STATISTICAL MOLECULAR THERMODYNAMICS

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Video 2.2

Non-ideal Gas Equations of State

TEMPERATURE AND THE GAS CONSTANT

The Ideal Gas obeys: $PV = nRT$ or $\boxed{P\overline{V} = RT}, \; \overline{V} = \frac{V}{n}$

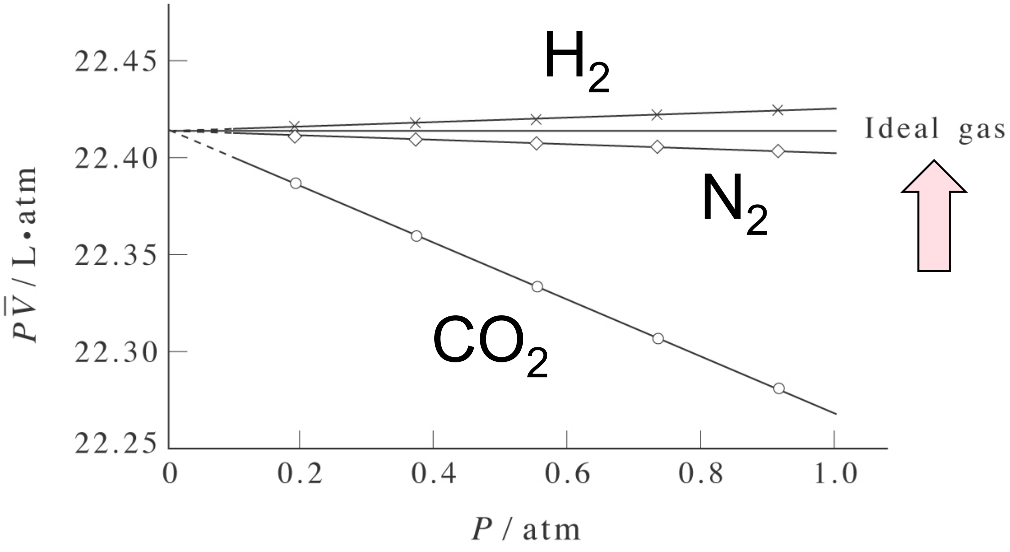
universal gas constant

molar volume

273.15 *K* measurements

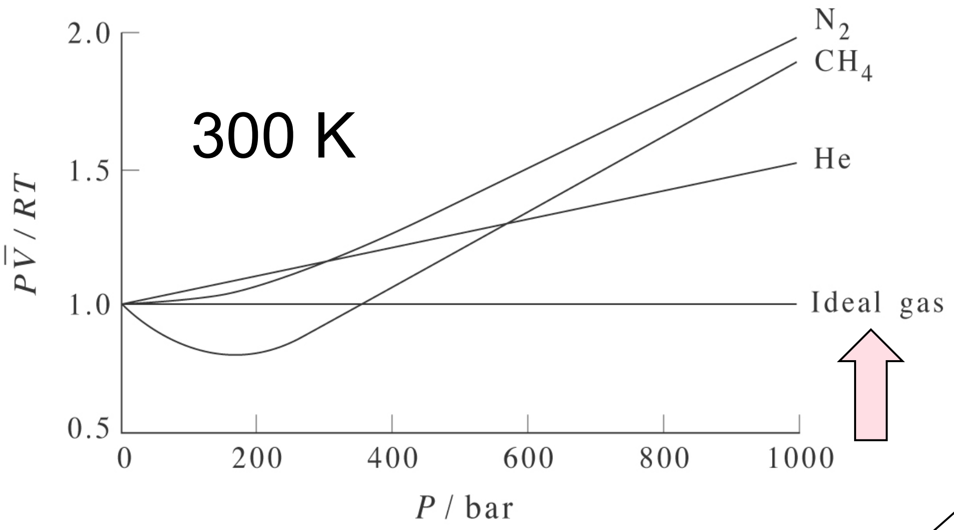
At low pressures, *all* gases converge to ideal behavior

