5.13. Real gases

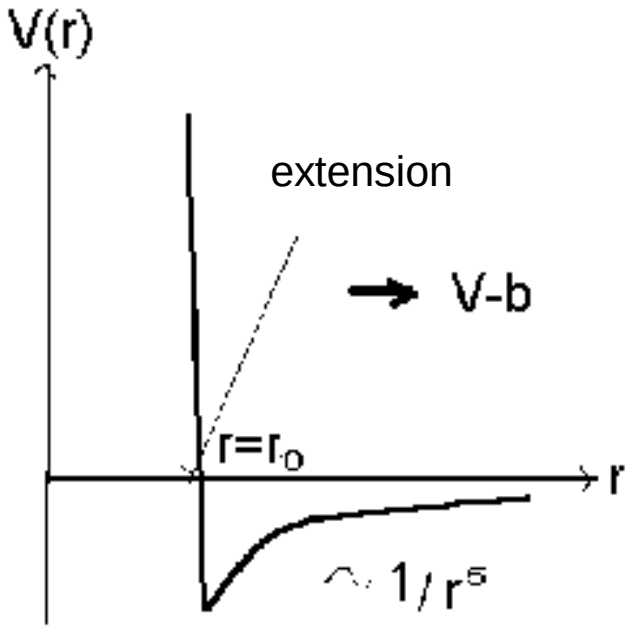
Deviation of the description of an ideal gas due to additional effects!
Van der Waals - Forces between molecules

a) Molecules of gases do have a volume proper

$$V \rightarrow V - b$$

b) At lower temperatures comes in the volume into description

b : Van der Waals Co-volume



Force beween molecules:

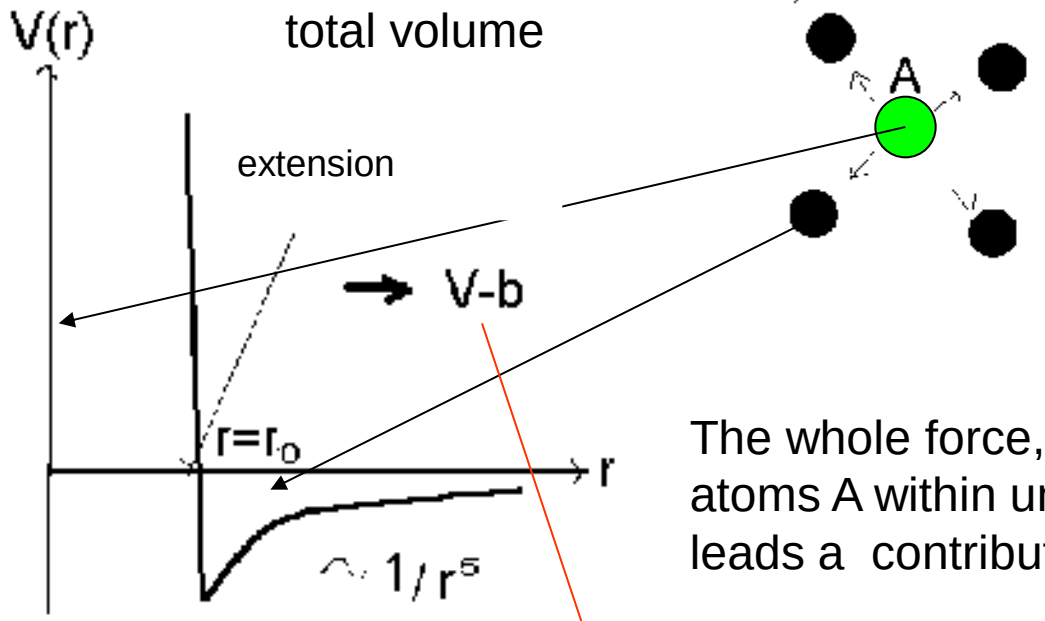
$$F \sim \frac{1}{r^6}$$

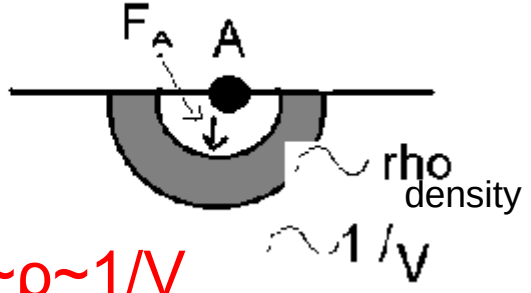
Changes pressure:

$$p \rightarrow p + \frac{a}{V^2}$$

The force act on the boundary surface only, gas-liquid
respectively gas- fixed wall. Inside cancels!

