MOLECULAR PHYSICS

CLASSICAL MECHANICS

Analysis of kinematics and dynamics properties of:

- **individual atoms (molecules) as material points in gases**
- **continuous set of atoms (molecules) in liquids**
- **continuously ordered set of atoms (molecules) in rigid bodies (solids)**

Description approach based on:

- **kinematics and dynamics laws: motion equations, Newton’s laws, continuity law, Bernoulli law, etc.**
- **conservation principles: momentum, energy, angular momentum.**

MOLECULAR PHYSICS

Analysis of physical phenomena in macroscopic systems of many atoms (molecules) like gas, liquid and solid, using primary physical parameter: TEMPERATURE

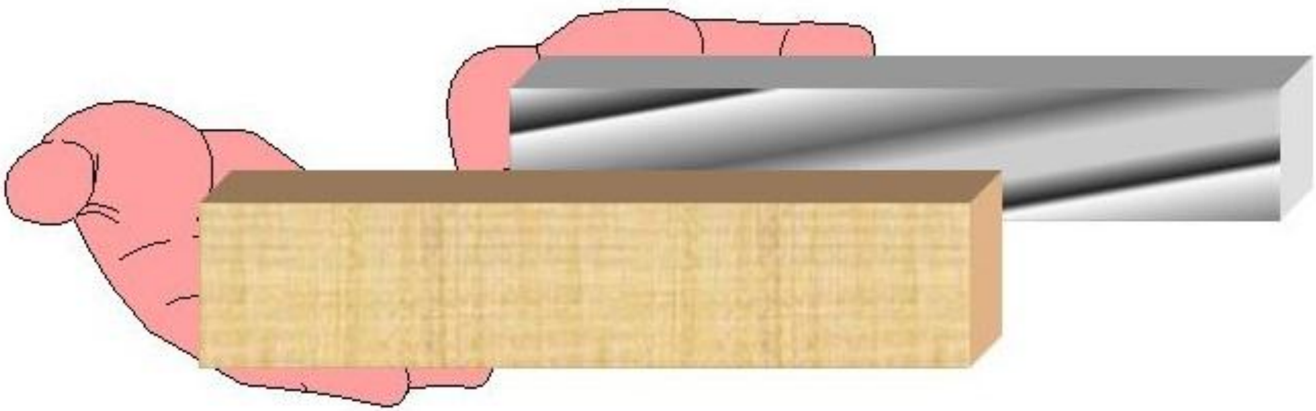
TEMPERATURE

Fundamental thermal parameter

basic property (attribute) of a body that determines its thermal equlibrium with another body - two temperature quantities:

- **SUBJECTIVE**

  impression - sensitivity (susceptibility) to heat (temperature)



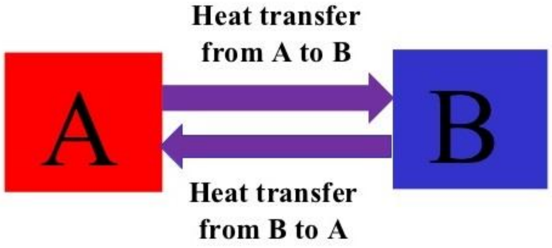
Common impression:
We always feel the metal as colder than wood at the same temperature

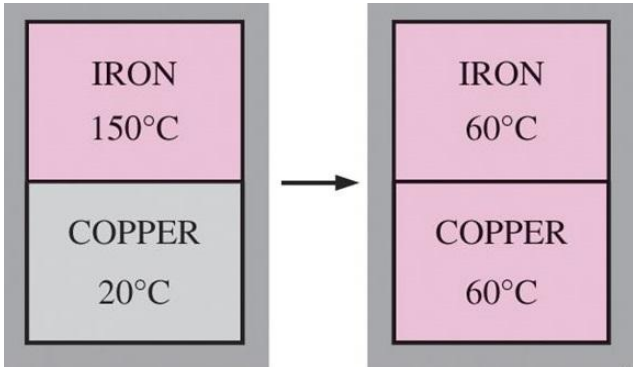
Why?:
Metal conducts the heat away from our hands, whereas wood does not conduct the heat away from our hands and feels warmer than metal.

TEMPERATURE

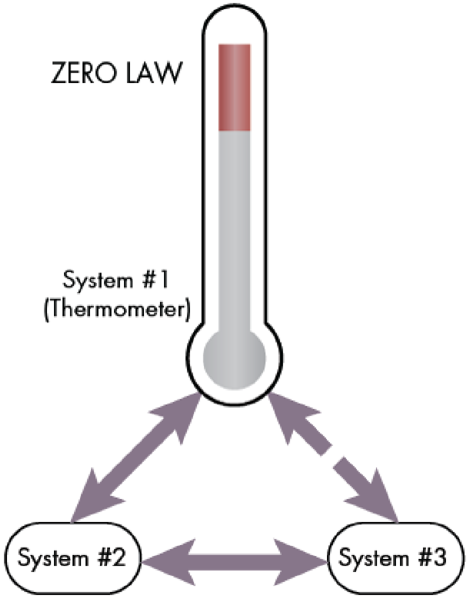
▪ OBJECTIVE - PHYSICAL

Measure of thermal equlibrium between two bodies (systems)





controlled via additional system – idea of thermometer



Thermal equlibrium between two systems in contact:

System 2 (temperature T_2) and system 3 (temperature T_3)

when $[T_2 = T_1] \wedge [T_3 = T_1] \Rightarrow [T_2 = T_3]$

- certain physical postulate - Zero thermodynamics law

Quantitative determination of temperature
- temperature scales: relative (empirical) and absolute (thermodynamics)

TEMPERATURE

RELATIVE (EMPIRICAL) TEMPERATURE SCALE

MAIN IDEAS

1596: Galileo - thermoscope for temperature variation

1612: Sartorio - thermoscope with scale without reference

1654: Ferdinand II (Grand Duke of Tuscany) – first liquid in glass system

1714: Fahrenheit

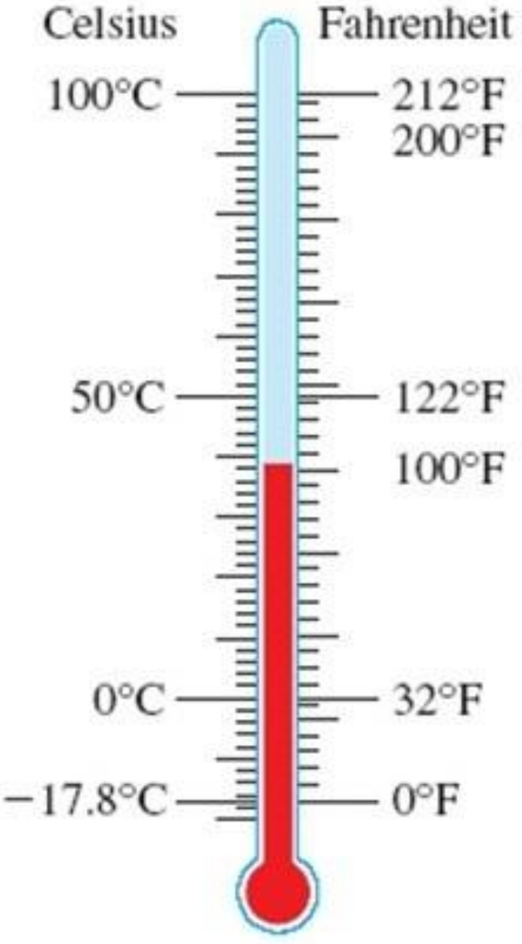
first Hg in glass system; scale of two boundary points: boiling water (180) and laboratory temperature (32?)

1731: Reamur

scale of two boundary points: freezing (0) and boiling water (80)

1742: Celsius

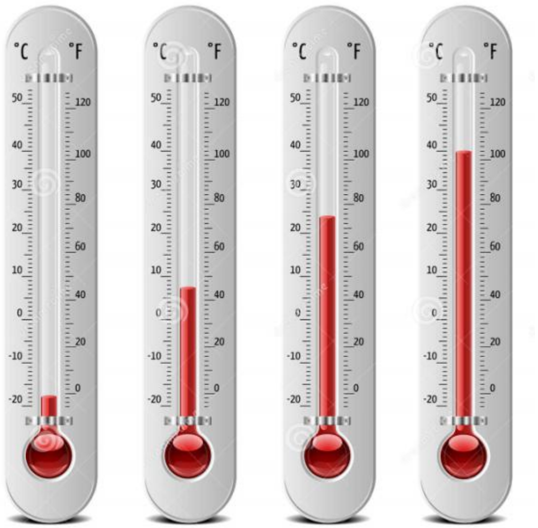
scale of two boundary points: water triple point (0°C) and water boiling point (100°C)



TEMPERATURE

RELATIVE (EMPIRICAL) TEMPERATURE SCALE

Two types of relative scale thermometers:



- **analog liquid thermometers:**

measurement of variation thermal expansion of liquids: alcohols, Hg (toxic!)

- **electronic digital thermometers:**

measurements of variation of thermal Seebeck effect at bimetalic junctions

Celsius practical scale since 1948.

