

ESO 201A: Thermodynamics

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Properties: part 5

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Learning objective

1. Introduce the concept of a pure substance.
2. Discuss the physics of phase change processes.
3. Illustrate the P-v, T-v and P-T property diagram, and P-v-T surfaces of pure substances.
4. Obtaining thermodynamic properties of a pure substance from a property table.
5. Define Ideal gas equation of state and demonstrate its use.
6. Introduce to compressibility.
7. Present the commonly used equation of states.

The Ideal Gas Equation 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.

$$P = R \left(\frac{T}{v} \right) \quad PV = RT \quad \text{Ideal gas equation of state}$$

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

R : gas constant

M : molar mass (kg/kmol)

R_u : universal gas constant

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

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

Different substances have different gas constants.

Mass = Molar mass x Mole number

$$m = MN$$

(kg)

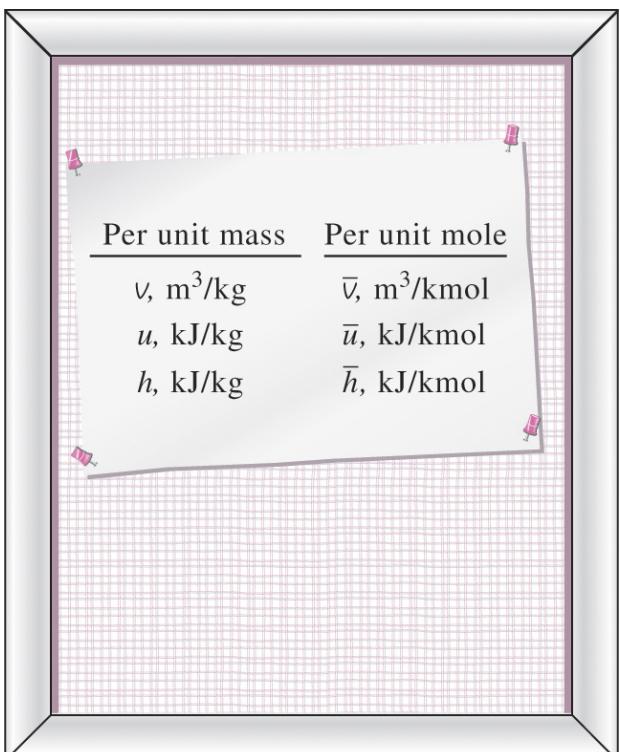
$$V = mV \longrightarrow PV = mRT$$

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

$$mR = (MN)R = NR_u \longrightarrow PV = NR_u T$$

Various expressions of ideal gas equation

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



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

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

The ideal-gas relation often is not applicable to real gases; thus, care should be exercised when using it.

