

The Ideal-gas & Equations of State

- **Equation of state:** Any equation that relates the pressure, temperature, and specific volume of a substance.
- The simplest and best-known equation of state for substances in the gas phase is the ideal-gas equation of state. This equation predicts the P - v - T behavior of a gas quite accurately within some properly selected region.
- At low pressures the volume of a gas is proportional to its temperature.

$$P = R \left(\frac{T}{v} \right)$$

$Pv = RT$ Ideal gas equation of state

$$R = \frac{R_u}{M} \quad (\text{kJ/kg} \cdot \text{K} \text{ or } \text{kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})$$

$$R_u = \begin{cases} 8.31447 \text{ J/mol} \cdot \text{K} \\ 8.31447 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\ 0.0831447 \text{ bar} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\ 1.98588 \text{ Btu/lbmol} \cdot \text{R} \\ 10.7316 \text{ psia} \cdot \text{ft}^3/\text{lbmol} \cdot \text{R} \\ 1545.37 \text{ ft} \cdot \text{lbf/lbmol} \cdot \text{R} \end{cases}$$

Substance	R , kJ/kg·K
Air	0.2870
Helium	2.0769
Argon	0.2081
Nitrogen	0.2968

R : gas constant

M : molar mass (kg/kmol)

R_u : universal gas constant

- *Gas* and *vapor* are often used as synonymous words.
- The vapor phase of a substance is customarily called a *gas* when it is above the critical temperature.
- *Vapor* usually implies a gas that is not far from a state of condensation.
- An **ideal gas** is an *imaginary* substance that obeys the relation

$$Pv = RT$$

In the range of practical interest, many familiar gases such as [air](#), [nitrogen](#), [oxygen](#), [hydrogen](#), helium, Argon, neon, krypton, and even heavier gases such as [carbon dioxide](#) can be treated as ideal gases with negligible error (often less than 1 %).

Mass = Molar mass $\times$ Mole
 number
 $m = MN$ (kg)

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{Ideal gas equation at two states for a fixed mass}$$

Per unit mass	Per unit mole
$v, \text{ m}^3/\text{kg}$	$\bar{v}, \text{ m}^3/\text{kmol}$
$u, \text{ kJ/kg}$	$\bar{u}, \text{ kJ/kmol}$
$h, \text{ kJ/kg}$	$\bar{h}, \text{ kJ/kmol}$