TEMPERATURE

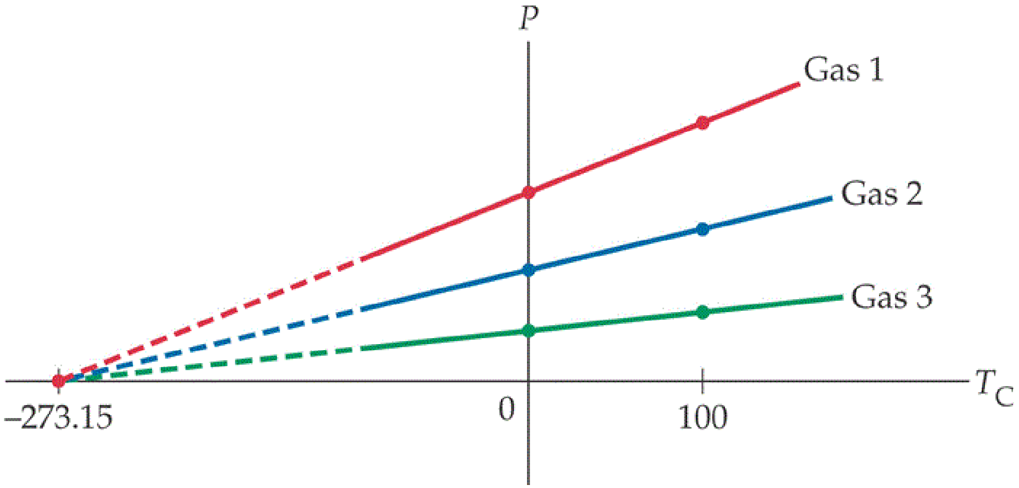
ABSOLUTE (THERMODYNAMICS) SCALE

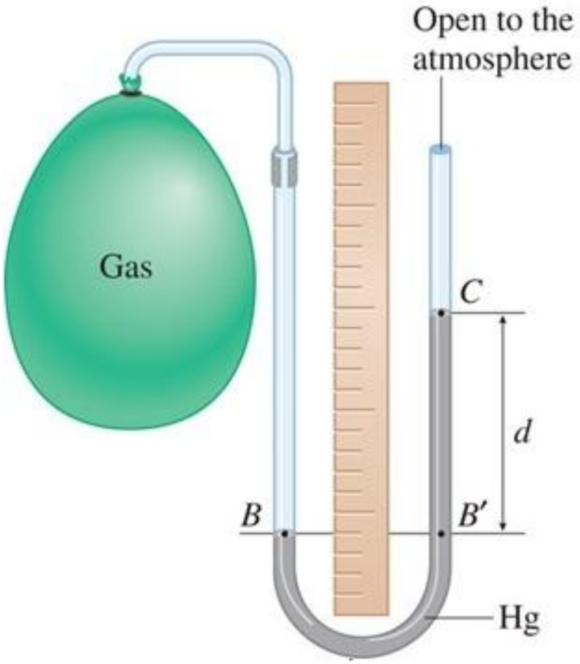
Idea: Lord Kelvin (1848)

Isochoric gas transition in glass vessel joint to U tube with Hg - according to empirical Charles relation

$$p(t)=p_0(1+\alpha\cdot t)=p_0\left(1+\frac{t}{273.16}\right)$$

- linear dependences of pressure vs temperature for all the gases



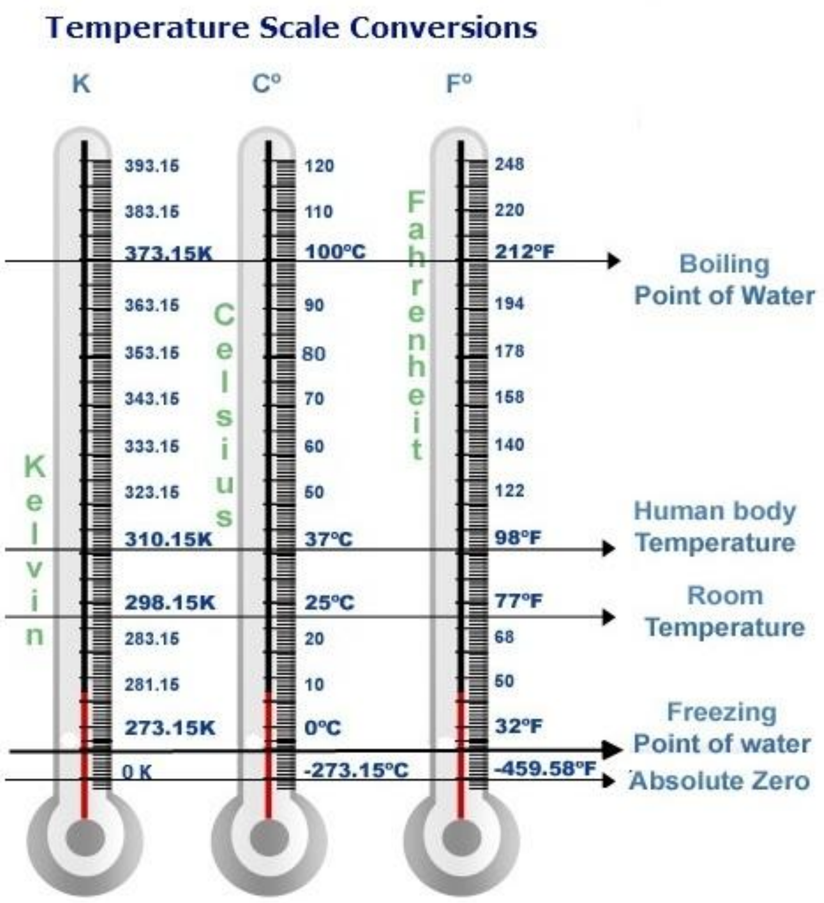


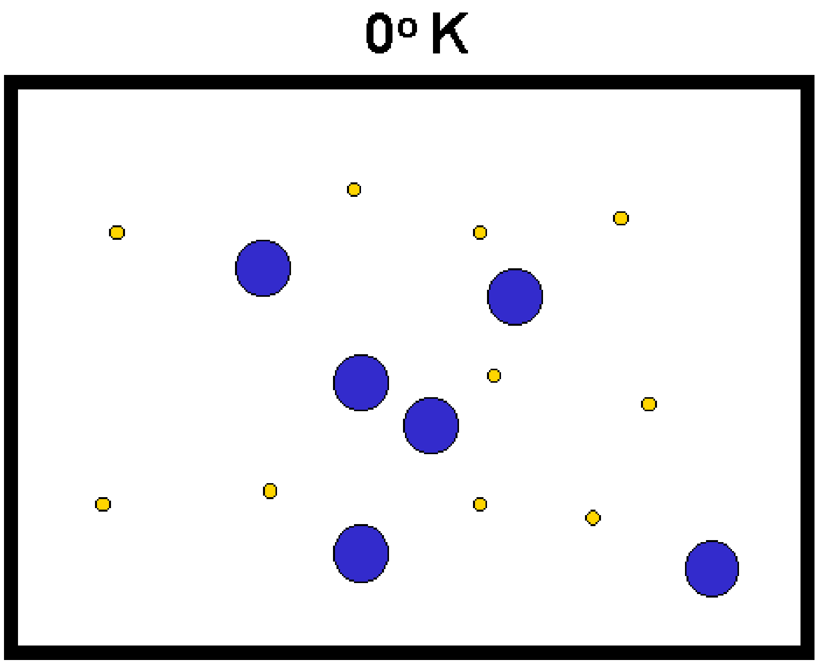
Extrapolation for all gases to 0 gives absolute zero point temperature t = -273.16° C - base of absolute Kelvin scale of T – 0 [K]

Kelvin basic temperature scale in SI system of units (SI) since 1954

TEMPERATURE

COMMONLY USED TEMPERATURE SCALES





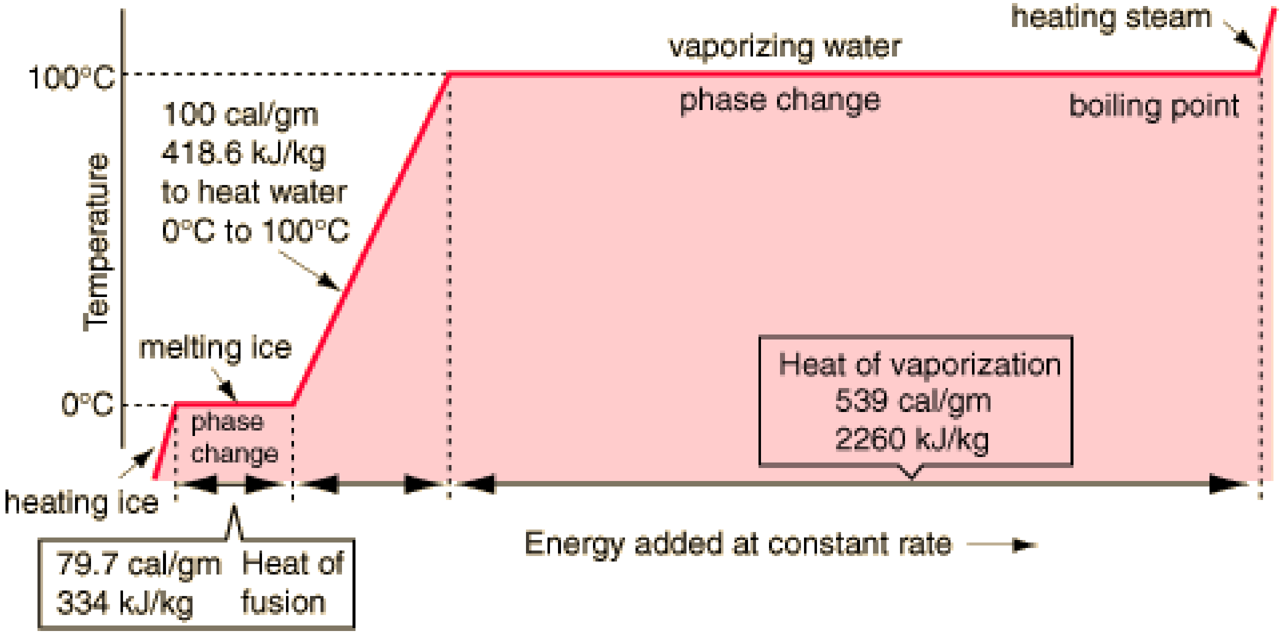
Temperature 0 K - minimal (zero point) energy of every atoms (molecules) - „freezing” effect of motion; Universe background radiation - 4 K (BBM)

Temperature: basic parameter determining every phase transitions

TEMPERATURE

IMPORTANCE

- Control of phase transition (aggregation states)



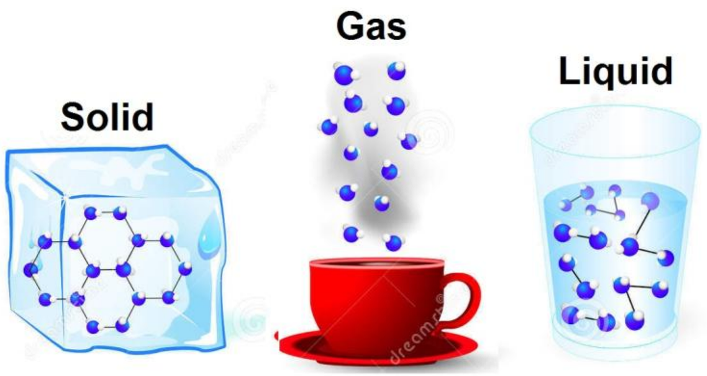
5 thermal processes at different latent heat of transitions:

- ice heating up to T=273 K $\Delta Q_{ih} = m \cdot c_i (273 - T)$
- ice melting at T=273 K $L_f = m \cdot l_f$
- water heating up to T=373 K $\Delta Q_{hw} = m \cdot c_w (T - 273)$
- water vaporisation at T=373 K $L_v = m \cdot l_v$
- steam heating at T>373K $\Delta Q_{vh} = m \cdot c_v (T - 373)$