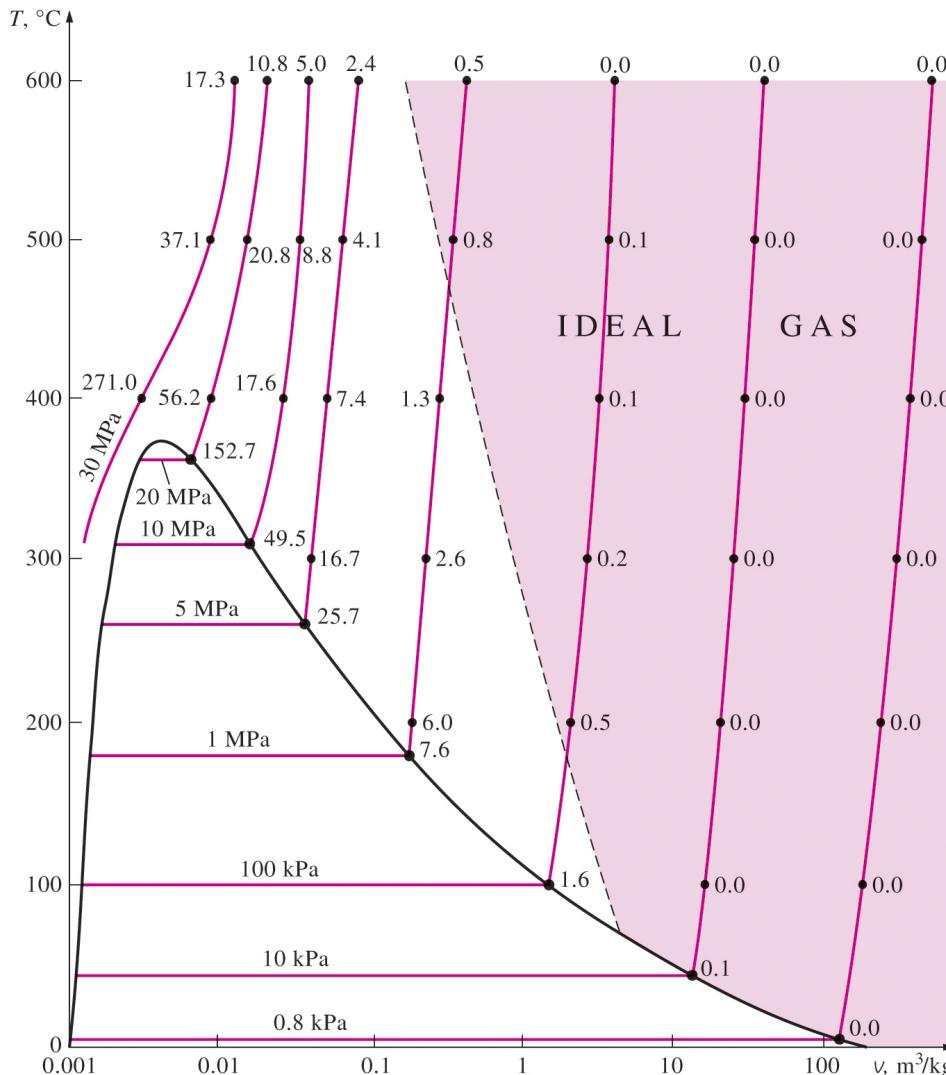
Properties per unit mole are denoted with a bar on the top.

Example

The gage pressure of an automobile tire is measured to be 210 kPa before a trip and 220 kPa after the trip at a location where the atmospheric pressure is 95 kPa. Assuming the volume of the tire remains constant and the air temperature before the trip is 25°C, determine air temperature in the tire after the trip.

Consider air is an ideal gas

Is water vapor an ideal gas ?



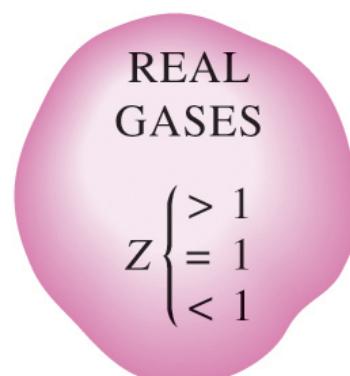
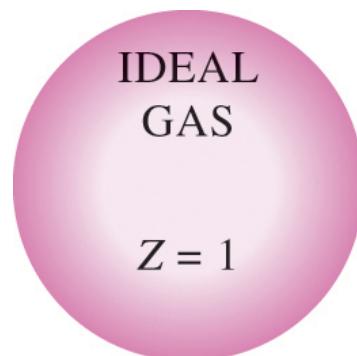
- At pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent).
- At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line.
- In air-conditioning applications, the water vapor in the air can be treated as an ideal gas. Why?
- In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.

Percentage of error ($(|v_{\text{table}} - v_{\text{ideal}}|/v_{\text{table}}) \times 100$) 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.

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 a given temperature and pressure.

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



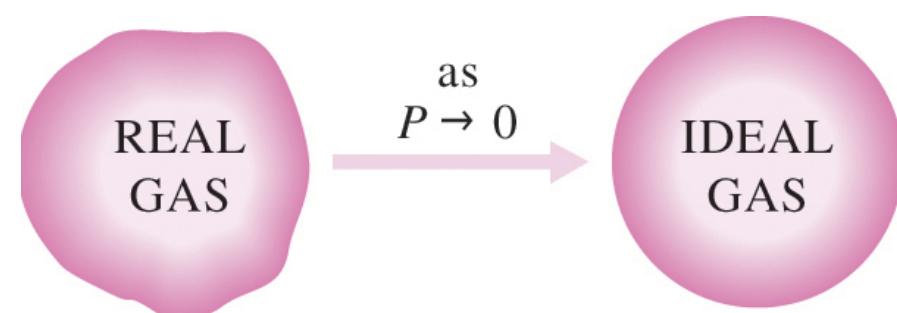
The compressibility factor is unity for ideal gases.

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).