Various
 expressions of
 ideal gas equation
 $Pv = RT$

$$V = m v \longrightarrow P V = m R T$$

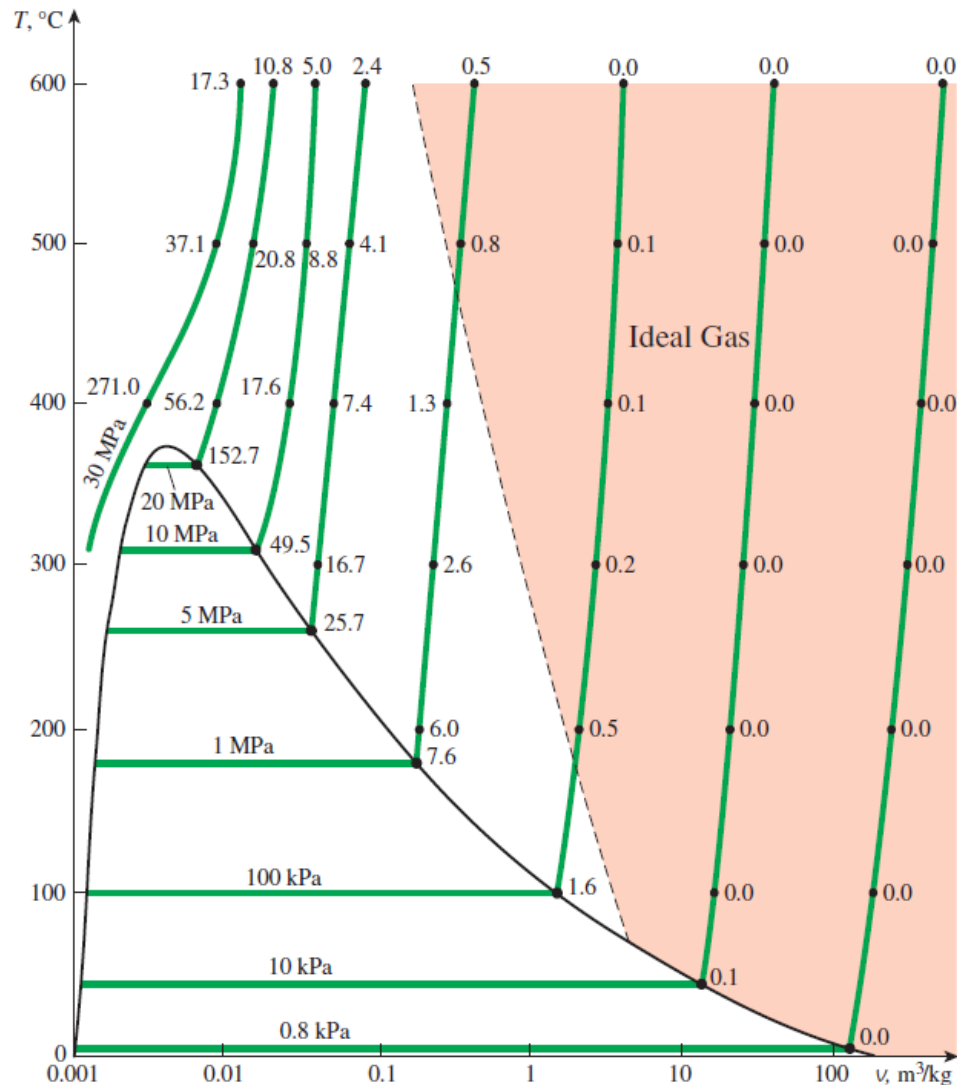
$$m R = (M N) R = N R_u \longrightarrow P V = N R_u T$$

$$V = N \bar{v} \longrightarrow P \bar{v} = R_u T$$

Properties per unit mole are denoted with a bar on the top.

Real gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).

Is Water Vapor an Ideal Gas?



- At pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent).

- At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line.

- Figure on the left shows the percentage of error involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas.**

Percentage of error

$$\left(\frac{|v_{\text{table}} - v_{\text{ideal}}|}{v_{\text{table}}} \times 100 \right)$$

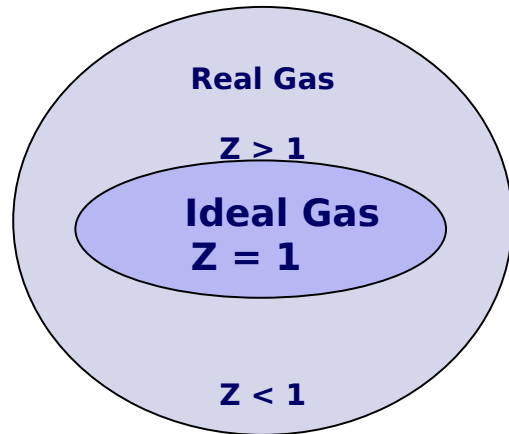
 involved in assuming steam to be an
 ideal gas, and the region where steam
 can be treated as an ideal gas with less
 than 1 percent error.

Compressibility Factor—a Measure Of Deviation From Ideal-gas Behavior

Compressibility

factor Z A factor that accounts for the deviation of real gases from ideal-gas behavior at P, V, T temperature and

$$Z = \frac{PV}{RT} \quad Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}$$



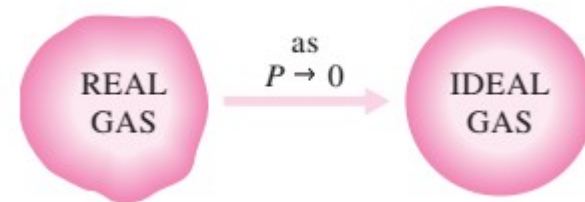
The compressibility factor is unity for ideal gases.

