стан
heat capacity	—	теплоємність
macroscopic	—	макроскопічний
mean kinetic energy	—	середня кінетична енергія
microscopic	—	мікроскопічний
molar heat capacity	—	молярна теплоємність
molar volume	—	молярний об’єм
monatomic gas	—	одноатомний газ
nonequilibrium	—	нерівноважний
number of degrees of molecule freedom	—	число ступенів свободи молекули

MOLECULAR PHYSICS. Glossary-2

perfect gas	—	ідеальний газ
pressure	—	тиск
state	—	стан
state equation	—	рівняння стану
specific heat capacity	—	питома теплоємність
specific volume	—	питомий об'єм
thermodynamics	—	термодинаміка
thermodynamic processes	—	термодинамічний процес
translatory degrees of freedom	—	поступальна ступінь свободи
triatomic gas	—	триатомний газ
true heat capacity	—	істинна теплоємність
rotatory degree of freedom	—	обертальна ступінь свободи
vibrational degree of freedom	—	коливальна ступінь свободи

MOLECULAR PHYICS. Glossary-3.

arithmetic mean velocity	—	середня швидкість
distribution	—	розподіл
equipartition principle of energy	—	принцип рівного розподілу енергії
internal energy	—	внутрішня енергія
probabilistic quantity	—	імовірнісна величина
the most probable velocity	—	істинна швидкість
equiprobable	—	рівноімовірний
diffusion	—	дифузія
heat conductivity	—	теплопровідність
free path of molecule	—	довжина вільного пробігу
	—	молекули

MOLECULAR KINETIC THEORY OF GAS

The molecular physics is a part of physics, which studies those properties of substance that are stipulated by its molecular structure.

The molecular kinetic theory is the basis of the molecular physics.

The liquid, solid, and gaseous states of a substence are called its ***aggreation states.***

The volume V, the temperature T, and the pressure p are the ***parameters of states.***

$F(V,T,p) = 0$ is the ***equation of state.***

The equilibrium state is such state of a system when all its parameters do not change on time for stable external conditions.

MOLECULAR KINETIC THEORY OF GAS (2)

$E = \sum_{i=1}^{N} \varepsilon_i$ is the energy of the gas molecules

N is the number of molecules

$\varepsilon_i = \frac{1}{2} m v_i^2$ is the energy of i-th molecule

m is the molecule mass

v is the molecule velocity

$$\langle \varepsilon_{tr} \rangle = \frac{1}{2} m \frac{\sum_{i=1}^{N} v_i^2}{N} = \frac{1}{2} m \langle v^2 \rangle$$

is the averaged energy of translation motion of molecules

$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} v_i^2}$ is the root mean square velocity

$\langle v \rangle = \frac{\sum_{i=1}^{N} v_i}{N} < \sqrt{\langle v^2 \rangle}$ is the averaged (mean) molecule velocity

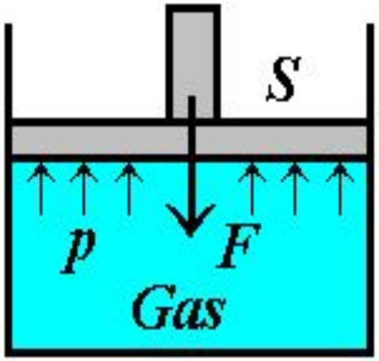
Example:

$i = 1,2 \ (N = 2)$

$v_1 = 3, \ v_2 = 5$

$$\langle v \rangle = \frac{3+5}{2} = 4; \ \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3^2+5^2}{2}} = 4{,}12; \ \langle v \rangle \approx \sqrt{\langle v^2 \rangle}$$

MOLECULAR KINETIC THEORY OF GAS (3)



$$p = \frac{F}{S}$$

The gas is ideal, which posseses by the following properties:

a) the size of molecules is much smaller than the averaged distance between molecules;
b) the molecule collisions are perfectly elastic;
c) the molecules do not attract or repulse.

$T = const,\ pV = const$ is the Boyle and Mariotte law *(the isothermal process)*

$p = const,\ \dfrac{V}{T} = const$ is the Gay-Lussac law *(the isobaric process)*

$V = const,\ \dfrac{p}{T} = const$ is the Charles law *(the isochoric process)*

$\dfrac{pV}{T} = const$ is the Clapeyron equation

$\dfrac{pV}{T} = \dfrac{M}{\mu}R$ is the Mendeleyev-Clapeyron equation

MOLECULAR KINETIC THEORY OF GAS

$\mu = \frac{M}{\nu}$ is the molar mass of the gas

ν is the number of moles

$$\nu = \frac{N}{N_A} = \frac{M}{\mu} = \frac{V}{V_\mu}$$

N is the number of molecules

N_A is the the Avagadro's number

V_μ is the volume of one mole of the gas

R the universal gas constant

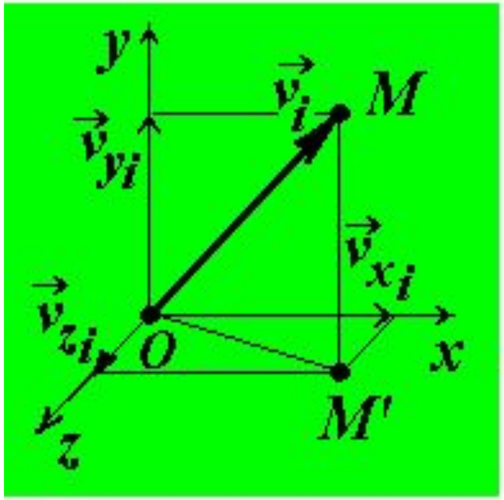
$k = \frac{R}{N_A}$ is the Boltzmann's constant

$n_0 = \frac{N_A}{V_\mu}$ is the number of molecules in the volume unit

The Avagadro law:
moles of different gases occupy equal volumes

The Dalton's law: the total pressure of a gaseous mixture equals the sum of purtial pressures

MOLECULAR KINETIC THEORY OF GAS

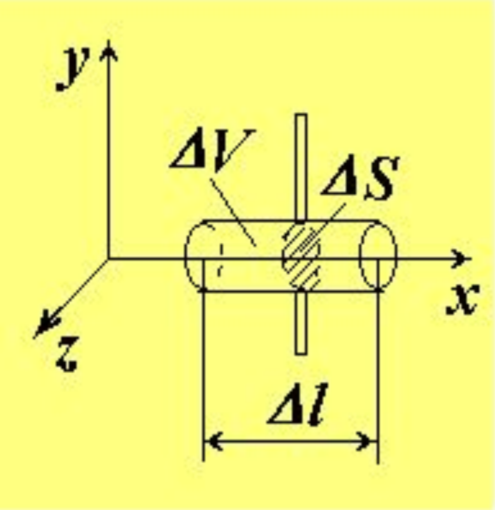


$$\langle\vec{v}^2\rangle=\frac{1}{N}\sum_{i=1}^{N}\vec{v}_i^2=\frac{1}{N}\sum_{i=1}^{N}\vec{v}_{x_i}^2=\frac{1}{N}\sum_{i=1}^{N}\vec{v}_{y_i}^2=\frac{1}{N}\sum_{i=1}^{N}\vec{v}_{z_i}^2\Rightarrow$$

$$\sqrt{\langle\vec{v}^2\rangle}=\sqrt{\langle\vec{v}_x^2\rangle+\langle\vec{v}_y^2\rangle+\langle\vec{v}_z^2\rangle}\approx\langle\vec{v}\rangle$$

$$n=\frac{\Delta N'}{\Delta V};\ \Delta N=\frac{1}{6}\Delta N';\ \Delta N=\frac{1}{6}n\Delta V;$$

$$\Delta V=\Delta l\,\Delta S;\ \Delta l=\langle\vec{v}\rangle\Delta t\ \Rightarrow$$



$$\Delta N=\frac{1}{6}n\,\Delta S\langle\vec{v}\rangle\Delta t$$

or

$$\Delta N\approx\frac{1}{6}n\,\Delta S\sqrt{\langle\vec{v}^2\rangle}\ \Delta t$$

MOLECULAR KINETIC THEORY OF GAS

THE CLAUSIUS EQUATION

We suppose that:

