# Thermodynamics II

## Volumetric Properties of Pure Fluids

## Chapter 3

# A pressure-temperature diagram

- the sublimation curve
- the fusion curve
- the vaporization curve
- the triple point
- the critical point

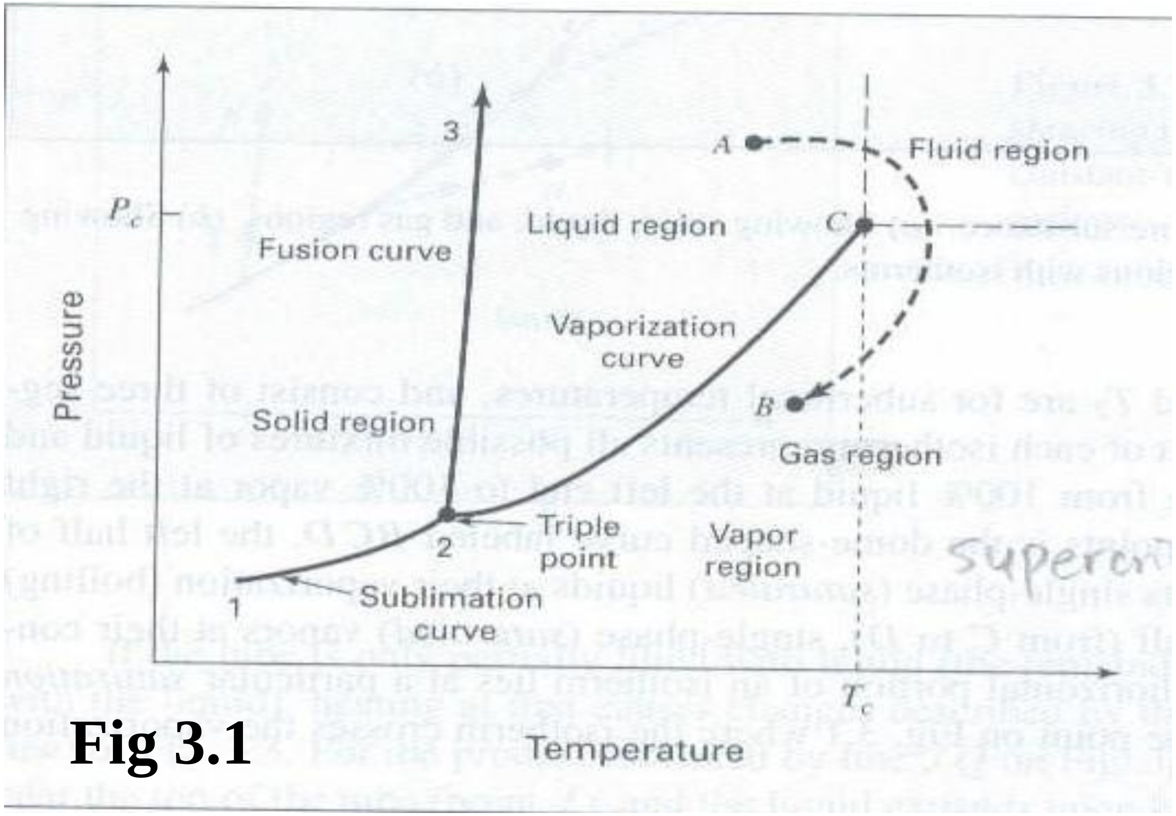


**Fig 3.1**

# A pressure-volume diagram

- The isotherms
  - the subcooled-liquid and the superheated-vapor regions
  - isotherms in the subcooled-liquid regions are steep because liquid volumes change little with large change in pressure
- The two-phase coexist region
- The triple point is the horizontal line
- The critical point