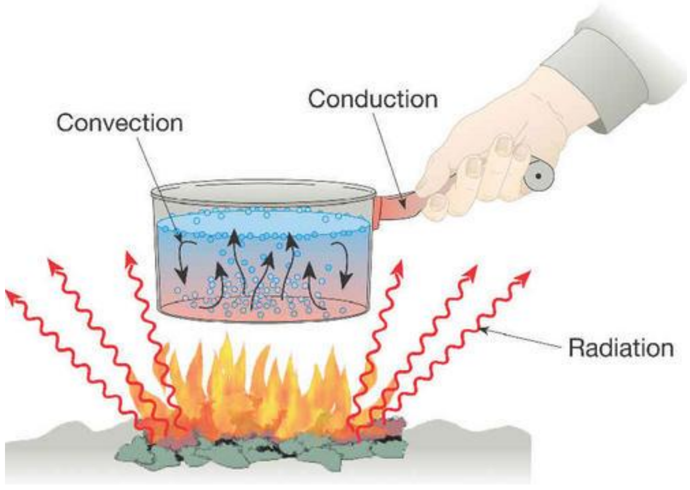
TEMPERATURE

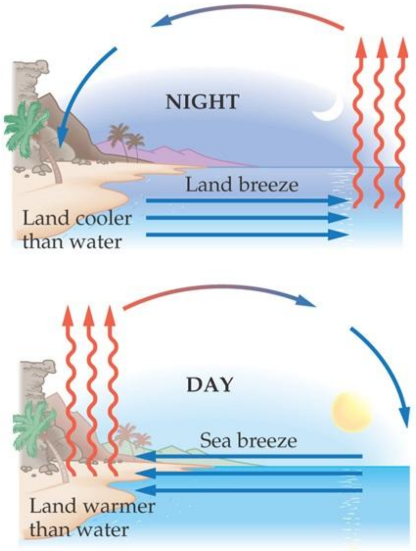
IMPORTANCE

- Decides on fundamental states of matter and phase transitions



- Decides on common heat transfers and thermal effects around us





GAS GENERAL PROPERTIES

GAS

Infinitive number of extremely small particles in continuous motion and collisions (mutual and internal) inside the vessel (Bernoulli - 1738)

As a system of huge amount of particles can be treated as:

- **Large collection (reservoir) of individual particles**

  individual properties of molecules considered - theoretical models based on microscopic parameters of every molecule:
  mass (m), velocity (υ), momentum (m·υ), kinetic energy (E_k)
  Domain of statistical physics

- **Continuous medium**

  individual properties of molecules neglected - empirical laws based on macroscopic quantities:
  - parameters of state: p, V, T, n
  - functions of state/process: U, Q, W, S, H depends on p.s.
  Domain of phenomenological thermodynamics

GAS PARAMETERS AND TRANSITIONS

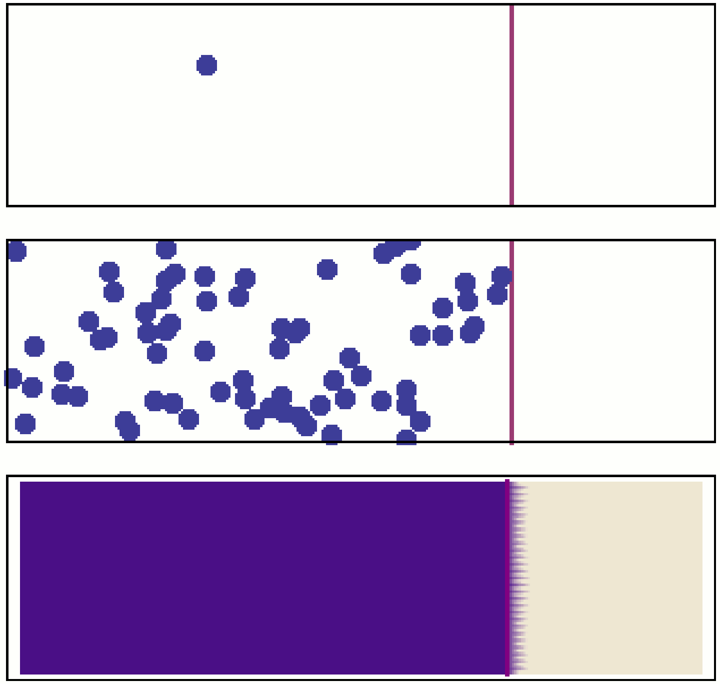
PARAMETERS OF STATE

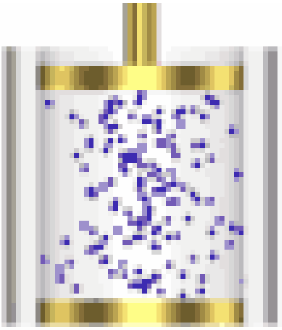
pressure p, volume V, temperature T, amount of gas n

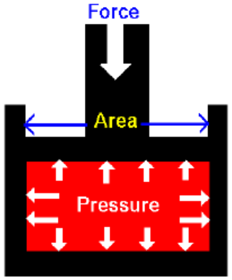
Primary parameter: gas pressure - Bernoulli (1738)

Gas as system of great number of particles fulfiling all the vessel

When closed by movable piston of weight F and area A - base for definition







Pressure force acts perpendicular to enclosing surfaces.

$$p = \frac{F\ (\text{Force})}{A\ (\text{Area})}$$

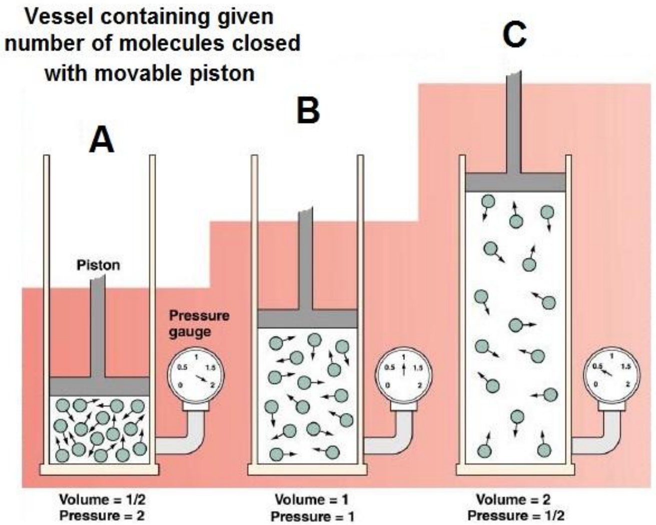
Pressure - macroscopic parameter od state

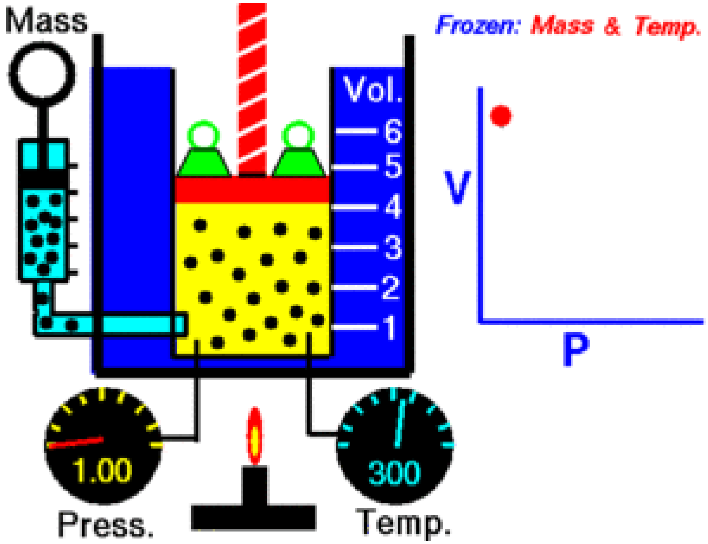
- base for quantitative description of macroscopic properties of gas system by empirical laws for gas transitions (processes)

- general shape of relations - linear dependences on main parameters

GAS TRANSITIONS

LAW OF ISOTHERM: T = const





Boyle-1662

Mariotte-1676

In vessel closed by movable piston at constant temperature gas pressure p is inversely proportional to its volume V

$$p = const \cdot \frac{1}{V}$$

At constant temperature product of ideal gas pressure and its volume remains always constant

$$p_1 \cdot V_1 = p_2 \cdot V_2 = p \cdot V = const$$

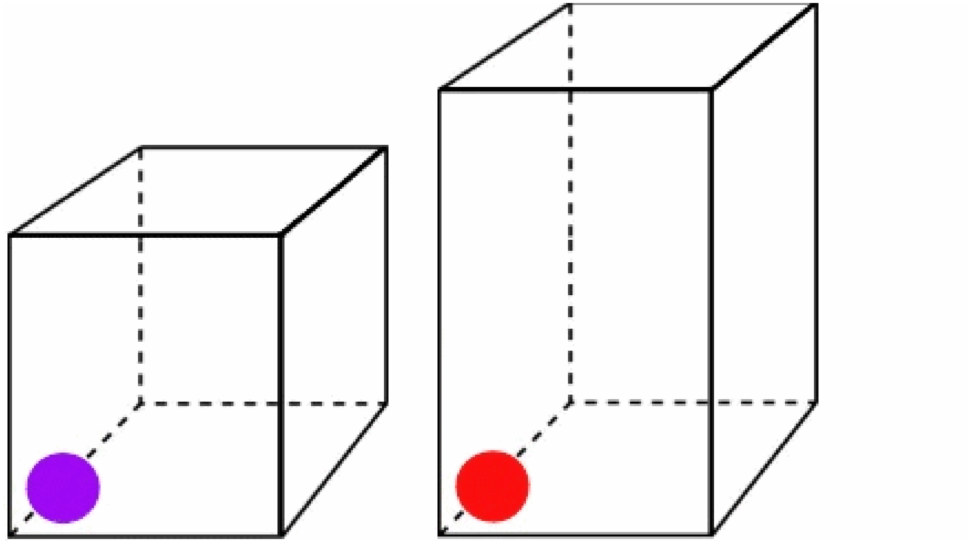
Domain of phenomenological thermodynamics

