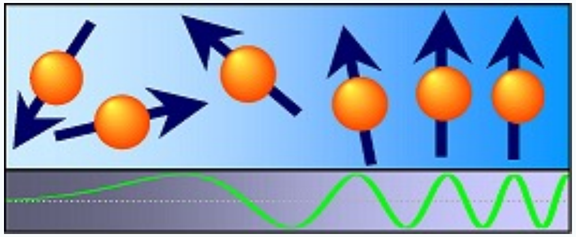
Experimental Physics EP2
Thermodynamics

– Real gases –

Van der Waals equation, Phase diagrams

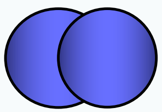


https://bloch.physgeo.uni-leipzig.de/amr/

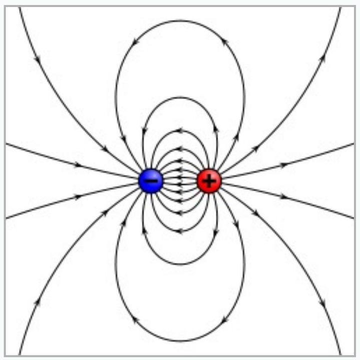
From ideal gases to real gases

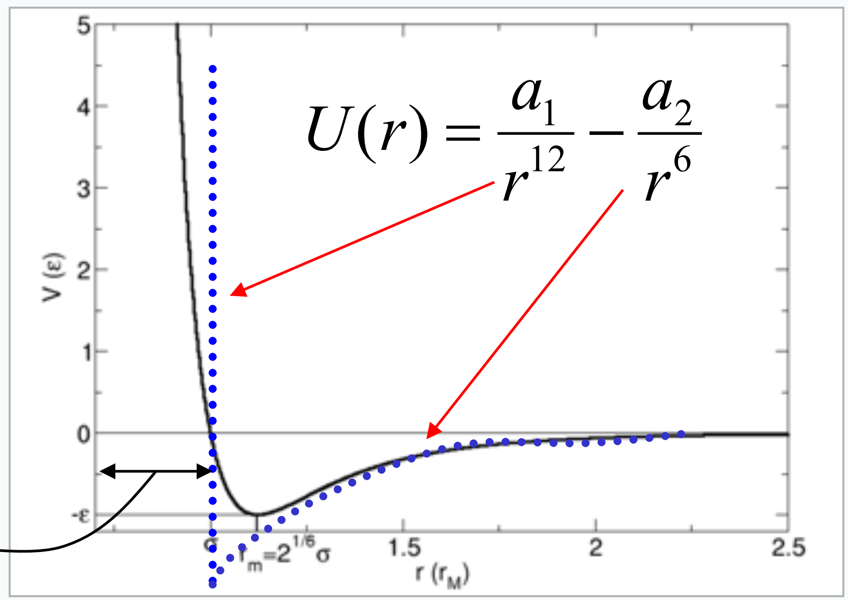
$$PV = \nu RT$$

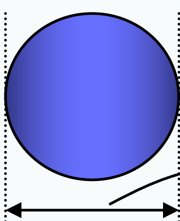
No chemically interacting (no covalent bonds)
Electrically neutral (no electrostatic interaction of ions)



- Repulsive force (Pauli's exclusion principle)
- Interaction between static dipoles (Keesom force)
- - static and induced dipole (induction, Debay force)
- - two induced dipole (London or dispersion forces)







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Hard-sphere model with attraction

Johannes van der Waals

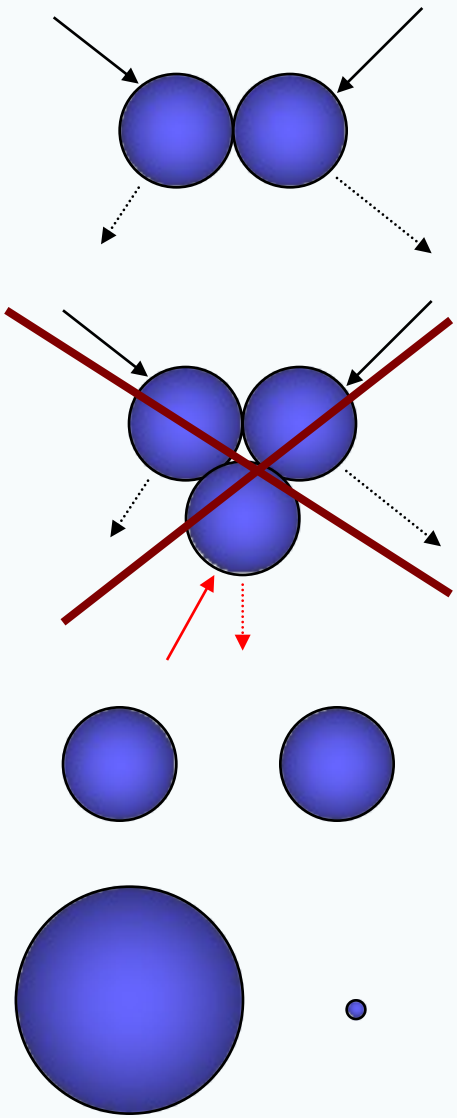
Born	23 November 1837 Leiden, Netherlands
Died	8 March 1923 (aged 85) Amsterdam, Netherlands

