Equation of state

Raj Pala,
rpala@iitk.ac.in
Department of Chemical Engineering,
Associate faculty of the Materials Science Programme,
Indian Institute of Technology, Kanpur.

What is not an equation of state?

Table 18-1 Classical Physics

Maxwell's equations

I. $\nabla \cdot E = \frac{\rho}{\epsilon_0}$ (Flux of E through a closed surface) = (Charge inside)/ϵ_0

II. $\nabla \times E = -\frac{\partial B}{\partial t}$ (Line integral of E around a loop) = $-\frac{d}{dt}$ (Flux of B through the loop)

III. $\nabla \cdot B = 0$ (Flux of B through a closed surface) = 0

IV. $c^2 \nabla \times B = \frac{j}{\epsilon_0} + \frac{\partial E}{\partial t}$ c^2(Integral of B around a loop) = (Current through the loop)/ϵ_0 + $\frac{\partial}{\partial t}$ (Flux of E through the loop)

[Conservation of charge $\nabla \cdot j = -\frac{\partial \rho}{\partial t}$ (Flux of current through a closed surface) = $-\frac{\partial}{\partial t}$ (Charge inside)]

Force law

$F = q(E + v \times B)$

Law of motion

$\frac{d}{dt}(p) = F$, where $p = \frac{mv}{\sqrt{1 - v^2/c^2}}$ (Newton's law, with Einstein's modification)

