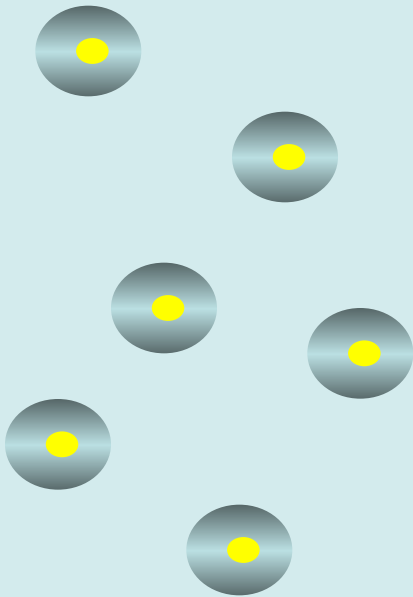


Water in the atmosphere

The names are: Mushroom, blind, blood, glazed rains. And still there is one particular one the people call “*TSAREVNA’S TEARS*”. That is the rain which can not be named by any other name but this.

The drops of this rain look larger than usual raindrops, They seem to fall slower from a small cloud. The Sun shining from a side and reflecting from the drops makes them as if they are made with gold. Being transparent, they bear blue color from that part of the sky which is not covered with clouds.

Gold and blue combination makes them so beautiful that the name “*tsarevna’s tears*” seems to be the most appropriate name for this rain.



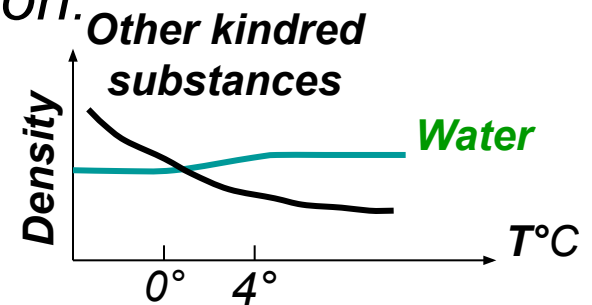
Distinctive properties of the water

The water in the atmosphere is found in all three phases:
vapor, liquid, and ice.

Special character of the *water density variation*.

$$(\rho_w)_{T=0^{\circ}C} = 1g / cm^3$$

$$(\rho_{ice})_{T \leq 0^{\circ}C} = 0.91g / cm^3$$



Water heat capacity significantly changes when congealing to the solid state. $C_w = 4187 J / kg \cdot K$ **That is** $C_{ice} = 2114 J / kg \cdot K$
not so for other kindred substances.

Water freezing and boiling temperature are much higher than that of other kindred chemical combinations.

Water melting and evaporation latent heat is rather high

$$L_m = 324 \text{ kJ/kg}$$

$$L = 2500 \text{ kJ/kg}$$

Water is a good solvent, it has chemical activity (iron rusts as contacting water)

Liquid water density varies with temperature a little. It can be regarded as constant (1 g/cm³), as well as ice (0.91 g/cm³).

Water vapor heat capacity can be also regarded as non-depended on temperature variation.

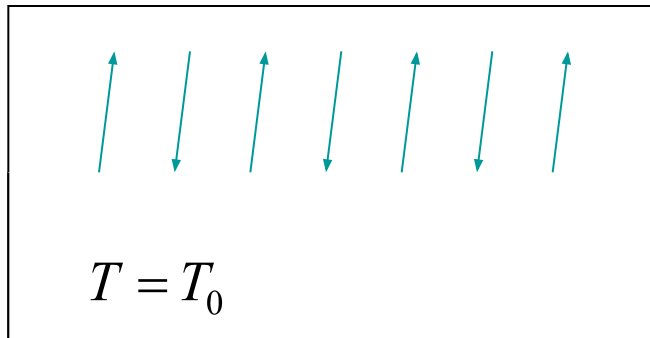
$$C_{wv} = 1386 \text{ J/kg} \cdot \text{K}$$