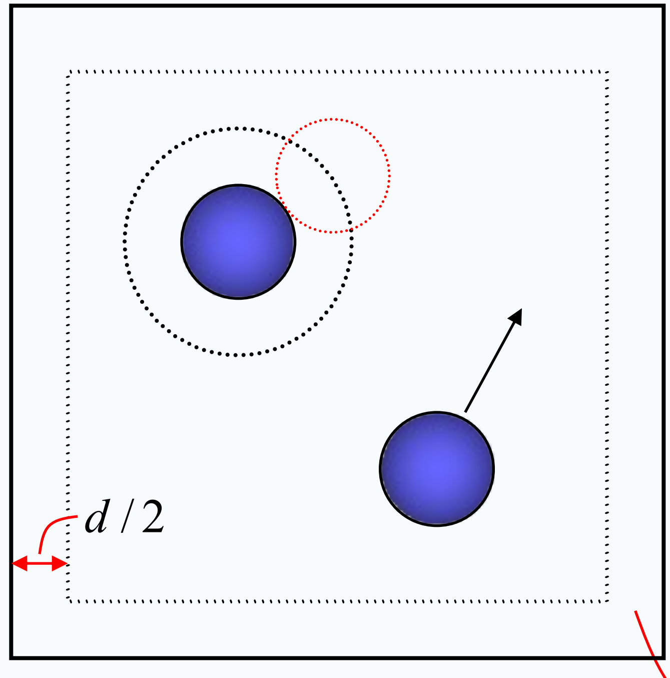
Nobel Prize for Physics (1910)

"for his work on the equation of state for gases and liquids"

Real gases: excluded volume effect

Only binary collisions





$$PV = \frac{2}{3}\left\langle E_{k,total}\right\rangle$$

$$N' = \frac{N}{2}$$

$$T' = 2T$$

$$P = n' k T'$$

?

$$P = \frac{N'}{V-b}kT' = \frac{NkT}{V-b}$$

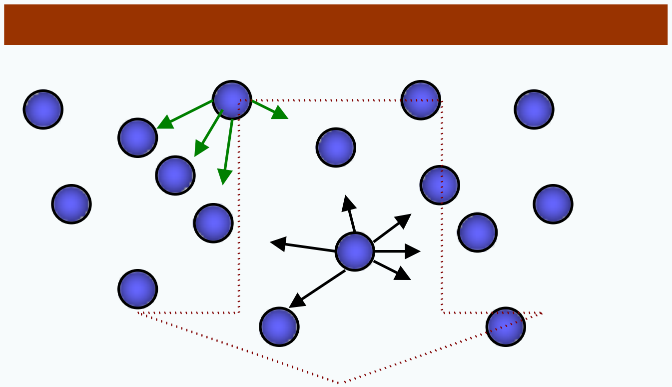
$$b = \frac{N}{2}\frac{4}{3}\pi d^3$$

$$A(d/2) << b$$

$$4\pi R^2 \tfrac{d}{2} << \tfrac{2}{3}\pi d^3 N$$

$$R << d\sqrt{N}$$

Real gases: role of attractive forces



$$P = nkT \quad \rightarrow \quad P + P_i = nkT$$

$$P_i = \frac{F}{S} \propto \frac{N \cdot f}{S} \propto \frac{C_1\rho \cdot C_2\rho}{S} \equiv \frac{a}{V^2}$$