- a) the gas is ideal;
- b) all molecules has the same velocities;
- c) the molecules move along the axises only.
- d) $p = \langle p \rangle$

Then: $E = \sum_{i=1}^{N} \varepsilon_i$,

$$\Delta N = \frac{1}{6} n \Delta S \, v \, \Delta t$$

where all definitions are given before

In accordance with the momentum conservation law:

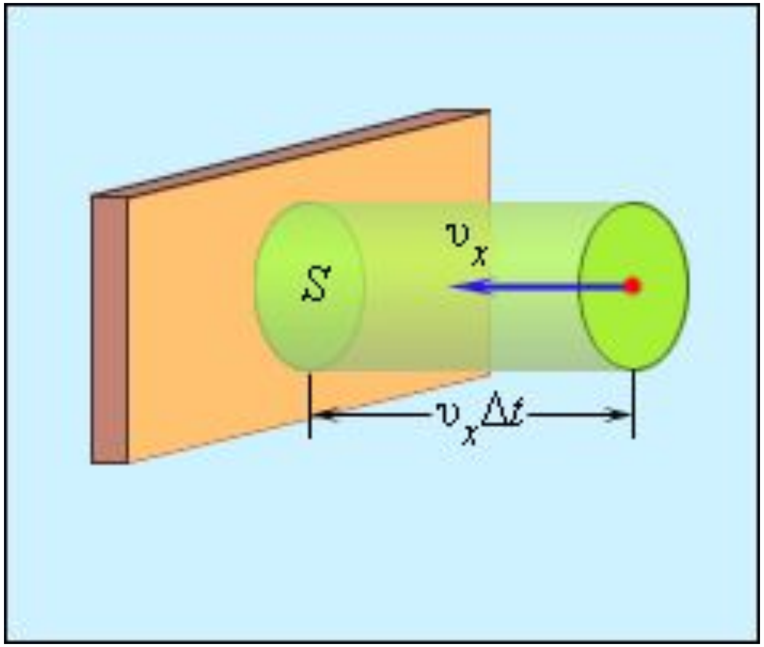
$$\Delta P_i = (-mv) - (mv) = -2mv$$

where ΔP_i is the momentum changing for an *i*-th molecules

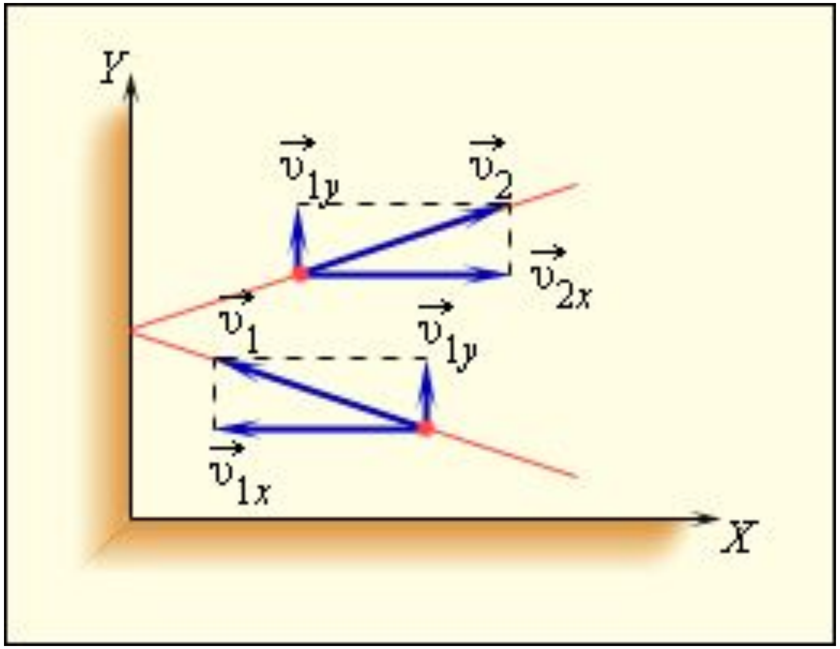
The total changing the momentum of the gas molecules is:

$$\Delta P = \sum_{i=1}^{N} \Delta P_i = (-2mv)\,\Delta N = (-2mv)\,\frac{1}{6} n \Delta S \, v \, \Delta t = -\frac{1}{3} nmv^2 \Delta S \Delta t$$

TO DERIVATION OF CLAUSIUS EQUATION



Calculation of collision number for molecules on the element of wall at square ***S*.**



Elastic collision of molecule with wall.

MOLECULAR KINETIC THEORY OF GAS

THE CLAUSIUS EQUATION

$$\Delta P = -\frac{1}{3} nmv^2 \Delta S \Delta t; \quad p = \frac{F}{\Delta S}; \quad F = p\Delta S$$

In accordance with the third law of dynamics: $-F = -p\Delta S$

In accordance with the second law of dynamics: $-F\Delta t = \Delta P = -p\Delta S\Delta t \Longrightarrow$

$\Longrightarrow -p\Delta S\Delta t = -\frac{1}{3} nmv^2 \Delta S\Delta t$ or $p = \frac{1}{3} nmv^2$; but $v^2 \approx \langle v^2 \rangle$

Hence:

$$p = \frac{1}{3} nm \langle v^2 \rangle$$

On the other hand:

$$\frac{1}{2} m \langle v^2 \rangle = \langle \varepsilon_{tr} \rangle$$

So, we can write:

$$p = \frac{2}{3} n \langle \varepsilon_{tr} \rangle$$

This is the Clausius equation – main equation of the molecular kinetic theory of gases

MOLECULAR KINETIC THEORY OF GAS

The Clausius equation: $p = \frac{2}{3} n \langle \varepsilon_{tr} \rangle$ $\quad n = \frac{N}{V}$ **then**

$$p = \frac{2}{3}\frac{N}{V}\langle \varepsilon_{tr} \rangle \Longrightarrow pV = \frac{2}{3} N \langle \varepsilon_{tr} \rangle;\ N\langle \varepsilon_{tr} \rangle = E_{tr} \Longrightarrow$$

$$\Longrightarrow \boxed{pV = \frac{2}{3} E_{tr}}$$

$N = \frac{M}{\mu} N_A$ $\quad pV = \frac{2}{3} N \langle \varepsilon_{tr} \rangle \Longrightarrow pV = \frac{2}{3}\frac{M}{\mu} N_A \langle \varepsilon_{tr} \rangle$ **On the other hand in accordance with the Mendeleyev-Clapeyron equation:** $pV = \frac{M}{\mu} RT$ **Hence:** $\frac{2}{3}\frac{M}{\mu} N_A \langle \varepsilon_{tr} \rangle = \frac{M}{\mu} RT$ **or**

$$\langle \varepsilon_{tr} \rangle = \frac{3}{2}\frac{R}{N_A} T = \frac{3}{2} kT$$

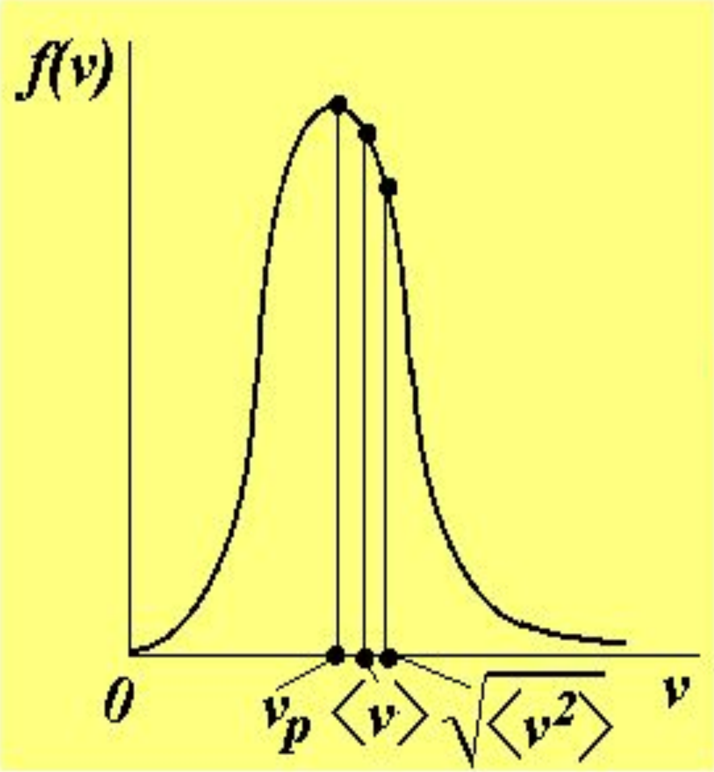
$$pV = \frac{2}{3} E_{tr} = \frac{2}{3} N \langle \varepsilon_{tr} \rangle = \frac{2}{3} N \frac{3}{2} kT \Longrightarrow p = \frac{N}{V} kT$$