$$C_{pw} = 1846 \text{ J/kg} \cdot \text{K}$$

$$C_v = 718 \text{ J/kg} \cdot \text{K}$$

$$C_p = 1005 \text{ J/kg} \cdot \text{K}$$

Evaporation and condensation



A number of molecules comes off, N_{off}

A number of molecules comes back, N_{back}

$N_{off} > N_{back} \rightarrow$ **Evaporation**

$N_{off} = N_{back} \rightarrow$ **Saturation state at $T = T_0$**

At $T_1 < T_0$ $N_{off} < N_{back} \rightarrow$ Condensation

If the temperature in the closed space increases to become $T_2 > T_1$, evaporation will begin again until $N_{off} = N_{back}$

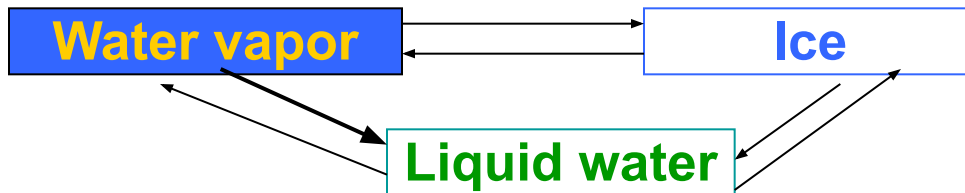
$e < E \rightarrow$ **Evaporation goes on** $N_{off} > N_{back}$

$e = E \rightarrow$ **Saturation has been reached** $N_{off} = N_{back}$

$e > E \rightarrow$ **Condensation takes place** $N_{off} < N_{back}$

Thermodynamics of the water phase transfer

The following processes for the water phase transfer from state 1 to state 2 are possible



The first law of thermodynamics can be applied to describe the water phase transfer processes

$$dq = du + edv$$

Let's introduce the notion of thermodynamic potential $\Phi = u + ev - T\varphi$

φ denotes entropy (it is a term known from general physics) $d\varphi = \frac{dq}{T}$

$$dq = Td\varphi = du + edv$$

$$du + edv - Td\varphi = 0$$

Transfer from one phase to another goes at the constant temperature

$$\int_{(1)}^{(2)} dq = T(\varphi_2 - \varphi_1) = (u_2 - u_1) + E(v_2 - v_1)$$

$$T\varphi_2 - T\varphi_1 = u_2 - u_1 + Ev_2 - Ev_1$$

$$\underbrace{u_1 + Ev_1 - T\varphi_1}_{\Phi_1} = \underbrace{u_2 + Ev_2 - T\varphi_2}_{\Phi_2} \quad \boxed{\Phi_1 = \Phi_2}$$

Thermodynamic potential remains unchanged at the water phase transfer from one state to another.

At temperature $T+dT$, $\Phi+d\Phi$, and $E+dE$, and $\Phi_1 + d\Phi_1 = \Phi_2 + d\Phi_2$

Recalling that $\Phi = u + ev - T\varphi$ $d\Phi = \underbrace{du + Edv - Td\varphi}_{=0} + vdE - \varphi dT$

$$d\Phi = vdE - \varphi dT,$$

$$\frac{dE}{dT} = \frac{\varphi_2 - \varphi_1}{v_2 - v_1}$$

$$v_1 dE - \varphi_1 dT = v_2 dE - \varphi_2 dT$$

$$(\varphi_2 - \varphi_1) dT = (v_2 - v_1) dE$$

$$dq = Td\varphi;$$

$$d\varphi = \frac{dq}{T};$$

$$\varphi_2 - \varphi_1 = \int_{(1)}^{(2)} \frac{dq}{T} = \frac{1}{T} \int_{(1)}^{(2)} dq = \frac{L_{1,2}}{T}$$

Here $L_{1,2}$ is specific latent heat that is released as water transfers from state 1 to state 2

$$\frac{dE}{dT} = \frac{L_{1,2}}{T(v_2 - v_1)} \rightarrow \text{Clausius - Clapeyron equation}$$

For practical purposes the quantity $2,72 \cdot T$ neglected because it is very small ($T^\circ\text{C}$). Therefore, the latent heat is adopted as constant.