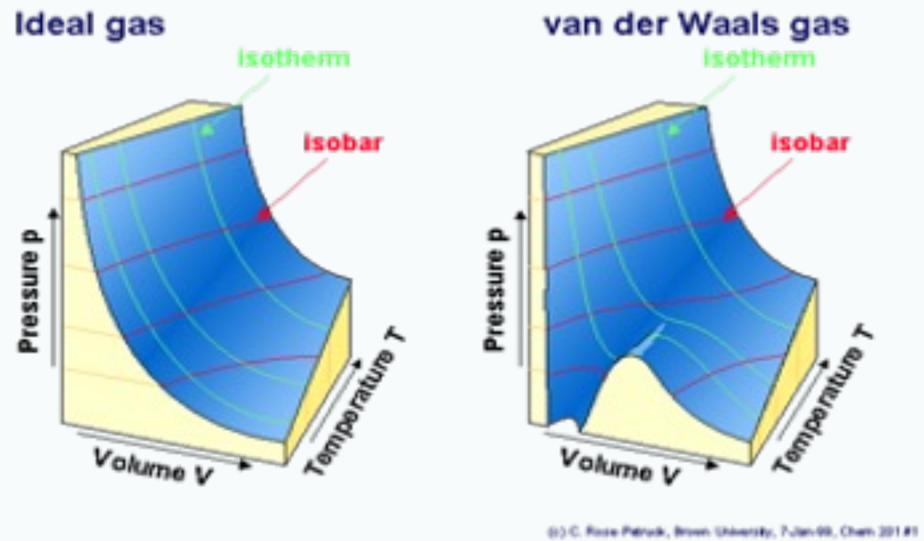
Van der Waals equation

$$PV = \nu RT$$

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

$$\left(P + \frac{a\nu^2}{V^2}\right)(V - \nu b) = \nu RT$$

Comparison of ideal and van der Waals gas



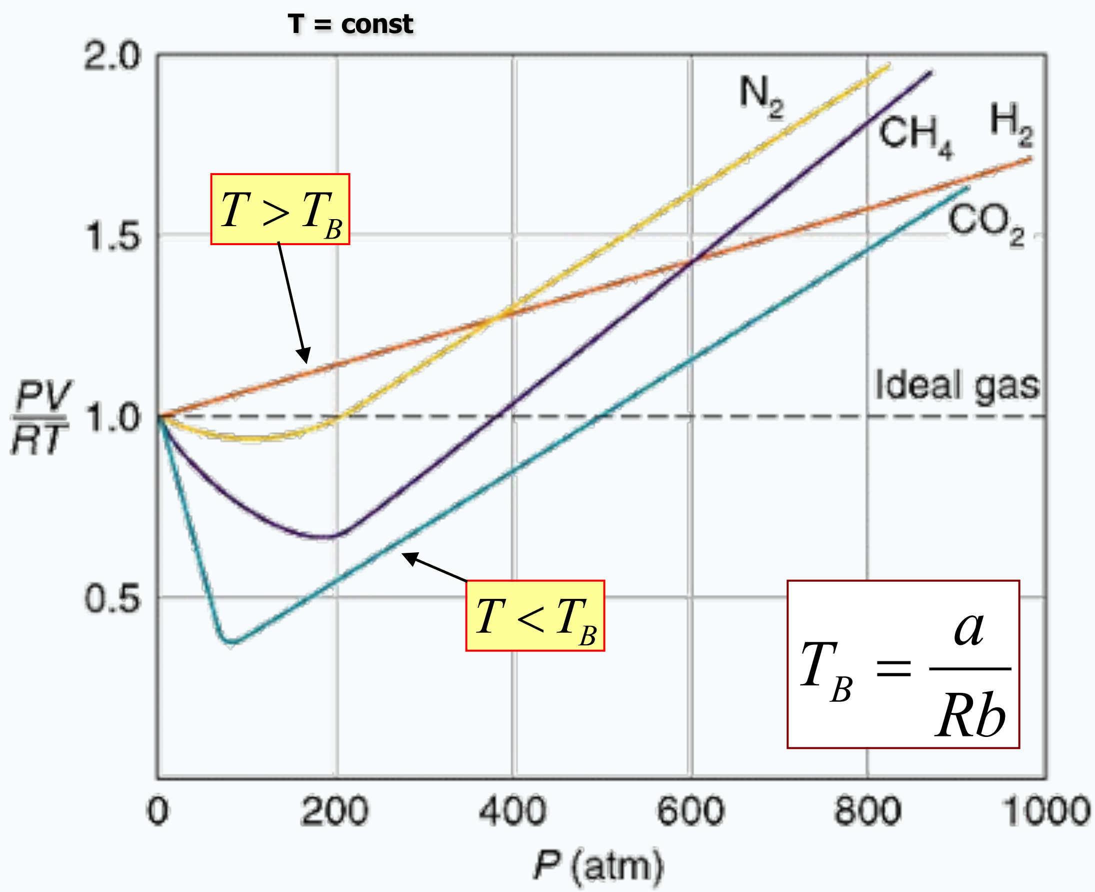
Real gases: PV versus density

$$\left(P + \frac{a\nu^2}{V^2}\right)(V - \nu b) = \nu RT$$

