

# **ELEMENTS OF MOLECULAR PHYSICS**

**Molecular Kinetic Theory  
of Gases**

## MOLECULAR PHYSICS. Glossary-1

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

## MOLECULAR PHYSICS. Glossary-2

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

## MOLECULAR PHYSICS. Glossary-3.

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

# MOLECULAR KINETIC THEORY OF GAS (1)

*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 substance are called its *aggregation 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)

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

$\epsilon_i = \frac{1}{2} m v_i^2$  is the energy of  $i$ -th molecule  
 $m$  is the molecule mass  
 $v$  is the molecule velocity

$\langle \epsilon_{tr} \rangle = \frac{1}{2} m \frac{\sum_{i=1}^N v_i^2}{N} = \frac{1}{2} m \langle v^2 \rangle$   
 is the averaged energy of translation motion of molecules

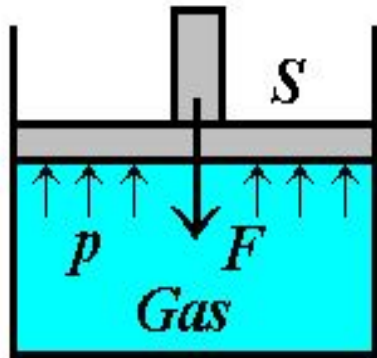
$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{1}{N} \sum_{i=1}^N v_i^2}$  is the root mean square velocity

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

Example:

$$i = 1, 2 \ (N = 2) \\ v_1 = 3, \ v_2 = 5 \quad \langle v \rangle = \frac{3+5}{2} = 4; \quad \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3^2+5^2}{2}} = 4.12; \quad \langle v \rangle \approx \sqrt{\langle v^2 \rangle}$$

## MOLECULAR KINETIC THEORY OF GAS (3)



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

The gas is ideal, which possesses 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.

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

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

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

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

$\frac{pV}{T} = \frac{M}{\mu}R$  is the Mendeleev-Clapeyron equation

# MOLECULAR KINETIC THEORY OF GAS

(4)

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

$\nu$  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

$V_\mu$  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

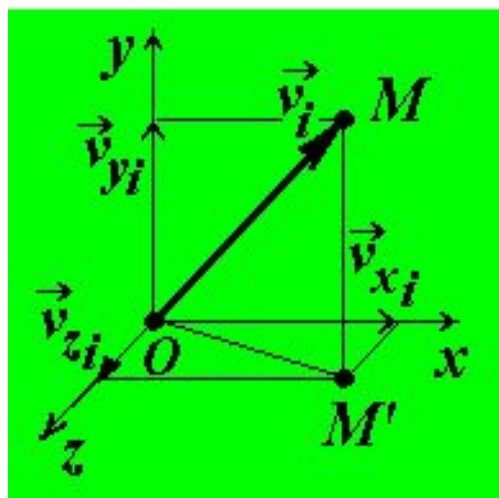
The Avagadro law:

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 (5)

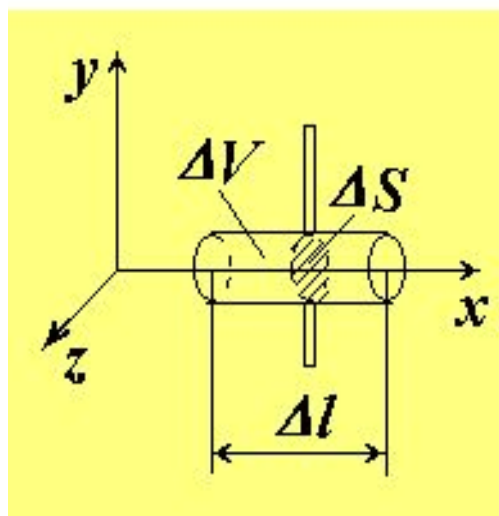


$$\langle \vec{v}^2 \rangle = \frac{1}{N} \sum_{i=1}^N \vec{v}_i^2 = \frac{1}{N} \sum_{i=1}^N \vec{v}_{xi}^2 = \frac{1}{N} \sum_{i=1}^N \vec{v}_{yi}^2 = \frac{1}{N} \sum_{i=1}^N \vec{v}_{zi}^2 \Rightarrow$$

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

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

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



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

or

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

# MOLECULAR KINETIC THEORY OF GAS (6)

## THE CLAUSIUS EQUATION

We suppose that:

- a) the gas is ideal;
- b) all molecules has the same velocities;
- c) the molecules move along the axes 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:

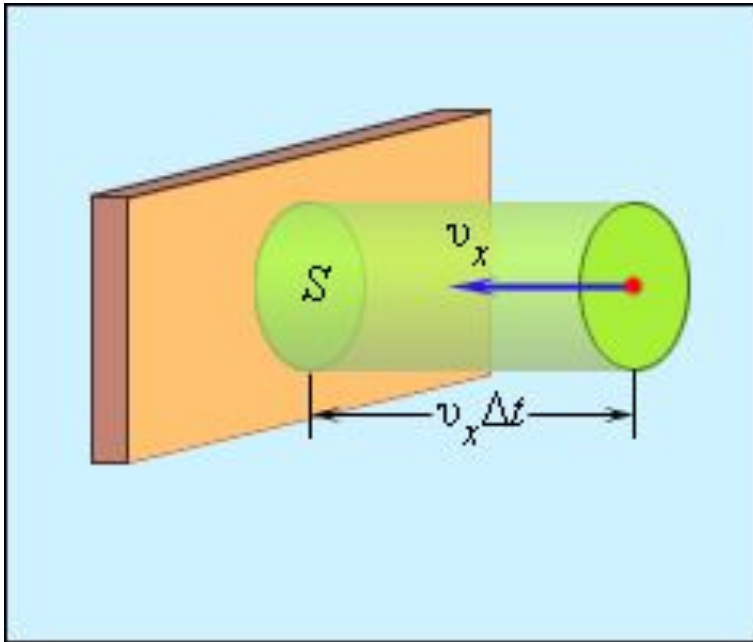
$$\Delta P_i = (-mv) - (mv) = -2mv$$

where  $\Delta P_i$  is the momentum changing for an  $i$ -th molecules

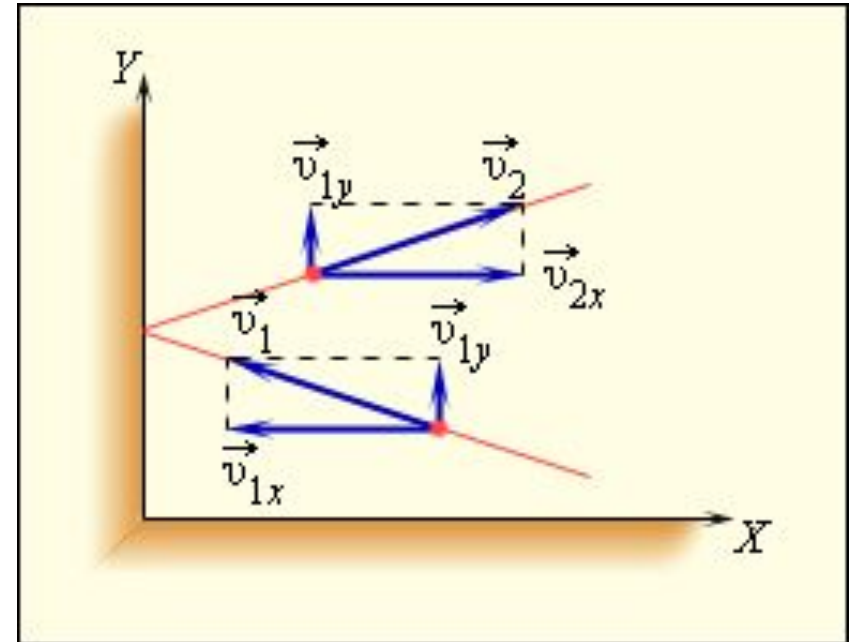
*The total changing the momentum of the gas molecules is:*

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

# 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 (7)

## 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:  $-F\Delta t = \Delta P = -p\Delta S\Delta t \Rightarrow$   
 $\Rightarrow -p\Delta S\Delta t = -\frac{1}{3}nmv^2\Delta S\Delta t$  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:

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

So, we can write:

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

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



## MOLECULAR KINETIC THEORY OF GAS (8)

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

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

$$\Rightarrow pV = \frac{2}{3} E_{tr}$$

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

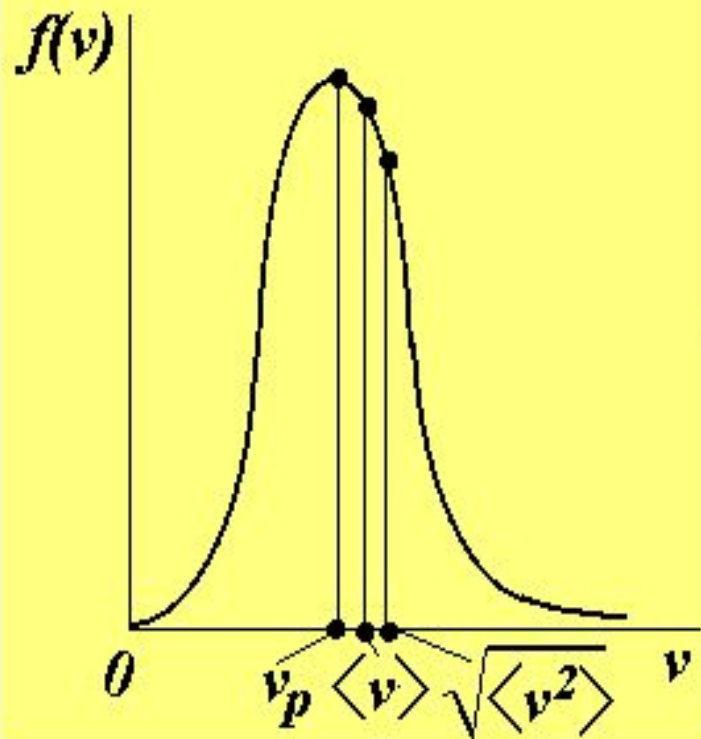
$$\langle \epsilon_{tr} \rangle = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} kT$$

