# Kinetic theory of gasses
# Phase transitions

Maxwell-Boltzmann distribution of molecule velocities. Diffusion. Ideal gas law, particular gas laws, phase diagram, phase equilibrium, Clausius-Clapeyron equation. Air humidity.

# Kinetic theory of gasses

- Maxwell-Boltzmann’s distribution
- Macroscopic phenomena based on microscopic matter structure
- Diffusion, gas viscosity
- Non-ideal Van der Waals’ gas

# Ideal gas

Non-interacting system of molecules

Reality – inert or diluted gasses

Internal energy – only kinetic energy of molecules

Kinetic theory of gasses

State equations – pressure, volume, temperature, number of molecules

# Molecular speed distribution

Molecules in an ideal gas move by variable velocities, their movement is straight and at constant speed between collisions

Assumptions:

1. No prefered velocity orientation in space
2. Different velocity coordinates in 3D space are independent

# Maxwell’s speed distribution

Velocity coordinate distribution

$$\rho(v_x) = \left( \frac{m_0}{2\pi k_\mathrm{B} T} \right)^{1/2} e^{-\frac{m_0 v_x^2}{2 k_\mathrm{B} T}}$$

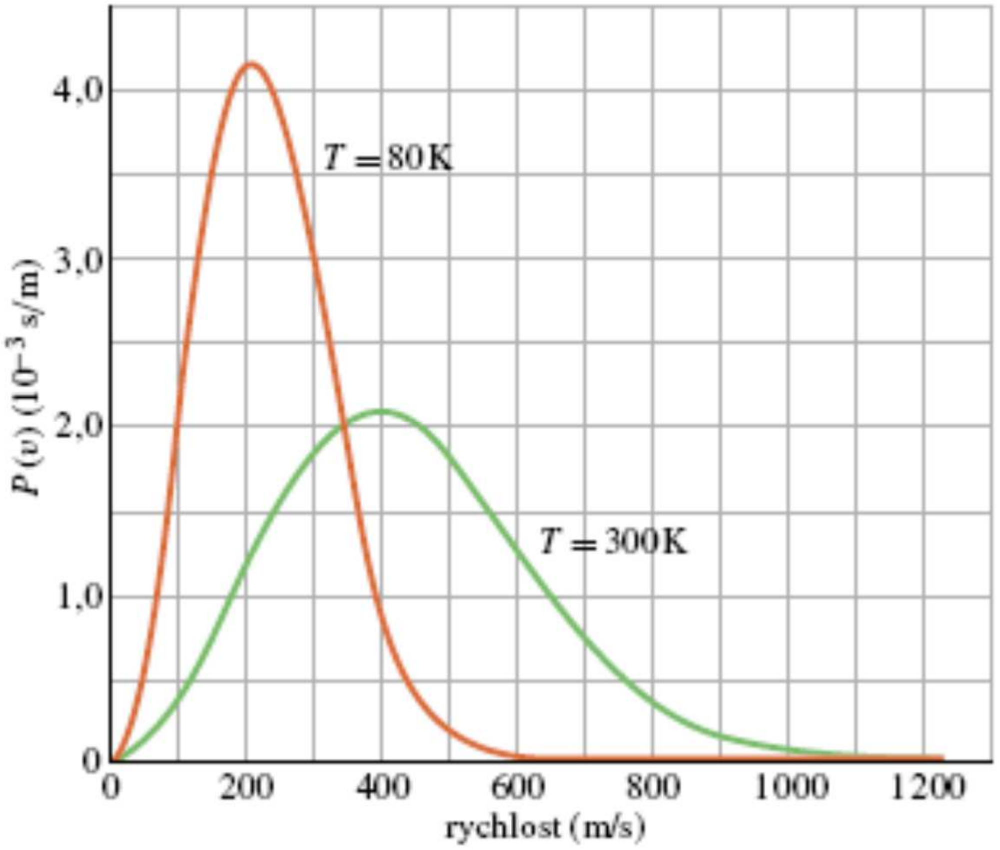
Velocity magnitude distribution

$$\rho(v) = 4\pi \left( \frac{m_0}{2\pi k_\mathrm{B} T} \right)^{3/2} v^2 e^{-\frac{m_0 v^2}{2 k_\mathrm{B} T}}$$

J.C.Maxwell, 1852

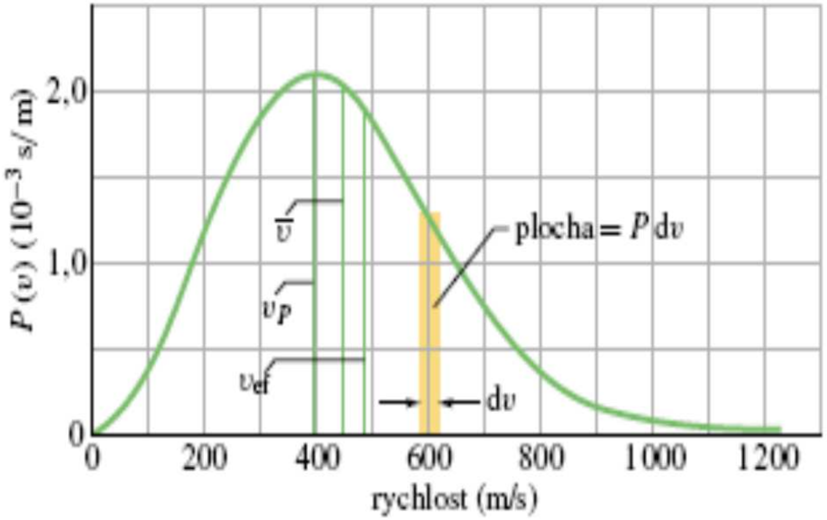
# Maxwell’s speed distribution

Molecules travel faster at higher temperatures – example for Oxygen



# Characteristics of distribution

Area below graph – oxygen at 300K



root-mean-square velocity 483ms$^{-1}$,
the most probable velocity 395ms$^{-1}$,
average velocity 445ms$^{-1}$

# Parameters of distribution

$$\rho(v) = 4\pi\left(\frac{m_0}{2\pi k_\mathrm{B} T}\right)^{3/2} v^2 e^{-\frac{m_0 v^2}{2k_\mathrm{B}T}}$$

- The most probable speed

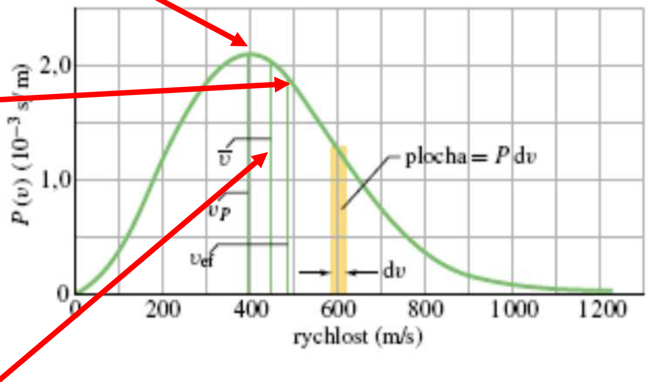
$$v_P = \sqrt{\frac{2k_B T}{m_0}}$$

- Root-mean-square speed

$$v_k = \sqrt{\frac{3k_B T}{m_0}}$$

- Average speed

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m_0}}$$



# Characteristic velocities

- The most probable speed

$$\frac{d\rho(v)}{dv} = 0$$

- Average speed

$$\overline{v} = \int_0^\infty v\rho(v)dv$$

- Root-mean-square speed

$$v_k = \sqrt{\overline{v^2}} = \int_0^\infty v^2\rho(v)dv$$

# Ideal gas in gravitational field

Gas molecules exhibit potential energy in gravity field

Density of molecules will differ as a function of position

$$\rho(h) = \rho(0)e^{-\frac{m_0 gh}{k_B T}}$$

Barometric formula for the pressure/density distribution in constant temperature medium

$$p(h) = p(0)e^{-\frac{m_0 gh}{k_B T}}$$

# Boltzmann’s distribution

Probability density = function of potential energy of particles

$$\rho(E_P) = \frac{e^{-\frac{E_P}{k_B T}}}{\int_0^\infty e^{-\frac{E_P}{k_B T}}\, dE_P}$$