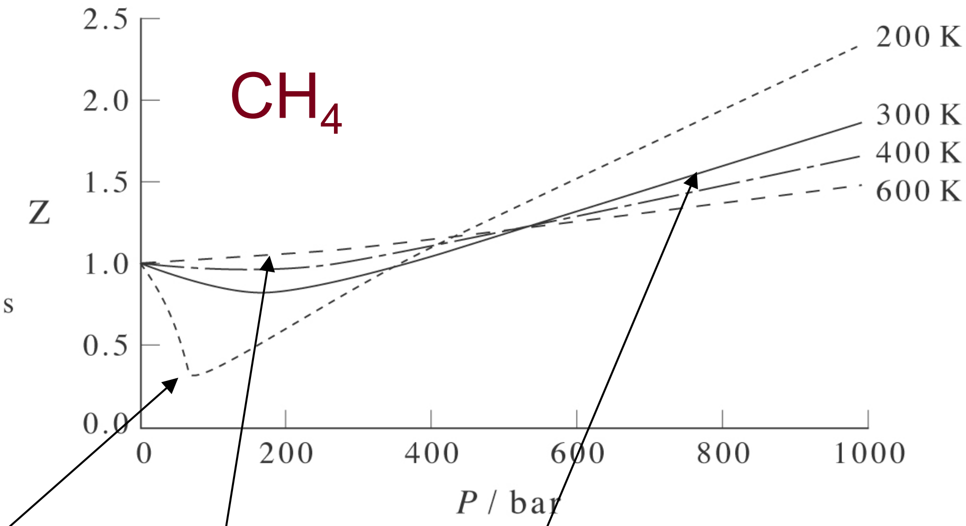
$$P\overline{V}(273.15) = 22.414 \text{ L} \bullet \text{atm} \bullet \text{mol}^{-1}$$



GASES ARE RARELY IDEAL

$$\frac{P\overline{V}}{RT} = Z$$ *compressibility* (unitless)