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

# MOLECULAR KINETIC THEORY OF GAS (9)

## MAXWELL DISTRIBUTION

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

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

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

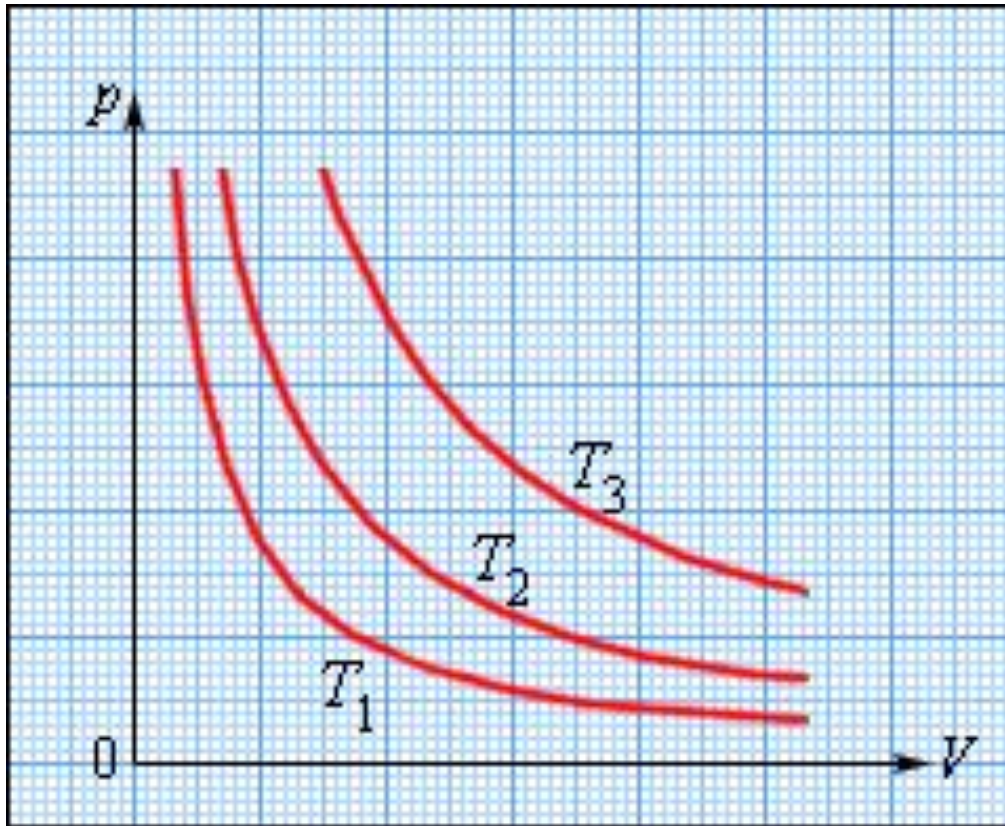
## **MOLECULAR KINETIC THEORY OF GAS**

**(10)**

**At home independently:**

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

# ISOTHERMAL PROCESS ( $T = \text{const}$ )

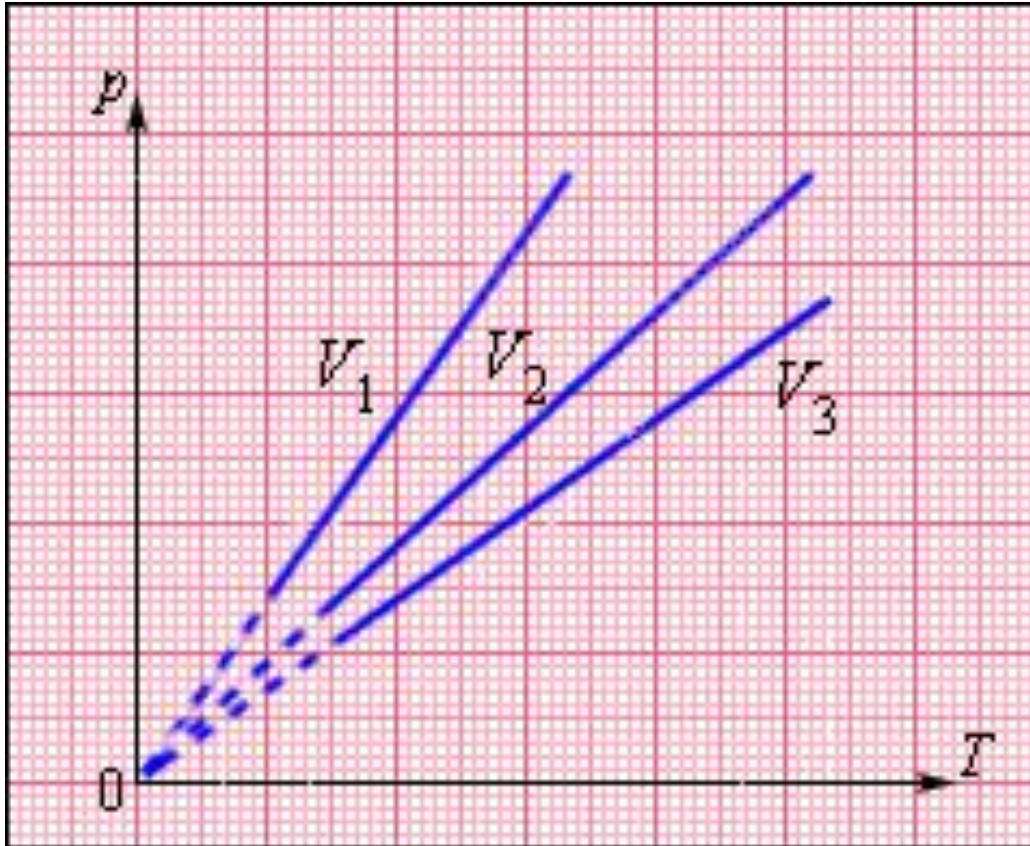


$$pV = \text{const.}$$

$$T_3 > T_2 > T_1$$



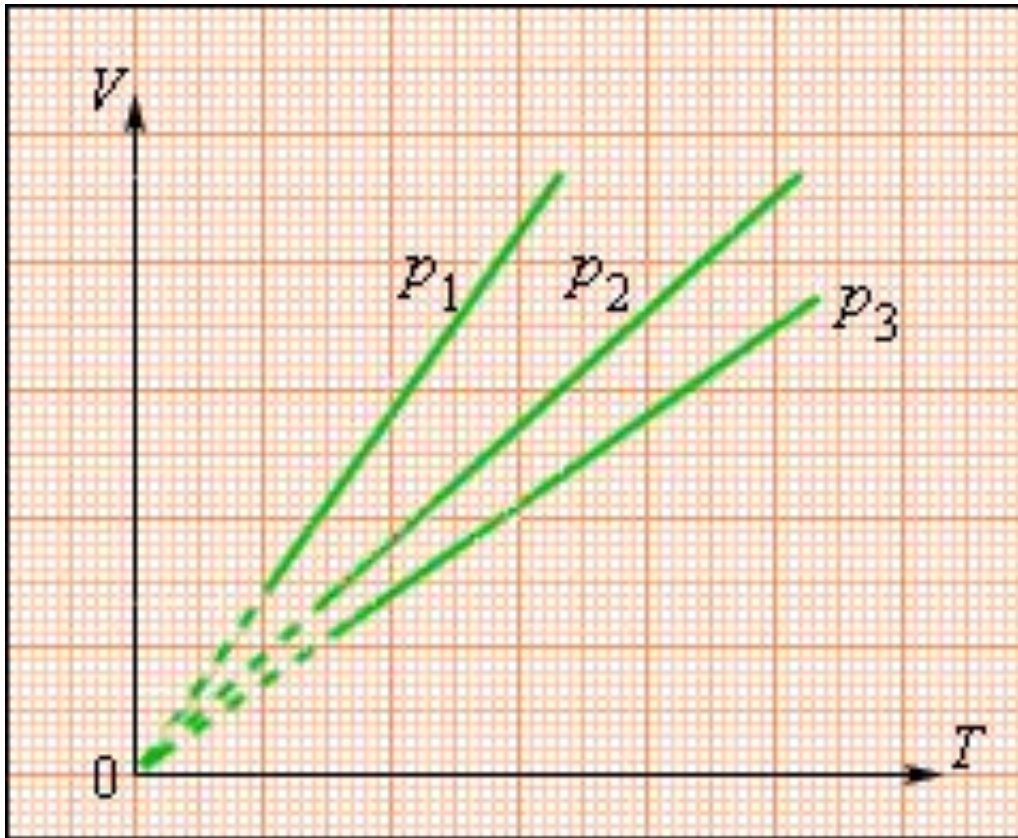
## ISOBARIC PROCESS ( $V = \text{const}$ )



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

$$V_3 > V_2 > V_1$$

# ISOBARIC PROCESS ( $p = \text{const}$ )



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

$$p_3 > p_2 > p_1$$

# 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 referred traditionally in the thermodynamics to as the internal energy.*

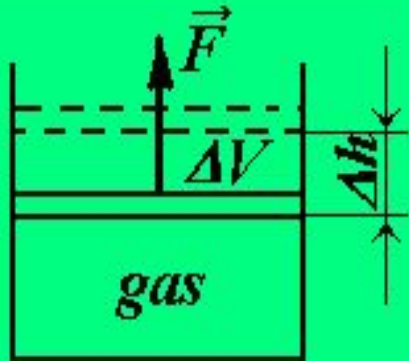
$U = U(V, T)$  *is the caloric equation*

*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

$\delta Q$  is the infinitesimal heat increment

$\delta A$  is the infinitesimal work increment

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

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

$$\oint_L dU = 0$$

$\delta Q$  and  $\delta A$  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:  $i = 6$ .