The farther away Z is from unity, the more the gas deviates from ideal-gas behavior.

Gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).

Question: What is the criteria for low pressure and high temperature?

Answer: The pressure or temperature of a gas is high or low relative to its critical temperature or pressure.



At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).

$$P_R = \frac{P}{P_{cr}}$$

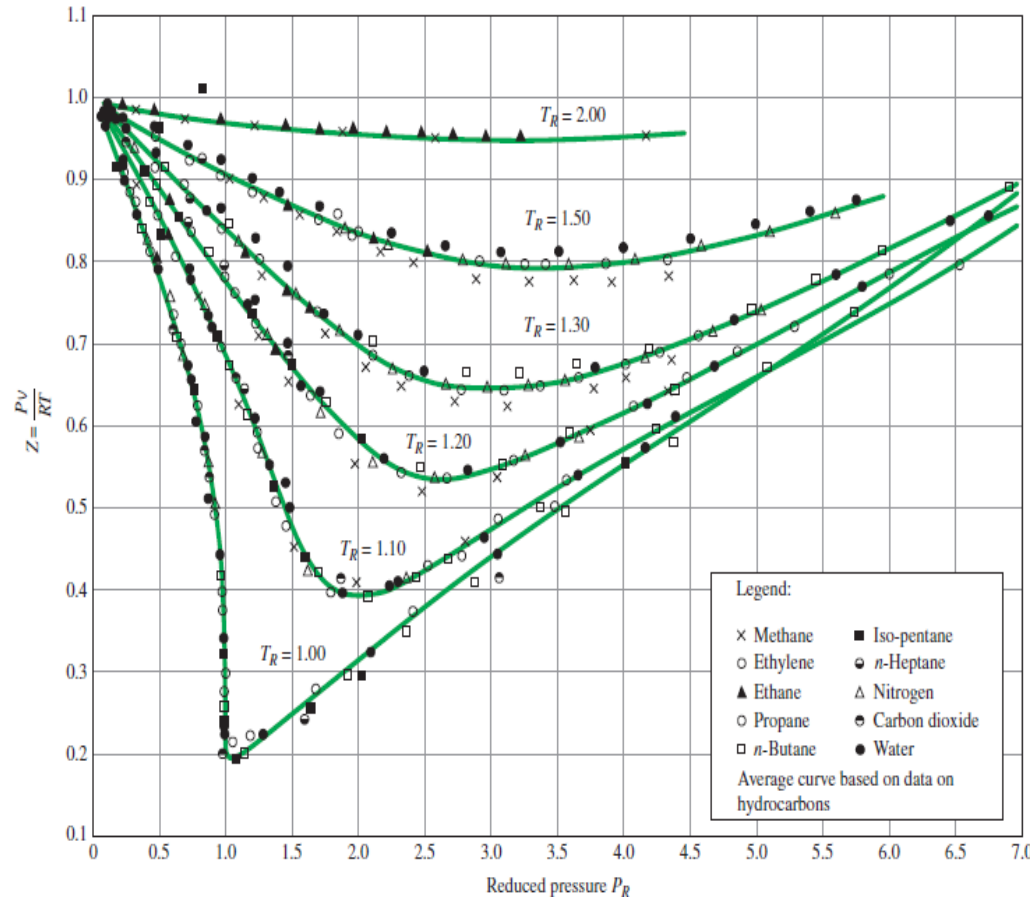
Reduced
pressure

$$T_R = \frac{T}{T_{cr}}$$

Reduced
temperatu
re

$$v_R = \frac{v_{actual}}{RT_{cr}/P_{cr}}$$

Pseudo-
reduced
specific
volume



It can be noticed that at many states the compressibility factor Z is approximately **unity**

1. At very low pressure ($P_R \ll 1$),
2. At high temperatures ($T_R > 2$) except when P_R

$\gg 1$. The Z factor is the same for all gases at the same reduced pressure and temperature.