$$PV = \frac{MRT}{M - b\rho} - \frac{a}{M}\rho$$

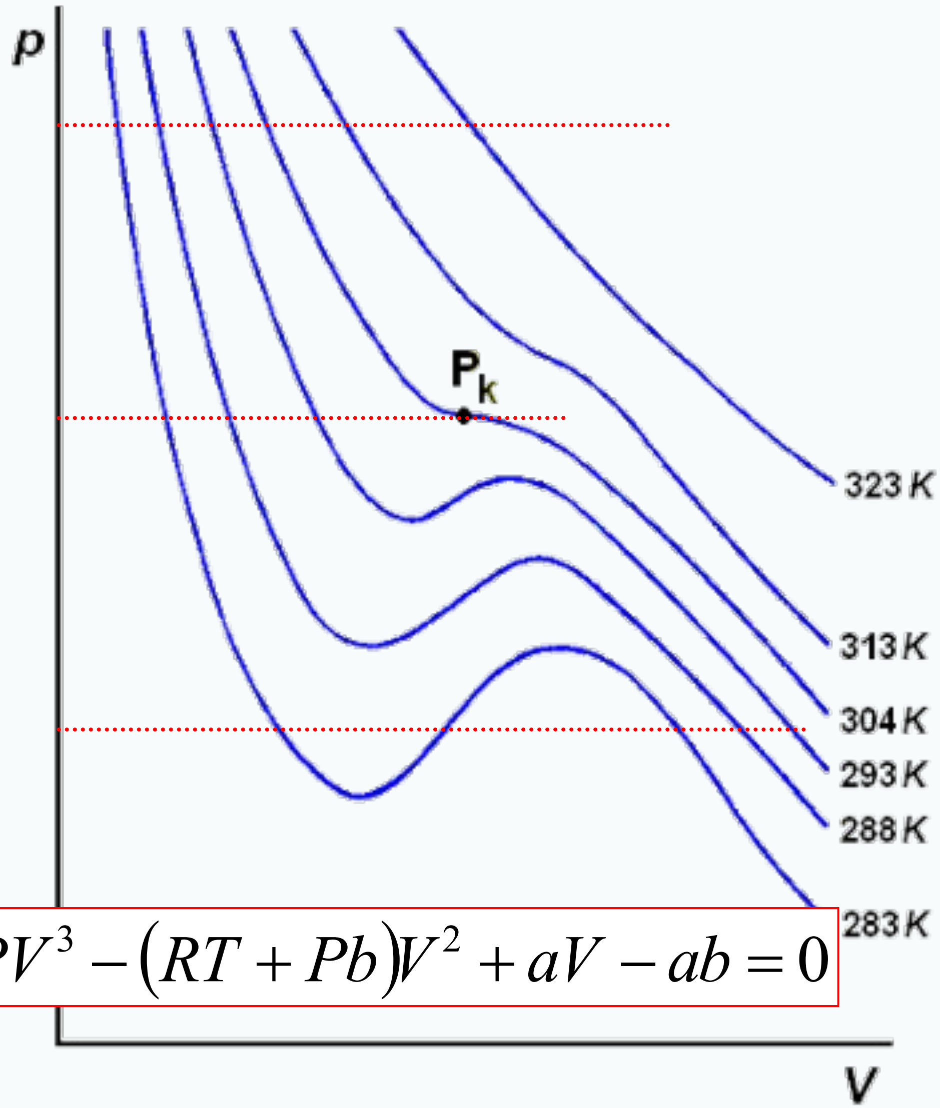
$$\frac{d(PV)}{d\rho} = 0$$

$$\rho_{\min} = \frac{M}{b}\left(1 - \sqrt{\frac{RTb}{a}}\right)$$

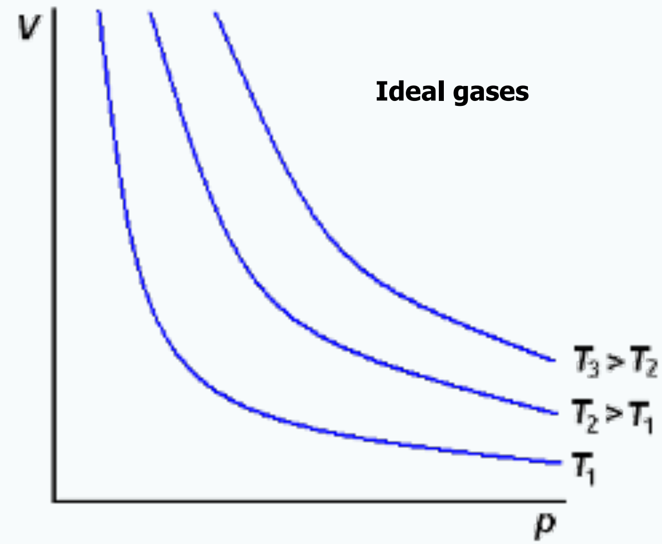


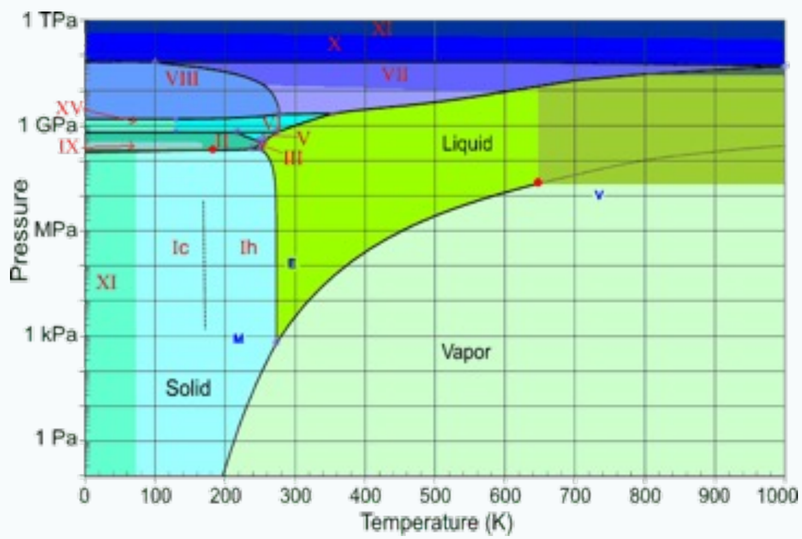
Gas	*a* (L²bar/mol²)	*b* (L/mol)
Hydrogen	0.2476	0.02661
Carbon dioxide	3.640	0.04267