MOLECULAR KINETIC THEORY OF GAS (9)

MAXWELL DISTRIBUTION

$f(v) = \frac{dN}{dv}$ is the Maxwell distribution function (the Maxewell distribution)

where dN is the number of molecules with velocities from v to $v + dv$



$$f(v) = 4\pi N v^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} exp\left\{-\frac{mv^2}{2kT}\right\}$$

All other values have been determined above

$$v = v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{\mu}} \qquad \frac{\sqrt{\langle v^2 \rangle}}{v_p} = 1.22$$

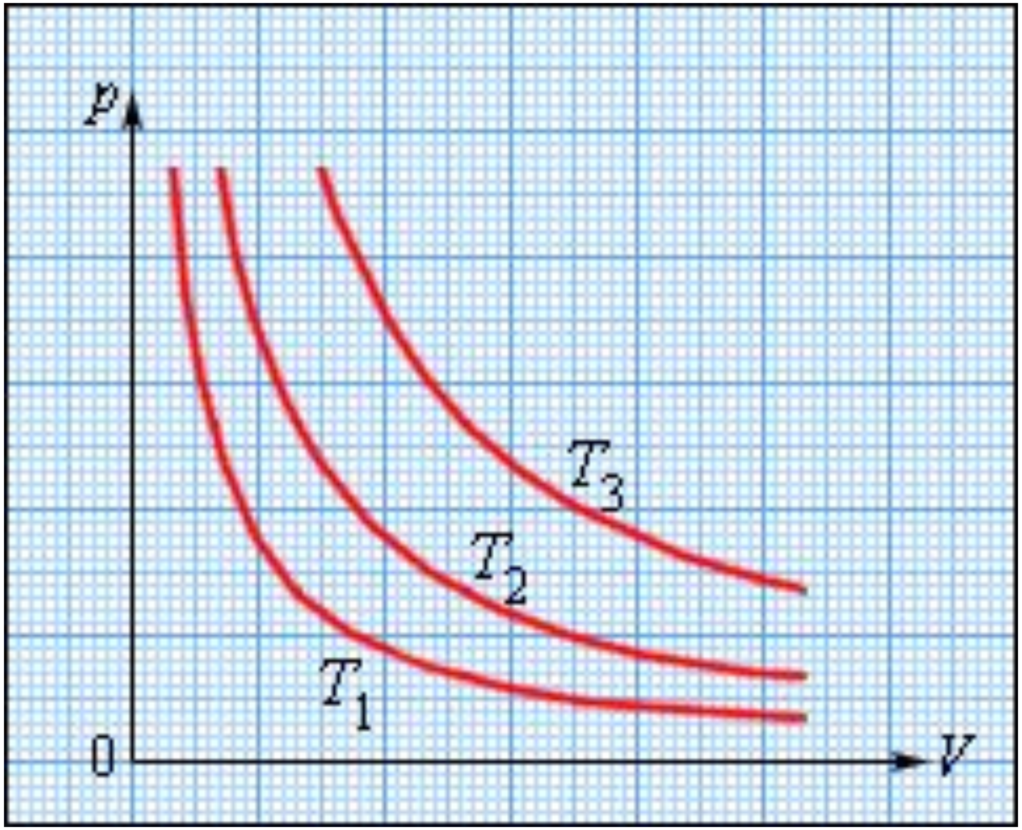
$$v = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{2kT}{m}} \qquad \frac{\langle v \rangle}{v_p} = 1.13$$

MOLECULAR KINETIC THEORY OF GAS

At home independently:

- a) to derive the Boltzmann barometric formula;
- b) the Boltzmann distribution.

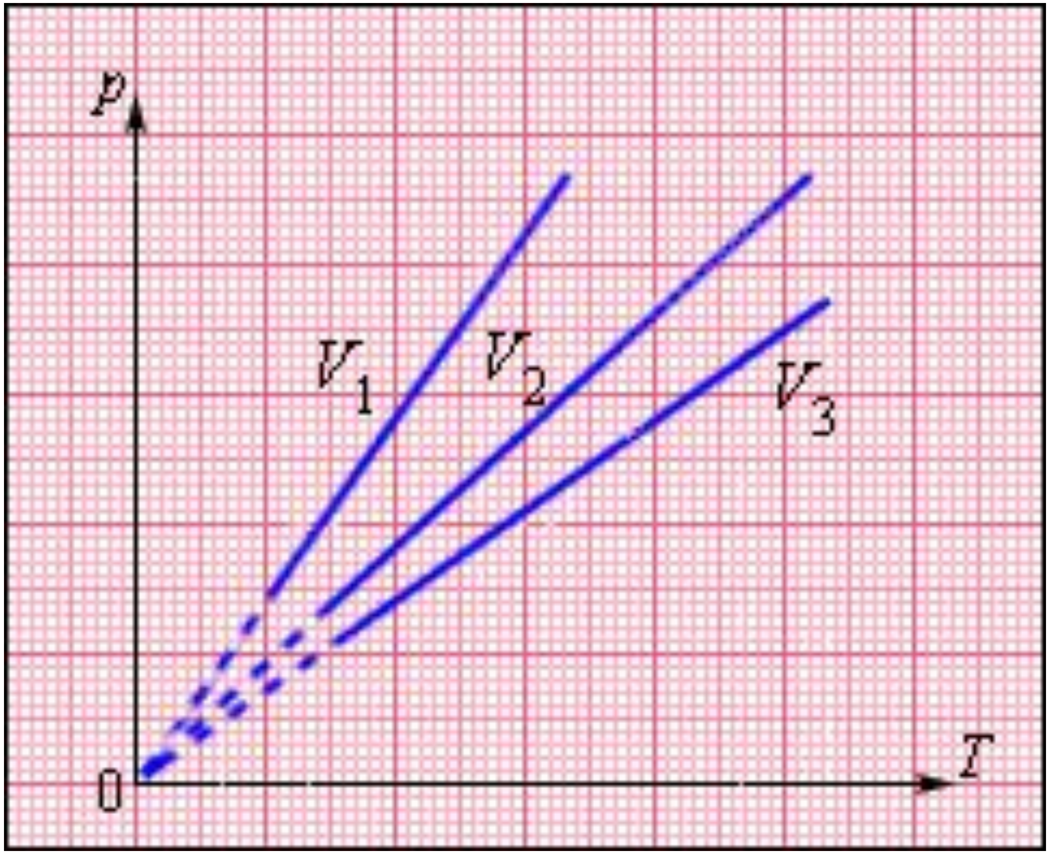
ISOTHERMAL PROCESS (T = const)



pV = const.