Principle of corresponding states

- Gases behaves differently at a given T and P
- Remarkably, they behave very much the same at T and P normalized with respect to their T_{cr} an P_{cr} values.

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

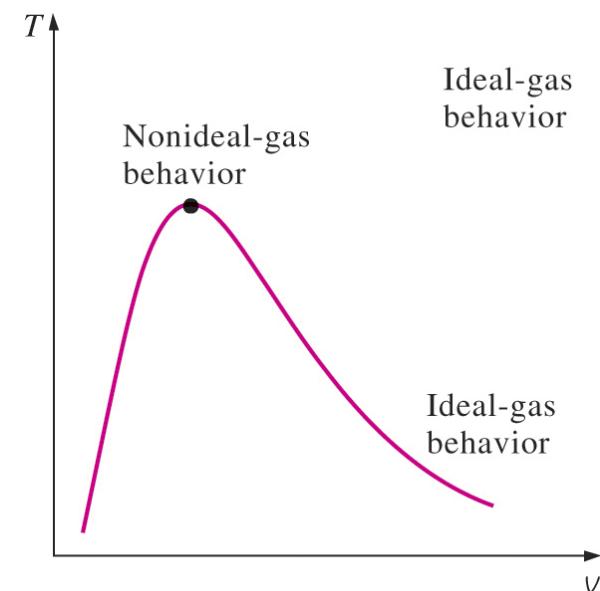
Reduced pressure

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

Reduced temperature

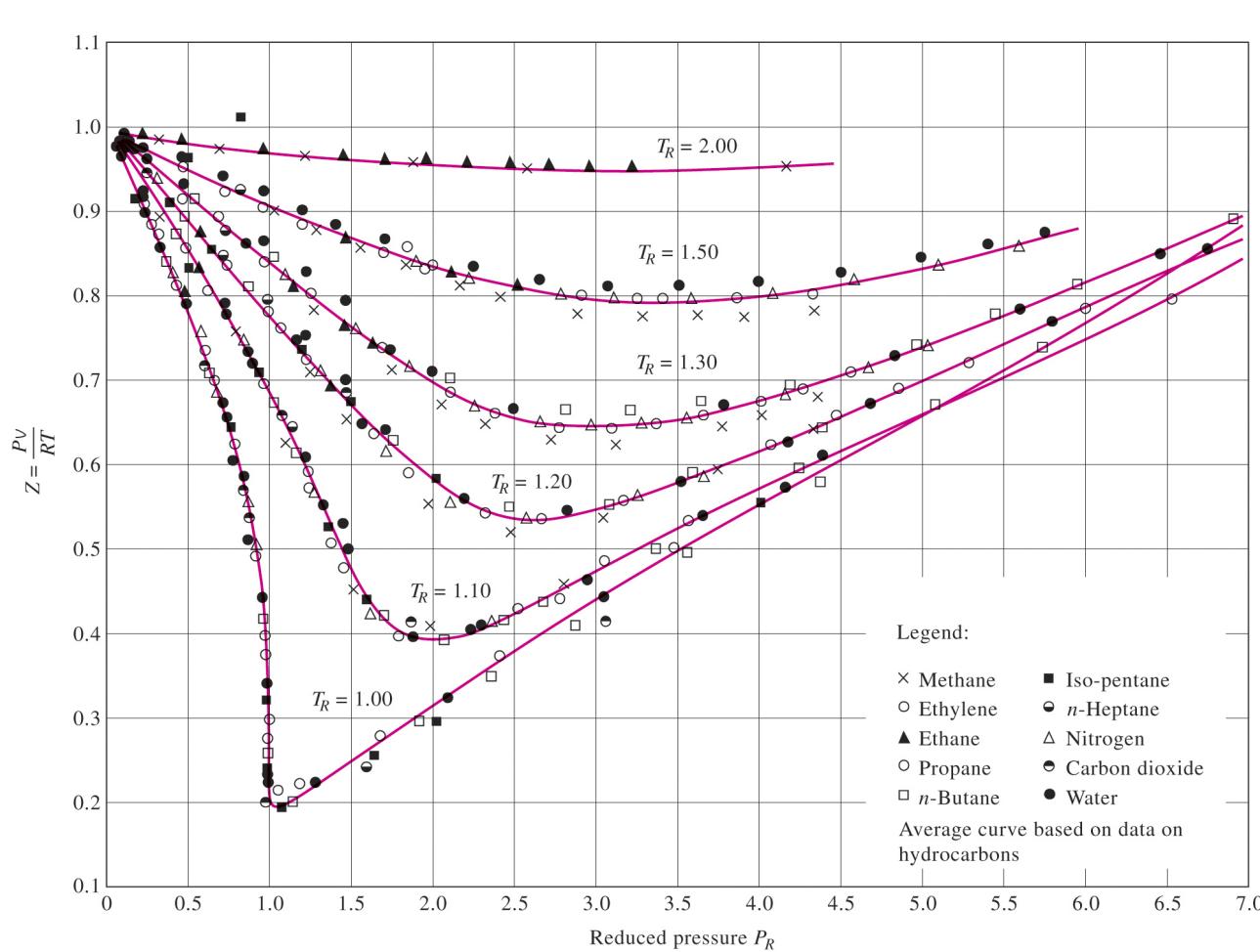
$$\nu_R = \frac{\nu_{\text{actual}}}{RT_{\text{cr}}/P_{\text{cr}}}$$