Size of particle lowers total volume





$F_A \sim \rho \sim 1/V$

The whole force,however, acts on all atoms A within unit volume and leads a contribution proportional 1/V

$$F \sim n_A \cdot F_A; n_A$$:Particles/Volume

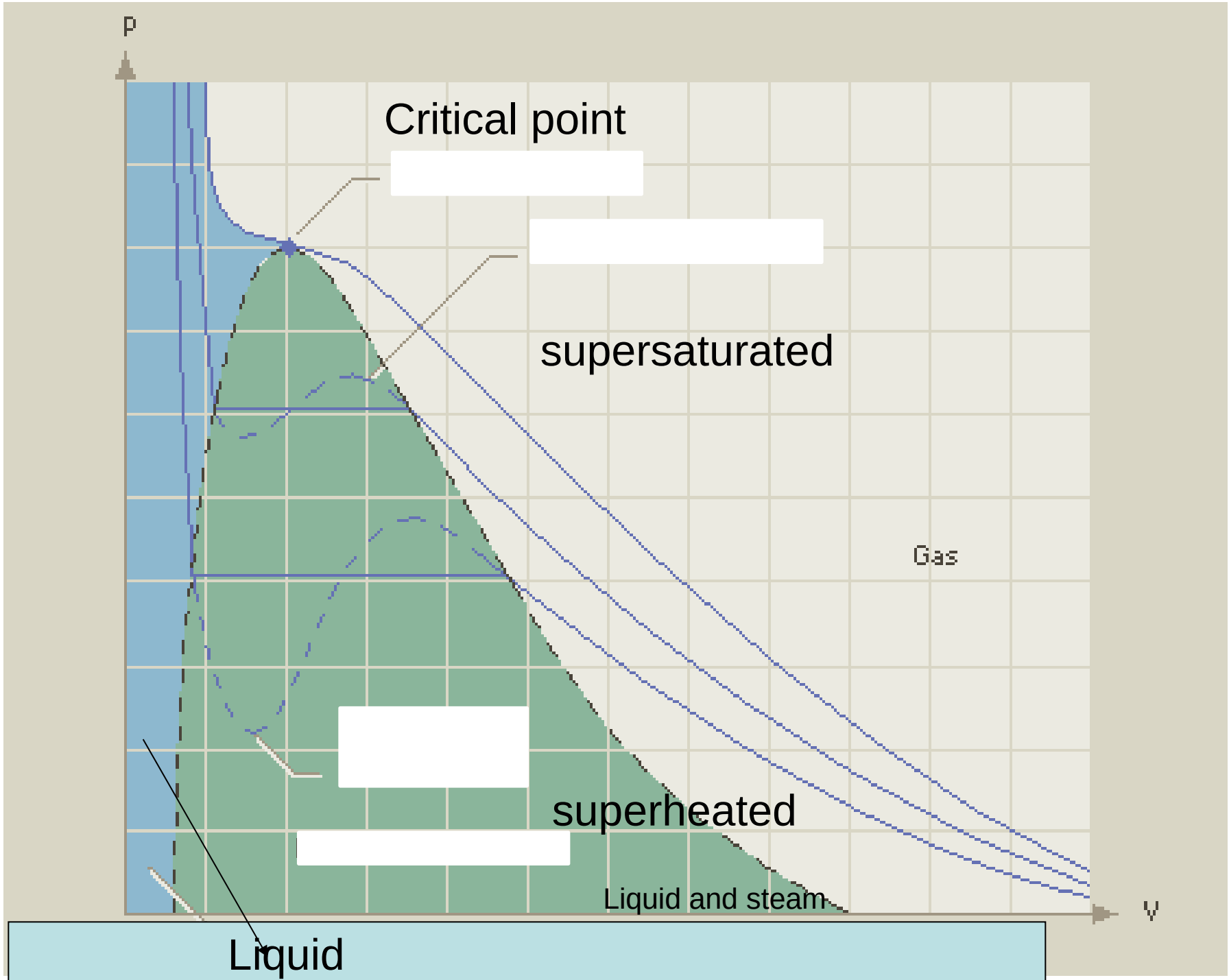
i.e.: additional inside pressure!

$$\Rightarrow p \rightarrow p + \frac{a}{V^2};$$

Equation of real gases

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

$$\Rightarrow V^3 - V^2(b + \frac{RT}{p}) + V \cdot \frac{a}{p} - \frac{a \cdot b}{p} = 0 \qquad p = \frac{V^2 RT - Va + ab}{V^2(V-b)}$$