Gravitation

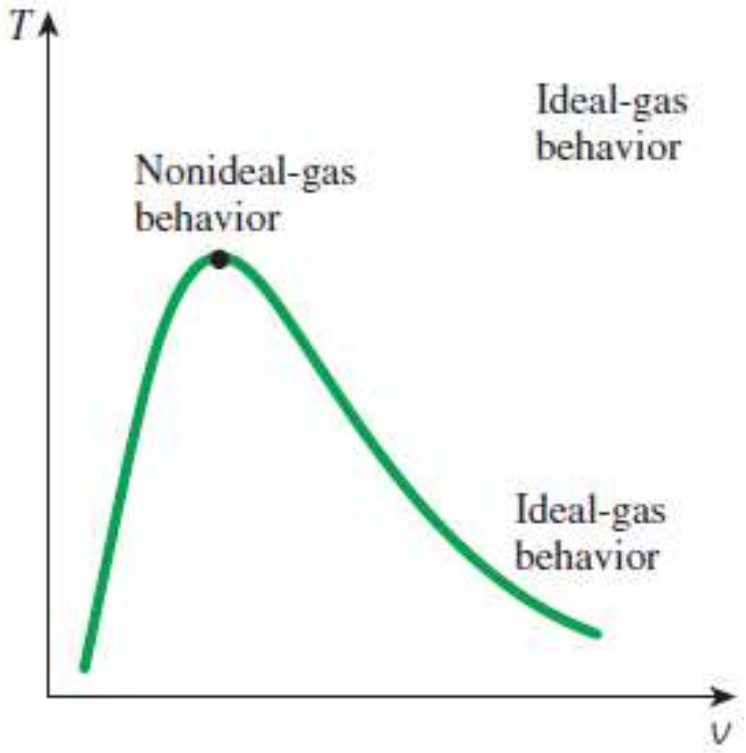
$F = -G\frac{m_1 m_2}{r^2} e_r$

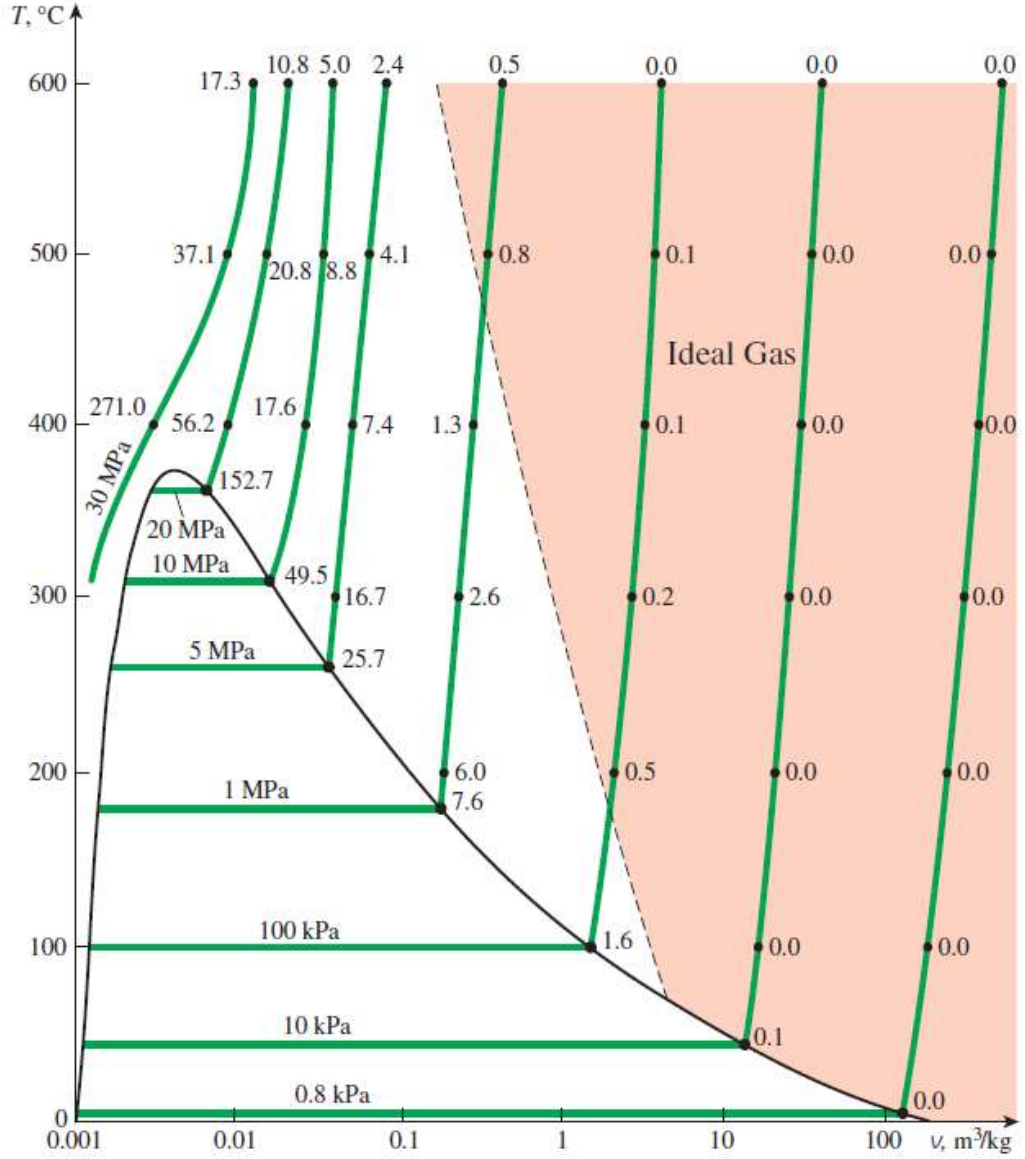
- Why care?
- ...Filling your cooking gas cylinder
- Can the Table of P, T & v be replaced by equation?