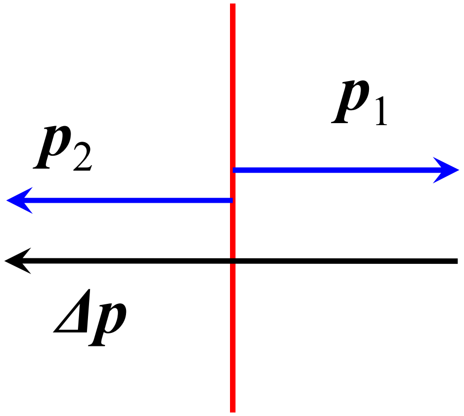
# Gas pressure

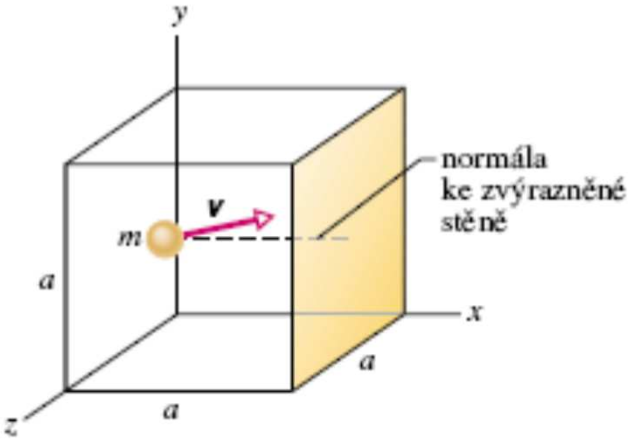
Molecules collide at the vessel walls

Change of impulse per 1s and $1\,\mathrm{m}^2$ is pressure

Change of impulse per particle at elastic collision

$$\Delta p = 2m_0 v$$

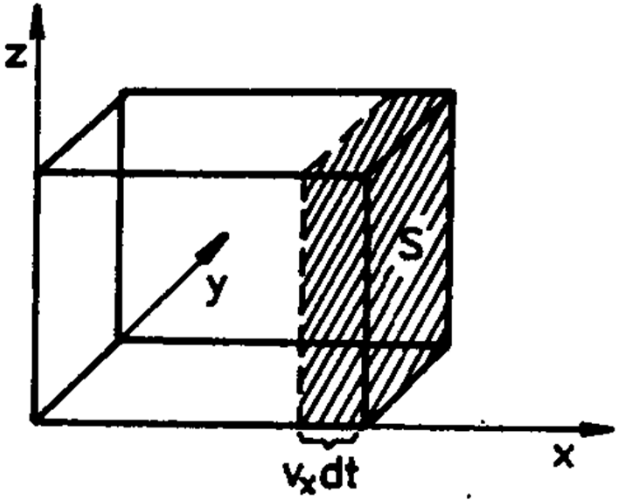




# Gas pressure

Number of molecules colliding at the wall per $\Delta t$

$$\Delta N = \frac{N}{V}(S v_x \Delta t)\Delta w(v_x)$$



$$\Delta w(v_x) = \rho(v_x)\Delta v_x$$

Exchanged impulse

$$\Delta P_x = \Delta N \cdot 2 m_0 v_x$$

Force on the wall

$$\Delta F = \frac{\Delta P_x}{\Delta t} = 2 m_0 \frac{N}{V} S(v_x^2 \rho(v_x)\Delta v_x)$$

# Gas pressure

Force $F = 2m_0 \frac{N}{V} S \int_{0}^{+\infty} v_x^2 \rho(v_x) dv_x$

Root-mean-square speed

$$\overline{v_x^2} = \int_{-\infty}^{+\infty} v_x^2 \rho(v_x) dv_x = 2 \int_{0}^{+\infty} v_x^2 \rho(v_x) dv_x$$

Pressure on the vessel wall

$$p = \frac{F}{S} = \frac{N}{V} m_0 \overline{v_x^2}$$

# Gas pressure

Magnitude of velocity

$$v_x^2 + v_y^2 + v_z^2 = v^2$$

Average

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2}$$

Gas pressure

$$\boxed{p = \frac{1}{3}\frac{N}{V}m_0\overline{v^2}}$$

# Ideal gas law and pressure

Equation of state $pV = nRT$

Root-mean-square speed

$$v_k = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M_m}}$$

# Root-mean-square speed

| T=300K | $H_2$ | He | $H_2O$ | $N_2$ | $O_2$ | $CO_2$ |
|---|---|---|---|---|---|---|
| $M_m$ [$g \cdot mol^{-1}$] | 2.02 | 4.0 | 18.0 | 28.0 | 32.0 | 44.0 |
| $v_k$ [$m \cdot s^{-1}$] | 1920 | 1370 | 645 | 517 | 483 | 412 |

# Kinetic energy of particles

Motion of single particle at root-mean-square speed

$$\overline{E_k} = \overline{\frac{1}{2} m_0 v^2} = \frac{1}{2} m_0 v_k^2$$

$$\boxed{\overline{E_k} = \frac{3}{2} k_B T}$$

Root-mean-square speed of molecules for an ideal gas is proportional to the temperature.

Boltzmann’s constant

$$k_B = \frac{R}{N_A} = 1.38 \cdot 10^{-23} JK^{-1}$$

# Internal gas energy

Sum of all kinetic energies of molecules

$$U = nN_A\overline{E_k} = nN_A\left(\frac{3}{2}k_BT\right) = \frac{3}{2}nRT$$

Internal energy of an ideal gas depends only on the temperature, not on volume, pressure etc.

Various nature of internal energy – translational, rotational, vibration, …

# Ideal gas law

$$pV = nRT$$

Universal gas constant

$R$=8.314Jmol$^{-1}$K$^{-1}$

Volume of 1 mole of gas at standard temperature and pressure (STP)