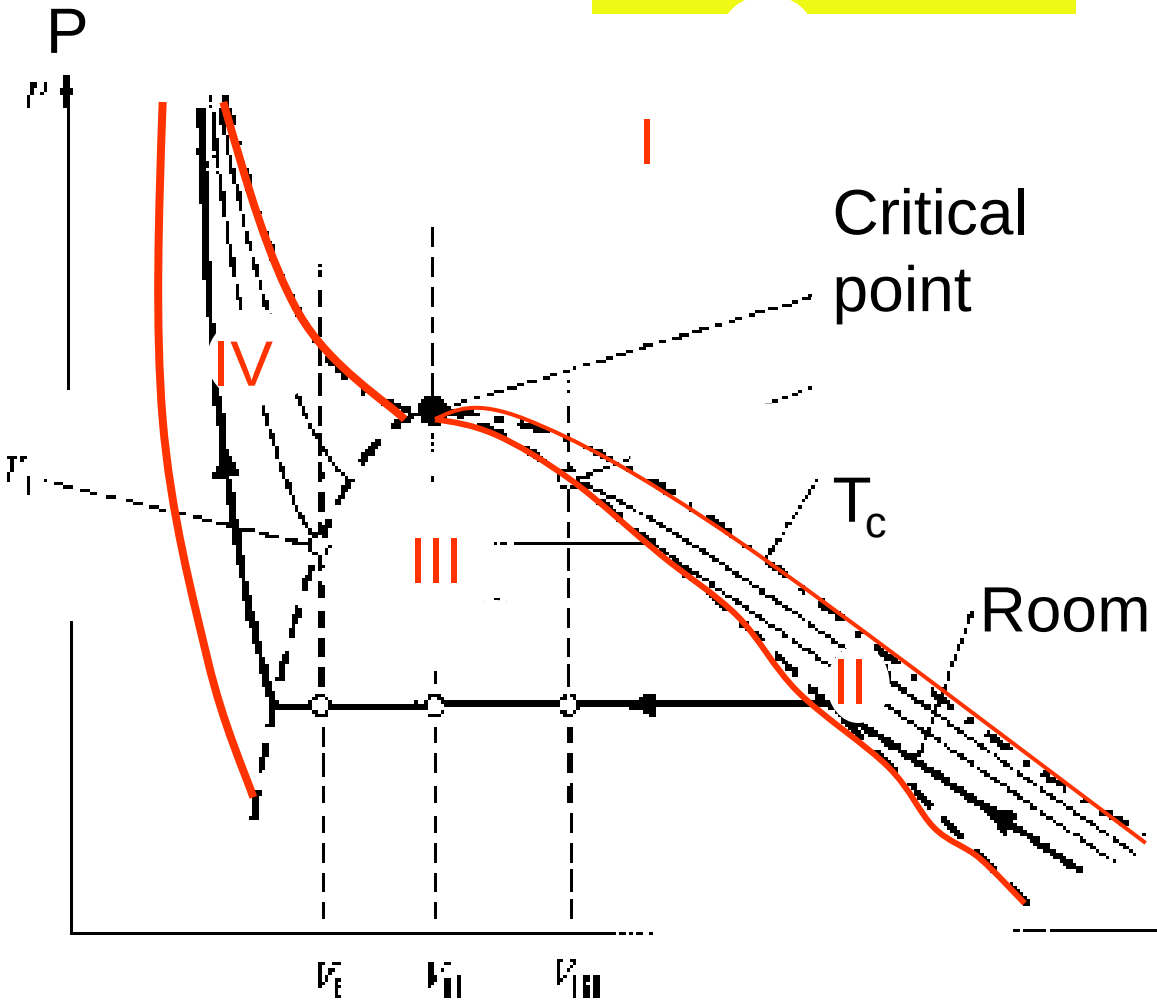

p
Critical point
supersaturated
Gas
superheated
Liquid and steam
V
Liquid

e.g: CO_2

In an interval of pressure dependent of tempetature

$[p_1, p_2] \Rightarrow$ No clearly classification of volume possible

All four regions meet at one point!