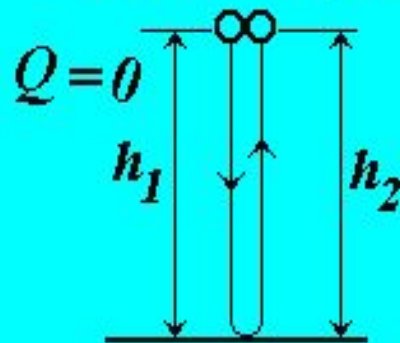
Mayer's theorem:

$$C_p - C_V = R$$

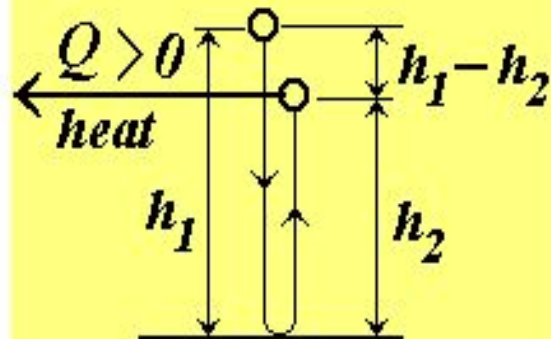
# THE SECOND LAW OF THERMODYNAMICS (1)

## INCIDENCE OF A SPHERE

*reversible process*



*irreversible process*



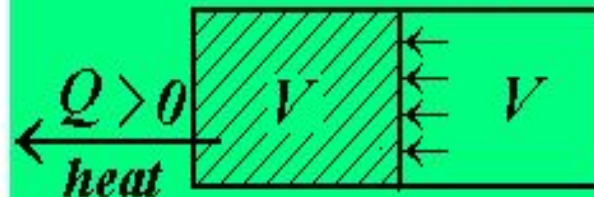
## EXPANSION OF A GAS



*take away  
the partition*



*restoration of  
the situation*



$\Omega$  - is the statistical weight  
(or the thermodynamic  
probability).

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

$$S = k \ln \Omega$$

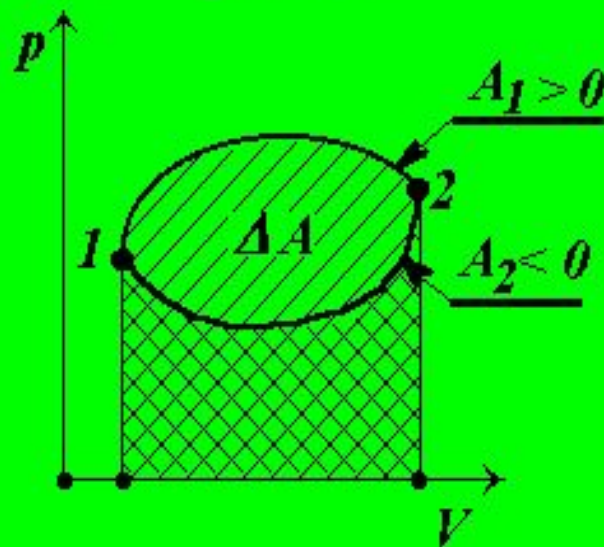
$S$  is the entropy  
 $k$  is the Boltzmann  
constant

The entropy is an measure  
of chaos in the system



# THE SECOND LAW OF THERMODYNAMICS (3)

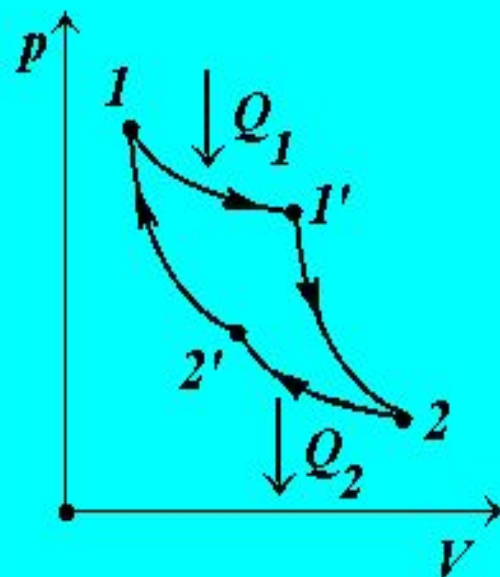
*The circular process*



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

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

*Carnot cycle*



$$1 - 1' \quad T = \text{const}$$

$$1' - 2 \quad Q = \text{const}$$

$$2 - 2' \quad T = \text{const}$$

$$2' - 1 \quad Q = \text{const}$$

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

$$T = \text{const}; \quad dU = 0$$

$$\delta Q = \delta A$$

$$Q = \text{const}; \quad \delta Q = 0$$

$$dU = -\delta A$$

*Carnot theorem*

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

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

$$\eta = \frac{\Delta A}{A_I} = \frac{Q_I - |Q_2|}{Q_I}$$



# THE SECOND LAW OF THERMODYNAMICS (3)

*The entropy of one mole of the ideal gas*

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

*The changing of entropy 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 entropy  $S = S_1$*

*The second law of thermodynamics  
(the Clausius formulation)*

$$dS \geq 0$$

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

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

*The Mendeleyev - Clapeyron  
for one mole of the ideal gas*

$$pV = RT$$

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

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

*In the case of irreversible process:*

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

*In the general case:*

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

# REAL GAS THEORY

(1)