$T3 > T2 > T1$

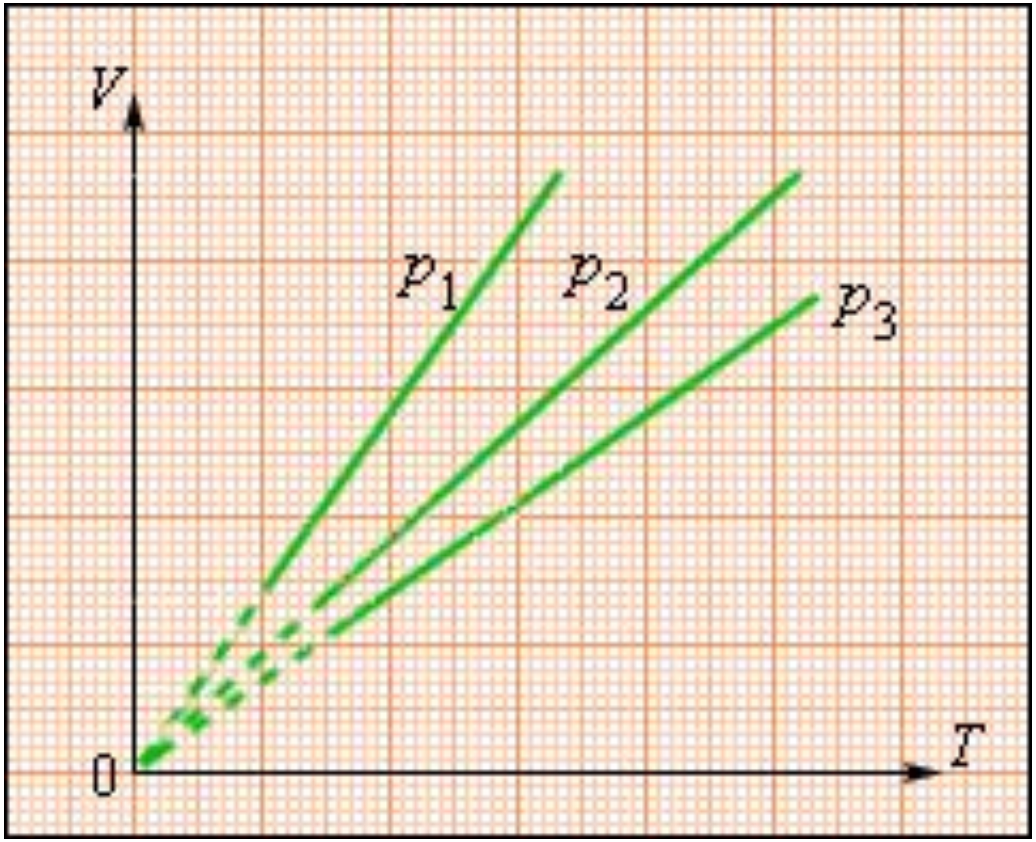
ISOBARIC PROCESS (*V* = const)



$$\frac{p}{T} = \text{const.}$$

*V*3 > *V*2 > *V*1

ISOBARIC PROCESS (*p* = const)



$$\frac{V}{T} = const$$

*p*3 > *p*2 > *p*1

THE FIRST LAW OF THERMODYNAMICS (1)

The internal (inner, intrinsic) energy of the system in general case includes:

a) the kinetic energy of the molecular chaotic motion;
b) the kinetic and potential energy of the molecular oscillations;
c) the potential energy of the intermolecular interactions;
d) the energy of the electron shells of molecules;
e) the energy of the nucleon interactions in nuclei.

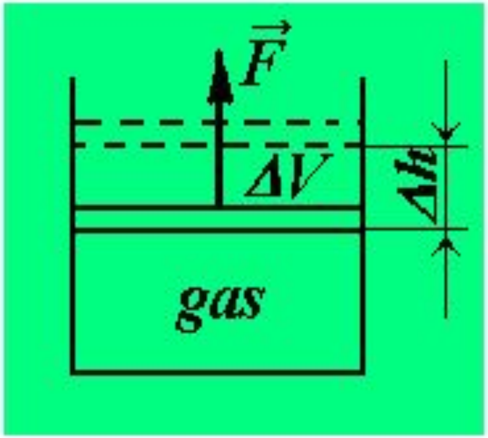
The first of them is reffered traditionally in the thermodynamics to as the internal energy.

$U = U(V,T)$ *is the caloric equation*

The internal energy is a single-valued function of the system state.

THE FIRST LAW OF THERMODYNAMICS

(2)



$\vec{F}$ is the force acted on external bodies

$$\delta Q = \delta A + dU$$

Q is the amount of heat

A is the work under external bodies

δQ is the infinitesimal heat increment

δA is the infinitesimal work increment

$\Delta A = F\,\Delta h$ is the work increment

$p = \dfrac{F}{S}$ is the pressure

S is the piston area

$\Delta V = S\,\Delta h$ is the volume increment

$$\Delta A = (pS)\,\Delta h = p\Delta V$$

dU is the total differential:

$$\oint_L dU = 0$$

δQ and δA are not the total differentials

THE FIRST LAW OF THERMODYNAMICS (3)

At home independently:

a) work under gas for the isoprocesses (isobaric and isothermal processes, derivation);

b) heat capacity, molar heat capacity, specific heat capacity;

c) heat capacity for the isoprocesses, including, the isochoric process (derivation), the isobaric (derivation), the isothermal process (derivation), the adiabatical process (derivation of the Poisson equation), and the politropic process (derivation);

d) derivation of the Mayer's formula;

e) heat capacity and number of molecule degrees of freedom.

THEOREM ABOUT UNIFORM DISTRIBUTION OF ENERGY ALONG DEGREES OF FREEDOM

For the system of molecules at thermodynamic equilibrium at temperature *T* the mean kinetic energy of molecules is the same for each degree of freedom and equal to $\frac{1}{2}kT$.

Molar specific heat capacity of ideal gas:

$$C_V = \frac{i}{2}R, \quad C_p = C_V + R = \frac{i+2}{2}R, \quad \gamma = \frac{C_p}{C_V} = \frac{i+2}{i},$$

Monoatomic gas: $i = 3$;

Two-atomic gas: $i = 5$;

Multi-atomic gas: $i = 6$.

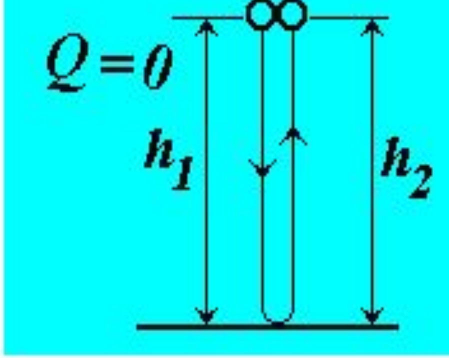
Mayer's theorem:

$$C_p - C_v = R$$

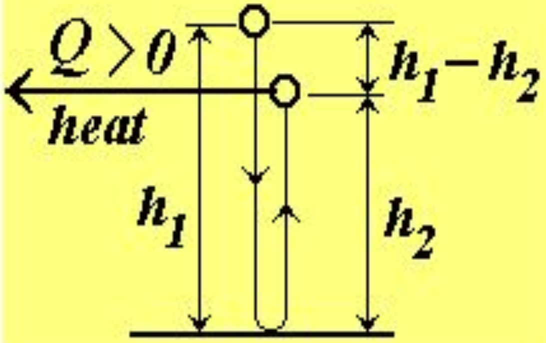
THE SECOND LAW OF THERMODYNAMICS (1)

INCIDENCE OF A SPHERE

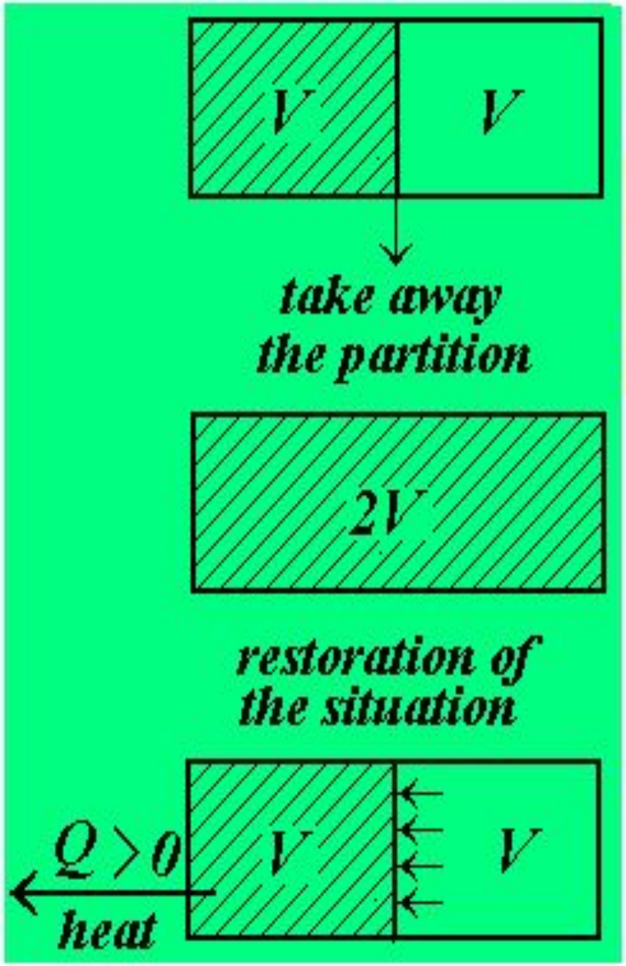
reversible process



irreversible process



EXPANSION OF A GAS



take away the partition

restoration of the situation

Ω - is the staistical weight (or the thermodynamic probability).