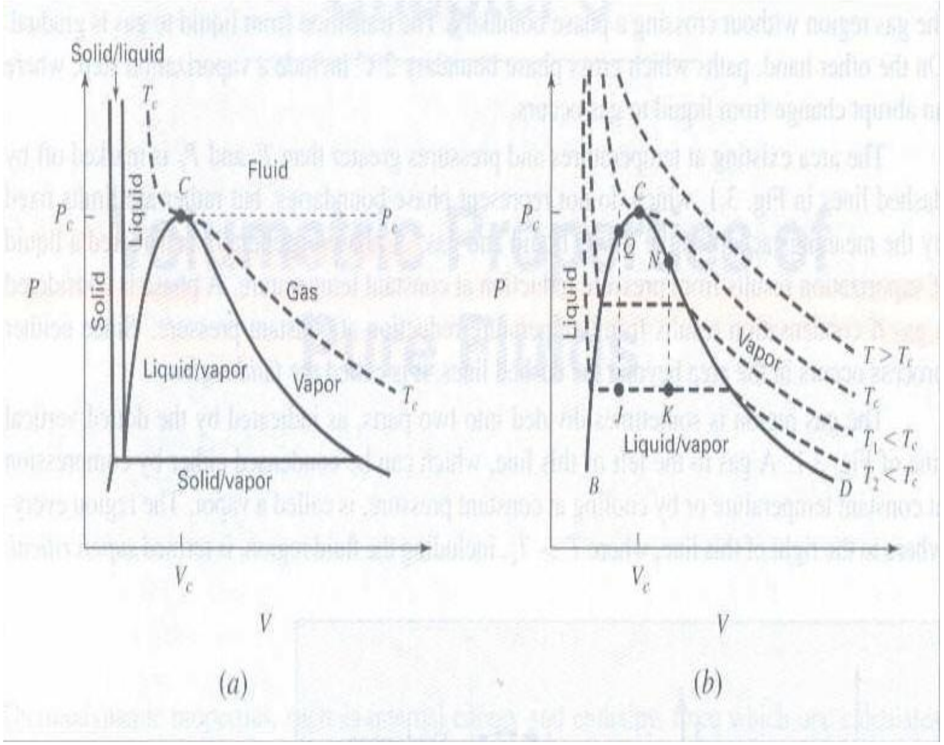


Fig 3.2

- Several processes are considered in thermodynamics:

- Reversible: $\boxed{dW = -PdV}$

-Isobaric process: $P$ = constant

- Isothermal process: $T$ = constant

- Adiabatic process: $Q$ = 0

- Isochoric process: $V$ = constant

- Isentropic S=constant

- Polytropic process: $\boxed{PV^{\delta} = \text{constant}}$ , where δ is constant

- Remember:
  - ▪ $Q$ and $W$ are path functions, while $U, V, H$, *and* $S$ are state functions.
  - ▪ In our text book, $Q$ and $W$ are heat and work added to the system, respectively.

# Ideal gas

- No interactions between molecules.
- gases at pressure up to a few bars may often be considered ideal and simple equations then apply
- the internal energy of gas depends on temperature only.
  - Z = 1; PV = RT
  - U = U (T)
  - $\boxed{C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} = C_V(T)}$ $\boxed{C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P = \frac{dH}{dT} = \frac{dU}{dT} + R = C_V + R = C_P(T)}$

    $\boxed{\Delta U = \int C_V dT}$ $\boxed{\Delta H = \int C_P dT}$
  - Mechanically reversible closed-system process, for a unit mass or a mole, $1^{st}$ –law of thermodynamics :

$$\boxed{dQ + dW = C_V dT} \xrightarrow[\boxed{dW = -PdV}]{} \boxed{dQ = \frac{C_V}{R} VdP + \frac{C_P}{R} PdV}$$