$p_0$=101325 Pa, $T$=273.15 K it is $V_\mathrm{m}$=22.4 liter

# Isothermal process ($T$=konst.)

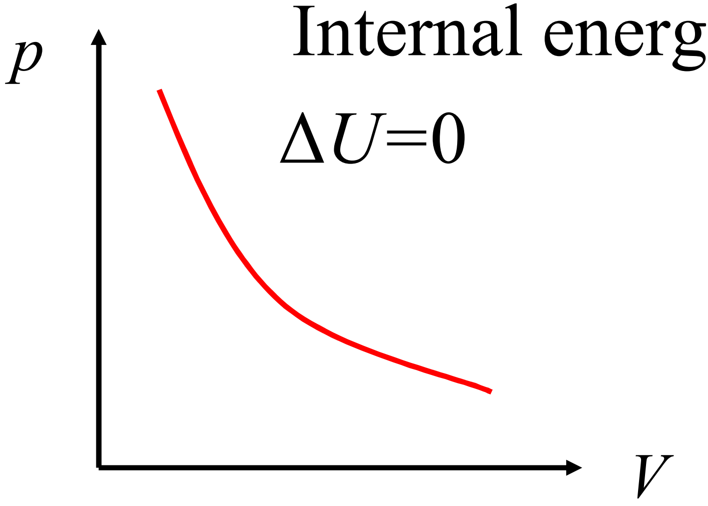
Boyle-Mariott's law $$pV = konst.$$

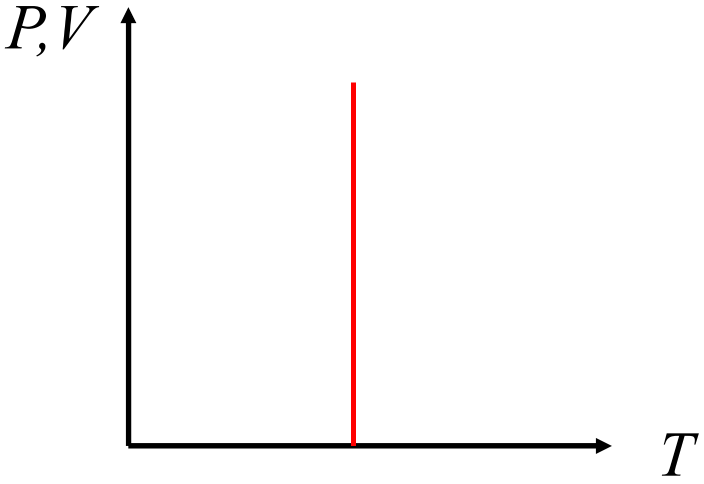
Work $A = nRT \ln \frac{V_2}{V_1}$

Heat $Q$=$A$

Internal energy

$\Delta U$=0





# Isovolumetric process ($V$=konst.)

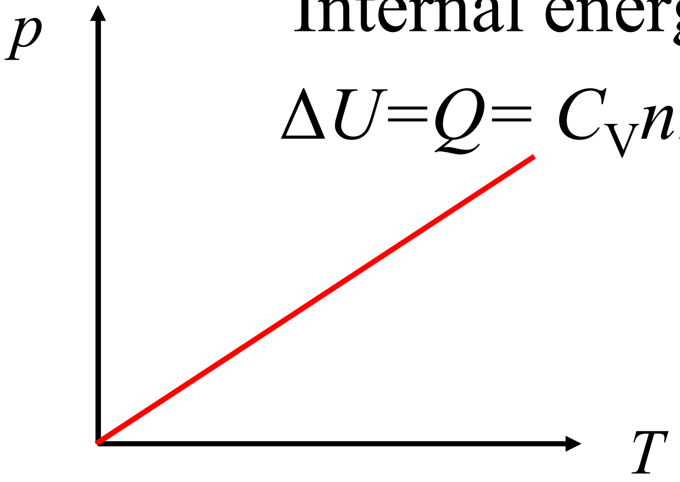
Charles' law $$\frac{p}{T} = konst.$$

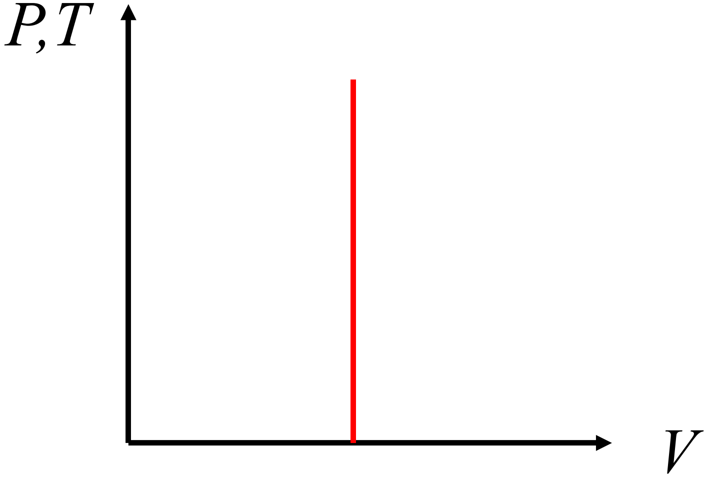
Work $A = 0$

Heat $Q$

Internal energy

$\Delta U = Q = C_{\mathrm{V}} n \Delta T$





# Isobaric process ($p$=konst.)

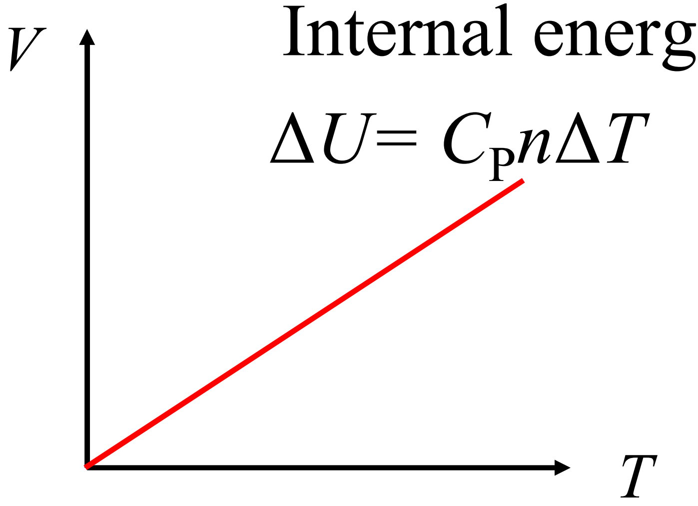
Gay-Lussac's law $\frac{V}{T} = konst.$

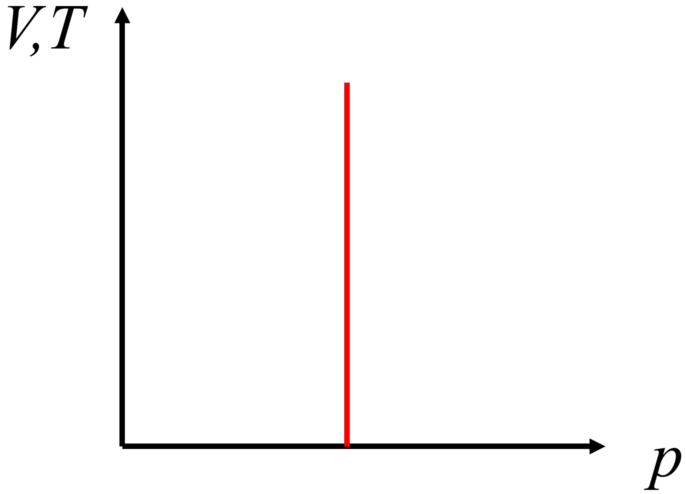
Work $A = p\Delta V$

Heat $Q=\Delta U-p\Delta V$

Internal energy

$\Delta U= C_p n\Delta T$





# Adiabatic process ($Q$=0)

$$pV^{\kappa} = konst.$$

+ ideal gas law

Poisson's constant $\kappa = \frac{C_P}{C_V}$

Using other variables

$$V^{\kappa-1}T = konst.$$

$$p^{1-\kappa}T^{\kappa} = konst.$$

# Poisson's constant

| | | | |
|---|---|---|---|
| Air | 1.40 | $SO_2$ | 1.29 |
| Hydrogen | 1.41 | $CO_2$ | 1.304 |
| Oxygen | 1.401 | $CH_4$ | 1.31 |

# Adiabatic process

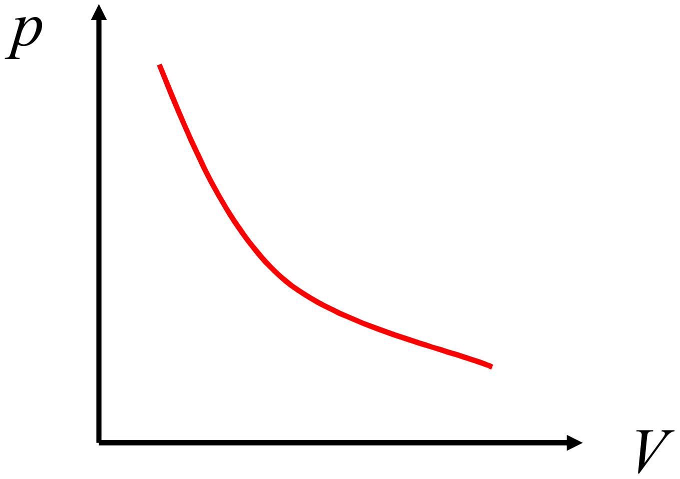
Work $$A = \int_{V_1}^{V_2} p\,dV$$

Heat $Q = 0$

Internal energy

$\Delta U = -A$

Adiabatic curve has higher slope then isothermal one



# Heat capacities for ideal gas

First law of thermodynamics $dQ = dU + pdV$

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

$$K_P - K_V = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p$$

Heat capacity at constant volume or pressure

$$K_V = \left(\frac{\partial U}{\partial T}\right)_V$$

# Mayer's formula

For an ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

Difference in heat capacities for isovolumetric and isobaric process

$$K_P - K_V = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p = nR$$

# Brownian motion

Unstable and random motion of tiny pollen particles (1μm) in liquid

Explanation - A.Einstein, M.Smoluchovski (1925-1927)

Non-compensated impulse transfer at pollen particles and water molecules

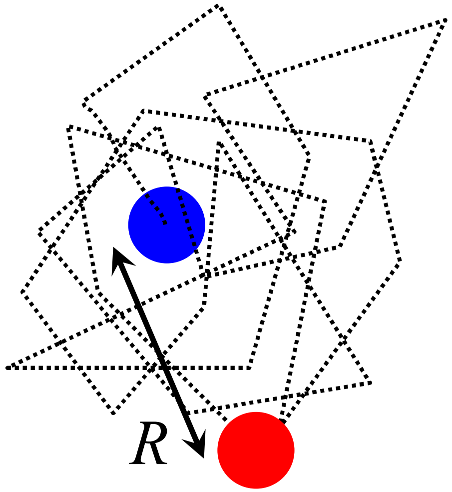
Experiments – J.B.Perrin (1910-15)

Avogadro's constant measurement

# Brownian motion

Root-mean-square displacement (mean “walk”) during time *t*

$$\overline{R^2} = \frac{k_B T}{\pi r \eta} t$$

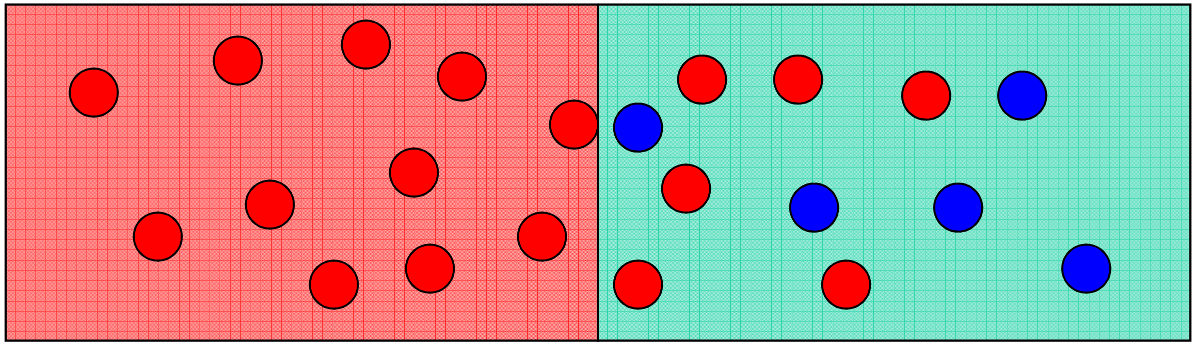


$\eta$ … dynamic viscosity [Pa.s]