This is a number of possible the system microstates which correspond to the given macrostate

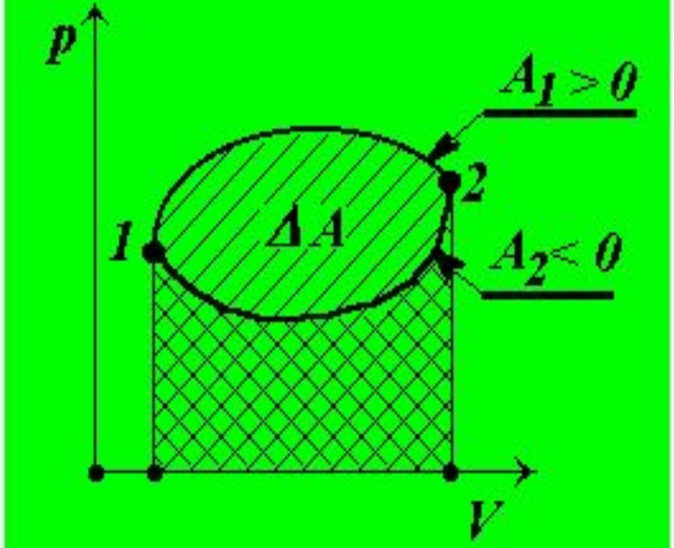
$$S = k \ln \Omega$$

S is the entrophy
k is the Boltzmann constant

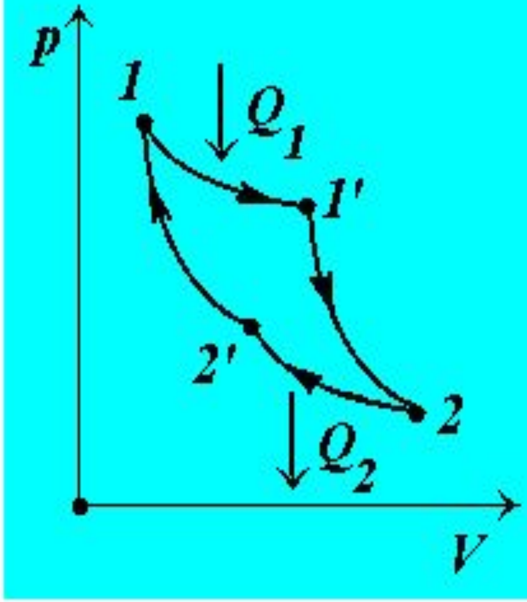
The entrophy is an measure of chaos in the system

THE SECOND LAW OF THERMODYNAMICS (3)

The circular process



Carnot cycle



1 - 1′ $T = const$

1′ - 2 $Q = const$

2 - 2′ $T = const$

2′ - 1 $Q = const$

$$\delta Q = dU + \delta A$$

$$T = const; \quad dU = 0$$

$$\delta Q = \delta A$$

$$Q = const; \quad \delta Q = 0$$

$$dU = -\delta A$$

$$\Delta A = A_1 - |A_2|$$

$$\eta = \frac{\Delta A}{A_1} = \frac{A_1 - |A_2|}{A_1}$$

Carnot theorem

$$\eta = \frac{T_1 - |T_2|}{T_1}$$

$$\Delta A = Q_1 - |Q_2|$$

$$\eta = \frac{\Delta A}{A_1} = \frac{Q_1 - |Q_2|}{Q_1}$$

THE SECOND LAW OF THERMODYNAMICS (3)

The entrophy of one mole of the ideal gas

$$S = R\ln V + C_V \ln T + S_0$$

The chanding of entrophy of the one mole of the ideal gas

$$\Delta S = S - S_1 = R\ln\frac{V}{V_1} + C_V \ln\frac{T}{T_1}$$

where for $V = V_1$ and $T = T_1$

the system entrophy $S = S_1$

The second law of thermodynamics (the Clausius formulation)

$$dS \geqslant 0$$

$$dS = R\frac{1}{V}dV + C_V\frac{1}{T}dT$$

$$TdS = \frac{RT}{V}dV + C_V dT$$

The Mendeleyev - Clapeyron for one mole of the ideal gas

$$pV = RT$$

$$TdS = p\,dV + C_V dT = \delta A + dU = \delta Q$$

$$dS = \frac{\delta Q}{T}$$ (but, for the reversible process only)

In the case of irrevercible process:

$$dS > \frac{\delta Q}{T}$$

In the general case:

$$dS \geqslant \frac{\delta Q}{T}$$

REAL GAS THEORY

(1)

The gaz can be considered ideal if:

a) the gas molecules can be considered as material points;

b) all collisions between the molecules are perfectly elastic;

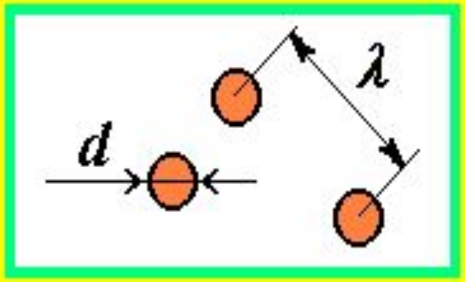
c) the attracting and repulsive forces do not act between the molecules.

The Mendeleyev - Clapeyron equation for 1 mole of the ideal gas:

$$\frac{pV}{RT} = f = 1$$

where f is the compessibility coefficient

The model of the real gas



d is the molecule diameter

λ is the distance between molecules

In the case of real gase the compressibility coefficient

$$f = \frac{pV}{RT} < 1$$

REAL GAS THEORY

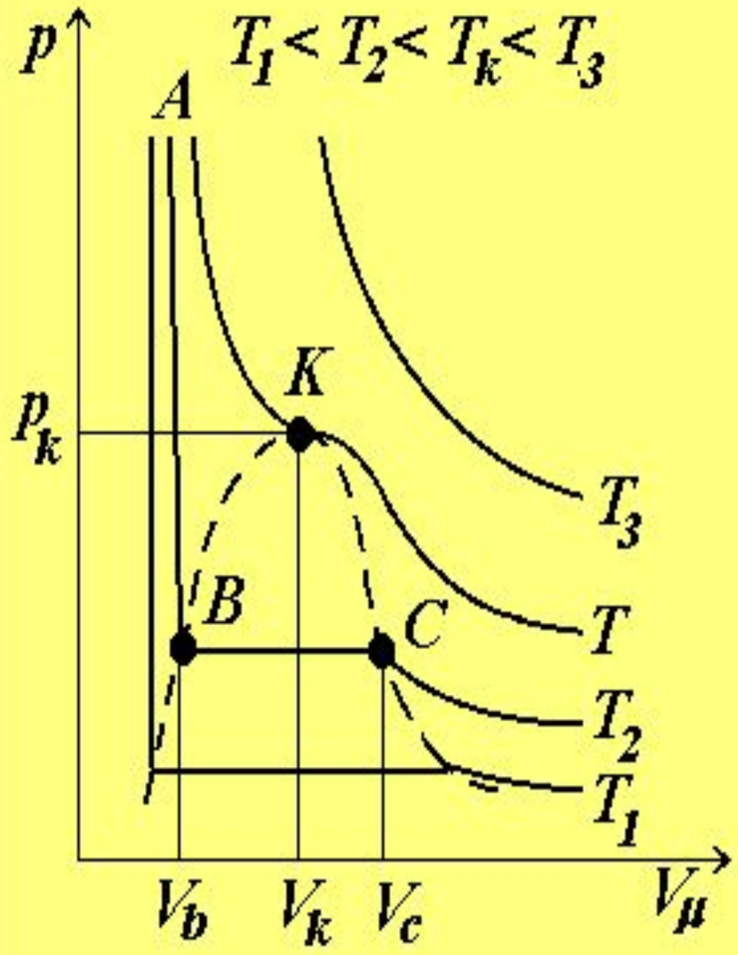
(2)