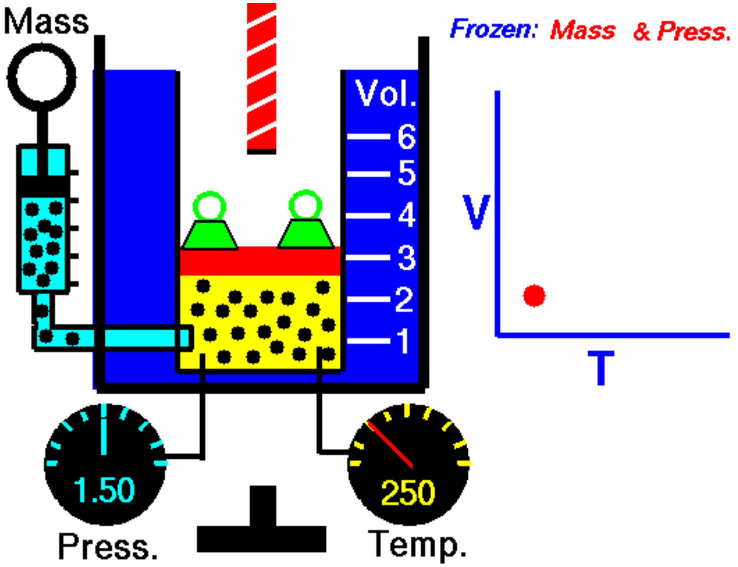
GAS TRANSITIONS

LAW OF ISOBARE: p = const

Charles - 1787

In vessel closed by movable piston at constant pressure its volume V increased linearly with temperature T





When temperature T increases by 1 degree its volume V increases by 1/273 according to formula

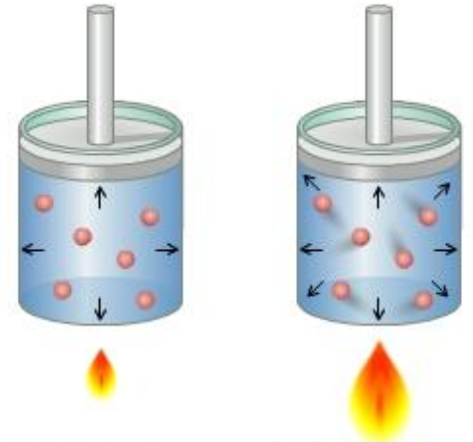
$$V = V_0(1 + \alpha \cdot t) = V_0\left(\frac{T}{273.16}\right) = V_0\left(\frac{T}{T_o}\right)$$

GAS TRANSITIONS

LAW OF ISOCHORE: V = const

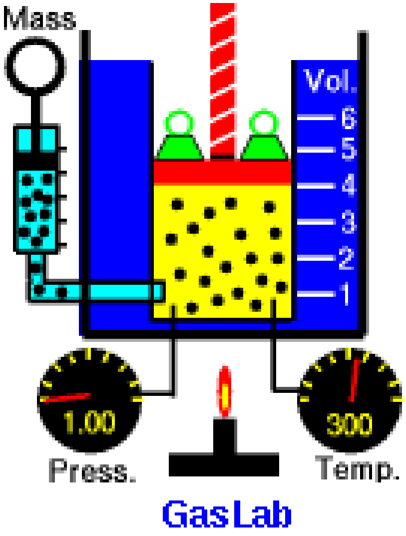
Guy-Lusac - 1802

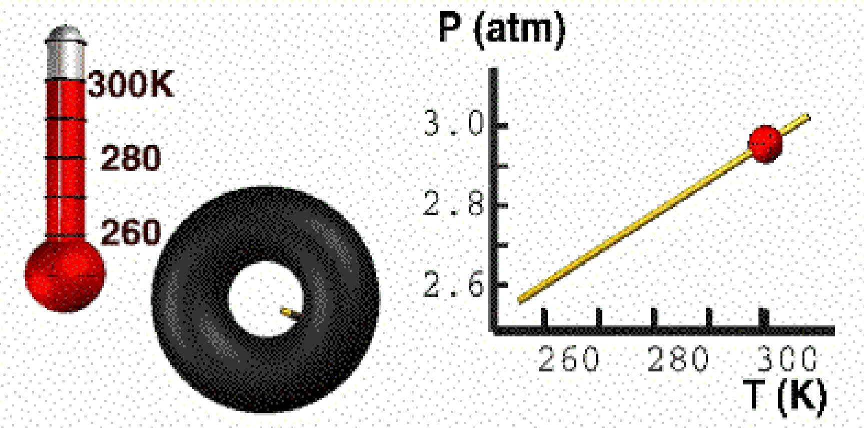
At constant gas volume V in vessel closed by fixed piston gas pressure p increases linearly with temperature T



Lower temperature
Lower pressure

Higher temperature
Higher pressure





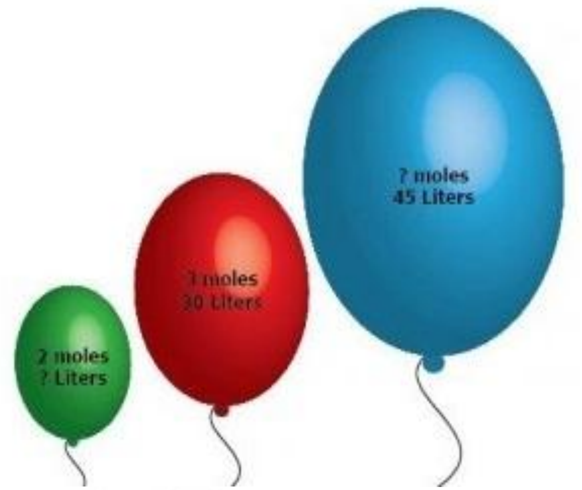
After increases of temperature T by 1 degree, the corresponding pressure increases by 1/273 according to formula

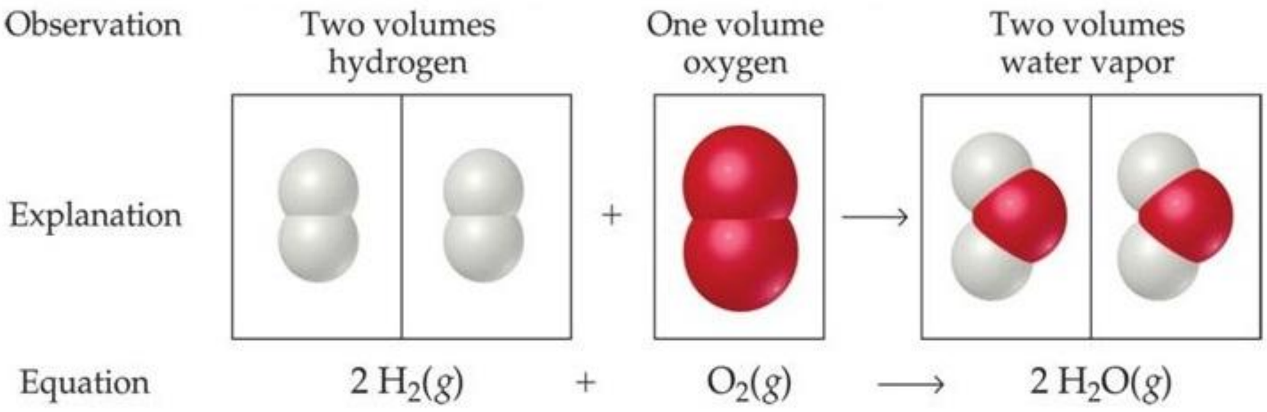
$$p(t) = p_0(1+\alpha\cdot t) = p_0\left(1+\frac{t}{273.16}\right) = p_o\frac{T}{T_o}$$

MODEL OF IDEAL GAS

AVOGADRO LAW (PRINCIPLE) - 1811

1 mole of all gases at normal conditions: p_o = 1 atm. (10^5 N/m^2) and T_o = 273 K exhibits unit volume of 22.4 dcm^3 and consists of $N_A = 6{\cdot}10^{23}$ molecules





GAS TRANSITIONS

UNIVERSAL GAS LAW

Clapeyron - 1834

Combining Avogadro's law and respective laws for gas two subsequent transitions:

- **isobaric expansion at p_o to volume V (Charles law)**

$$V = V_o\left(\frac{T}{T_o}\right)$$

- **isothermic expansion at T to pressure p (Boyle's-Mariotte's law)**

$$p = p_o\left(\frac{V_o}{V}\right)$$

Clapeyron's combined equation of state of ideal gas

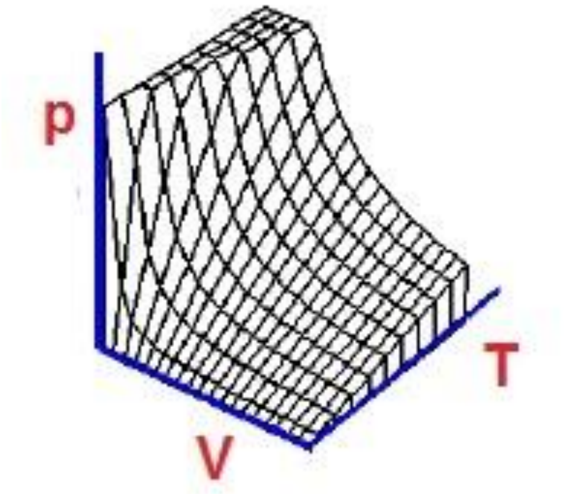
$$\frac{p_o V_o}{T_o} = \frac{p_1 \cdot V_1}{T_1} = \frac{p_2 \cdot V_2}{T_2} = \frac{p \cdot V}{T} = R = 8.31\left[\frac{J}{mol \cdot K}\right]$$

Common proof:

rises of ballon with hot gas inside of less density with respect to cold air of higher density

GAS TRANSITIONS

UNIVERSAL GAS LAW



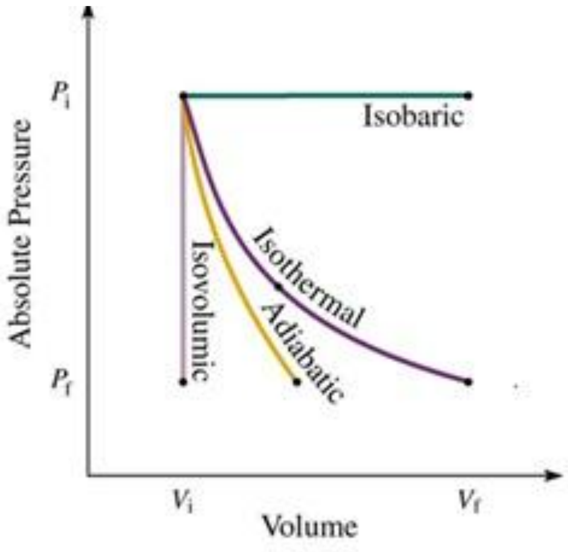
For n moles of arbitrary gas of mass *m* and molecular weight *M* Clapeyron's equation

$$p \cdot V = \frac{m}{M} R \cdot T = n \cdot R \cdot T$$

Thus, gas density

$$\rho = \frac{m}{V} = \frac{M \cdot p}{R \cdot T}$$

For *n* = 1 mole of gas combined equation of state of ideal gas describes constant function
- surface of thermodynamics states in space of variables - gas state parameters p, V and T