# Diffusion

Transport of particles – concentration changes

- Homo-diffusion
- Hetero-diffusion



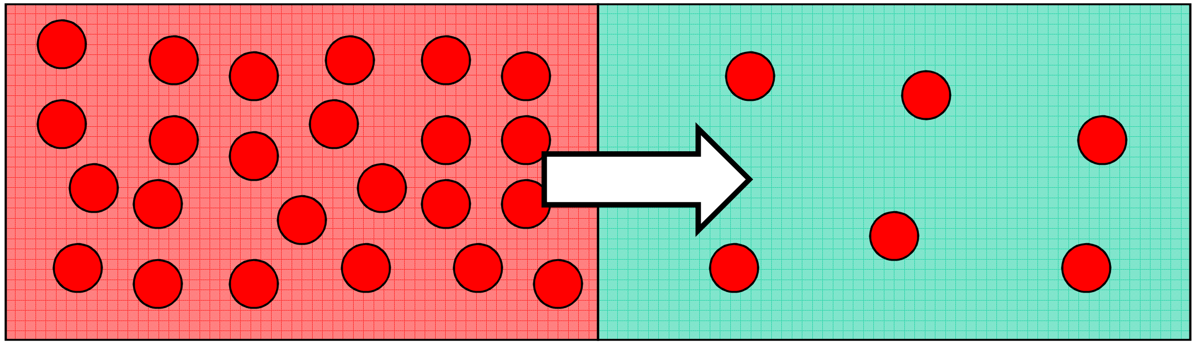
Transfer of fragrances, aerosols, fog, smoke etc. in gasses, particles in colloidal suspensions etc.

# Diffusion

- Concentration gradient
- Rate of diffusion – diffusion coefficient

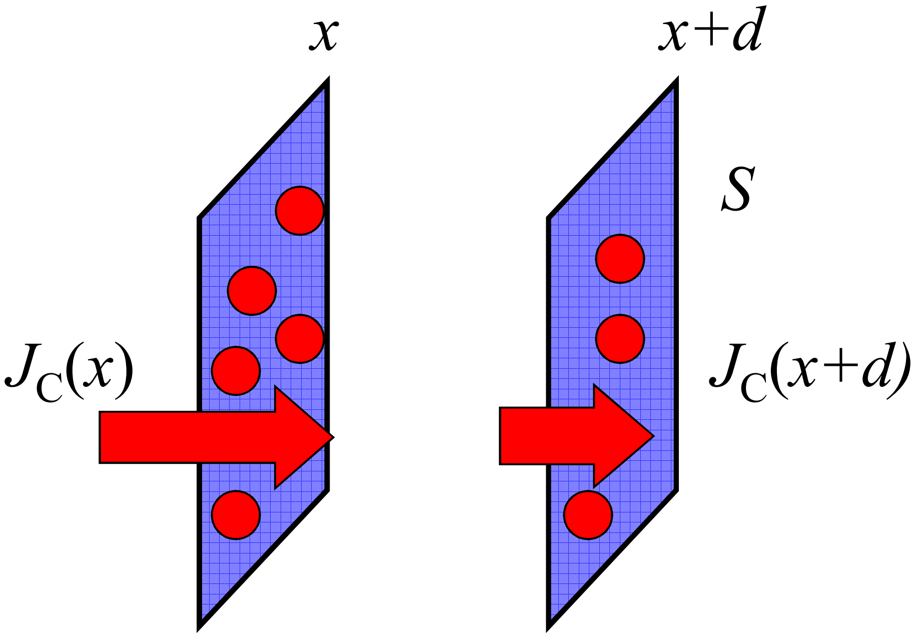
First Fick's law

$$J_C = D\frac{\Delta C}{\Delta x}, \qquad [D] = m^2 s^{-1}$$



# Second Fick's law

Change in concentration in volume *V* is equal to the difference of diffusion ratio (in- and out-coming)

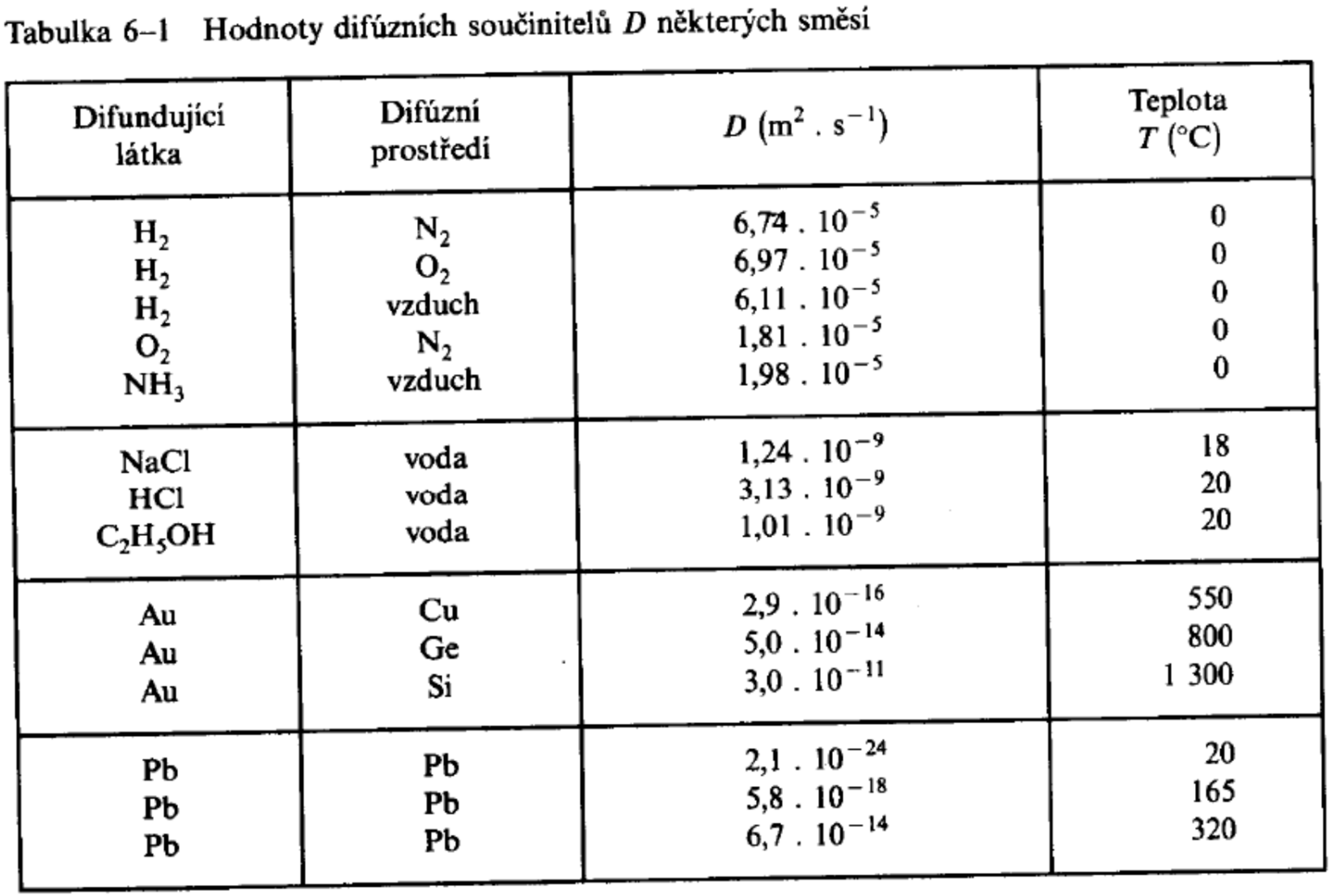


$$V\frac{\Delta C}{\Delta\tau} = S[J_C(x+d) - J_C(x)]$$

$$\frac{\Delta C}{\Delta\tau} = \frac{\Delta J_C}{\Delta x}$$

$$\boxed{\frac{\partial C}{\partial\tau} = D\frac{\partial^2 C}{\partial x^2}}$$

# Diffusion coefficients



Tabulka 6–1 Hodnoty difúzních součinitelů $D$ některých směsí

| Difundující látka | Difúzní prostředí | $D$ ($m^2 . s^{-1}$) | Teplota $T$ (°C) |
|---|---|---|---|
| $H_2$ | $N_2$ | $6{,}74 . 10^{-5}$ | 0 |
| $H_2$ | $O_2$ | $6{,}97 . 10^{-5}$ | 0 |
| $H_2$ | vzduch | $6{,}11 . 10^{-5}$ | 0 |
| $O_2$ | $N_2$ | $1{,}81 . 10^{-5}$ | 0 |
| $NH_3$ | vzduch | $1{,}98 . 10^{-5}$ | 0 |
| NaCl | voda | $1{,}24 . 10^{-9}$ | 18 |
| HCl | voda | $3{,}13 . 10^{-9}$ | 20 |
| $C_2H_5OH$ | voda | $1{,}01 . 10^{-9}$ | 20 |
| Au | Cu | $2{,}9 . 10^{-16}$ | 550 |
| Au | Ge | $5{,}0 . 10^{-14}$ | 800 |
| Au | Si | $3{,}0 . 10^{-11}$ | 1 300 |
| Pb | Pb | $2{,}1 . 10^{-24}$ | 20 |
| Pb | Pb | $5{,}8 . 10^{-18}$ | 165 |
| Pb | Pb | $6{,}7 . 10^{-14}$ | 320 |