The Van der Waals equation for 1 mole of a real gas

$$\left(p+\frac{a}{V_\mu^2}\right)\left(V_\mu-b\right)=RT$$

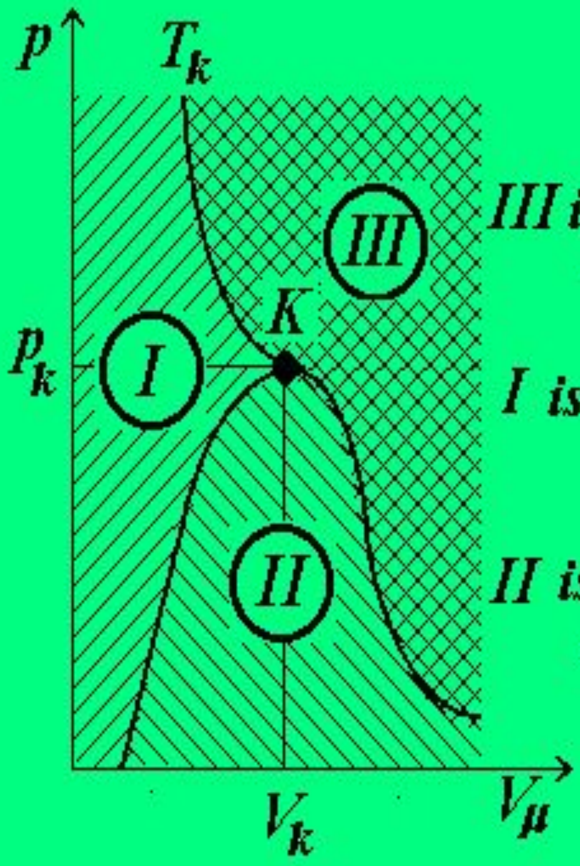
The Van der Waals equation for $\frac{M}{\mu}$ moles of a real gas

$$\left(p+\frac{a}{V^2}\frac{M^2}{\mu^2}\right)\left(V-\frac{M}{\mu}b\right)=\frac{M}{\mu}RT$$



REAL GAS THEORY (3)