Every point at this surface describes the thermodynamic states of the gas

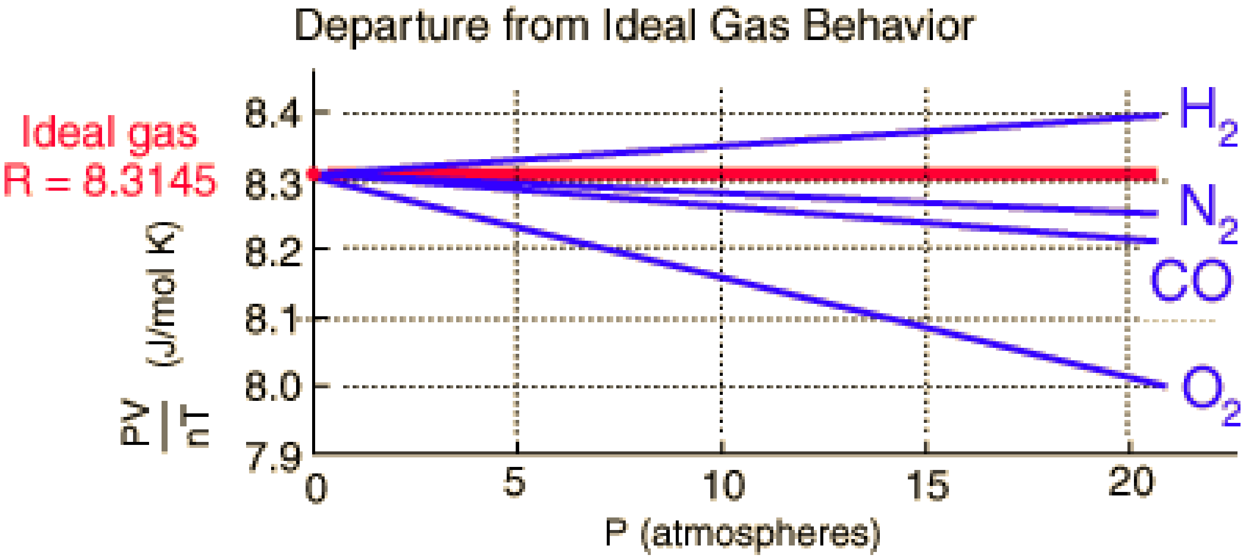
Thermodynamic states projected on *pV*, *VT* and *pT* planes
- particular dependences for chosen thermodynamic processes

GAS TRANSITIONS

UNIVERSAL GAS LAW LIMITATIONS

Limited applicability of empirical gas transition laws including Clapeyron's equation only for low pressure *p* and not very high temp. *T*

For high gas pressure (combined with high temperature) considerable departure from a Clapeyron's equation



because gas molecules are treated as located in empty space (without own volume) and do not undergo mutual interactions

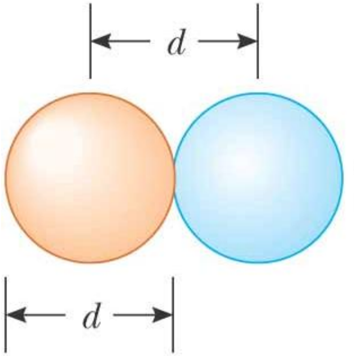
Solution: Van der Waals corrections of both limitations (1873)

REAL GAS TRANSITIONS

• CORRECTIONS FOR OWN VOLUME OF REAL GAS

All the molecules having own volume can only fill free space of vessel

Own volume of molecule of diameter *d*



$$V_m = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{1}{6}\pi \cdot d^3$$

Around every molecule *2d* space without other molecule

$$V_{sph} = \frac{4}{3}\pi \cdot d^3 = 8V_m$$

Volume inaccessible to any other molecule of *n* = 1 mole of gas

$$b = \frac{1}{2}V_{sph} \cdot N_A = 4V_m \cdot N_A$$

Limited free (empty) space of total volume V filled by *n* = 1 mole of gas

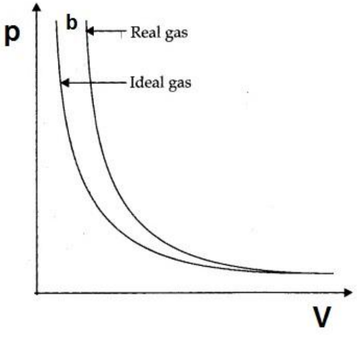
$$V_f = V - b$$

what should be taken into account as

Graphical illustration:

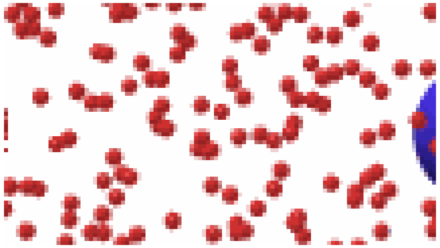
$$pV_f = p(V - b) = const$$

hyperbola (isotherm) *pV* shifted by *b* value along *V*



REAL GAS TRANSITIONS

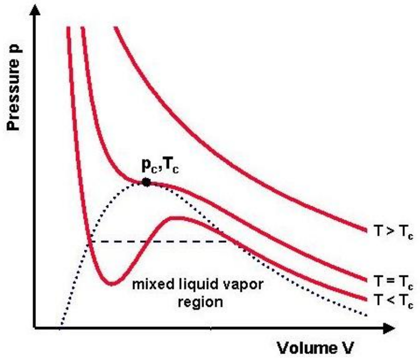
- CORRECTION FOR MUTUAL INTERACTIONS



Weak interaction of real gas molecules via dipolar Van der Waals forces at very short distance in vessel close to walls in thin layer σ (few nm) (compensated only in centre) - additional internal pressure

Taking into account both corrections (for *n* = 1 mole)

$$p_i = \frac{F_\sigma}{A} \cdot n_\sigma \approx \rho^2 \approx \frac{1}{V^2} = \frac{a}{V^2}$$

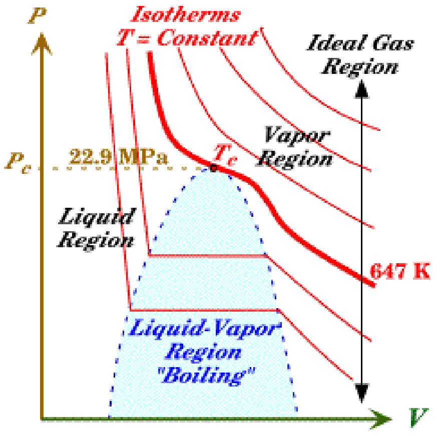


Final combined equation of real gas of Van der Waals

$$(p + p_i)(V - b) = \left(p + \frac{a}{V^2}\right)(V - b) = R \cdot T = const$$

After transformation

$$p = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{R \cdot T \cdot V^2 - a(V-b)}{V^2(V-b)}$$



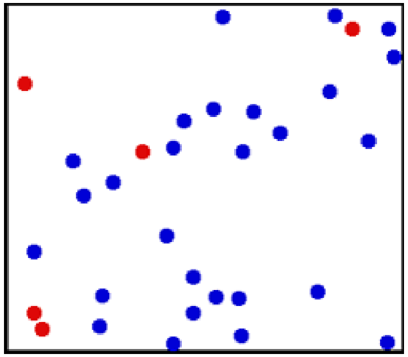
From isotherms of real gas 3 various V values and 3 various regions (phases): vapor - liquid-vapor – liquid - direct consequence: triple point of water at n.c.

KINETIC THEORY OF IDEAL GAS

GAS

infinitive number of extremely small particles in motion/collisions - without shape always ocupies whole vessel - Bernoulli (1738)

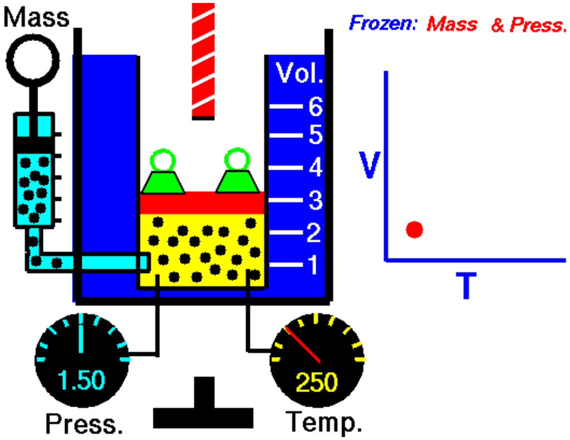
Two approaches:



- **Large collection (reservoir) of individual particles** being treated as material points having basic kinematic and dynamic microscopic parameters: mass m, velocity υ, momentum m·υ and kinetic energy E_k

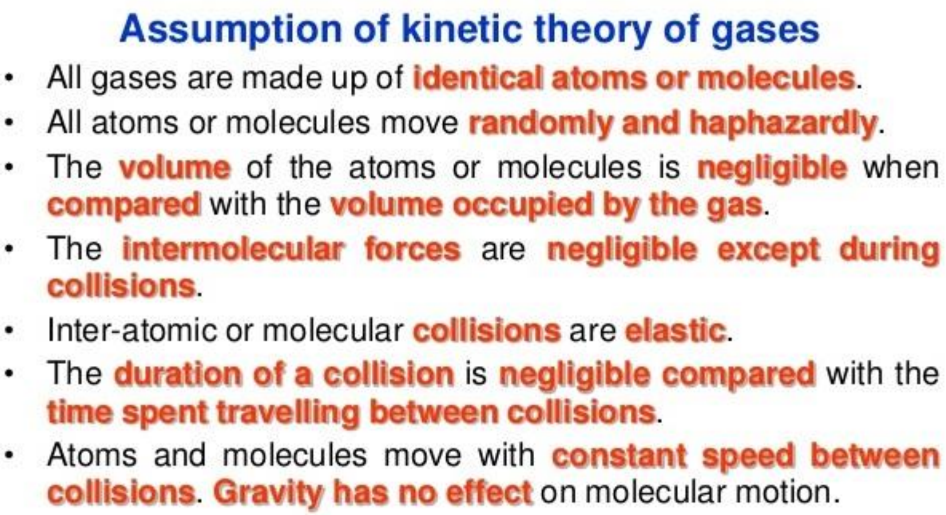
- **Continuous medium** in which individual properties of molecules neglected using empirical laws based on macroscopic gas parameters of state: p, V, T, n, which determine functions of state/process:

  - internal energy U
  - heat of transition (process)(Q),
  - mechanical work (W)
  - enthalpy H
  - entrophy S



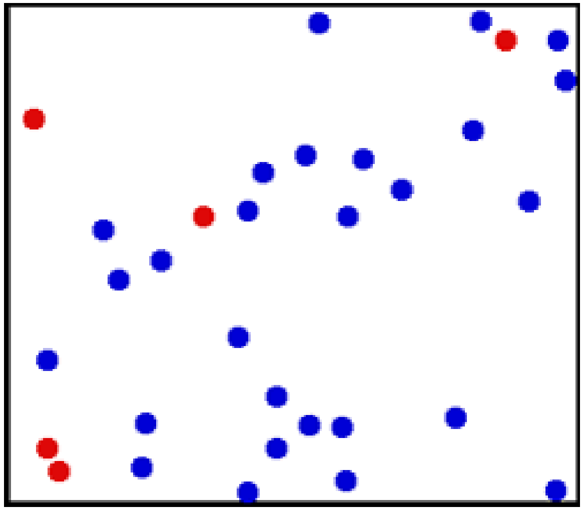
KINETIC THEORY OF IDEAL GAS

Joining of two worlds: large collection of individual particles being at least the continuous medium: M-B-C contributions (1849-1865)



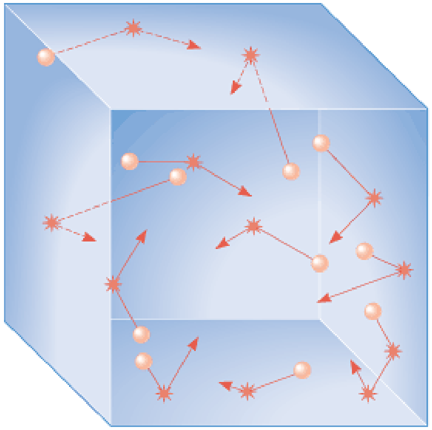
Assumption of kinetic theory of gases

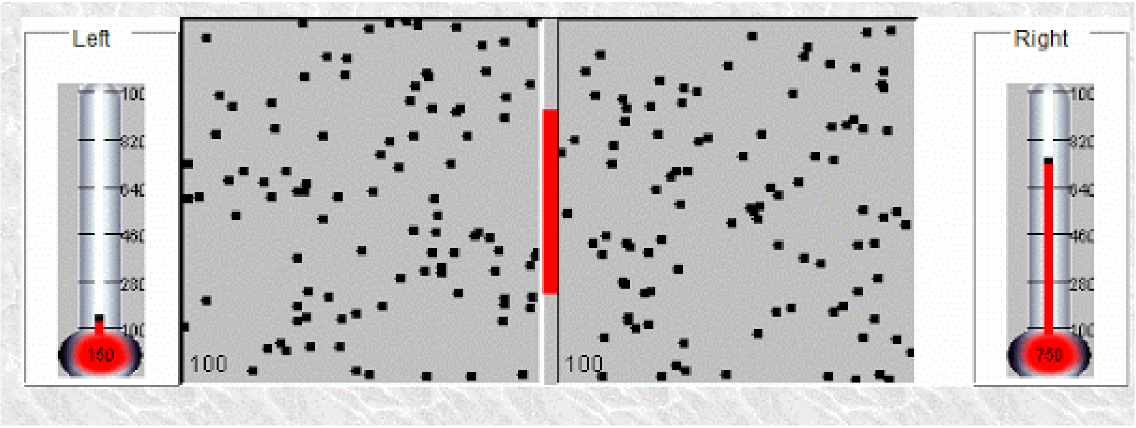
- All gases are made up of **identical atoms or molecules**.
- All atoms or molecules move **randomly and haphazardly**.
- The **volume** of the atoms or molecules is **negligible** when **compared** with the **volume occupied by the gas**.
- The **intermolecular forces** are **negligible except during collisions**.
- Inter-atomic or molecular **collisions** are **elastic**.
- The **duration of a collision** is **negligible compared** with the **time spent travelling between collisions**.
- Atoms and molecules move with **constant speed between collisions**. **Gravity has no effect** on molecular motion.



Maxwell

Boltzmann

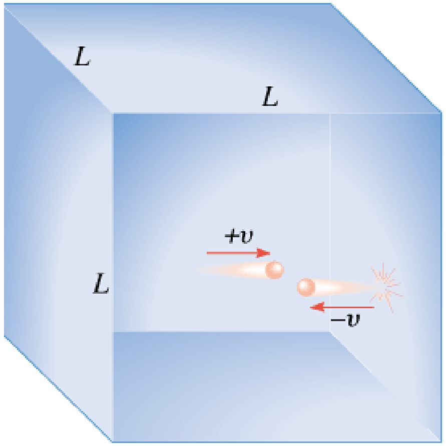




Clausius

KINETIC THEORY OF IDEAL GAS

KINETIC INTERPRETATION OF PRESSURE



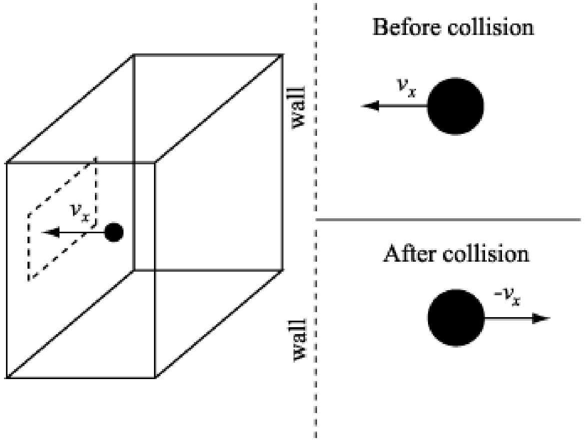
One dimensional motion of gas molecules of mass *m* and velocity υ inside a cubic vessel of edge *L* – elastic ⊥ collisions with walls of vessel and rebounding

Net force of every gas molecule along *x* direction

$$F_x = \frac{\Delta P_x}{\Delta t} = \frac{-m\cdot\upsilon_x - m\cdot\upsilon_x}{2L/\upsilon_x} = -\frac{m\cdot\upsilon_x^2}{L}$$

Absolute net pressure on wall of *N* molecules

$$p_x = N\frac{F_x}{A} = N\frac{m\cdot\bar{\upsilon}_x^2}{L^3} = N\frac{m\cdot\bar{\upsilon}_x^2}{V}$$



Because of no favorite direction $\bar{\upsilon}^2 = \bar{\upsilon}_x^2 + \bar{\upsilon}_y^2 + \bar{\upsilon}_z^2$

Thus $\bar{\upsilon}_x^2 = \bar{\upsilon}_y^2 = \bar{\upsilon}_z^2 = \frac{1}{3}\bar{\upsilon}^2$

According to Pascal law $p = p_x + p_y + p_z$

Gas pressure in vessel - Boltzmann equation

$$p = \frac{1}{3}\frac{N}{V}m\cdot\bar{\upsilon}^2 = \frac{1}{3}m\cdot n_V\cdot\bar{\upsilon}^2 = \frac{1}{3}\rho\cdot\bar{\upsilon}^2$$

where: $\bar{\upsilon}^2$ **- average square velocity**

KINETIC THEORY OF IDEAL GAS

KINETIC INTERPRETATION OF TEMPERATURE

Combining Boltzmann and Clapeyron equations for 1 mole of ideal gas

$$p \cdot V = \frac{1}{3} m \cdot n_V \cdot V \cdot \overline{\upsilon}^2 = \frac{1}{3} m \cdot N_A \cdot \overline{\upsilon}^2 = \frac{2}{3} N_A \cdot \overline{E} = R \cdot T$$

Where: $\overline{E} = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} k \cdot T$ **- average kinetic energy of single molecule**

and $k = 1.4\ 10^{-19}$ **[J/K] - Boltzmann constant**

Average kinetic energy for 1 mole of gas - ideal gas internal energy

$$U = N_A \cdot \overline{E}_k = N_A \frac{3}{2} k \cdot T = \frac{3}{2} R \cdot T$$

For isochoric process (transition): V = const

$$\frac{dU}{dT} = \frac{3}{2} R = C_V$$

where: C_V - heat capacity at constant volume
At room temperature ideal gas C_V = 12.5 [J/mol K]

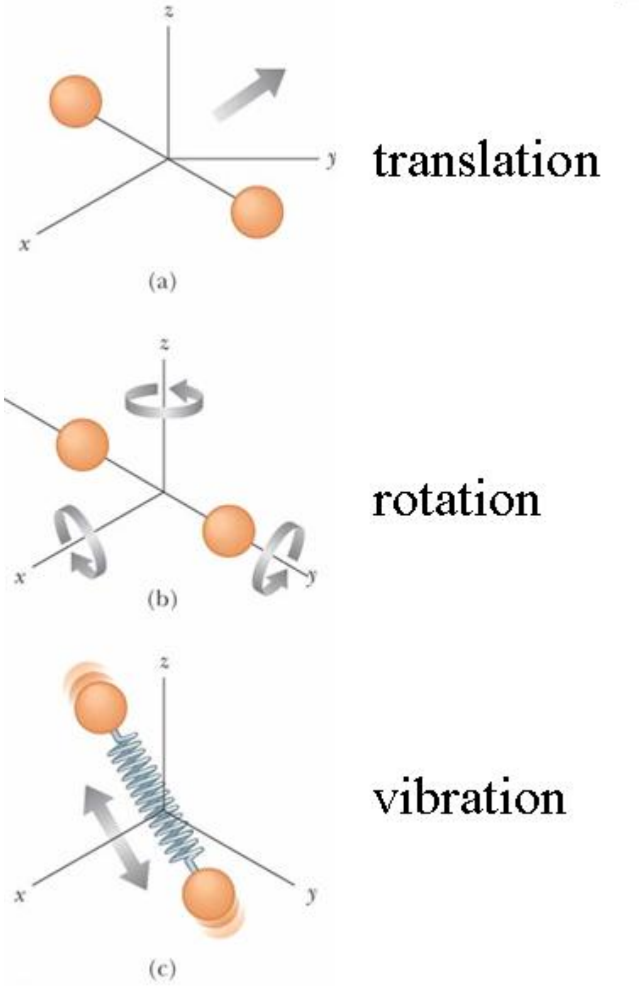
However, only valid for monoatomic inert gases: He, Ne
Boltzmann's explanation basing on concept: DEGREE OF FREEDOM