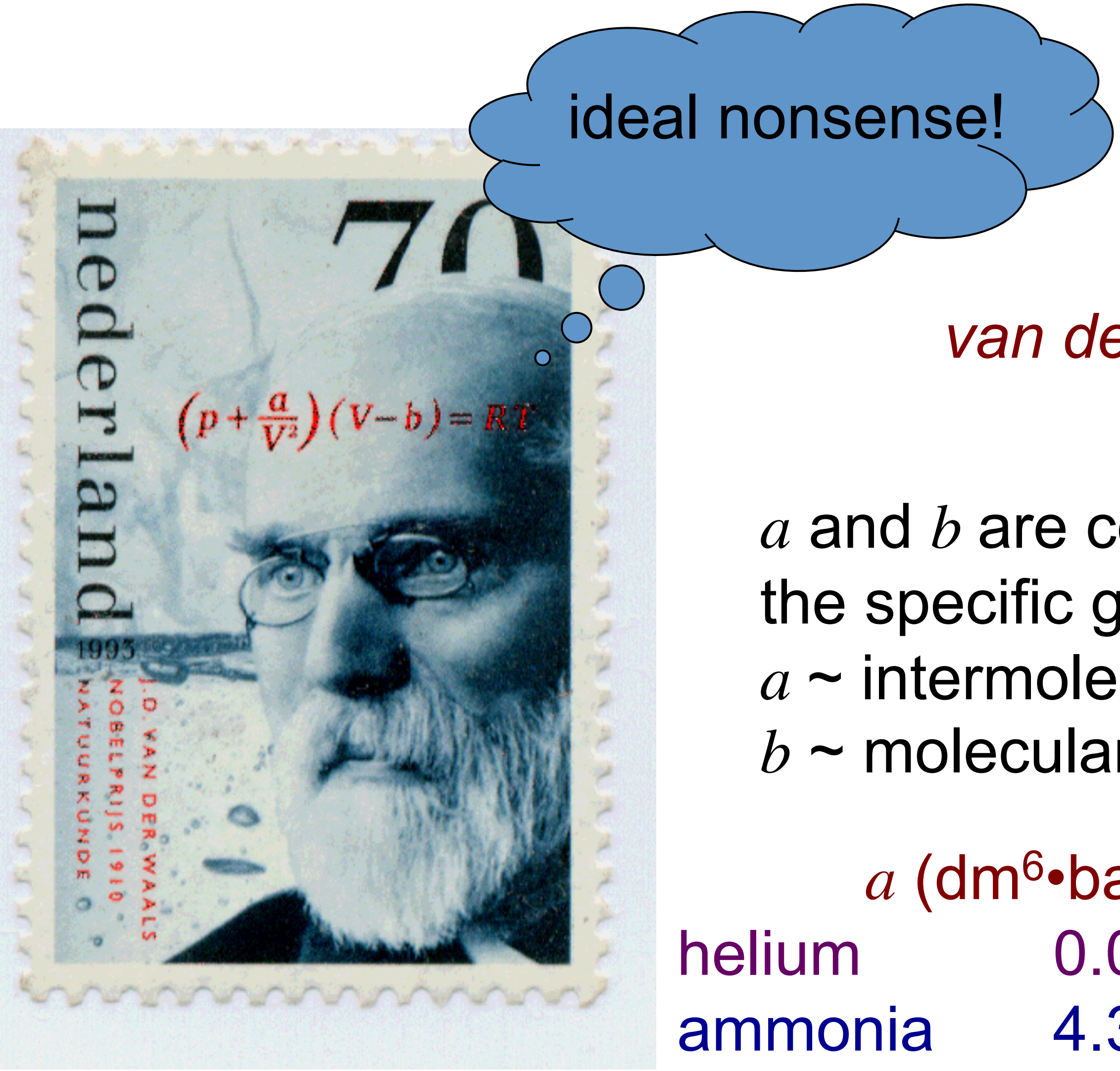
Low T and low P: attractive forces

$$\overline{V}_{\text{real}} < \overline{V}_{\text{ideal}}$$

High T or high P: repulsive forces

$$\overline{V}_{\text{real}} > \overline{V}_{\text{ideal}}$$

JOHANNES DIDERIK VAN DER WAALS



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

van der Waals equation of state

a and b are constants that depend on the specific gas in question:

a ~ intermolecular interaction strength

b ~ molecular size

	a ($\text{dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}$)	b ($\text{dm}^3\cdot\text{mol}^{-1}$)
helium	0.035	0.024
ammonia	4.304	0.037

Various Cubic Equations of State

van der Waals

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

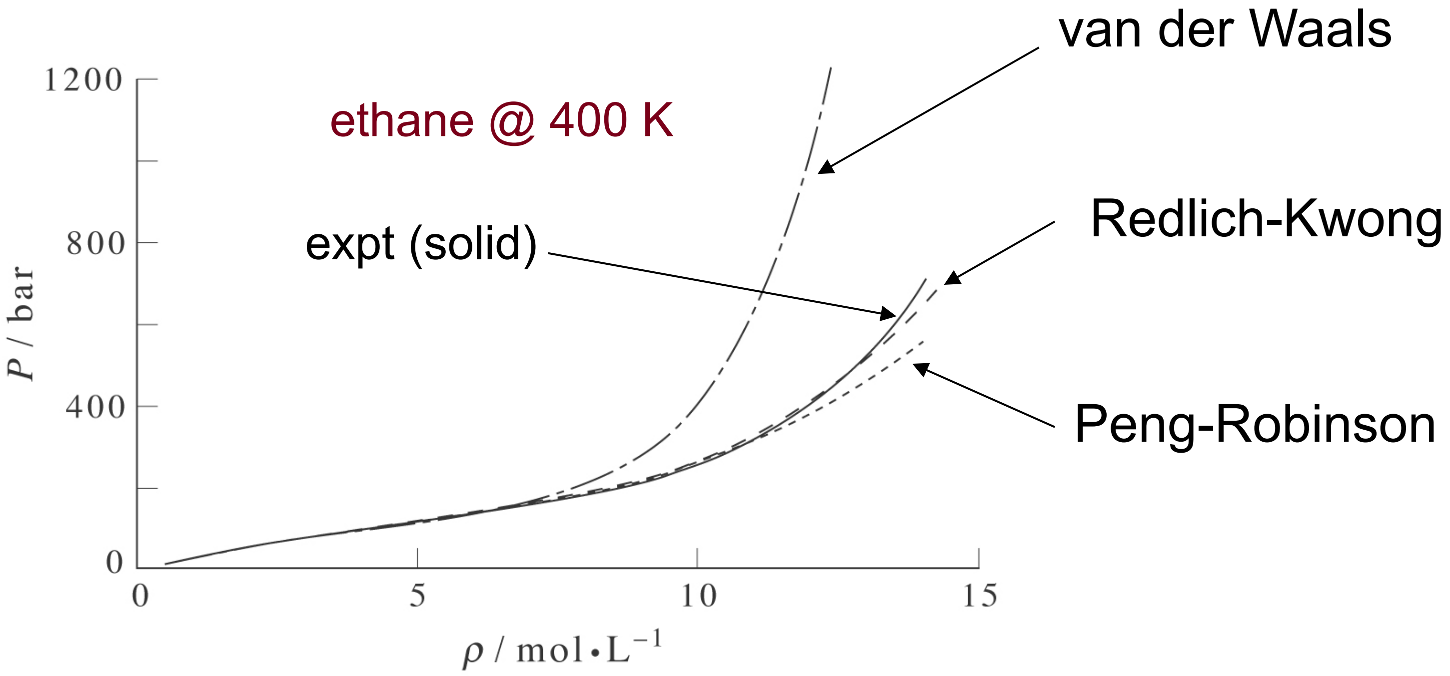
Redlich-Kwong

$$P = \left(\frac{RT}{\overline{V} - B}\right) - \left(\frac{A}{T^{1/2}\,\overline{V}\left(\overline{V} + B\right)}\right)$$