For the process 1. Liquid water \longleftrightarrow 2. Water vapor

$$L_{1,2} = L = L_0 + 2,72 \cdot T = 2500 + 2,72T \text{ kJ/kg}$$

$$\boxed{v_2 \gg v_1} \quad L = L_0 = 2500 \text{ kJ/kg} = \text{const}$$

$$\frac{dE}{dT} = \frac{L}{T \cdot v_2} \quad Ev = R_w T$$

$$v = \frac{R_w T}{E}$$

$$\frac{dE}{dT} = \frac{LE}{R_w T^2}$$

$$T = -50^\circ\text{C} \Rightarrow 2,72 \cdot T = -136$$

$$L = 2364 \text{ kJ/kg}$$

$$T = 50^\circ\text{C} \Rightarrow 2,72 \cdot T = 136$$

$$L = 2636 \text{ kJ/kg}$$

The formula above can be transformed in the following way:

$$\frac{dE}{dT} = \frac{LE}{R_w T^2} \rightarrow \frac{dE}{E} = \frac{LdT}{R_w T^2} \rightarrow \int_{E_0}^E \frac{dE}{E} = \frac{L}{R_w} \int_{T_0}^T \frac{dT}{T^2}$$

Adopting \rightarrow

$$\begin{aligned} T_0 &= 273.15K \\ E_0 &= 6.1078hPa \\ R_w &= 460 J/kg \cdot K \end{aligned}$$