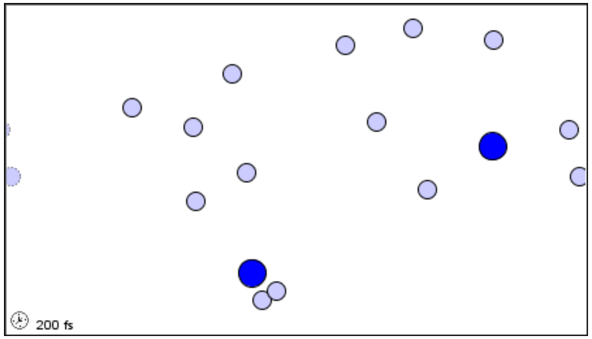
KINETIC THEORY OF IDEAL GAS

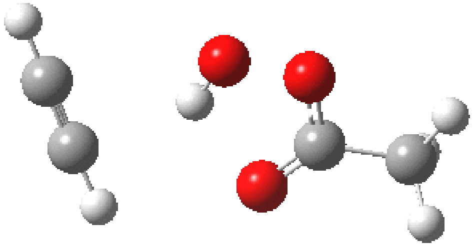
IDEAL GAS DEGREES OF FREEDOM

Definition: number of independent manner of thermal motion of gas molecules (energy storage)

- **monoatomic gas: $i = 3$ (only 3 transl. - 3 axes)**
- **diatomic gas: $i = 5$ (as above + 2 rot.)**
- **polyatomic gas: $i = 6$ (3 transl. + 3 rot.)**







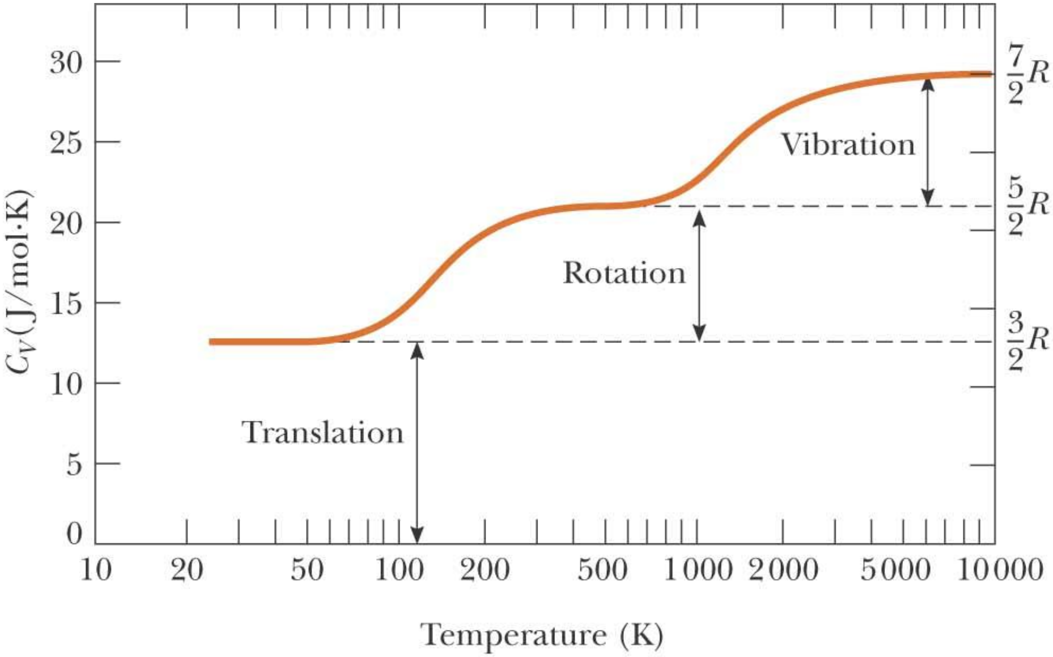
For molecular H_2
$i = 3 + 2 = 5$, thus $C_V = 20.7$ [J/mol K] !
Good correlation with the experimental data

However, additional limitation appeared, it is only valid at room temperature (RT)

KINETIC THEORY OF IDEAL GAS

IDEAL GAS DEGREES OF FREEDOM

Boltzmann's additional explanation of high temperature value of C_V
- the additional motions (oscilations) of every gas molecules



With increasing of T – abrupt variation by constant value

$$\bar{E}_i = \frac{1}{2} k \cdot T$$

Final conclusion: for every degree of freedom - unit kinetic energy

- principle of equipartition of energy of single gas molecules

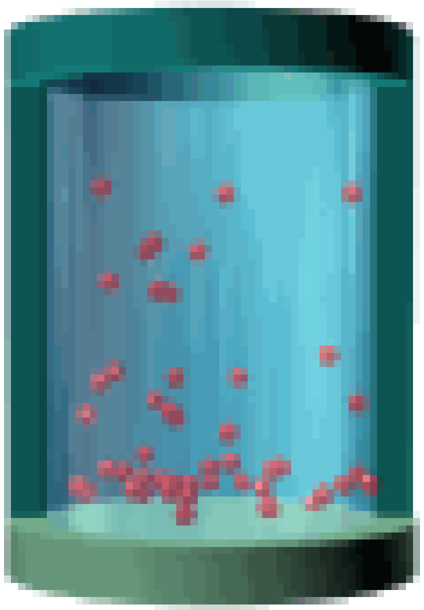
KINETIC THEORY OF IDEAL GAS

GAS IN ATMOSPHERE

Gas pressure in atmosphere depends on *h* over see level - gravitation

Because gas pressure in atmosphere decreases with *h*

$$dp = -\rho \cdot g \cdot dh = \frac{M \cdot p}{R \cdot T} \cdot g \cdot dh$$



Relative decrease of gas pressure

$$\int_{p_o}^{p} \frac{dp}{p} = -\frac{M}{R \cdot T} g \int_{o}^{h} dh$$

After integration $$ln \frac{p}{p_o} = -\frac{M \cdot g \cdot h}{R \cdot T}$$

Thus

$$p = p_o \cdot exp(-\frac{M \cdot g \cdot h}{R \cdot T})$$

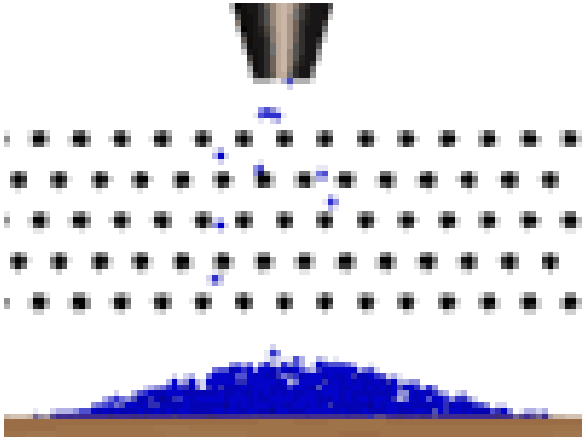
Barometric equation – law of atmosphere

- increasing of height over sea level by 11 [m] - decreasing of air pressure in atmosphere by 1 hPa - good correlation with natural data

General relation: $n = n_o (exp - \frac{E}{k \cdot T})$ **- Boltzmann distribution function**

KINETIC THEORY OF IDEAL GAS

MAXWELL – BOLTZMANN DISTRIBUTION FUNCTION



Main limitation of primary kinetic theory – average square (rms) velocity of molecules

$$\overline{\upsilon}^2 = \upsilon_{rms}^2 = \frac{3}{2}\frac{R\cdot T}{m\cdot N_A} = 3\frac{k\cdot T}{m} = 3\frac{R\cdot T}{M}$$

In reality, velocity distribution in space because of huge amount (10^9 /s) of mutual collisions

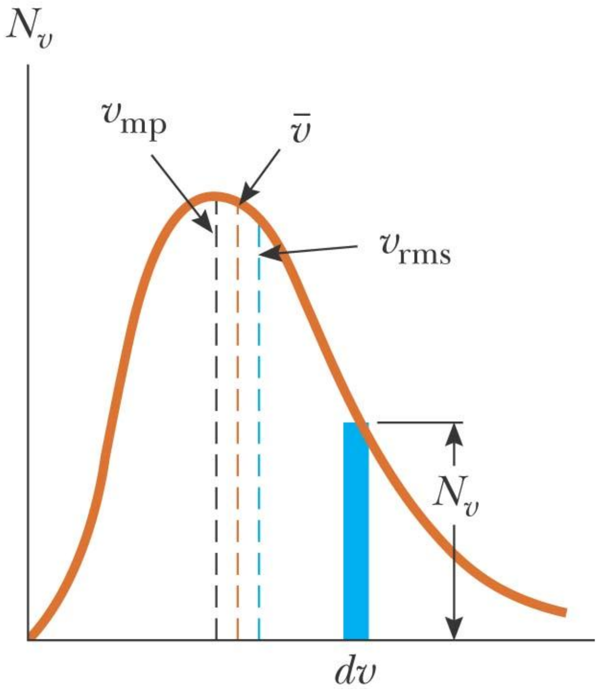
Fraction of molecules of respective velocities

$$\frac{dN}{N} = f(\upsilon)d\upsilon = \frac{4kT}{\sqrt{\pi}}\frac{\overline{\upsilon}^2}{\upsilon_p^2}\exp(-\frac{\overline{\upsilon}^2}{\upsilon_p^2})d\upsilon$$

where: $\upsilon_{mp} = \sqrt{\frac{2R\cdot T}{M}}$ **- most probable velocity**

However, a majority molecules exhibit velocity close to its average value

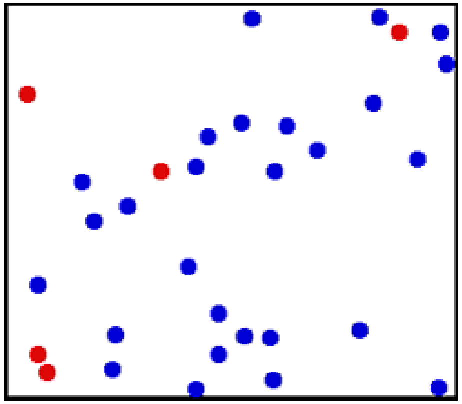
$$\overline{\upsilon} = \sqrt{\frac{8R\cdot T}{\pi\cdot M}}$$