Peng-Robinson

$$P = \left(\frac{RT}{\overline{V} - \beta}\right) - \left(\frac{\alpha}{\overline{V}\left(\overline{V} + \beta\right) + \beta\left(\overline{V} - \beta\right)}\right)$$

VARIOUS CUBIC EQUATIONS OF STATE

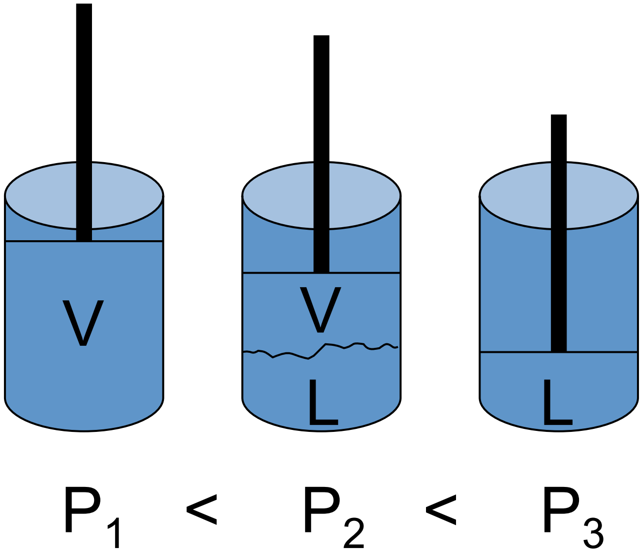


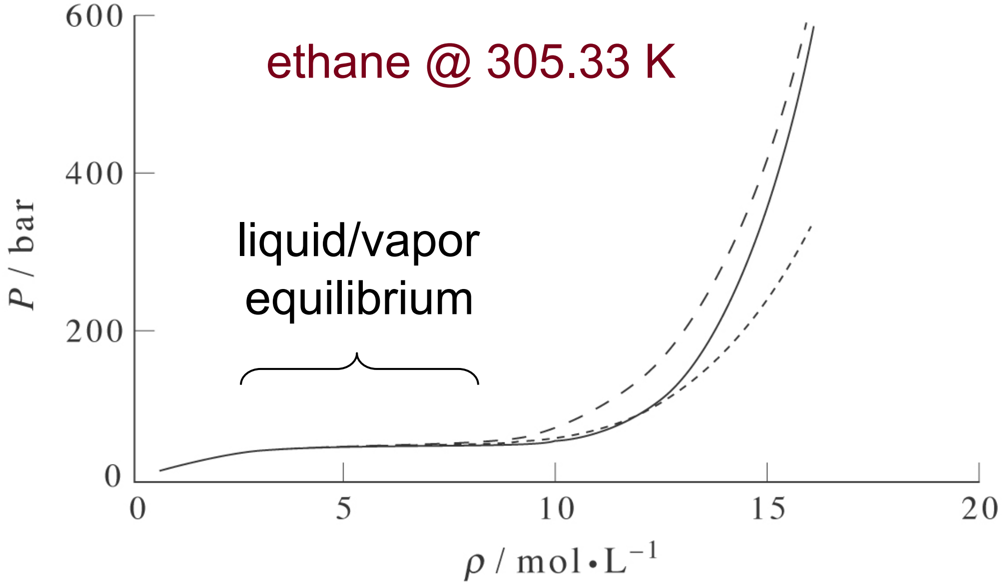
Improved performance of the more complex equations of state at very high pressures

$$\overline{V}^{-1} = \rho \quad \left(\mathrm{mol} \bullet \mathrm{L}^{-1}\right)$$

$$1\ \mathrm{L} = 1\ \mathrm{dm}^3$$

VARIOUS CUBIC EQUATIONS OF STATE





While Redlich-Kwong and Peng-Robinson perform reasonably well into the liquid phase, at a certain point the van der Waals equation of state predicts negative pressures!

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

$$\underset{\lim \rho \to \infty}{=} RT\rho - a\rho^2$$