Pseudo-reduced specific volume



Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

Compressibility chart



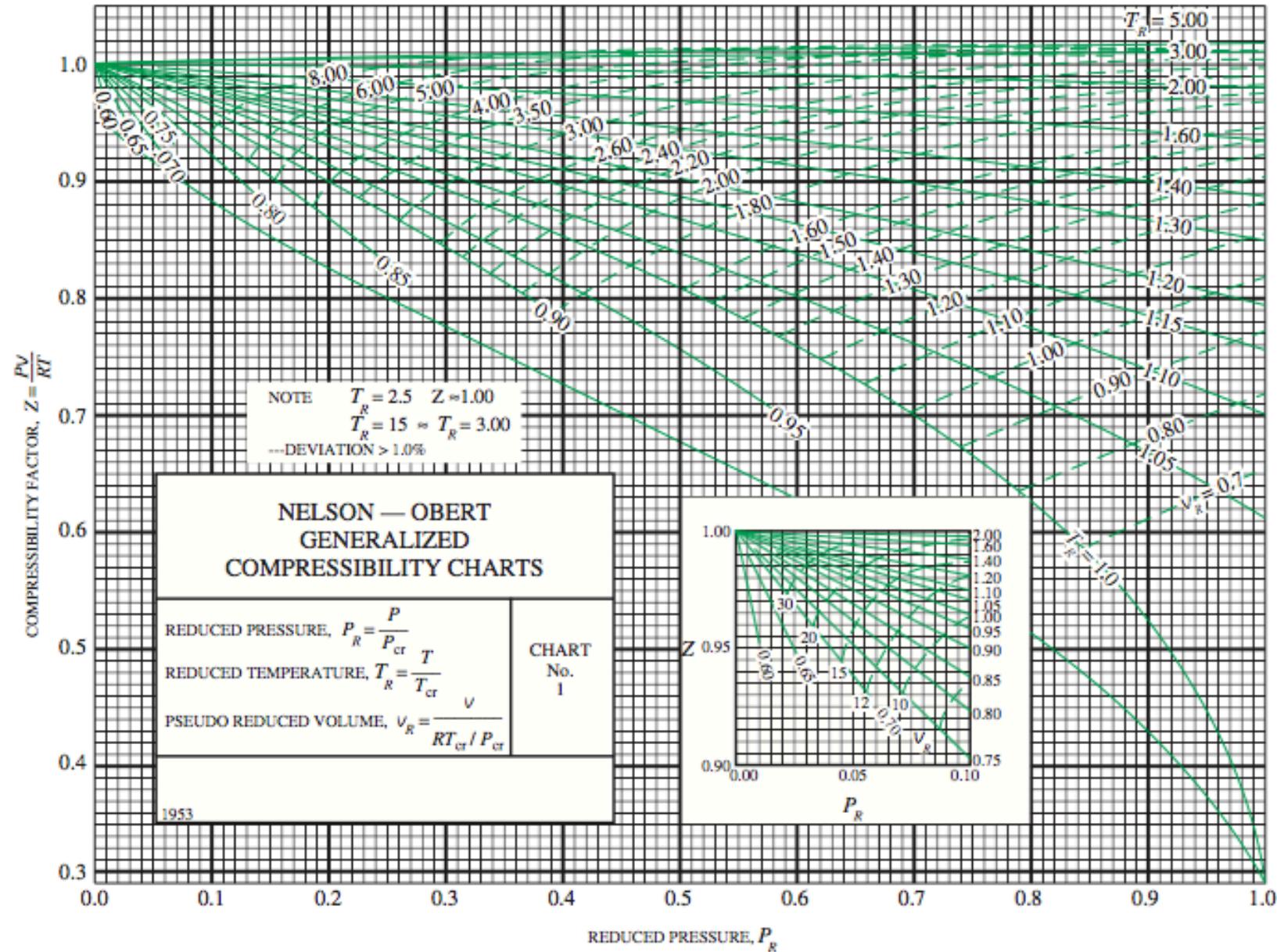
$$\left. \begin{aligned} P_R &= \frac{P}{P_{\text{cr}}} \\ v_R &= \frac{v}{RT_{\text{cr}}/P_{\text{cr}}} \end{aligned} \right\} Z = \dots \quad (\text{Fig. A-15})$$