$$\ln \frac{E}{E_0} = \frac{L}{R_w} \left(\frac{1}{T_0} - \frac{1}{T} \right)$$

$$E = E_0 \times 10^{\frac{8.62T}{273.15+T}}$$

$$E_i = E_0 \times 10^{\frac{9.76T}{273.15+T}}$$

$$E = E_0 \times 10^{\frac{aT}{b+T}}$$

Magnus formula

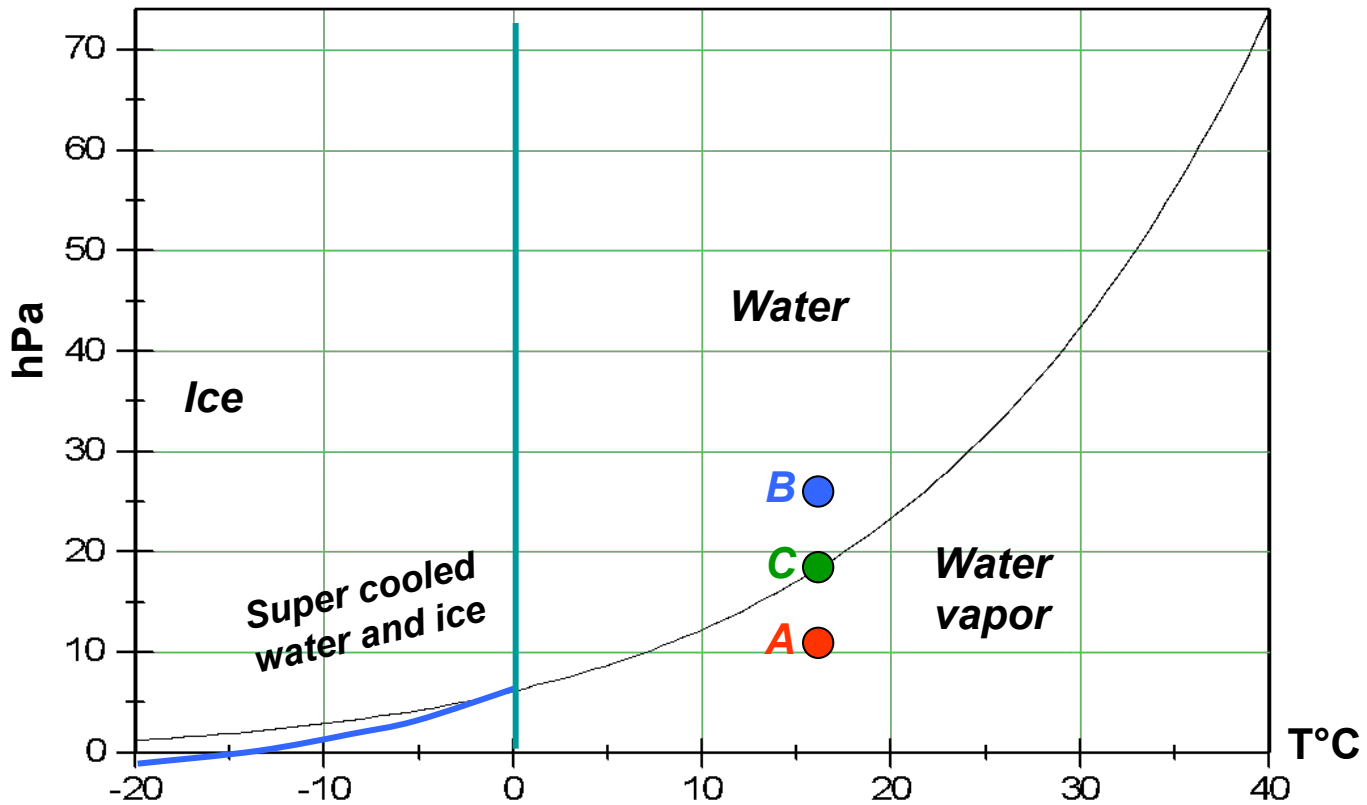
Doing the same reasoning, we'll obtain the similar formula for sublimation process.



Much better results were obtained with empirically determined coefficients "a" and "b"