# Dynamic viscosity of gas

Independent from the density and pressure of an ideal gas

$$\eta = \frac{1}{4\pi r^2}\sqrt{\frac{m_0 k_B T}{\pi}}$$

Reality – small dependence on pressure – e.g. $CO_2$

$10^5$Pa $\eta=14.9\cdot10^{-6}$ Pa·s

300Pa $\eta=14.7\cdot10^{-6}$ Pa·s

Measurement of gas viscosity could give molecule radius $r$

# Real gasses

Mutual molecular interactions exist

Such effect must be taken into account – e.g. impossible compression to the zero volume etc.

Approximative equations of state

- Van der Waals' equation
- Virial expansion

# Non-ideal gas equation of state

J.D.van der Waals, 1873

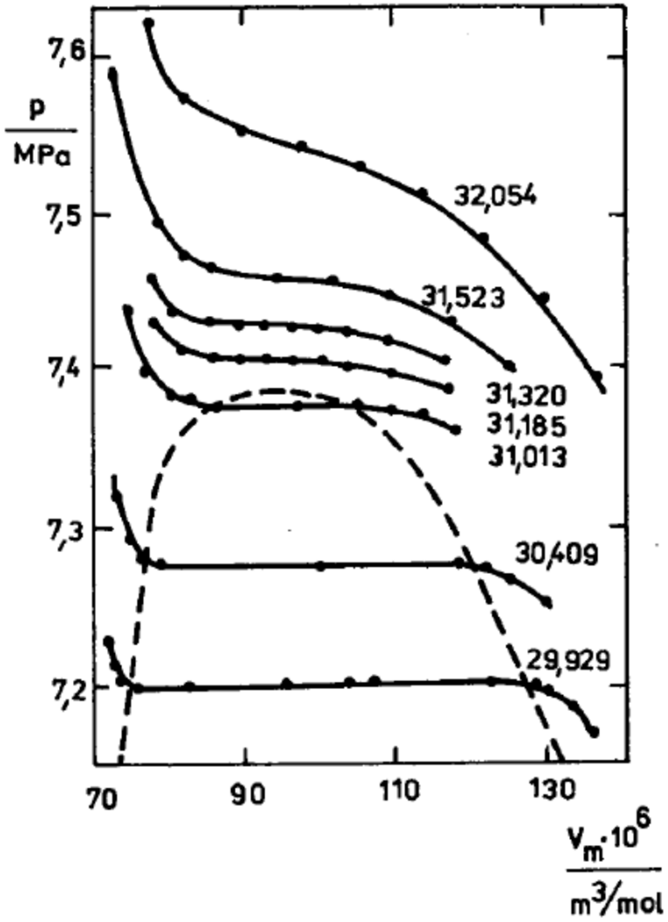
$$\left(p+\frac{a}{V_m^2}\right)\left(V_m-b\right)=RT$$

Molar volume $V_\mathrm{m}=V/n$

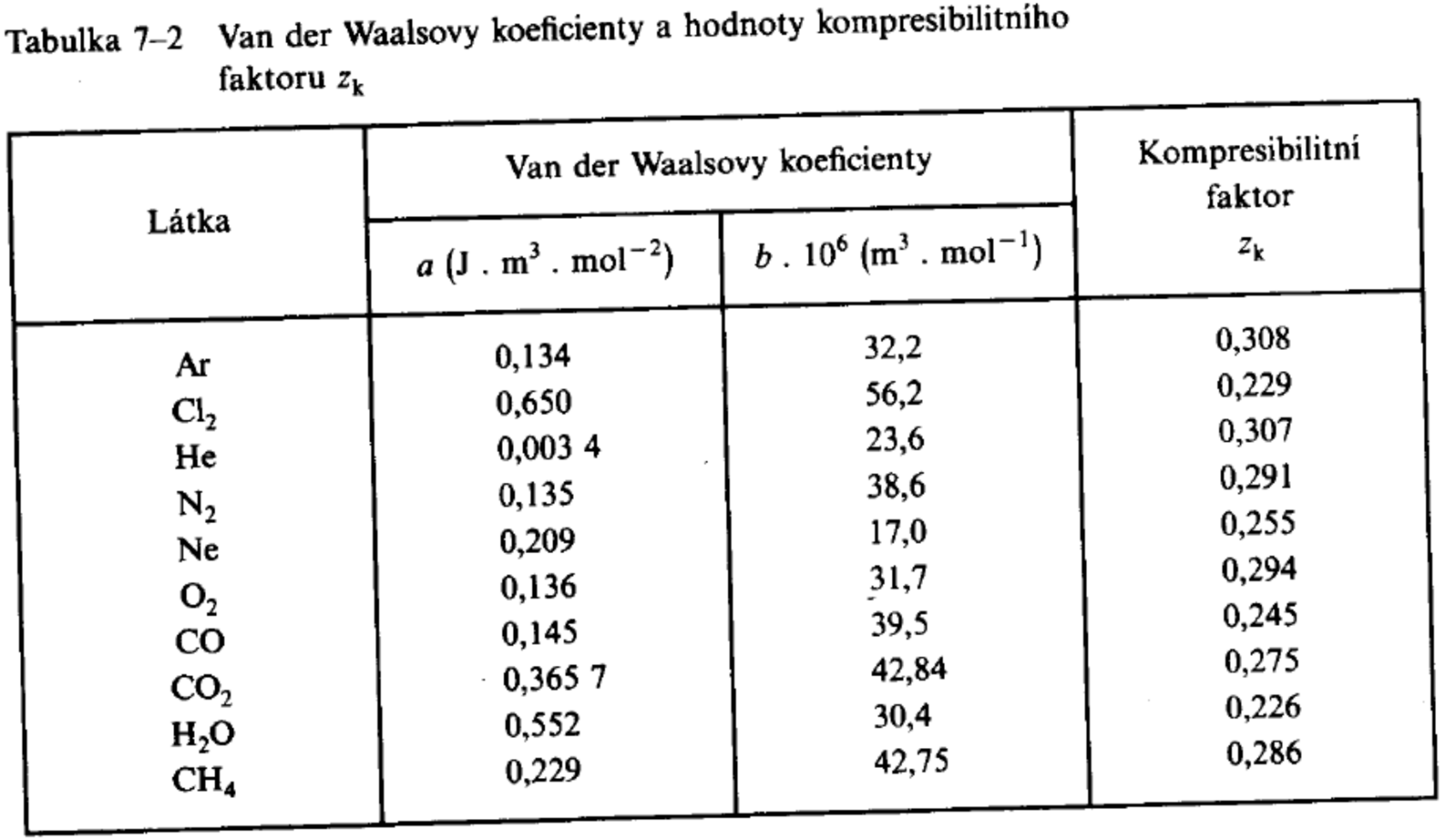
Constants $a$,$b$ are characteristics of attractive and repulsive forces among molecules – different for different gasses

# Isothermal curves of van der Waals' gas

Michels 1937 – isothermal curves for $CO_2$



# Van der Waals' coefficients



Tabulka 7–2 Van der Waalsovy koeficienty a hodnoty kompresibilitního faktoru $z_k$

| Látka | Van der Waalsovy koeficienty | | Kompresibilitní faktor $z_k$ |
|---|---|---|---|
| | $a$ (J . m$^3$ . mol$^{-2}$) | $b$ . 10$^6$ (m$^3$ . mol$^{-1}$) | |
| Ar | 0,134 | 32,2 | 0,308 |
| $Cl_2$ | 0,650 | 56,2 | 0,229 |
| He | 0,003 4 | 23,6 | 0,307 |
| $N_2$ | 0,135 | 38,6 | 0,291 |
| Ne | 0,209 | 17,0 | 0,255 |
| $O_2$ | 0,136 | 31,7 | 0,294 |
| CO | 0,145 | 39,5 | 0,245 |
| $CO_2$ | 0,365 7 | 42,84 | 0,275 |
| $H_2O$ | 0,552 | 30,4 | 0,226 |
| $CH_4$ | 0,229 | 42,75 | 0,286 |