Van der Waals isotherms



$$PV^3 - (RT + Pb)V^2 + aV - ab = 0$$





Critical parameters

$$P_c V^3 - (RT_c + P_c b)V^2 + aV - ab = 0$$

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

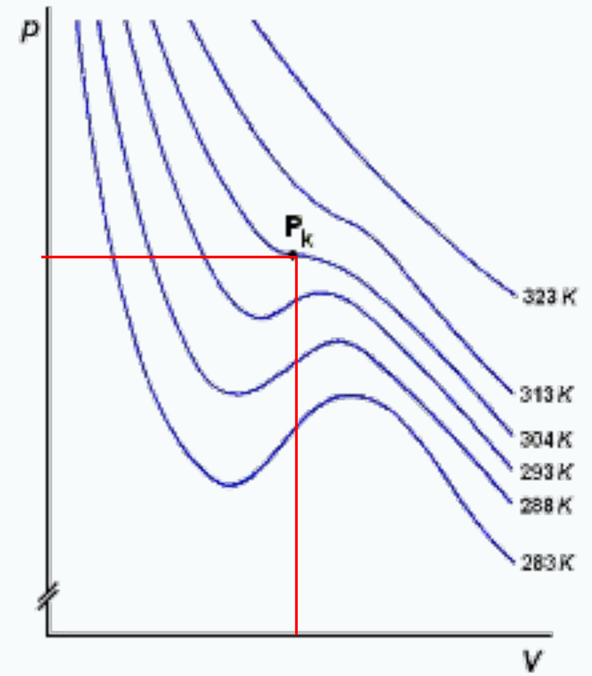
$$V_k = 3b \qquad P_k = \frac{a}{27b^2} \qquad T_k = \frac{8a}{27Rb}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

Reduced form of the Van der Waals equation

$$\upsilon = \frac{V}{V_k} \qquad p = \frac{P}{P_k} \qquad t = \frac{T}{T_k}$$

$$\left(p + \frac{3}{\upsilon^2}\right)\left(\upsilon - \frac{1}{3}\right) = \frac{8}{3}t$$