*The gas can be considered ideal if:*

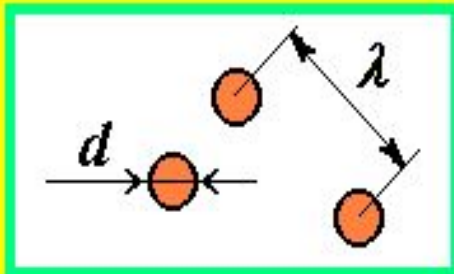
- a) the gas molecules can be considered as material points;*
- b) all collisions between the molecules are perfectly elastic;*
- c) the attracting and repulsive forces do not act between the molecules.*

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

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

*where  $f$  is the compressibility coefficient*

*The model of the real gas*



*$d$  is the molecule diameter  
 $\lambda$  is the distance between molecules*

*In the case of real gas the compressibility coefficient*

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

# REAL GAS THEORY

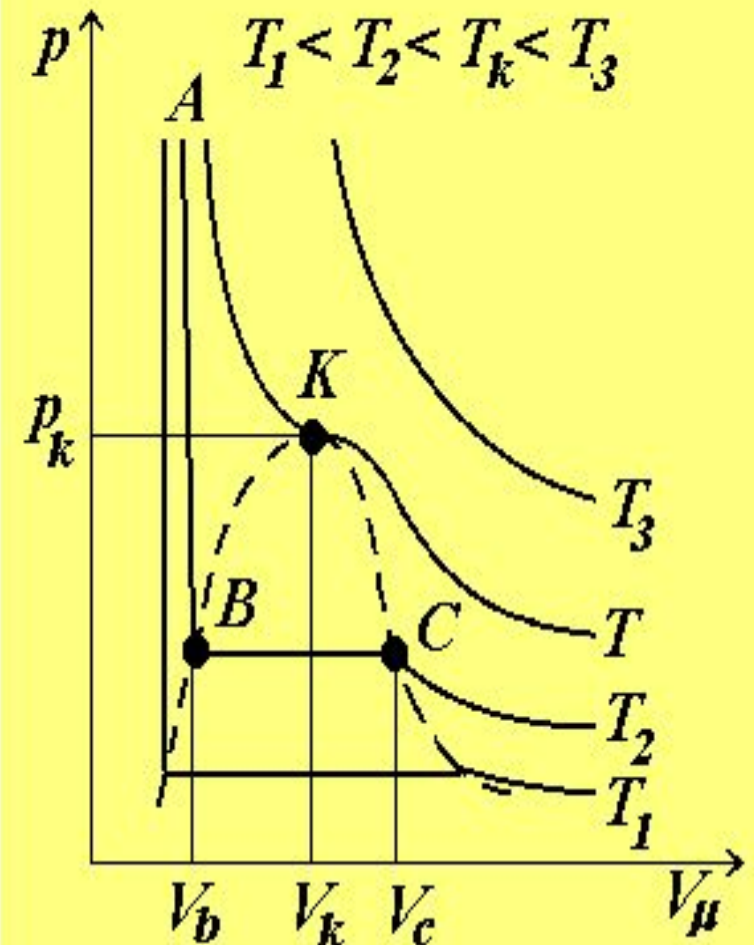
(2)

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

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

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

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

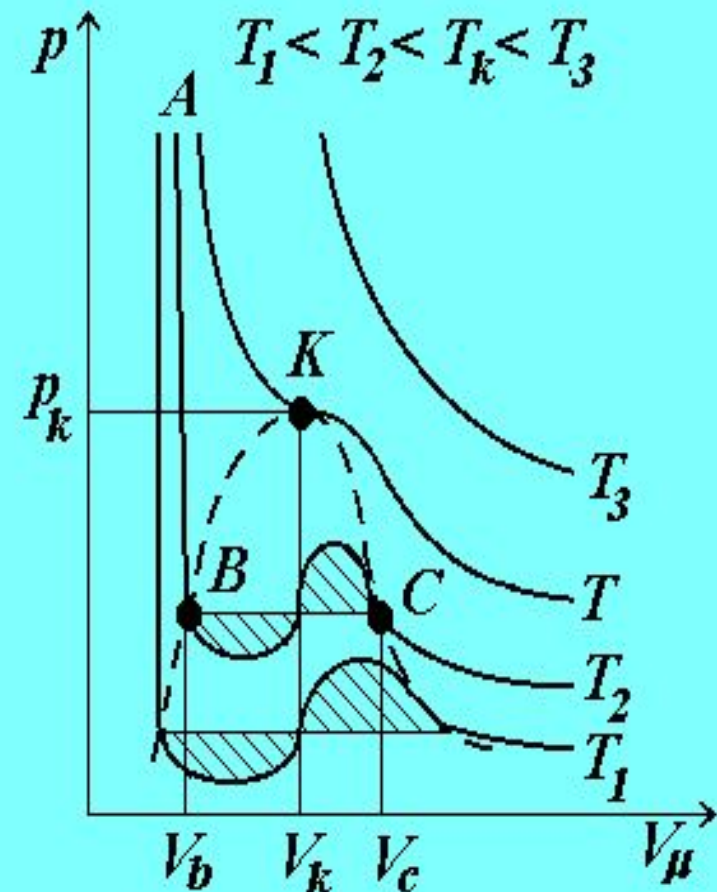
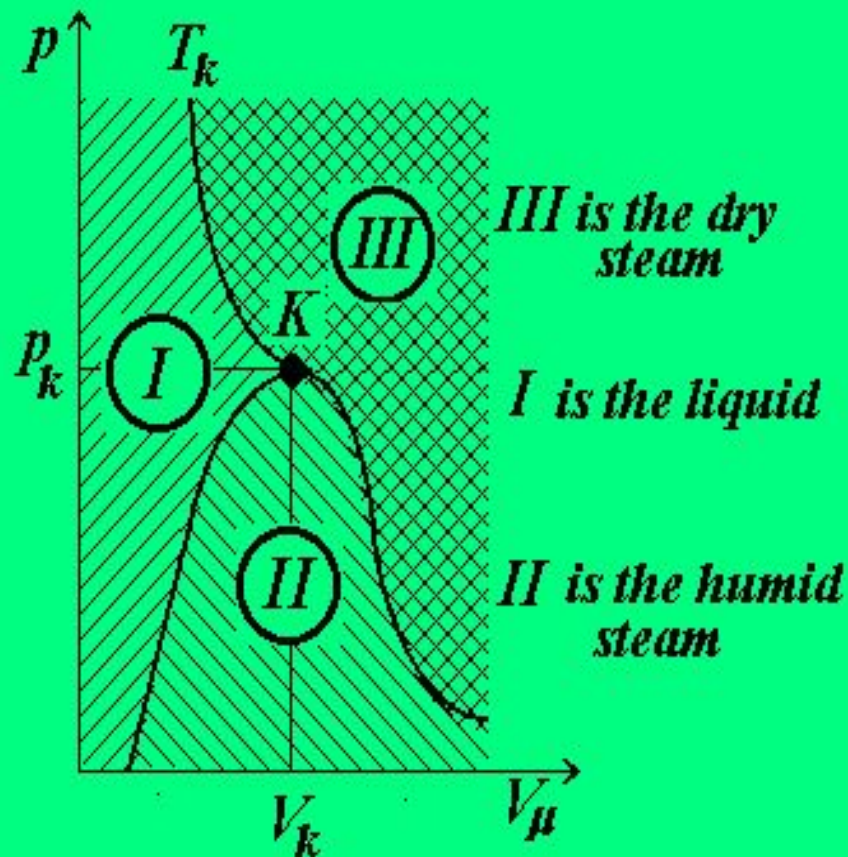