- **For ideal gas undergoing a mechanically reversible isobaric process:**

$$W = -\int PdV$$

$$W = -R(T_2 - T_1)$$

$$Q = \Delta H = \int C_P \, dT \qquad (\text{const } P)$$

- **For ideal gas undergoing a mechanically reversible isochoric process:**

$$\mathrm{W = O}$$

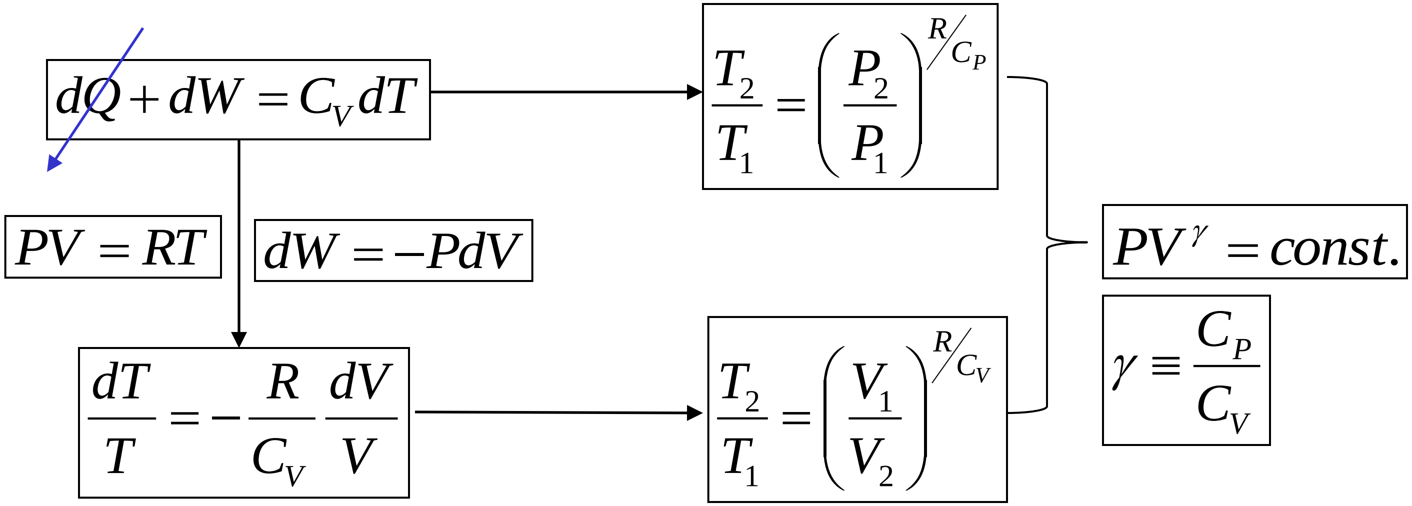
$$Q = \Delta U = \int C_V \, dT \qquad (\text{const } V)$$

- **For ideal gas undergoing a mechanically reversible isothermal process:**

$$\Delta U = \Delta H = 0$$

$$Q = -W = \mathrm{RT\ln}\frac{V_2}{V_1} = -RT\ln\frac{P_2}{P_1} \qquad (\text{const } T)$$

- **For ideal gas with constant heat capacities undergoing a mechanically reversible adiabatic process:**



$$\cancel{dQ} + dW = C_V dT$$

$$PV = RT$$

$$dW = -PdV$$

$$\frac{dT}{T} = -\frac{R}{C_V}\frac{dV}{V}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_P}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_V}$$

$$PV^{\gamma} = const.$$

$$\gamma \equiv \frac{C_P}{C_V}$$

  - for monatomic gases, $\gamma = 1.67$
  - for diatomic gases, $\gamma = 1.4$
  - for simple polyatomic gases, such as $CO_2$, $SO_2$, $NH_3$, and $CH_4$, $\gamma = 1.3$

- **For ideal gas with constant heat capacities undergoing a mechanically reversible adiabatic process:**

$$W = -\int P dV \qquad \boxed{PV^{\gamma} = const.}$$

$$W = \frac{RT_2 - RT_1}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

$$W = \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right]$$

- **For ideal gas undergoing polytropic reversible process:**

$$PV^{\delta} = \text{constant}$$

$$TV^{\delta-1} = \text{constant}$$

$$TP^{(1-\delta)/\delta} = \text{constant}$$

$$W = \frac{RT_1}{\delta - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right]$$

$$Q = \frac{(\delta - \gamma)RT_1}{(\delta - 1)(\gamma - 1)}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right]$$

**Example 3.2** Air is compressed from an initial condition of 1 bar and 25°C to a final state of 5 bar and 25 °C by three different mechanically reversible processes in a closed system. (a) heating at constant volume followed by cooling at constant pressure; (b) isothermal compression; (c) adiabatic compression followed by cooling at constant volume. Assume air to be an ideal gas with the constant heat capacities, $C_V = (5/2)R$ and $C_P = (7/2)R$. Calculate the work required, heat transferred, and the changes in internal energy and enthalpy of the air in each process.