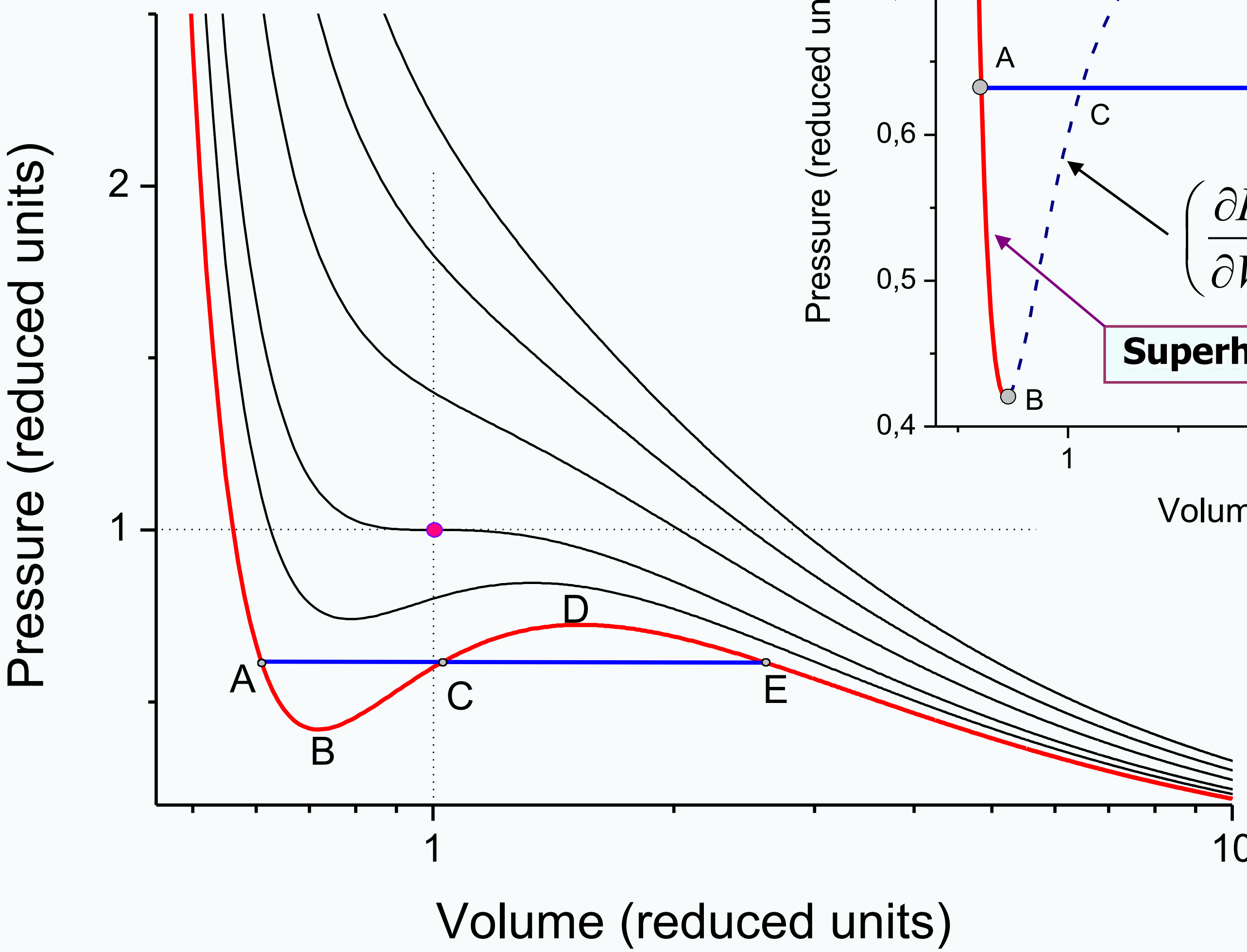


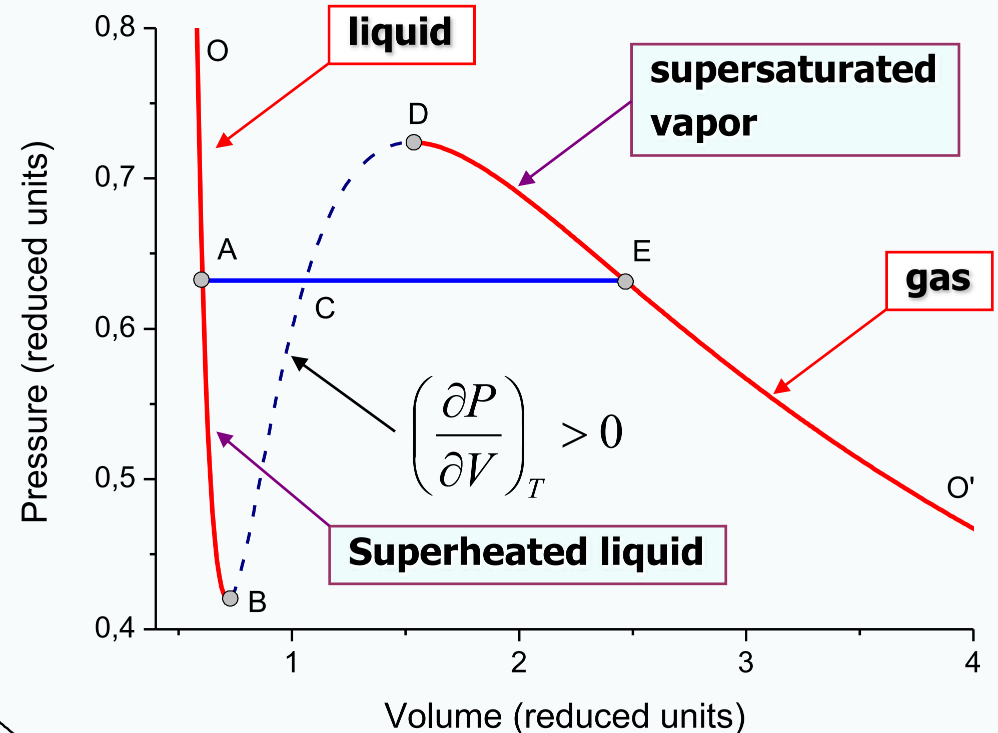
In the reduced form, the isotherms for all gases coincide.
- Theorem of corresponding states -