# Virial expansion

Compressibility factor

$$z = \frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \ldots$$

Virial coefficients B, C, D, …

H.Kamerling-Onnes, 1901 – infinite expansion series

Van der Waals's equation

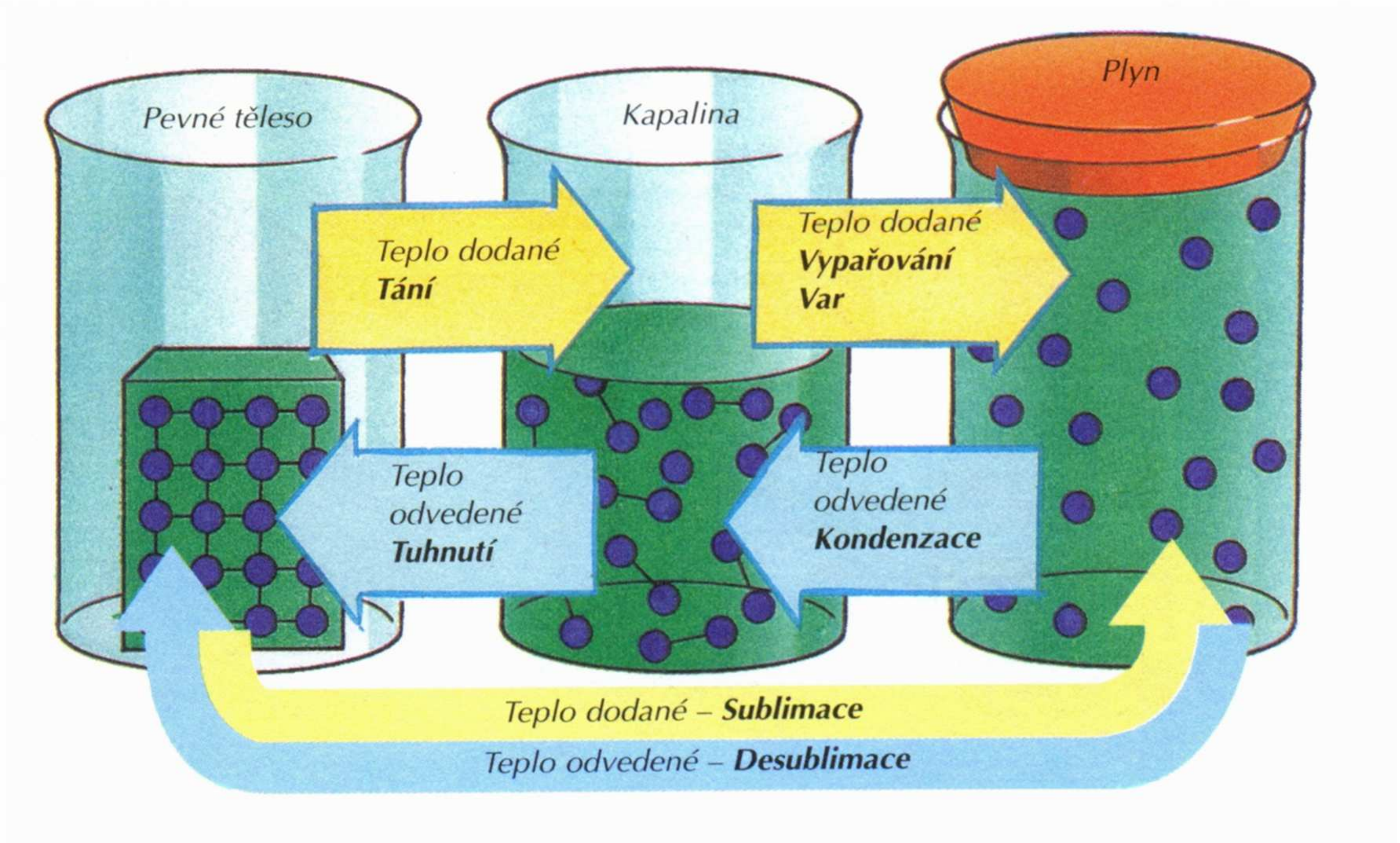
$$B(T) = b - a/RT, \quad C(T) = b^2$$

# Phases

- Phase transitions
- Phase diagram
- Calorimetry
- Air humidity

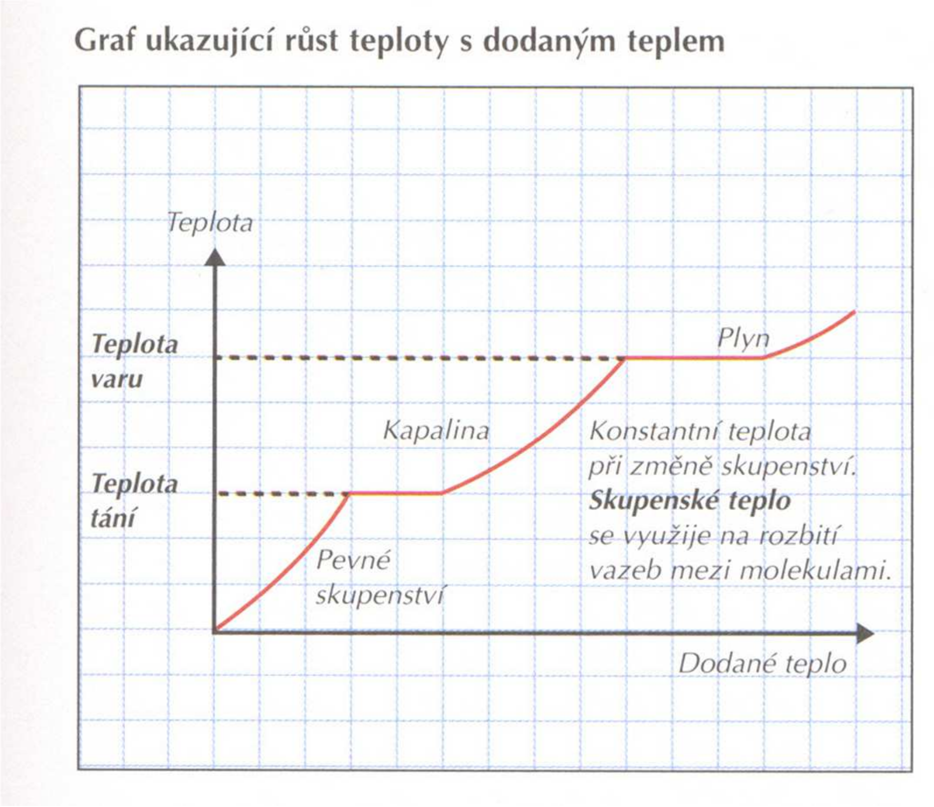
# Phase transitions

melting, boiling, sublimation, solidification, condensation



# Latent heat – temperature increase

Heat delivered to the substance for the change of phase

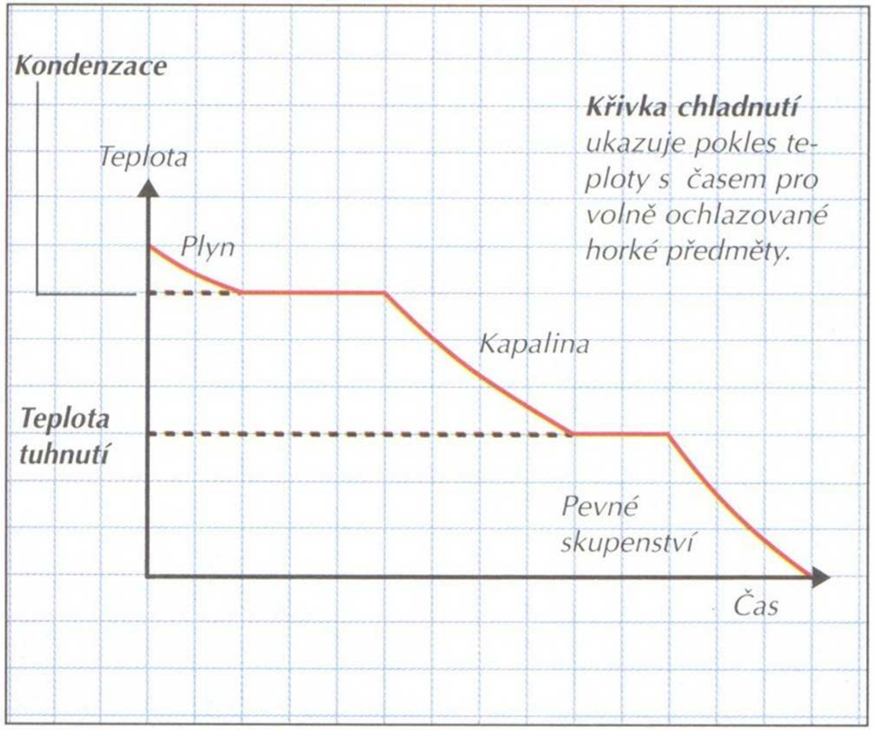

Graf ukazující růst teploty s dodaným teplem

Konstantní teplota při změně skupenství. **Skupenské teplo** se využije na rozbití vazeb mezi molekulami.