Z can also be determined from a knowledge of P_R and v_R .

Comparison of Z factors for various gases.

Generalized compressibility chart

(a) Low pressures, $0 < P_R < 1.0$



OTHER EQUATIONS OF STATE

Several equations have been proposed to represent the P - v - T behavior of substances accurately over a larger region with no limitations.

Van der Waals Equation of State

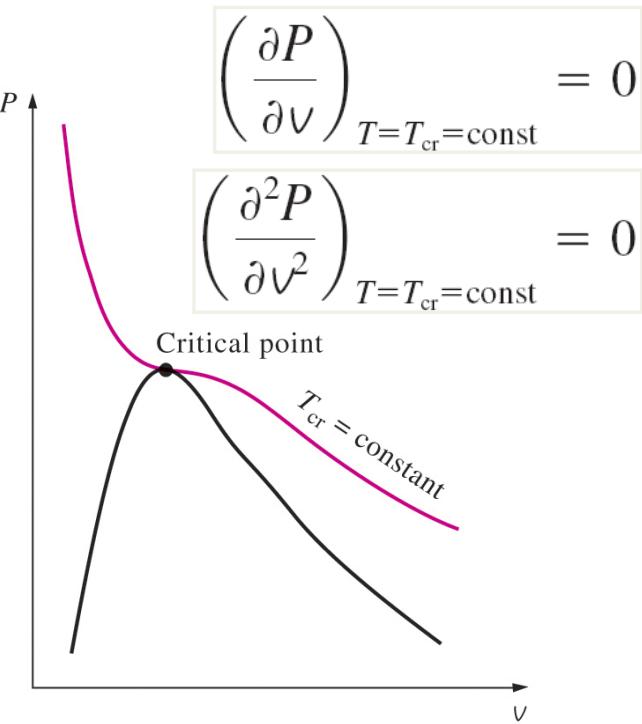
$$\left(P + \frac{a}{v^2} \right) (v - b) = RT$$

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

This model includes two effects not considered in the ideal-gas model: the *intermolecular attraction forces* and the *volume occupied by the molecules themselves*. The accuracy of the van der Waals equation of state is often inadequate.



Critical isotherm of a pure substance has an inflection point at the critical state.



Beattie-Bridgeman Equation of State

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

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

The five constants are given in Table 3–4 for various substances. It is known to be reasonably accurate for densities up to about $0.8\rho_{\text{cr}}$.