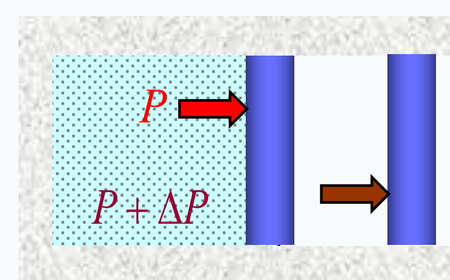
Phase transitions

$$\left(\frac{\partial P}{\partial V}\right)_T < 0$$

condition of thermodynamic stability



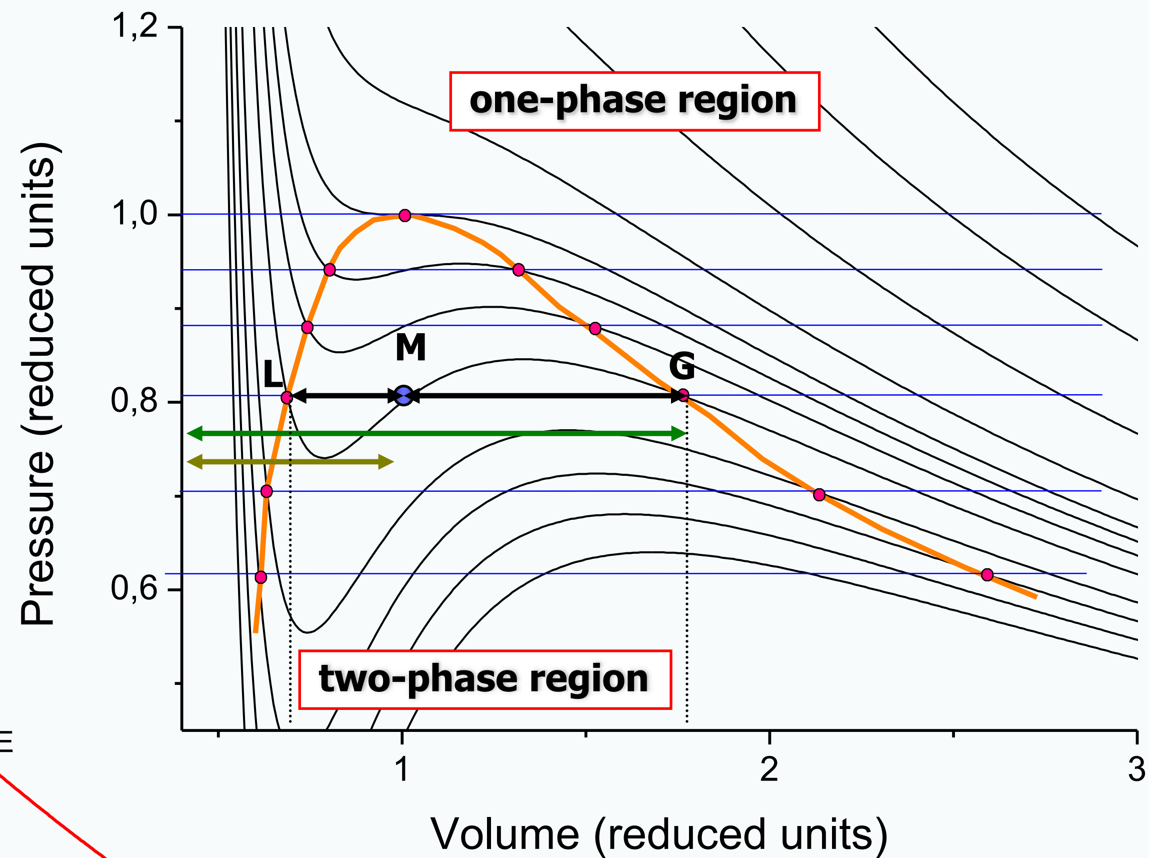


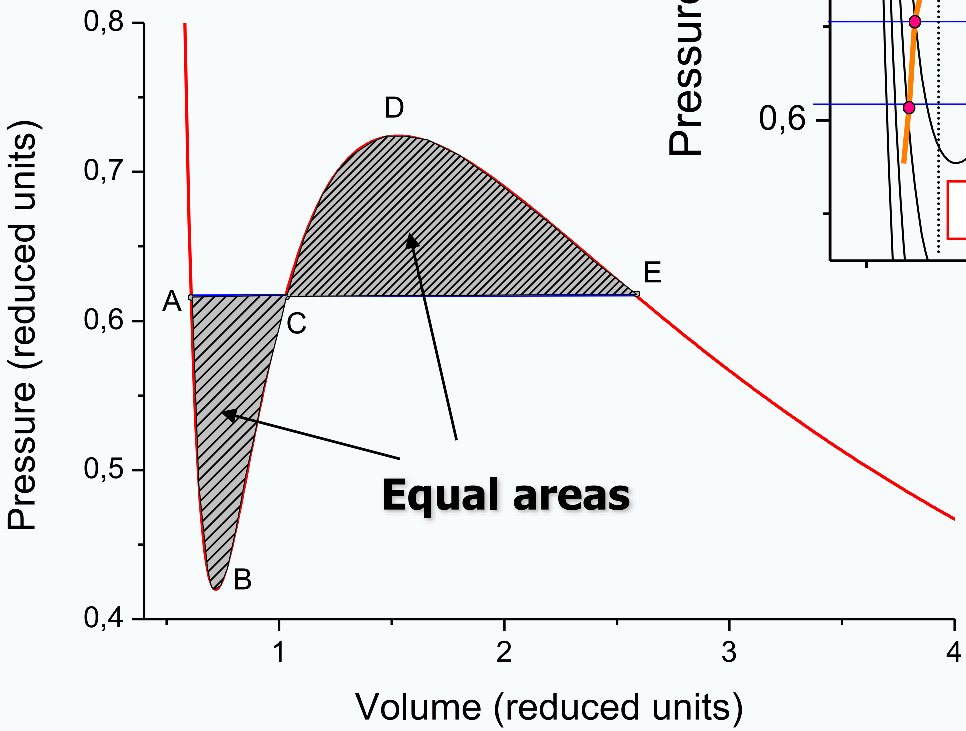


The Maxwell construction

$$\oint \frac{\delta Q}{T} = 0$$

$$\int_{ACE} PdV = \int_{ABCDE} PdV$$

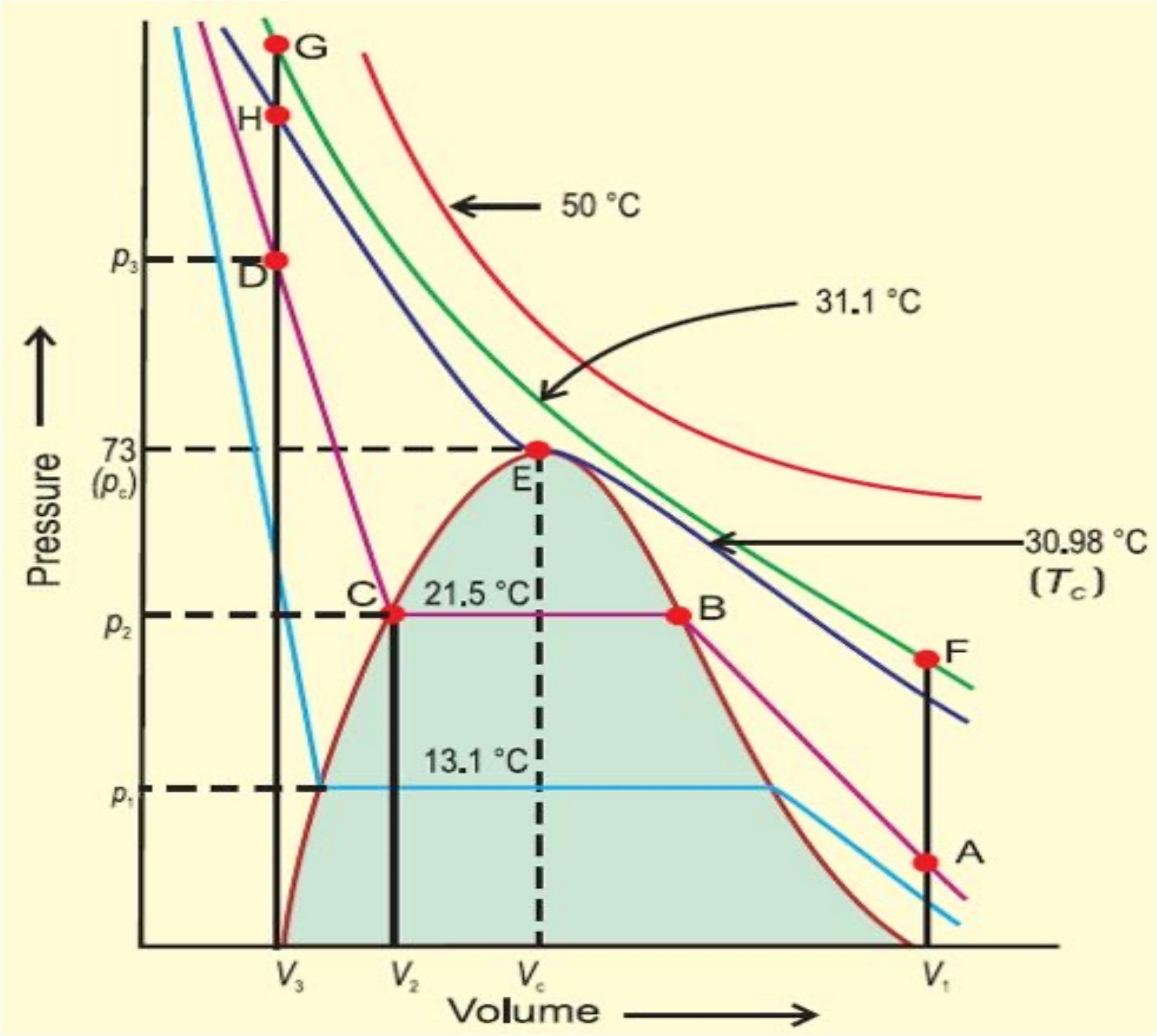




$$\frac{m_{gas}}{m_{liq}} = \frac{|ML|}{|MG|}$$

the level rule

CO_2



G
H
50 °C
p_3
D
31.1 °C
Pressure
73
(p_c)
E
30.98 °C
(T_c)
C
21.5 °C
B
p_2
F
13.1 °C
p_1
A
V_3
V_2
V_c
V_1
Volume

To remember!

- **Van der Waals forces do refer to all forces except covalent bonding and electrostatic interaction between ions.**

- **Van der Waals equation takes account of the excluded volume and of the van der Waals forces, improving thus the ideal gas law.**

- **This equation leads not only to quantitative improvement, but to qualitative ones.**

- **Van der Waals equation predicts gas-liquid phase transition and coexistence.**

- **In the reduced form, van der Waals equation is the same for all fluids.**