# Latent heat – temperature decrease

Heat taken from the substance for the change of phase

Graf ukazující pokles teploty při ochlazování předmětu



***Křivka chladnutí*** *ukazuje pokles teploty s časem pro volně ochlazované horké předměty.*

# Latent heat

Heat needed for the change of phase

Necessary for the change of matter structure

$$L = lm$$

Specific latent heat

$$l = \frac{L}{m} \quad [Jkg^{-1}]$$

# Specific latent heat

| Substance | melting | | boiling | |
|---|---|---|---|---|
| | $T$[°C] | $l$[kJkg$^{-1}$] | $T$[°C] | $l$[kJkg$^{-1}$] |
| Fe | 1535 | 289 | 2750 | 6340 |
| Cu | 1084 | 204 | 2567 | 4790 |
| Al | 660 | 399 | 2467 | 10500 |
| $H_2O$ | 0 | 334 | 100 | 2256 |

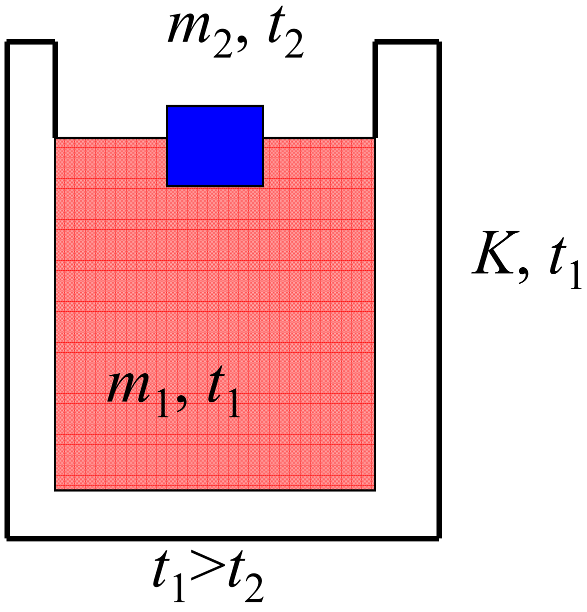
# Calorimetric equation

Simplification of the first law of thermodynamics in case of negligible work done ($A<<Q$)

$$Q_{in} = Q_{out}$$

# Example of calorimetry

$$m_2c_2(t_{melt}-t_2)+m_2l_2+m_2c_2'(t-t_{melt})=m_1c_1(t_1-t)+K(t_1-t)$$

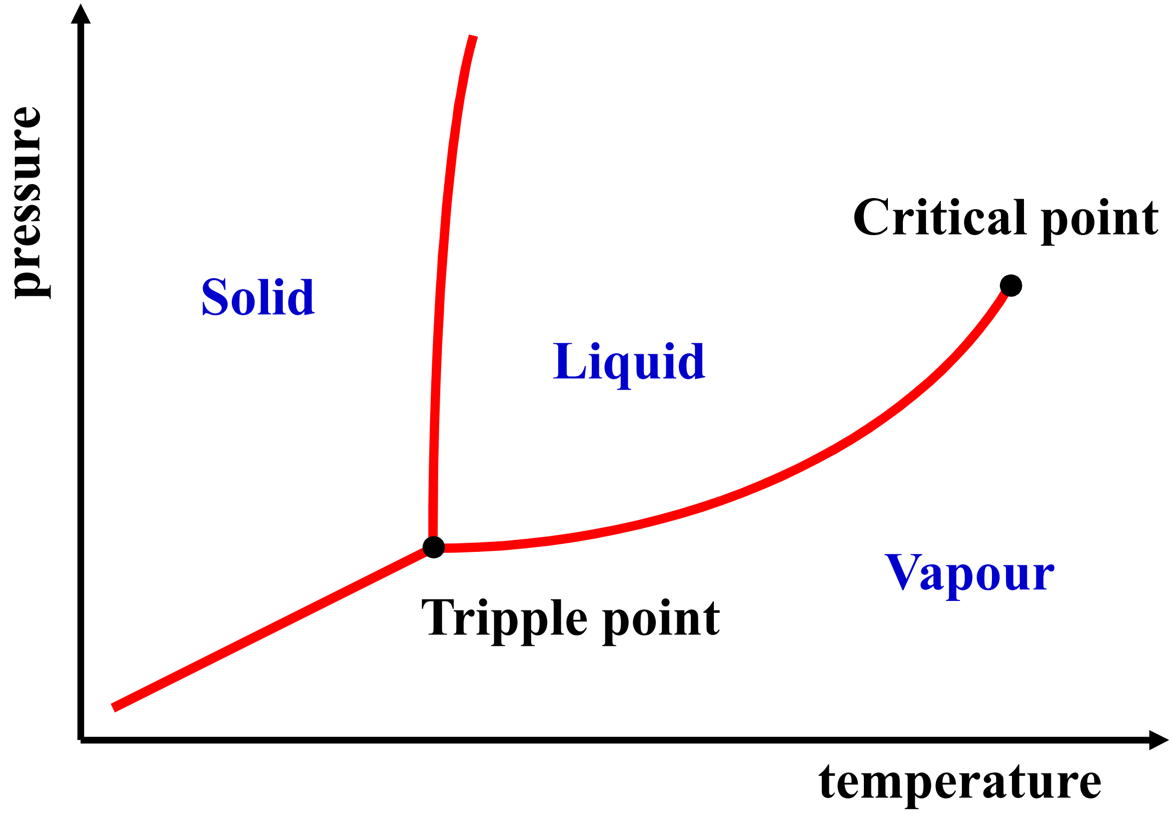


Final temperature $t_2<t<t_1$

“whisky on the rocks”

# Phase diagram

Equilibrium between phases – coexistence



# Clausius – Clapeyron's equation

Change of phase transition temperature with pressure

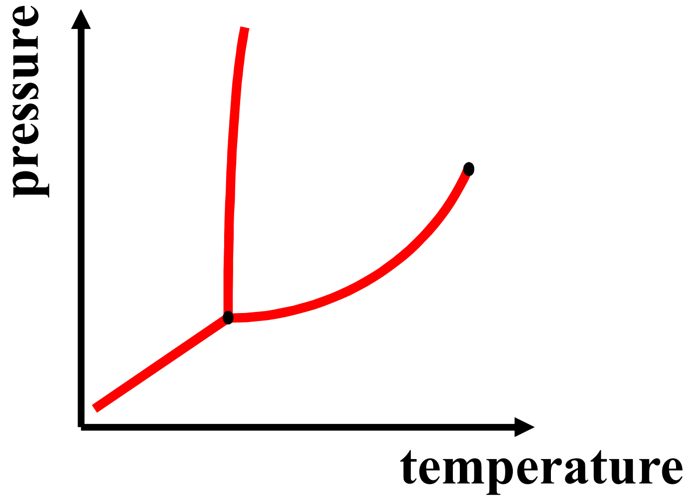
$$v_2 - v_1 = \frac{l}{T}\frac{\Delta T}{\Delta p}$$