# REAL GAS THEORY

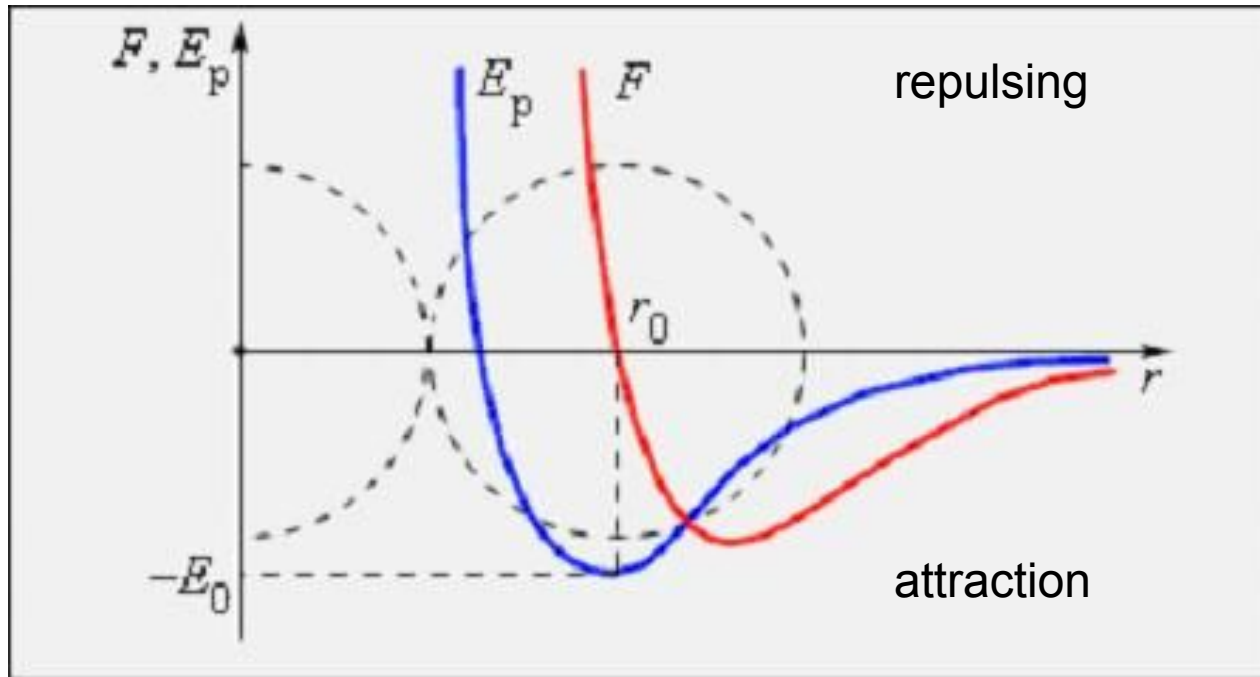
(3)

The phase diagram



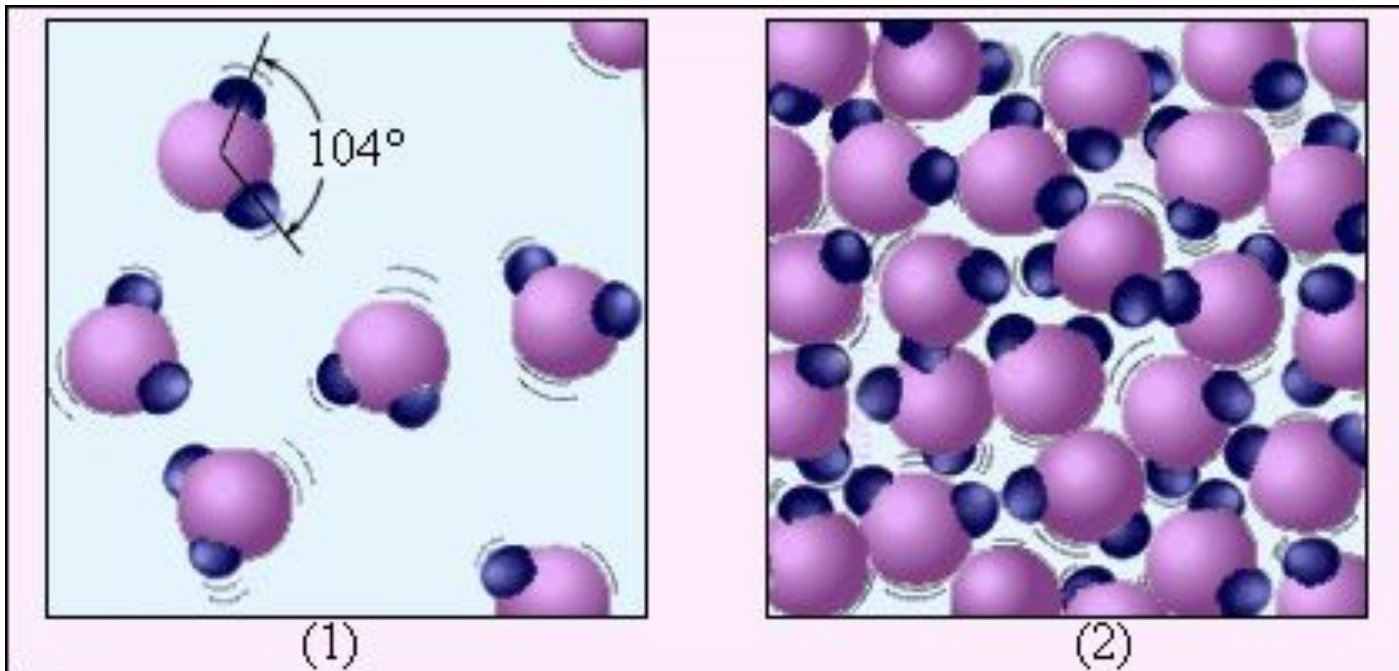
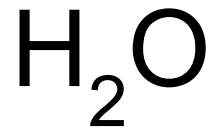
$$p_k = \frac{1}{27} \frac{a}{b^2}; \quad V_k = 3b; \quad T_k = \frac{8}{27} \frac{a}{bR}$$