Fig: https://www.shutterstock.com/; Wiki

Ideal "gas" behavior & …

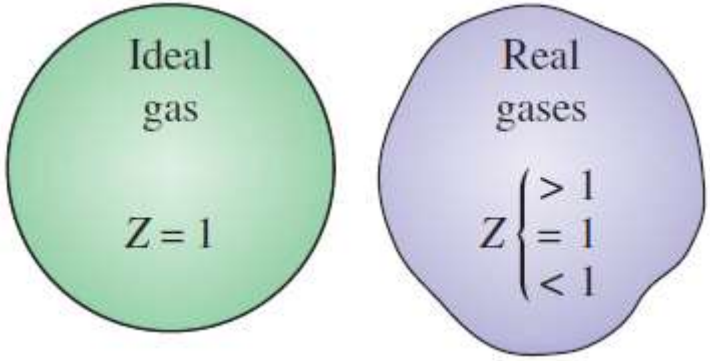
- PV=nRT
- Operational P & T
- Higher T, lesser relative interaction energy





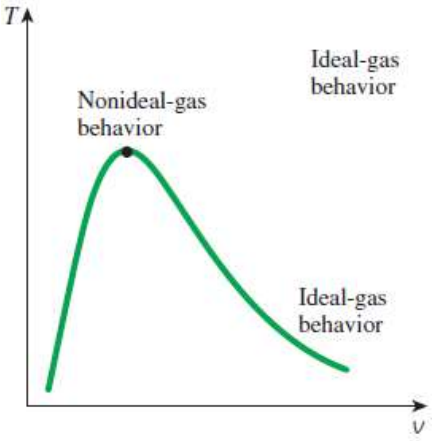
Figs: Cengel & Boles, TD

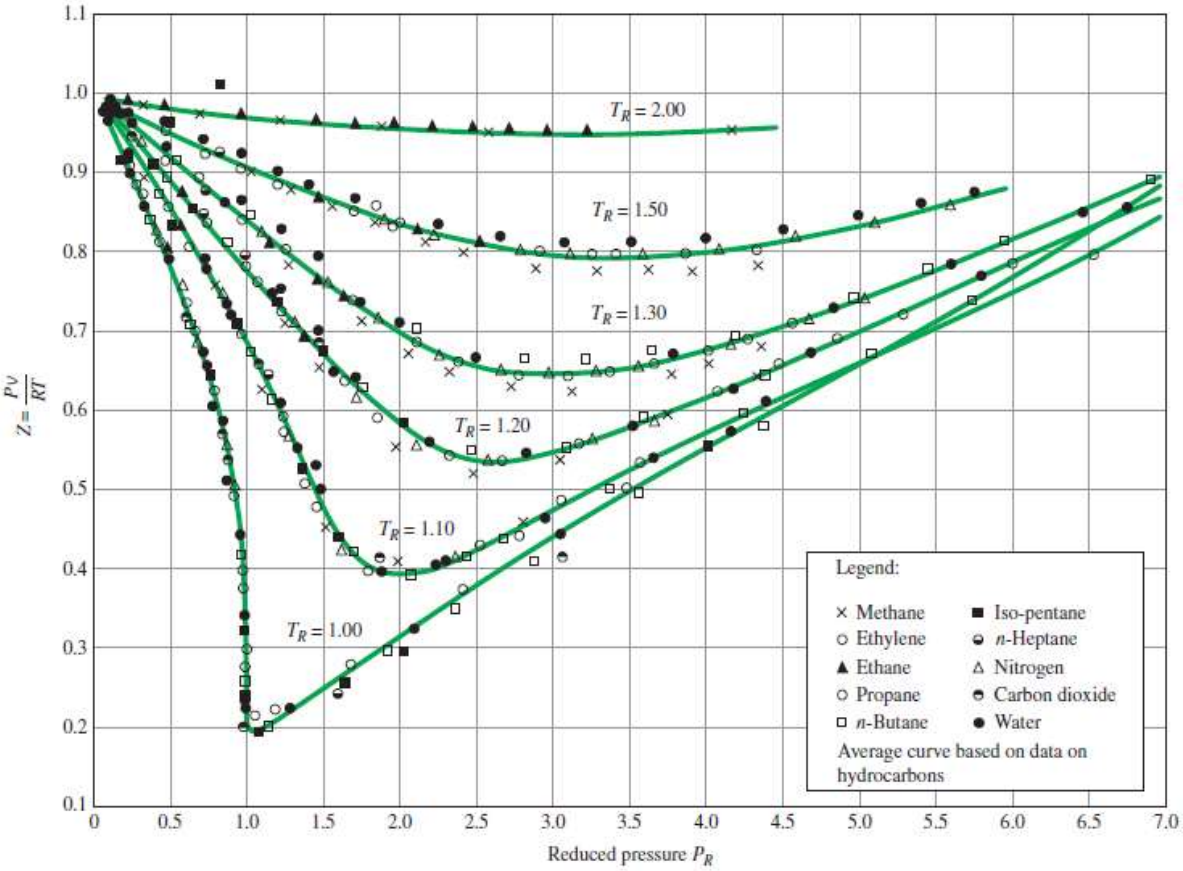
Non-Ideality & Compressibility factor



$$P\nu = ZRT$$

$$Z = \frac{P\nu}{RT} \qquad Z = \frac{\nu_{actual}}{\nu_{ideal}}$$





$$P_R = \frac{P}{P_{cr}} \qquad T_R = \frac{T}{T_{cr}}$$

Reduced pressure

Reduced temperature

$$\nu_R = \frac{\nu_{actual}}{RT_{cr}/P_{cr}}$$

Pseudo-reduced specific volume

Fig: Cengel & Boles

Van der waals EOS

- "Finite size" of gases