Benedict-Webb-Rubin Equation of State

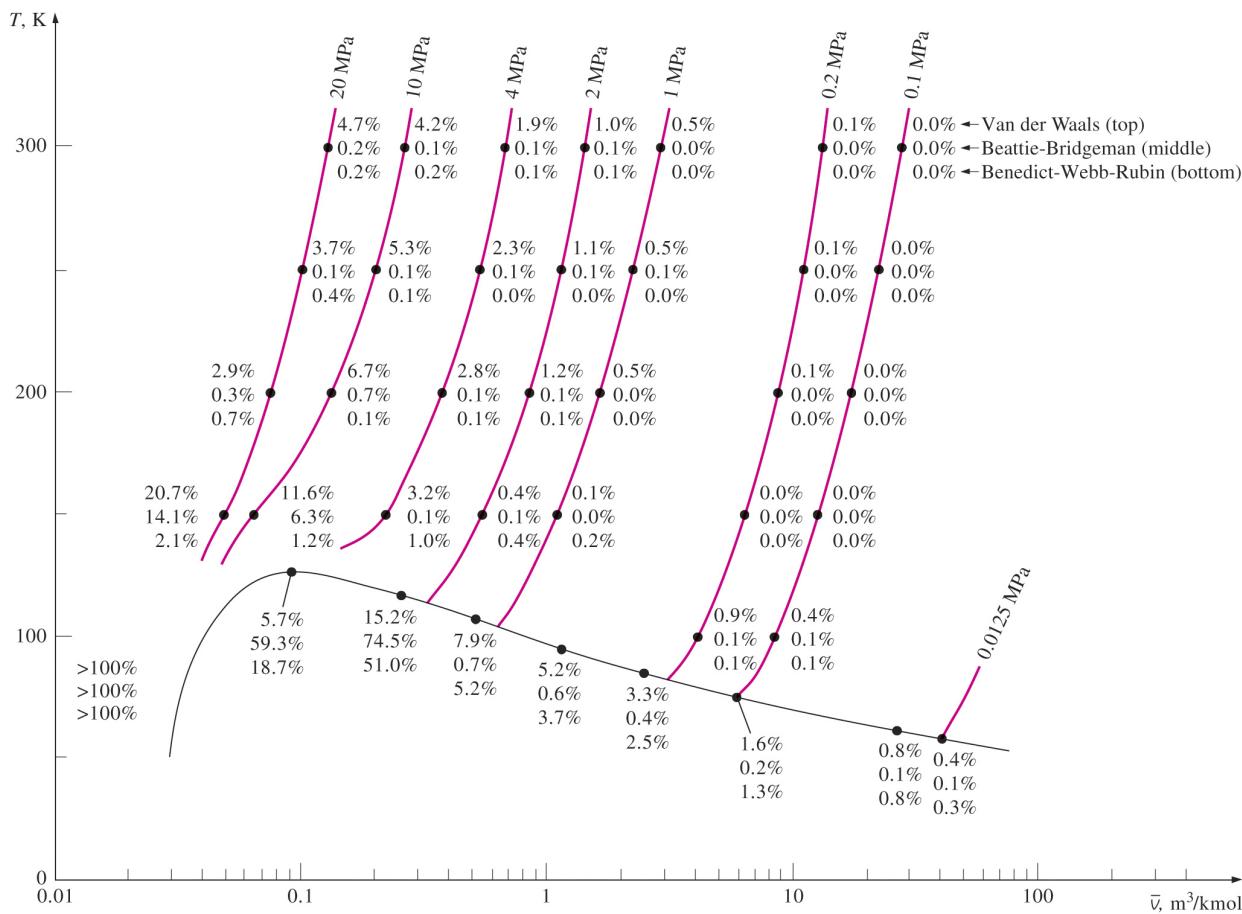
$$P = \frac{R_u T}{\bar{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2} \left(1 + \frac{\gamma}{\bar{v}^2} \right) e^{-\gamma/\bar{v}^2}$$

The eight constants are given in Table 3–4. This equation can handle substances at densities up to about $2.5\rho_{\text{cr}}$.

Virial Equation of State

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

The coefficients $a(T)$, $b(T)$, $c(T)$, and so on, that are functions of temperature alone are called *virial coefficients*.



Percentage of error involved in various equations of state for nitrogen
 $(\% \text{ error} = [(|v_{\text{table}} - v_{\text{equation}}|)/v_{\text{table}}] \times 100)$.

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

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

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

Strobridge: 16 constants.
 More suitable for computer calculations.

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

Complex equations of state represent the *P-v-T* behavior of gases more accurately over a wider range.

Summary

- Pure substance
- Phases of a pure substance
- Phase-change processes of pure substances
 - Compressed liquid, Saturated liquid, Saturated vapor, Superheated vapor
 - Saturation temperature and Saturation pressure
- Property diagrams for phase change processes
 - The $T-v$ diagram, The $P-v$ diagram, The $P-T$ diagram, The $P-v-T$ surface
- Property tables
 - Enthalpy
 - Saturated liquid, saturated vapor, Saturated liquid vapor mixture, Superheated vapor, compressed liquid
 - Reference state and reference values
- The ideal gas equation of state
 - Is water vapor an ideal gas?
- Compressibility factor
- Other equations of state