# 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



**Vapor of water**

**Liquid water**

Scale of molecules drawing is  $5 \times 10^7$ .



# TRANSFER PHENOMENA IN GASES

(1)

The transfer phenomena:

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

$$l = \frac{1}{\sqrt{2} \pi d^2 n} \quad \text{is the averaged path (track) length}$$

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

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

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

*Example:*

$$d \approx 2 \cdot 10^{-10} \text{ m}$$

$$n \approx 2.7 \cdot 10^{25} \text{ m}^{-3}$$

$$p \approx 1 \text{ atm}$$

$$T \approx 273 \text{ K}$$

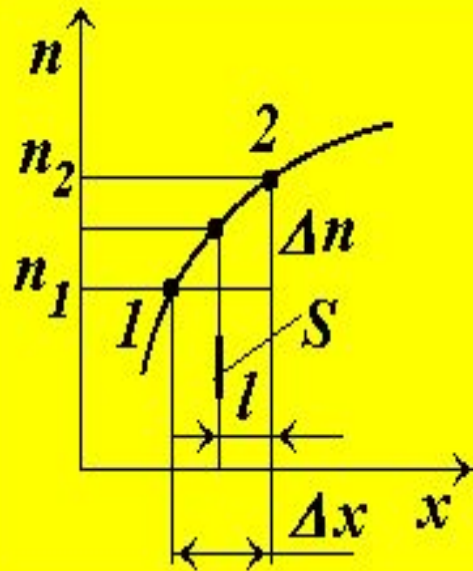
$$l \approx 10^{-7} \text{ m}$$

*What is the vacuum?*

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

# TRANSFER PHENOMENA IN GASES

(2)



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

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

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

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

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

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

$$J = -D \text{ grad } n \quad \text{This is the Fick law}$$

# TRANSFER PHENOMENA IN GASES

(4)

Analogously to derive (independently):

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

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  $q = -\lambda \text{ grad } T$

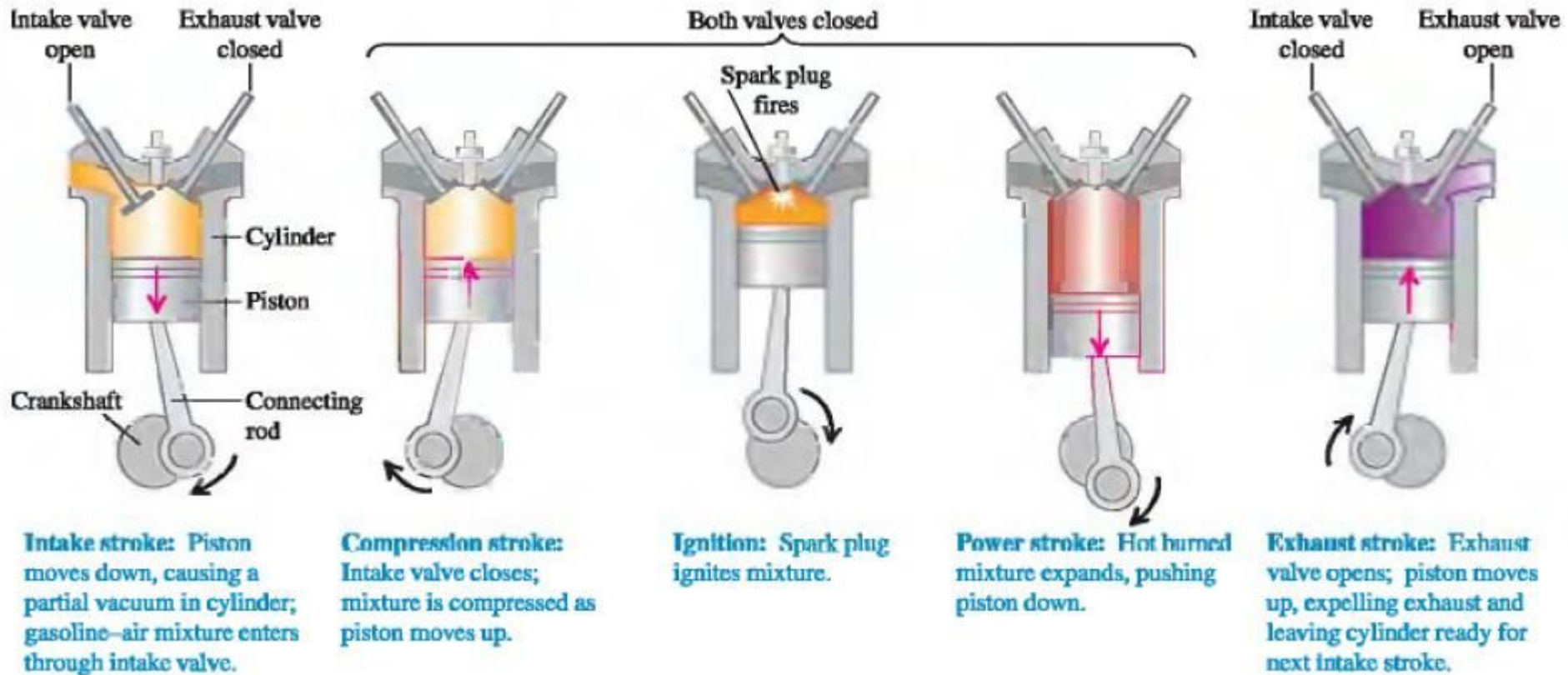
where  $q$  is the heat (thermal) flow  $\lambda = \frac{1}{2} l n k \langle v \rangle$  is the heat conduction coefficient (thermal conductivity)