For water	a=7.63	b=241.9
For ice	a=9.5	b=265.5

Magnus curve

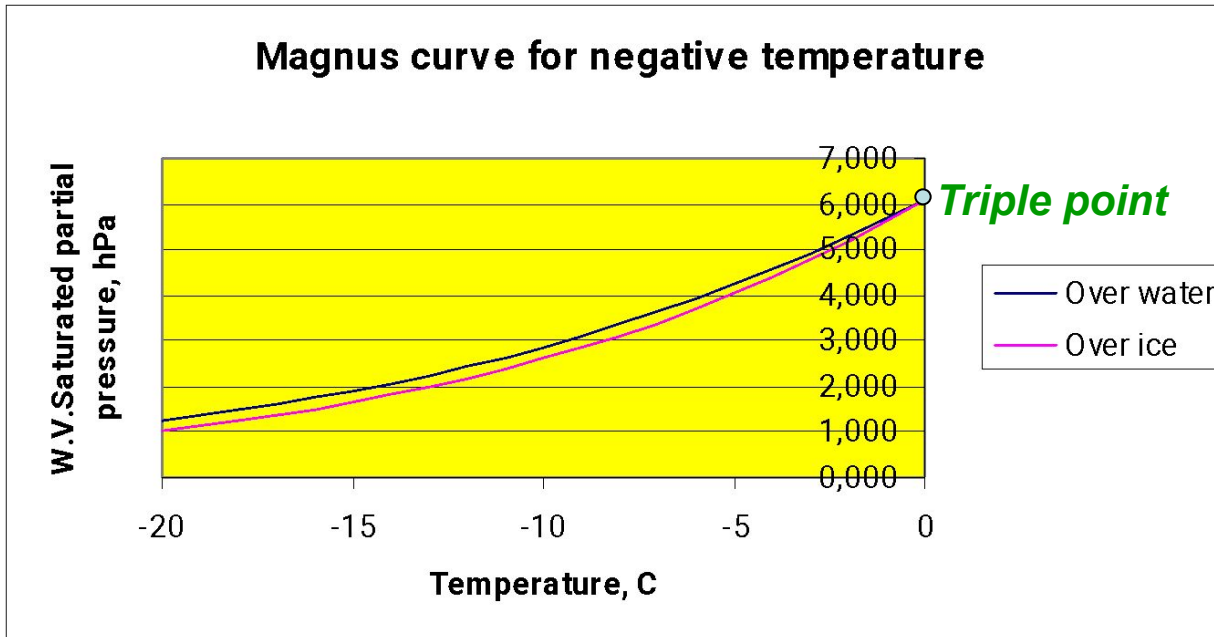


A-Under saturated air

B-Super saturated air

C-Saturated air

Triple point



The triple point corresponds to $T_0=273,16\text{ K}$ ($0,01^\circ\text{C}$), $E_0=6,1114\text{ hPa}$

At $T>0,01$ water can be in two phases: liquid and vapor.

At $T\leq 0,01$ water can be found in any phase.

Due to adhesion forces the equilibrium water vapor pressure over super cooled water is larger than over ice.

Other factors influencing the saturation water vapor pressure

These factors are curvature of the evaporating surface, salt solution, and electric charges.



**Convex
(dome)**

Easier come off



Flat



Concave

Hard come off

$$E_{Dome} > E_{Flat} > E_{Concave}$$

In the atmosphere we deal with convex surfaces (droplets). To determine the saturation water vapor pressure over droplet of the radius r , meteorologists use Thomson's formula.

$$\ln \frac{E_r}{E} = \frac{2\sigma}{R_w \cdot \rho_w \cdot T \cdot r} \quad \text{For practical purposes } \frac{2\sigma}{R_w \rho_w T} \approx 1,2 \cdot 10^{-7} \text{ cm} = \text{const} = C_r$$

$$\frac{E_r}{E} = 1 + \frac{C_r}{r} \quad E_r = E \left(1 + \frac{C_r}{r} \right) \quad 12$$

σ is surface tension coefficient

When using original Thomson's formula, it is worth knowing that the surface tension coefficient depends upon temperature as indicated in the table.

$T^{\circ}\text{C}$	-5	0	10	20	30
$\sigma \text{ mJ/m}^2$	76.42	75.64	72.22	71.75	71.18

In fact, the parameter C_r is not constant, but its variation is so small that we may neglect them.

The ration E_r/E can be calculated for different values of the droplet radius.

$R \text{ cm}$	10^{-7}	$5 \cdot 10^{-7}$	10^{-6}	10^{-5}	10^{-4}
E_r/E	332	124	113	101,2	100,1

For the condensation to start over very small droplets ($r \leq 10^{-7}$) the super saturation must be 300 – 400%. If the droplet radius is $r \leq 10^{-4}$ the saturation is about 100%. It means that curvature, at this case, doesn't influence saturation, and, hence, condensation.

In the real atmosphere water vapor condenses over so called condensation nuclei (ядрах конденсации) that are particles of various salts. Thus, the droplets actually are chemical solutions. The saturation over solution is always smaller than over pure water (at the same temperature).

$$E_{r,m} = E_r \left(1 + \frac{C_m m}{M + m} \right)^{\frac{\rho_w}{\rho_w'}}$$

m is the mass of the salt dissolved in the droplet, M is the solution mass (mass of the droplet), ρ_w' is the solution density, ρ_w is pure water density, C_m is coefficient depending on the nature of the salt.

Presence in droplets of **electric charges (Q)** should also be accounted for.

$$\ln \frac{E_{r,Q}}{E} = \frac{2\sigma}{R_w \cdot \rho_w \cdot T \cdot r} - \frac{Q^2}{8\pi\epsilon_0\epsilon \cdot r^4} \times \frac{1}{R_w \cdot \rho_w \cdot T}$$

ϵ_0 Is dielectric permissivity

ϵ Is electric constant