I: For T $\succ T_c$(Critical temperature)

CO_2 gaseous

II: For $T \prec T_c$

Phase steam exists

III:Coexistence steam-liquid

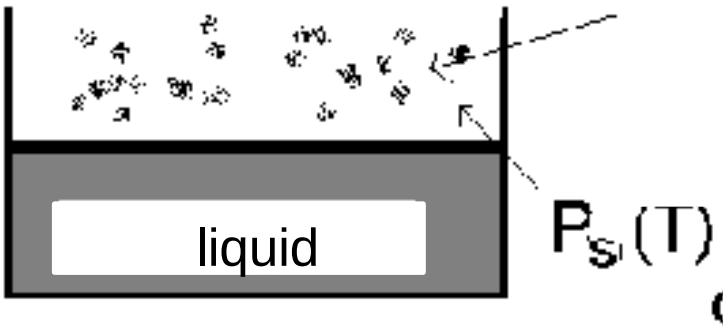
Access: Isotherme compression

IV: Liquid :compressibility small

Here: $T_c = 31^0, P_c = 73 \cdot 10^5 Pa,$ for one Mol CO_2 : V= 97cm^3

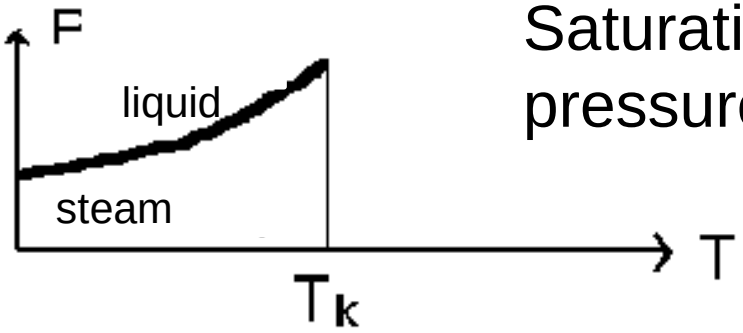
States of aggregations: Phases

Phasetransition →liquid ←→solid ←→ gaseous



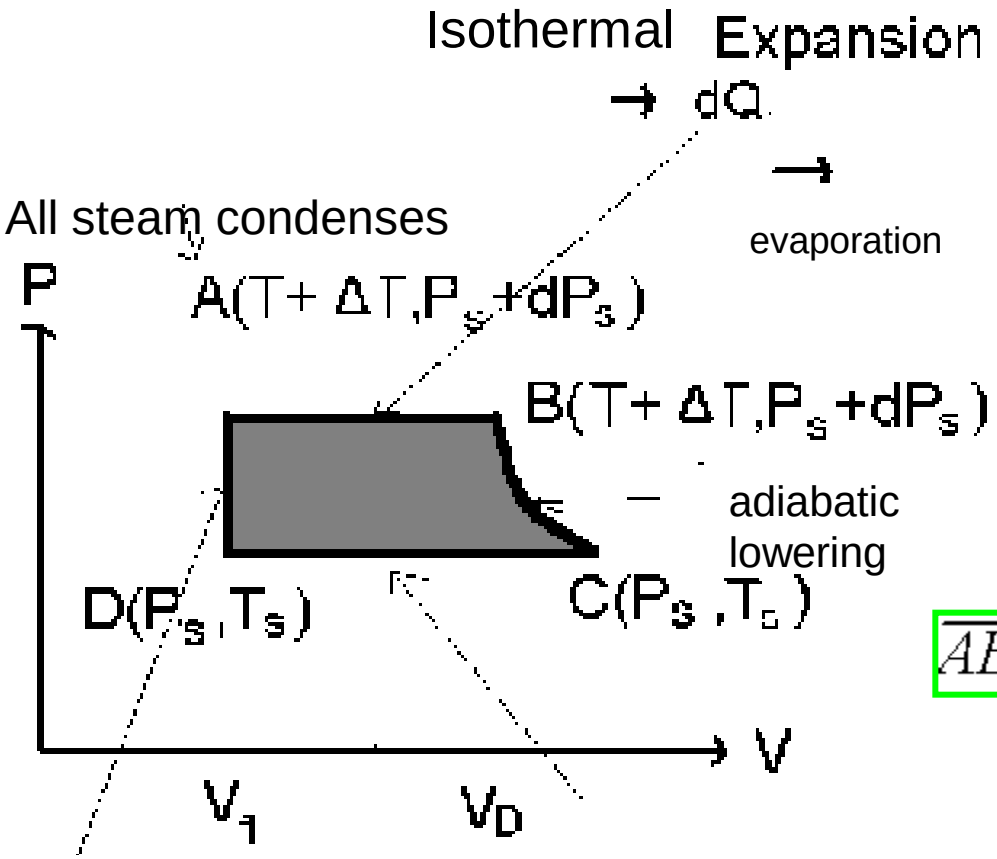
A part evaporates

Coexistence of phases:
As many molecules evaporate as condense.