All other values have been determined before



# INTERNAL COMBUSTION ENGINE

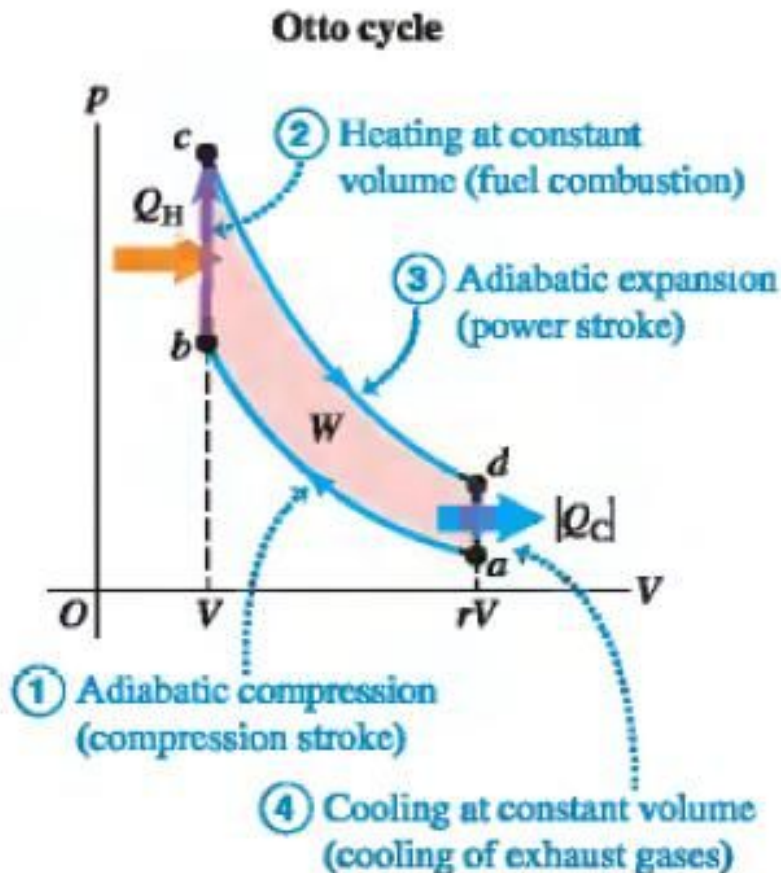
Cycle of a four-stroke internal-combustion engine.



# THE $p$ - $V$ -DIAGRAMS FOR GASOLINE ENGINE AND FOR DIESEL CYCLE

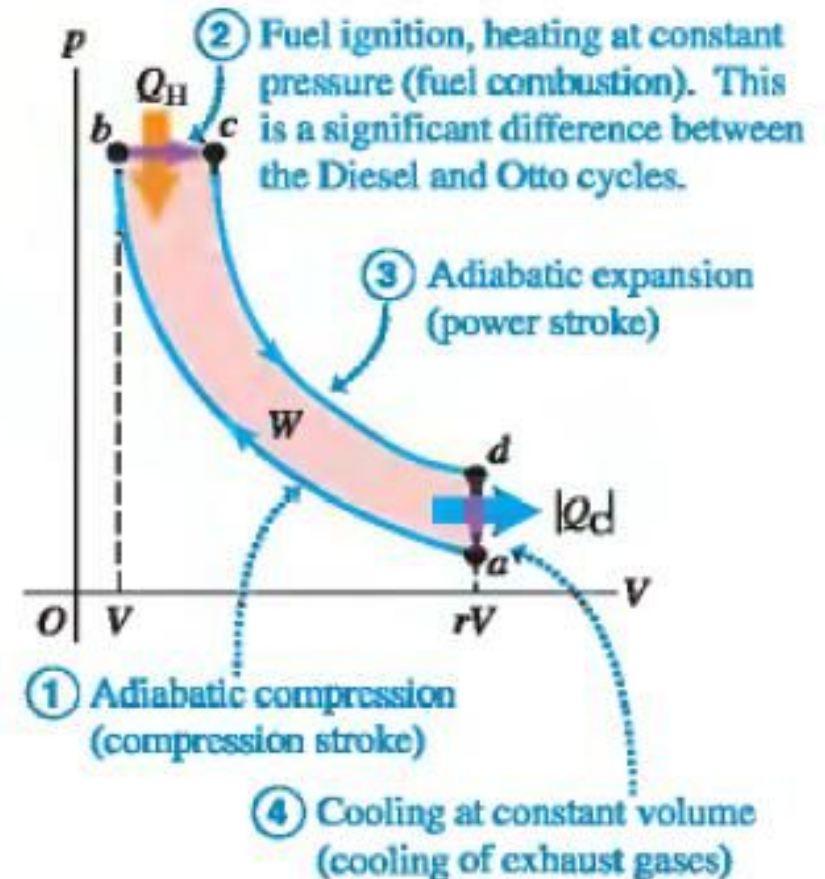
## Internal-Combustion Engines

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.

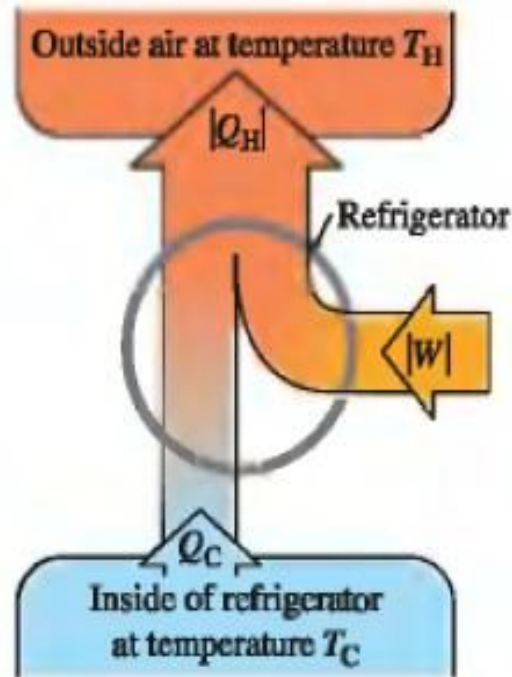
## Diesel cycle



# 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.