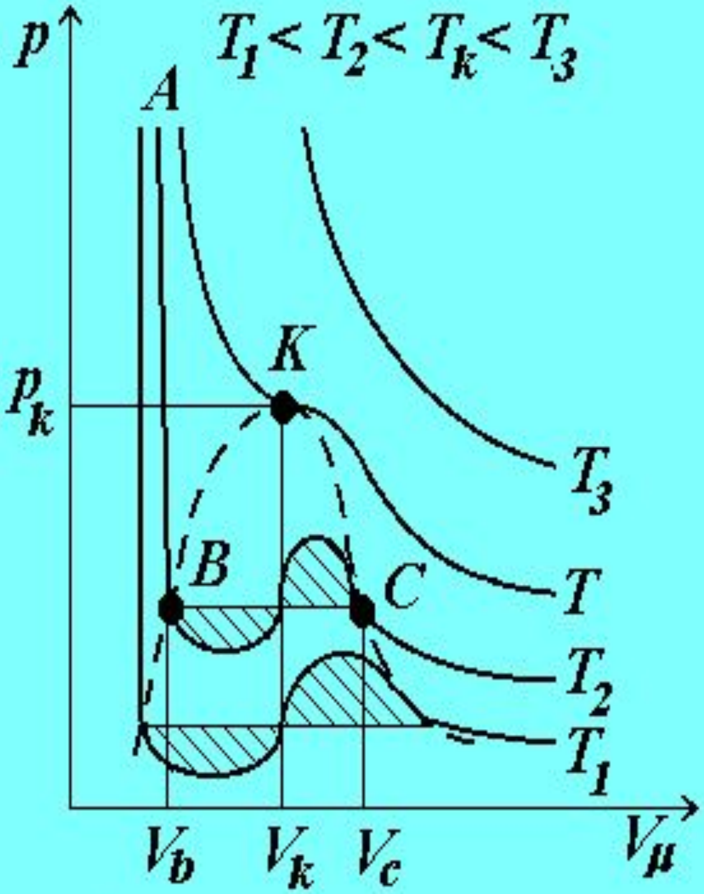
The phase diagram



III is the dry steam

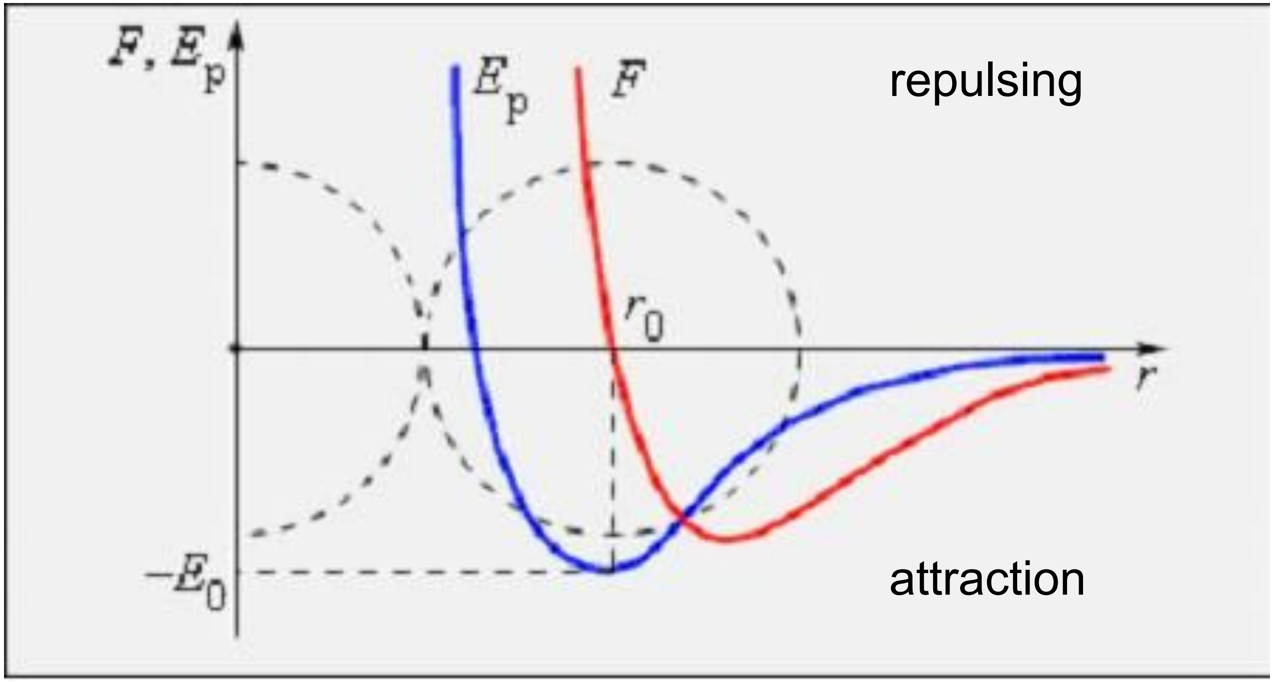
I is the liquid

II is the humid steam



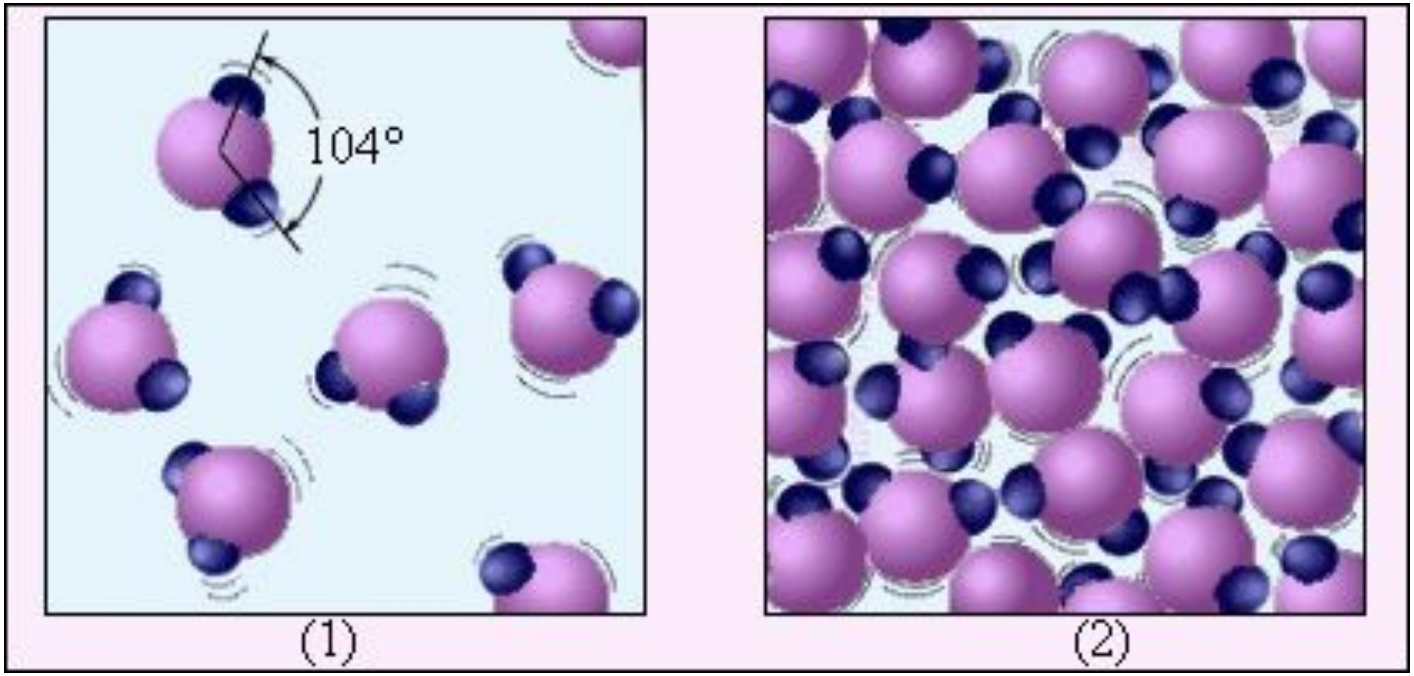
$$p_k = \frac{1}{27}\frac{a}{b^2}; \quad V_k = 3b; \; T_k = \frac{8}{27}\frac{a}{bR}$$

Force of interaction of two gas molecules as the function of distance between their centers



- $2r_0=d$ is a diameter of molecule;
- F is a force of interaction;
- E_p is a potential energy of interaction;
- E_0 is the energy of connection, or potential well depth

INCREASE OF DISTANCE BETWEEN MOLECULES OF WATER AT VAPORIZING



H_2O

Vapor of water

Liquid water

Scale of molecules drawing is 5 x 10^7.

TRANSFER PHENOMENA IN GASES

(1)

The transfer phehomena:
- a) the diffusion;
- b) the internal (viscous) friction;
- c) the heat (thermal) conductivity.

The chaotic motion of molecules is the common cause of all these phenomena.

$$l = \frac{1}{\sqrt{2}\pi d^2 n}$$

is the averaged path (track) length

where: d **is the molecule diameter**
n **is the gas concentration**

$$n = \frac{p}{kT} \qquad l = \frac{kT}{\sqrt{2}\pi d^2 p}$$

Example:

$d \approx 2\cdot 10^{-10} m$
$n \approx 2.7\cdot 10^{25} m$
$p \approx 1\ atm$
$T \approx 273\ K$

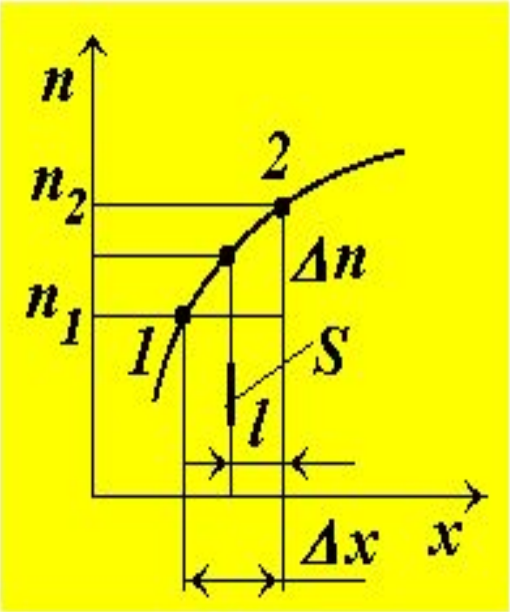
$l \approx 10^{-7}\ m$

What is the vacuum?

$p \approx 10^{-3} tor \qquad l \approx 10\ cm$

TRANSFER PHENOMENA IN GASES

(2)



$$J = \frac{\Delta N}{\Delta S \Delta t}$$

$$(\leftarrow)\, \Delta N_- = -\frac{1}{6} n_2 \langle v \rangle \Delta S \Delta t$$

$$(\rightarrow)\, \Delta N_+ = -\frac{1}{6} n_1 \langle v \rangle \Delta S \Delta t$$

$$\Delta N = \Delta N_+ - \Delta N_- = -\frac{1}{6}(n_1 - n_2)\langle v \rangle \Delta S \Delta t$$

$$J = -\frac{1}{6}(n_1 - n_2)\langle v \rangle = -\frac{1}{3}\langle v \rangle l \frac{(n_1 - n_2)}{2l}$$

$J = -D\frac{(n_1 - n_2)}{2l}$ where: D is the coeficient of diffusion ; but $\Delta x \approx 2l$

therefore: $J \approx -D\frac{\Delta n}{\Delta x} = -D \, grad \, n$

$J = -D \, grad \, n$ This is the Fick law

TRANSFER PHENOMENA IN GASES (4)

Analogously to derive (independetly):

the Newton law $f_{fr} = -\eta \, grad \, v$

where f_{fr} is the internal friction force

$\eta = \frac{1}{3} l n m \langle v \rangle$ is the coefficient of viscosity

the Fourier law $q = -\lambda \, grad \, T$

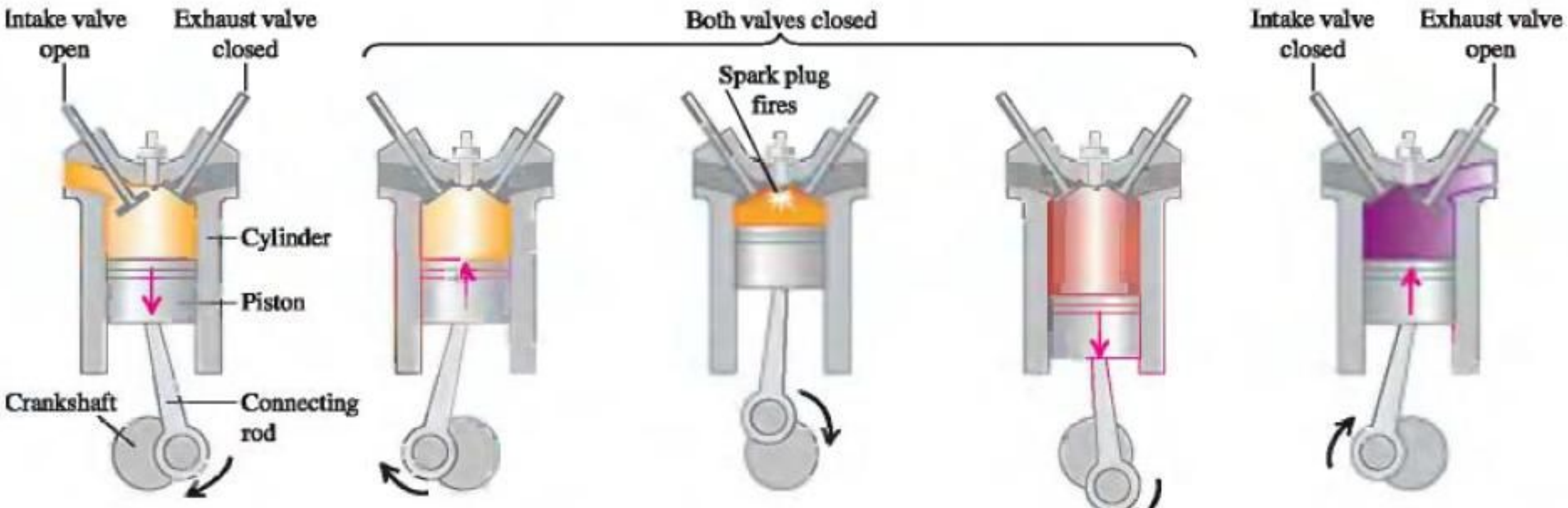
where q is the heat (thermal) flow

$\lambda = \frac{1}{2} l n k \langle v \rangle$ is the heat conduction coefficient (thermal conductivity)

All other values have been determined before

INTERNAL COMBUSTION ENGINE

Cycle of a four-stroke internal-combustion engine.