Saturation vapor pressure

Thermodynamic cycle in the region liquid – gaseous



$$\overline{AB}\ :\ \Delta W_1 = (p_s + dp_s)(V_{fl} - V_D)$$

$$\overline{CD}\ :\ \Delta W_2 = p_s(V_D - V_{fl})$$

isothermal compression
(steam gets condensed)
dQ 2 gets free

$$\Rightarrow \eta = \frac{|\Delta W|}{\Delta Q} = \frac{(V_D - V_{fl})\cdot dp_s}{\Lambda} = \frac{\Delta T}{T}$$

$$\Delta W = \Delta W_1 + \Delta W_2 = (V_{fl} - V_D)\cdot dp_s$$

$$\Rightarrow \boxed{\Lambda = T\frac{(V_D - V_{fl})\cdot dp_s}{dT}} \quad Clausius - Clapeyron$$

$$\Rightarrow \boxed{\Lambda = T\frac{(V_D - V_{fl})\cdot dp_s}{dT}} \quad Clausius - Clapeyron$$

Λ : Evaporation heat per Mol
One sees two portions:

1. $V_{fl} \rightarrow V_D$: Increase of volume

2. Work for an increase of the mean distance of molecules

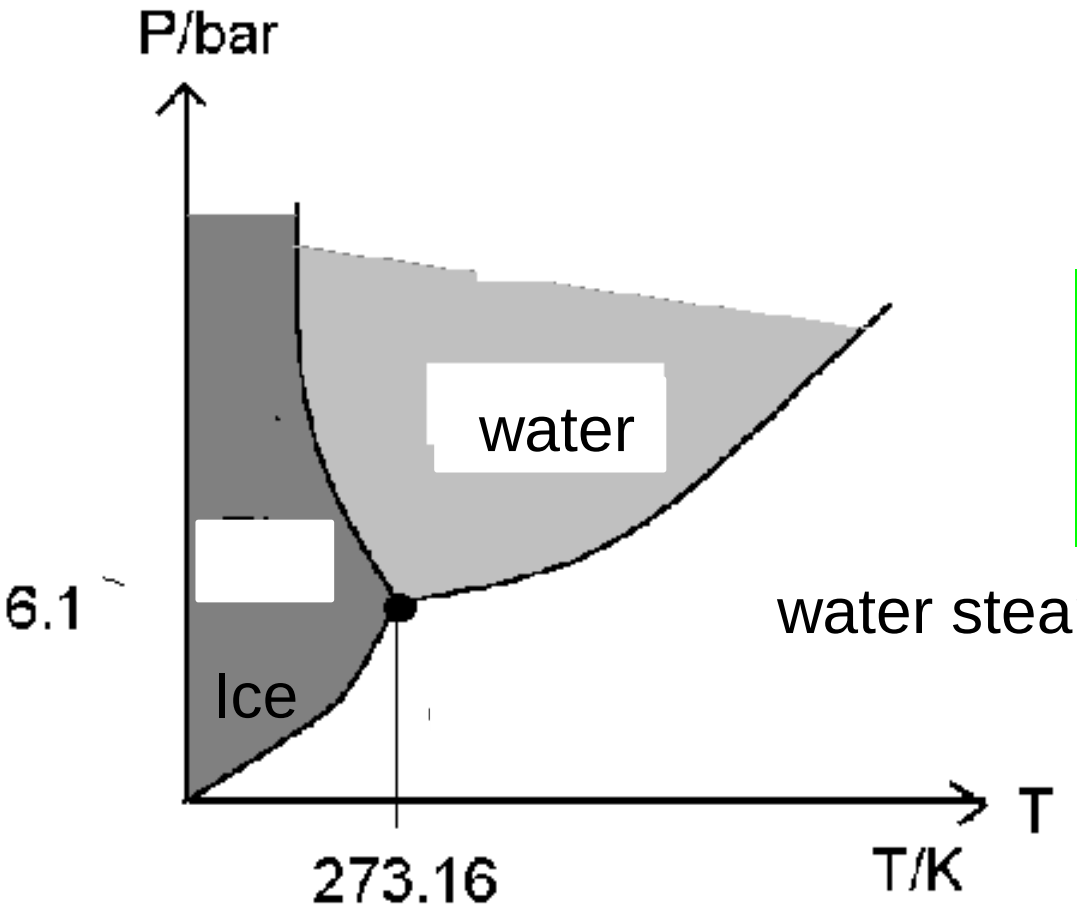
2.>>>1. Example: 1dm^3 H_2O liquid, expands at 100^0

to 1.7m^3

Work against pressure of 1bar: $p \cdot dV = 170kJ$

Total evaporation heat: 2080kJ

Coexistence of three phases, Triplepoint



At tripelpoint all three phases can exist at the same time.
Borderline: Gaseous - solid:
Line of sublimation