- Interactions: Electrodynamical & excluded volume
- Constraints on EOS: Inflection at critical point
- Noble Prize for Physics-1910

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

$$a = \frac{27R^2T_{cr}^2}{64P_{cr}} \quad b = \frac{RT_{cr}}{8P_{cr}}$$

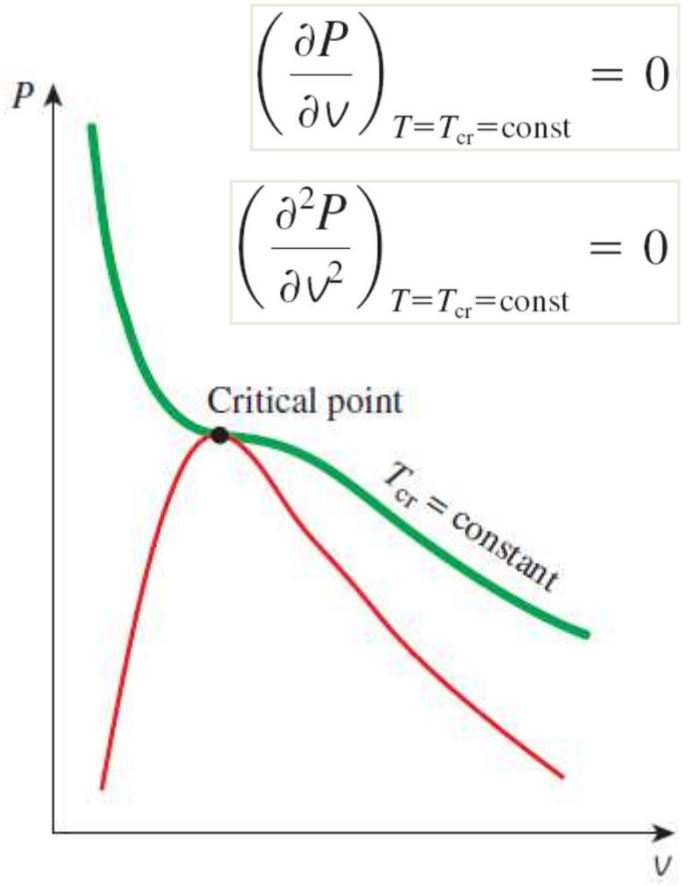


Fig: Cengel & Boles

Who is the second man on Moon?-All other EOS!

van der Waals: 2 constants.
Accurate over a limited range.

Beattie-Bridgeman: 5 constants.
Accurate for $\rho \leq 0.8\rho_{cr.}$

Benedict-Webb-Rubin: 8 constants.
Accurate for $\rho \leq 2.5\rho_{cr.}$

Strobridge: 16 constants.
More suitable for
computer calculations.