This is called the **principle of corresponding states**.

Comparison of Z factors for various gases.

Pseudo reduced specific volume

When P and v or T and v are given,
generalized chart can still be used

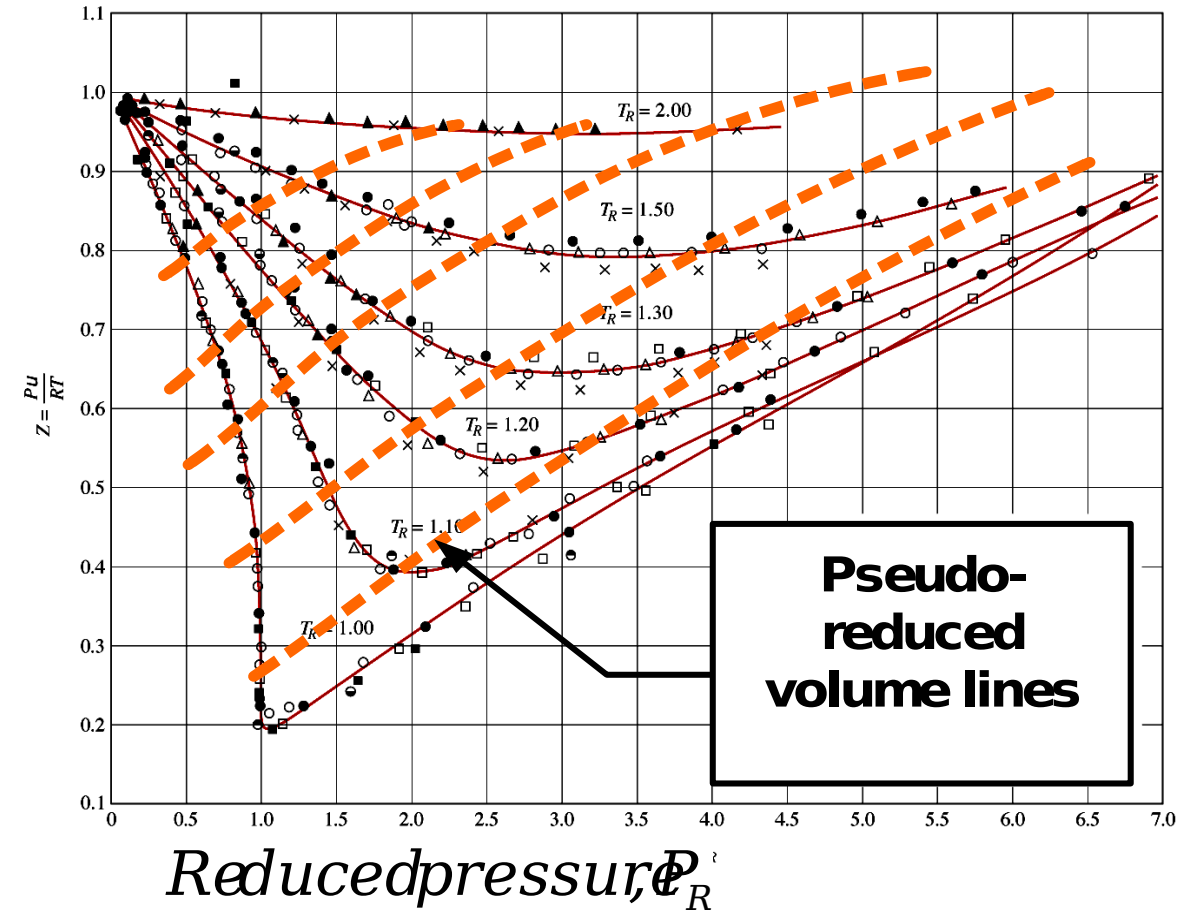
2- T_R and v_R

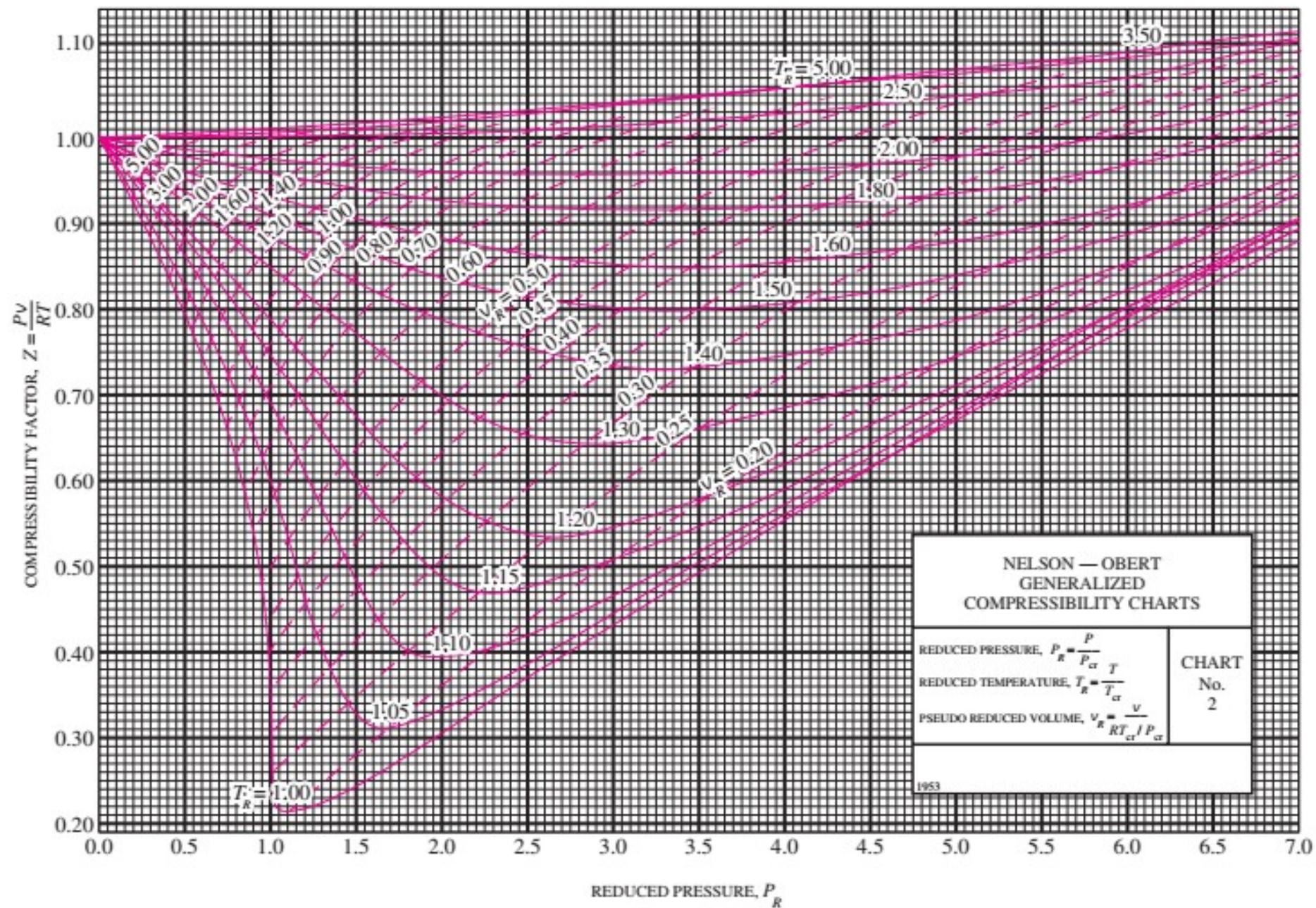
3- P_R and v_R

$$Z \equiv \frac{Pv}{RT}$$

v_R is pseudo reduced
specific volume defined
as:

$$v_R = \frac{v_{actual}}{RT_{cr}/P_{cr}}$$





Other equations of state

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

where

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

Beattie-Bridgeman:
$$P = \frac{R_u T}{\bar{v}^2} \left(1 - \frac{c}{\bar{v} T^3}\right) (\bar{v} + B) - \frac{A}{\bar{v}^2}$$

where

$$A = A_0 \left(1 - \frac{a}{\bar{v}}\right) \quad \text{and} \quad B = B_0 \left(1 - \frac{b}{\bar{v}}\right)$$

Benedict-Webb-Rubin:

$$P = \frac{R_u T}{\bar{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2}\right) \frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a \alpha}{\bar{v}^6} \\ + \frac{c}{\bar{v}^3 T^2} \left(1 + \frac{\gamma}{\bar{v}^2}\right) e^{-\gamma/\bar{v}^2}$$

where R_u is the universal gas constant and $\bar{v}$ is the molar specific volume.

Constants that appear in the Beattie-Bridgeman and the Benedict-Webb-Rubin equations of state

(a) When P is in kPa, $\bar{v}$ is in m^3/kmol , T is in K, and $R_u = 8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K}$, the five constants in the Beattie-Bridgeman equation are as follows:

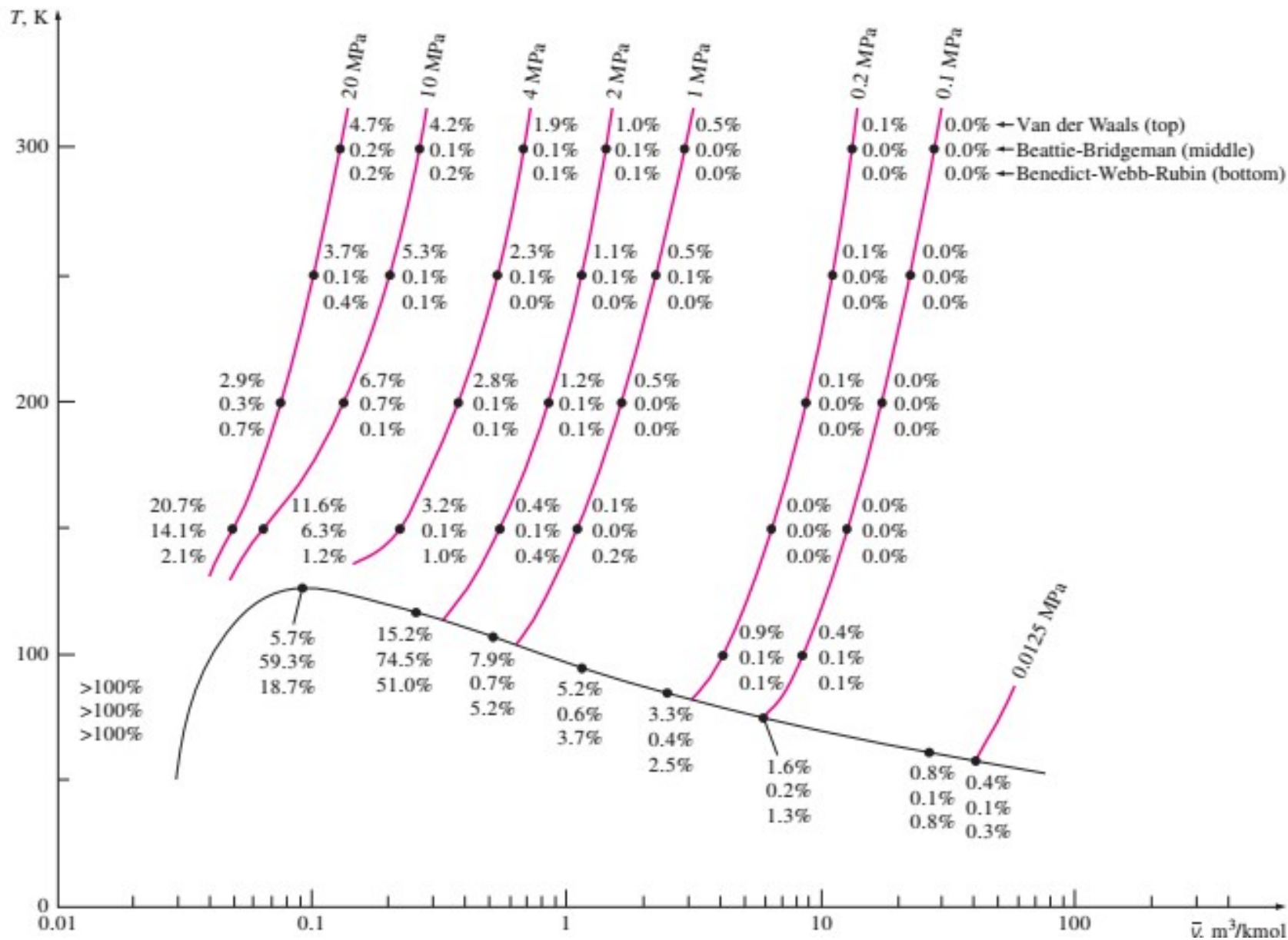
Gas	A_0	a	B_0	b	c
Air	131.8441	0.01931	0.04611	-0.001101	4.34×10^4
Argon, Ar	130.7802	0.02328	0.03931	0.0	5.99×10^4
Carbon dioxide, CO_2	507.2836	0.07132	0.10476	0.07235	6.60×10^5
Helium, He	2.1886	0.05984	0.01400	0.0	40
Hydrogen, H_2	20.0117	-0.00506	0.02096	-0.04359	504
Nitrogen, N_2	136.2315	0.02617	0.05046	-0.00691	4.20×10^4
Oxygen, O_2	151.0857	0.02562	0.04624	0.004208	4.80×10^4