Intake stroke: Piston moves down, causing a partial vacuum in cylinder; gasoline–air mixture enters through intake valve.

Compression stroke: Intake valve closes; mixture is compressed as piston moves up.

Ignition: Spark plug ignites mixture.

Power stroke: Hot burned mixture expands, pushing piston down.

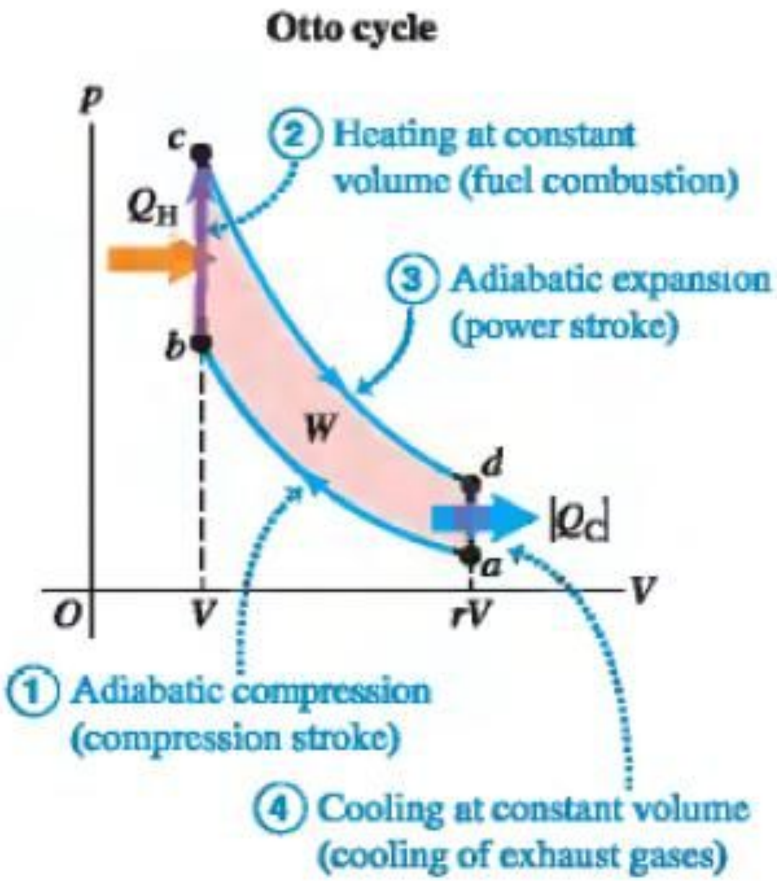
Exhaust stroke: Exhaust valve opens; piston moves up, expelling exhaust and leaving cylinder ready for next intake stroke.

THE *p*-*V*-DIAGRAMS FOR GASOLINE ENGINE AND FOR DIESEL CYCLE

Internal-Combustion Engines

The pV-diagram for the Otto cycle, an idealized model of the thermodynamic processes in a gasoline engine.

The pV-diagram for the idealized Diesel cycle.



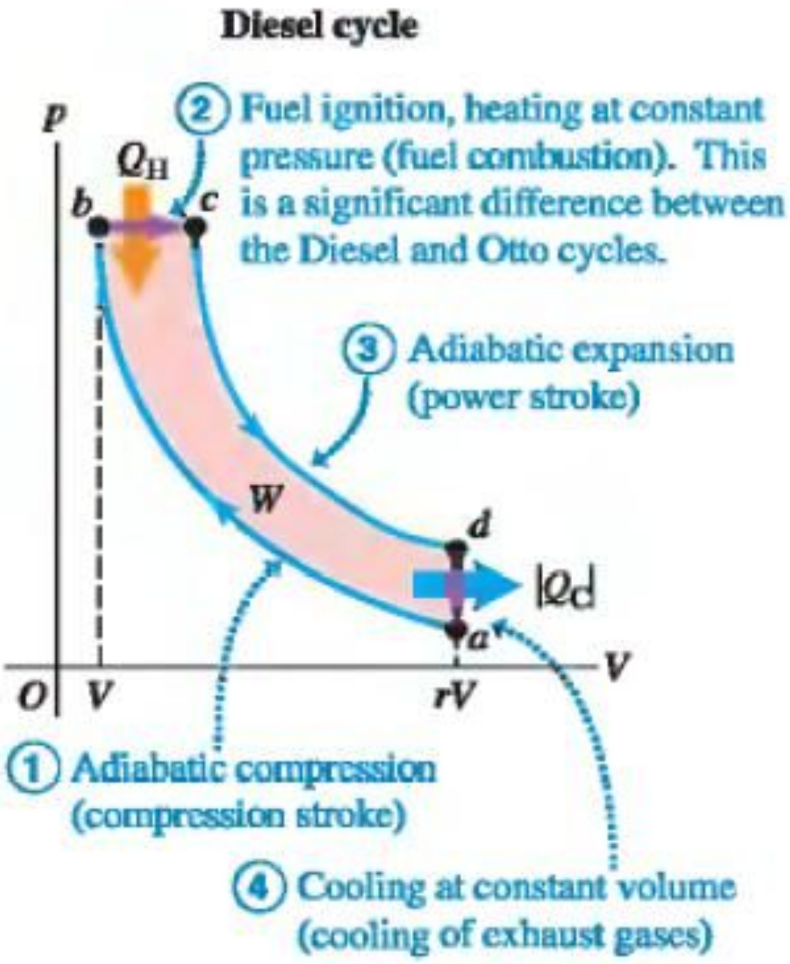
Otto cycle

② Heating at constant volume (fuel combustion)

③ Adiabatic expansion (power stroke)

① Adiabatic compression (compression stroke)

④ Cooling at constant volume (cooling of exhaust gases)



Diesel cycle

② Fuel ignition, heating at constant pressure (fuel combustion). This is a significant difference between the Diesel and Otto cycles.

③ Adiabatic expansion (power stroke)

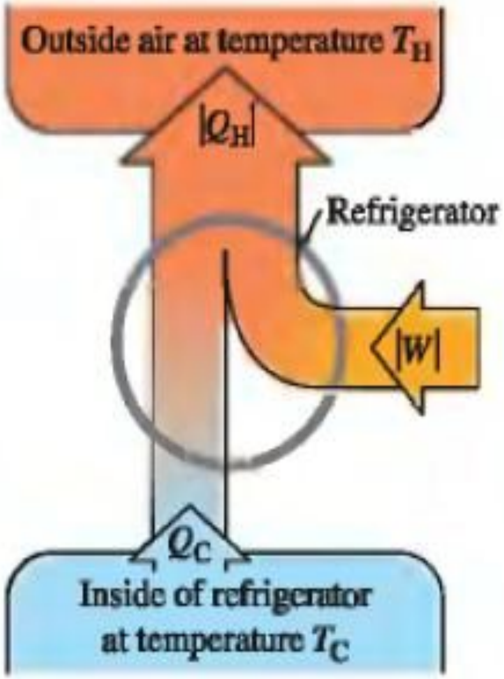
① Adiabatic compression (compression stroke)

④ Cooling at constant volume (cooling of exhaust gases)

ENERGY FLOW FOR REFRIGERATOR AND FOR AIR CONDITIONER

Refrigerators

Schematic energy-flow diagram of refrigerator.



Air conditioner

An air conditioner works on the same principle as a refrigerator.