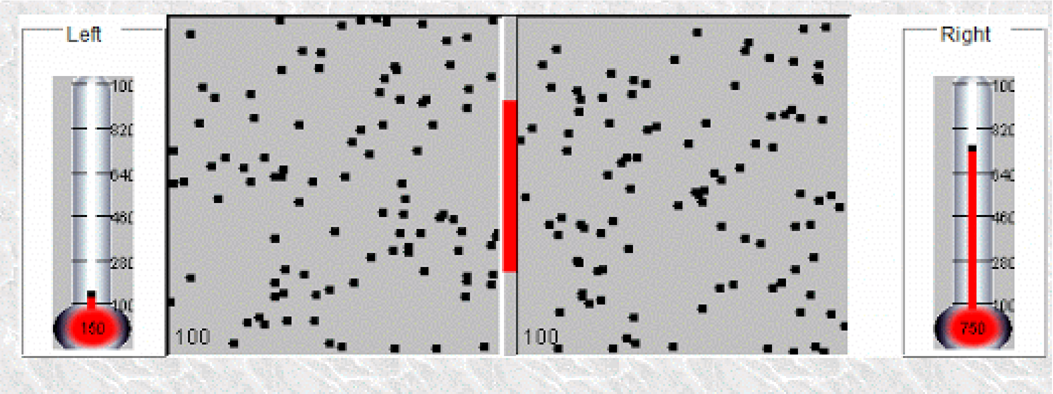


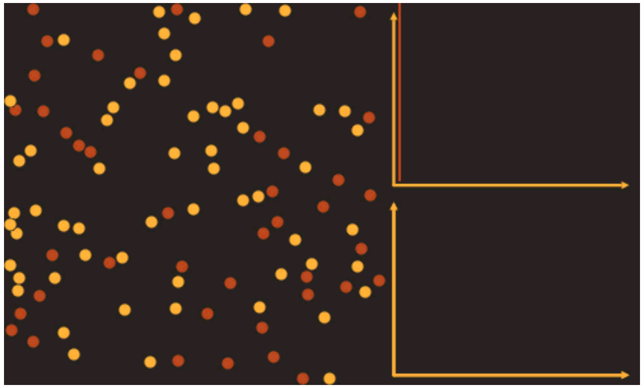
KINETIC THEORY OF IDEAL GAS

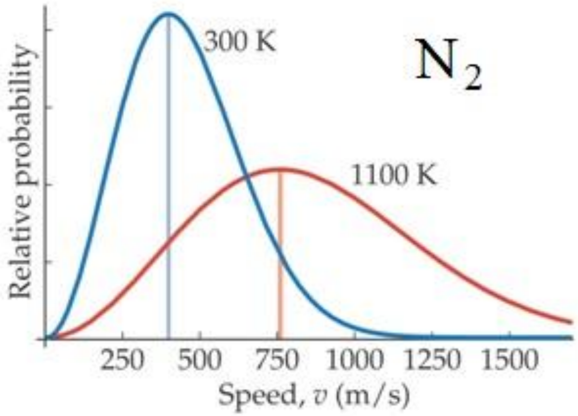
MAXWELL – BOLTZMANN DISTRIBUTION FUNCTION

Interpretation of temperature dependent gas velocity









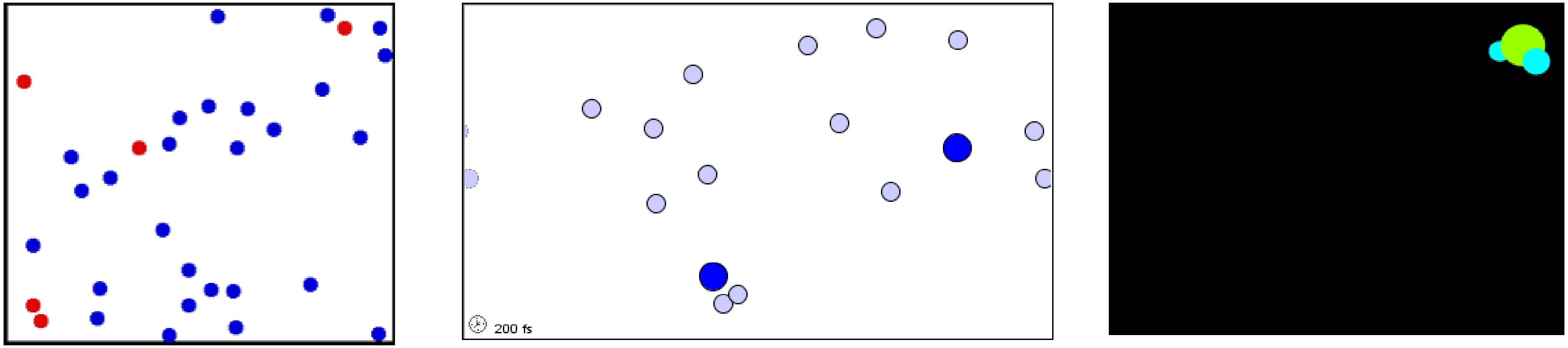
Explanation of common effects:

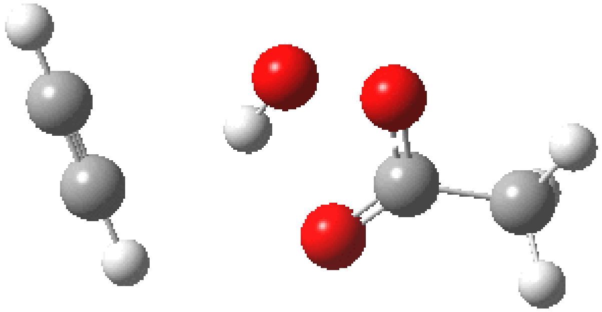
- fast evaporation of liquids at boiling temperature T_b
- slow evaporation of liquids even evidently below boiling T_b (common evaporation of water from open glass at 300 K)

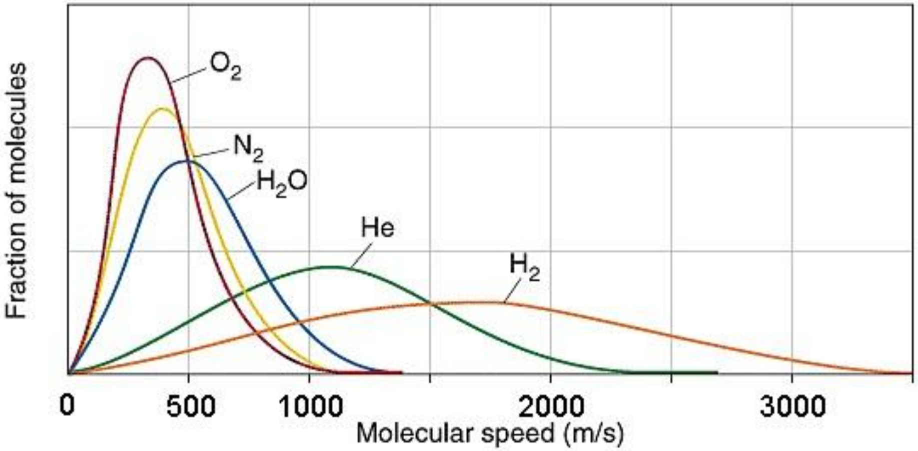
KINETIC THEORY OF IDEAL GAS

MAXWELL – BOLTZMANN DISTRIBUTION FUNCTION

Interpretation of mass (dimension) dependent gas velocity







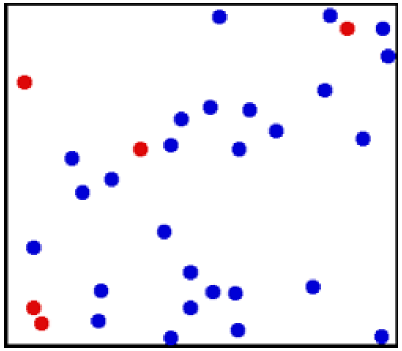
Explanation of common effects:

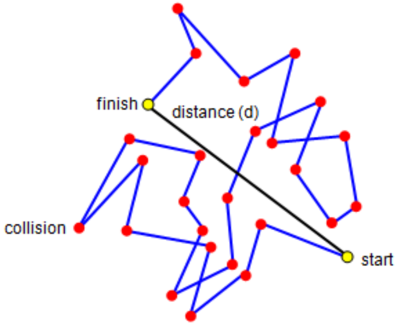
- absence of H_2 in Earth atmosphere (smallest gravitational attraction)
- absence of atmosphere at Moon

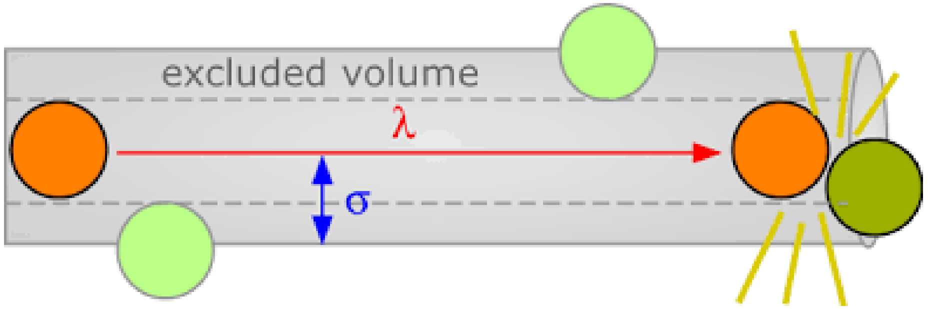
KINETIC THEORY OF IDEAL GAS

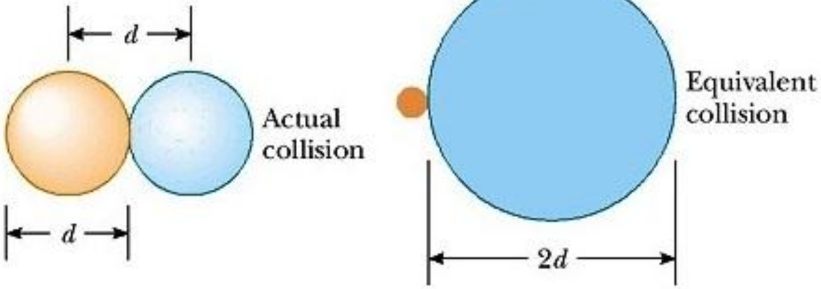
MEAN FREE PATH OF GAS MOLECULES

Average distance between collisions









$$\lambda = \frac{R \cdot T}{\sqrt{2} \cdot \pi \cdot d^2 \cdot N_A \cdot p} = \frac{T}{p} \cdot \frac{k}{\sqrt{2} \cdot \pi \cdot d^2}$$

Typical values at RT:

- in air at n.c. for $n_V \approx 10^{19}$ [cm^3] $\lambda \approx 10^{-7}$ [m]
- in vacuum at pressure $p = 10^{-3}$ [hPa] $\lambda \approx 10^{-1}$ [m]
- in ultrahigh vacuum at pressure $p = 10^{-8}$ [hPa] $\lambda \approx 10^{3}$ [m]

Great importance in clean technology under UHV conditions