Virial: may vary.
Accuracy depends on the
number of terms used.

$$P = \frac{RT}{v} + \frac{a(T)}{v^2} + \frac{b(T)}{v^3} + \frac{c(T)}{v^4} + \frac{d(T)}{v^5} + \dots$$

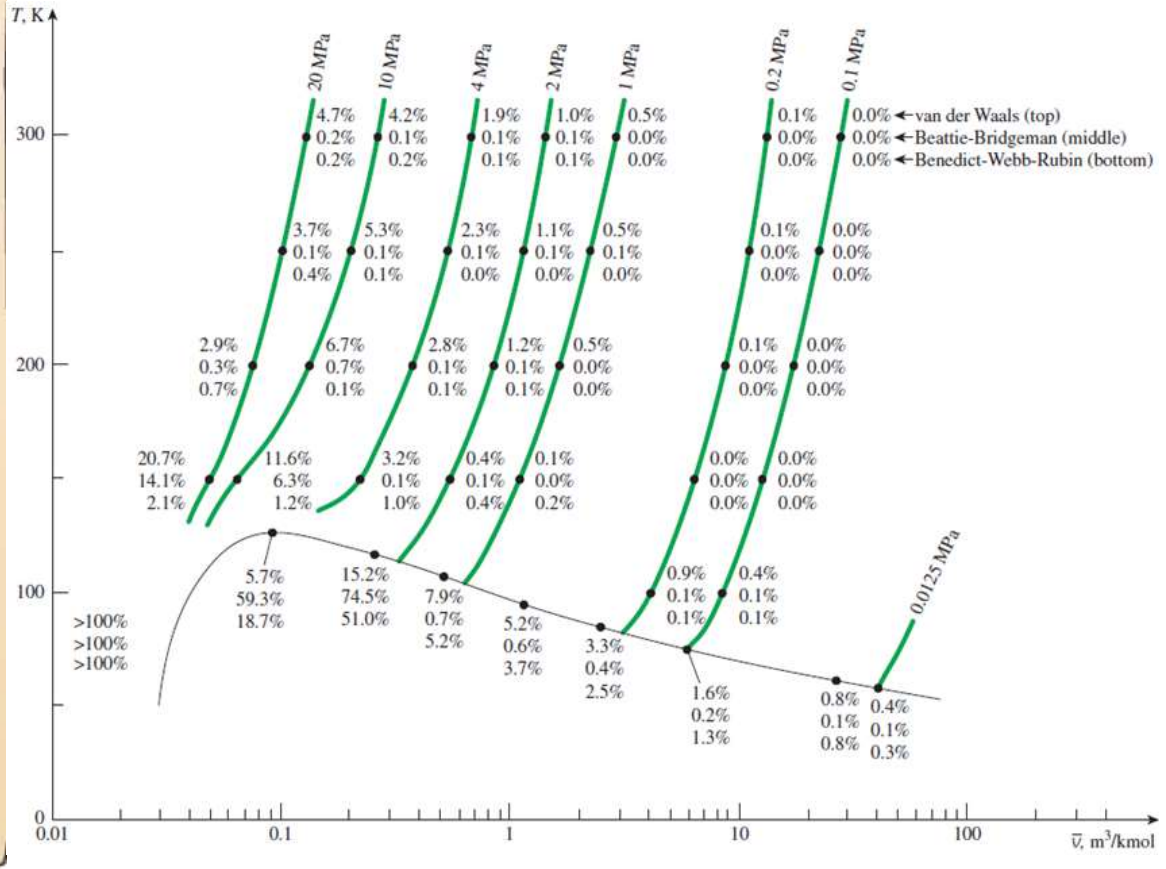


Fig: Cengel & Boles

- a(T), b(T)...Virial Coefficients
- Statistical Thermodynamics/Mechanics: Maria Goeppert Mayer-2nd woman to win Physics Noble Prize (for Nuclear Shell Model)