$l$…specific latent heat

$v_2$, $v_1 = 1/\rho_1$ … specific volumes of phases

$T$… phase transition temperature

$p$…pressure



# Clausius – Clapeyron's equation

Water – ice melting point

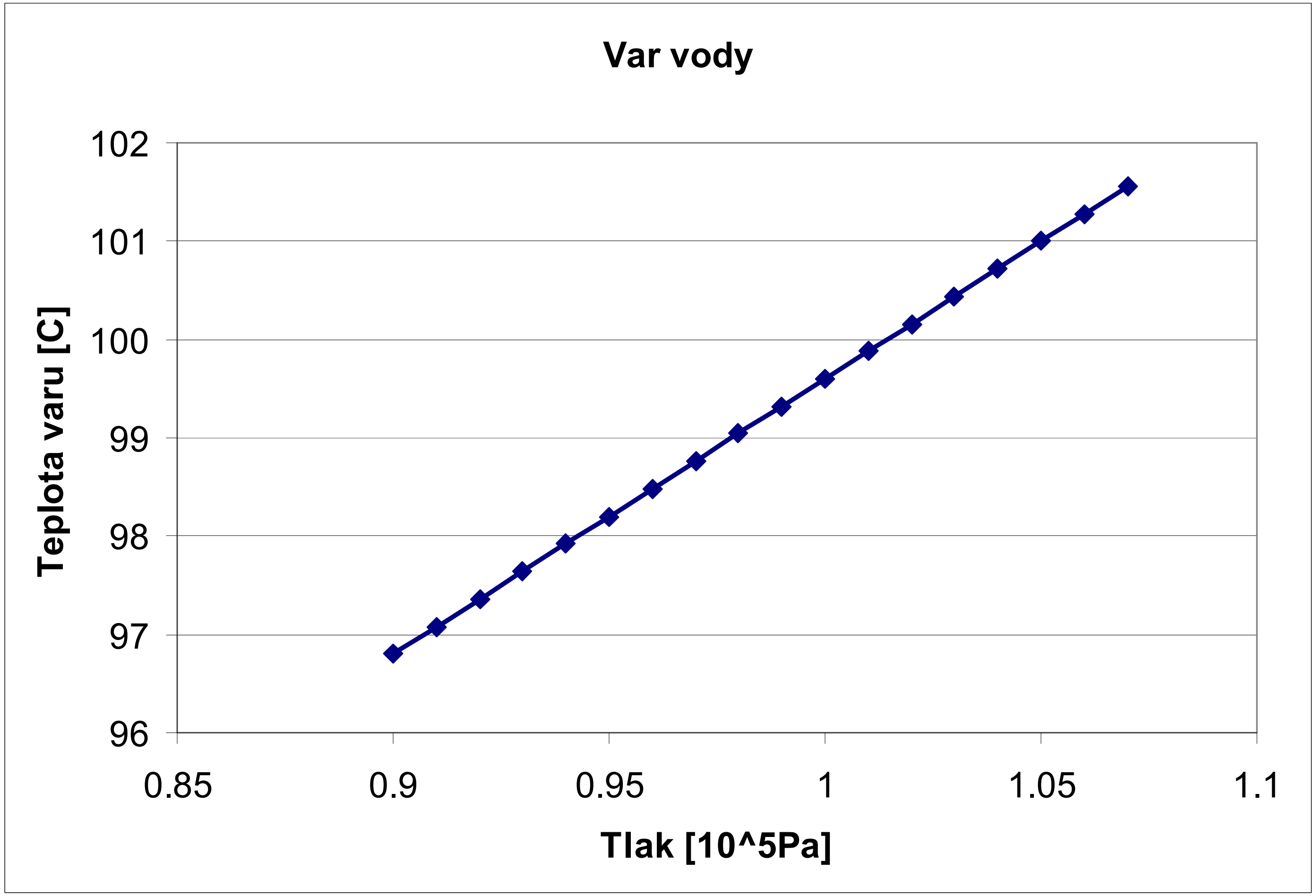
$$\frac{\Delta T}{\Delta p} = \frac{(v_2 - v_1)T}{l} = -9 \cdot 10^{-8} KPa^{-1}$$

Specific latent heat $l$= 334000Jkg$^{-1}$, $v$=1/$\rho$, $\rho_2$=1000kgm$^{-3}$ water, $\rho_1$=900kgm$^{-3}$ ice, $T$=273K melting point

Change of melting point below ice-skate

(S=10$^{-3}$m$^2$, G=1000N, $\Delta$T=-0.09K)

# Boiling point of water



# Air humidity

- Absolute = mass of water vapour per 1m$^3$ of air

$$\Phi = \frac{m}{V} \quad [kgm^{-3}]$$

- Relative

$$\varphi = \frac{\Phi}{\Phi_{\max}} \quad [\%]$$

Optimum humidity for humans 65-70%

# Saturated vapour

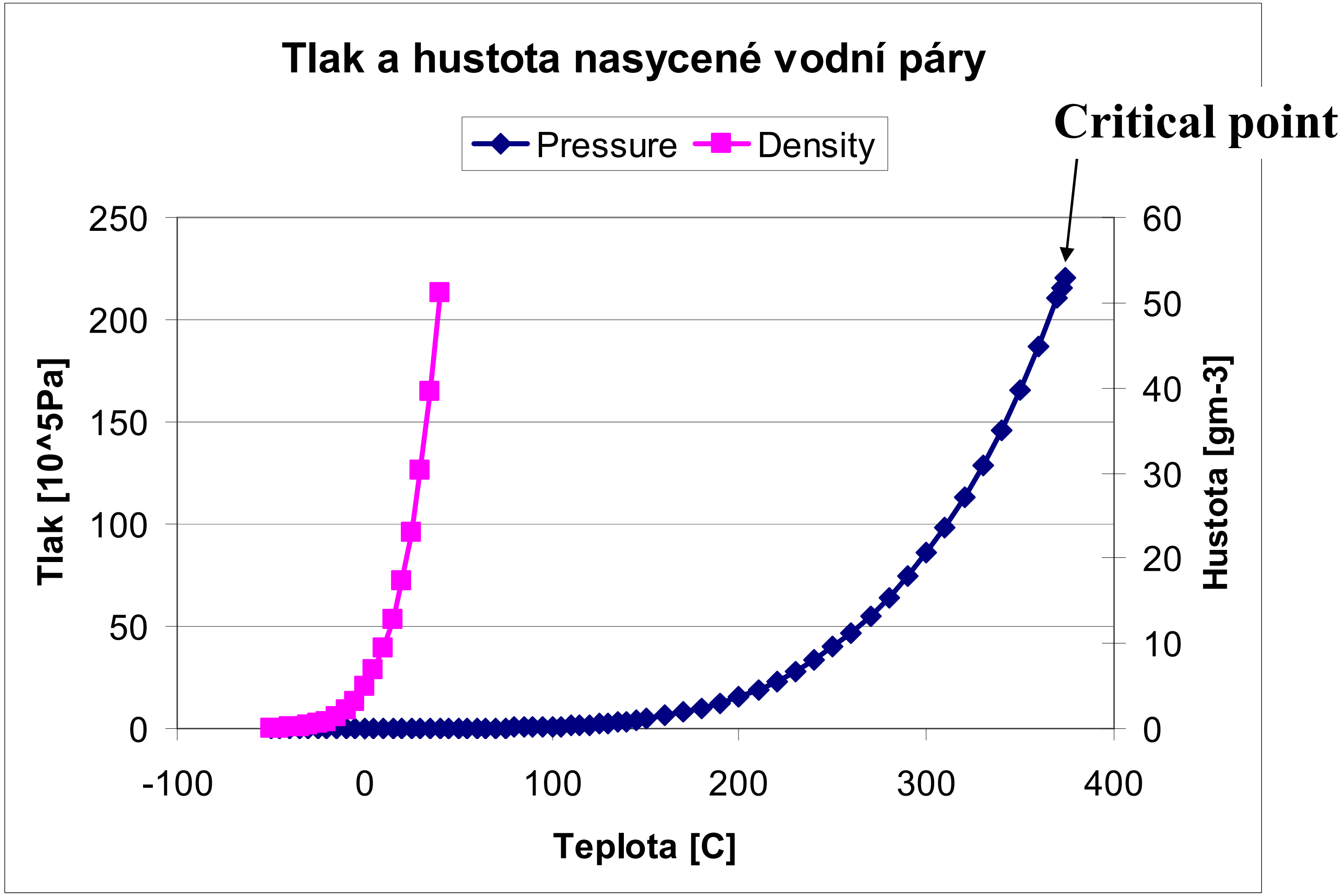
- Equilibrium between ratios of particles changing phase from liquid to vapour and back

Maximum vapour content is limited in an air $\Phi_{max}$

Dew point ($t_S$[°C]) – temperature of saturated vapour at given vapour content, i.e. temperature when condensation starts

$t_S<0^oC$ white frost, $t_S>0^oC$ dew

# Saturated water vapour



# Air humidity, dew point – example

| $t$[°C] | $\Phi_{max}$[gm$^{-3}$] |
|---|---|
| 30 | 30.4 |
| 25 | 23.0 |
| 20 | 17.3 |
| 15 | 12.8 |
| 10 | 9.4 |
| 5 | 6.8 |
| 0 | 4.9 |
| -5 | 3.3 |

50% humidity at 20°C, i.e. 8.7gm$^{-3}$ of water vapour

$\Phi_{max}$=8.7gm$^{-3}$
Water vapour is saturated at the temperature close to 9°C
Dew point is 9°C

# Literature

Pictures used from the books:

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and material data from tables:

BROŽ, J., ROSKOVEC, V., VALOUCH, M.: Fyzikální a matematické tabulky, SNTL Praha 1980