Source: Gordon J. Van Wylen and Richard E. Sonntag, *Fundamentals of Classical Thermodynamics*, English/SI Version, 3rd ed. (New York: John Wiley & Sons, 1986), p. 46, table 3.3.

(b) When P is in kPa, $\bar{v}$ is in m^3/kmol , T is in K, and $R_u = 8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K}$, the eight constants in the Benedict-Webb-Rubin equation are as follows:

Gas	a	A_0	b	B_0	c	C_0	α	γ
n-Butane, C_4H_{10}	190.68	1021.6	0.039998	0.12436	3.205×10^7	1.006×10^8	1.101×10^{-3}	0.0340
Carbon dioxide, CO_2	13.86	277.30	0.007210	0.04991	1.511×10^6	1.404×10^7	8.470×10^{-5}	0.00539
Carbon monoxide, CO	3.71	135.87	0.002632	0.05454	1.054×10^5	8.673×10^5	1.350×10^{-4}	0.0060
Methane, CH_4	5.00	187.91	0.003380	0.04260	2.578×10^5	2.286×10^6	1.244×10^{-4}	0.0060
Nitrogen, N_2	2.54	106.73	0.002328	0.04074	7.379×10^4	8.164×10^5	1.272×10^{-4}	0.0053

Source: Kenneth Wark, *Thermodynamics*, 4th ed. (New York: McGraw-Hill, 1983), p. 815, table A-21M. Originally published in H. W. Cooper and J. C. Goldfrank, *Hydrocarbon Processing* 46, no. 12 (1967), p. 141.



Percentage of error involved in various equations of state for nitrogen (% error = $\left[\left(\frac{v_{\text{table}} - v_{\text{EoS}}}{v_{\text{table}}} \right) \times 100 \right]$)