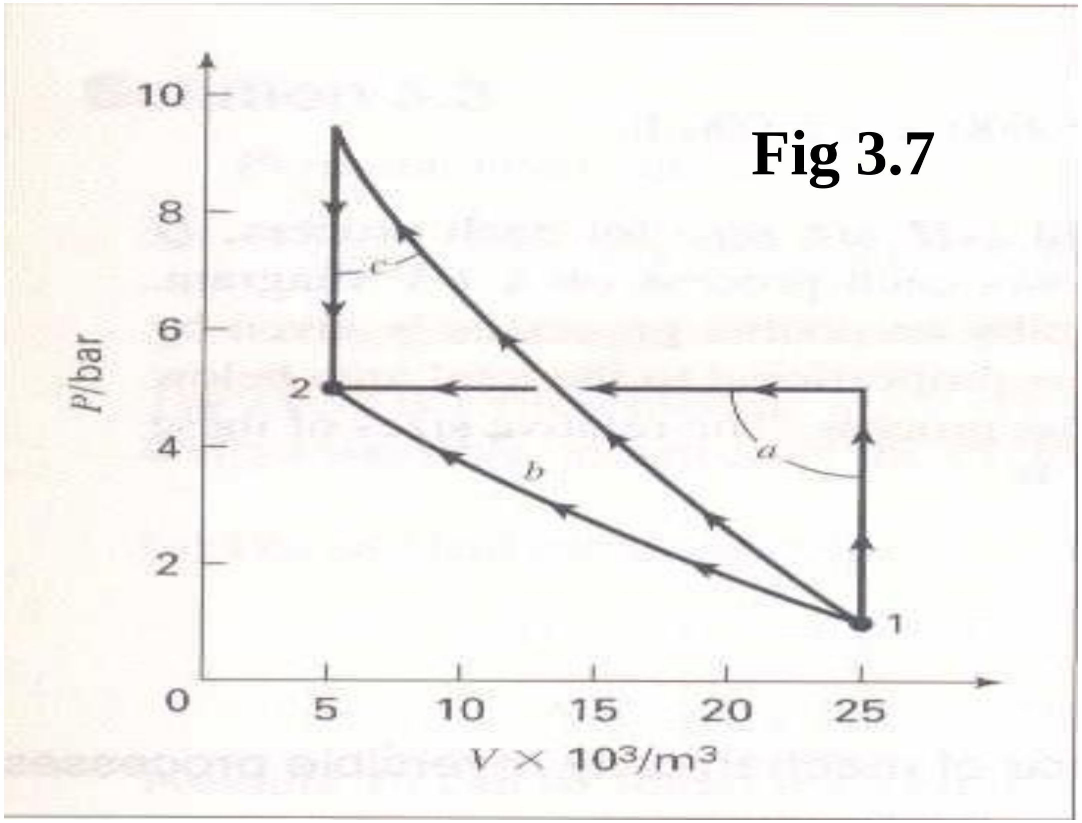


**Fig 3.7**

Choose the system as 1 mol of air, contained in an imaginary frictionless piston /cylinder arrangement.

For R = 8.314 J/mol.K, $C_V$ = 20.785, $C_P$ = 29.099 J/mol.K

The initial and final molar volumes are: $V_1$ = 0.02479 $m^3$ and $V_2$ = 0.004958 $m^3$

The initial and final temperatures are identical: $\Delta U = \Delta H = 0$

(a) $Q = C_V\Delta T + C_P\Delta T = -9915$ J; $W = \Delta U - Q = 9915$ J

(b) $Q = -W = RT\ln\left(\frac{P_1}{P_2}\right) = -3990$ J

(c) adiabatic compression: $\boxed{T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 567.57\ K}$ $\boxed{P_2 = P_1\left(\frac{V_1}{V_2}\right)^{\gamma} = 9.52\ bar}$

$$\boxed{W = C_V\Delta T = 5600\ J}$$

cooling at constant V, W = 0.

overall, W = 5600 J, $Q = \Delta U - W = -5600$ J.

# Irreversible process

- Remember that changes in state functions as enthalpy and internal energy depend only on the initial and final states of the system.
- Thus, previous equations that relate changes in state functions only are valid for ideal gases regardless of the process reversible/irreversible in both closed and open systems
- This is NOT true for Q or W since they are path function.
- The work of an irreversible process is calculated:
  - First, the work is determined for a mechanically reversible process.
  - Second, if the process produces work (negative value), the value for the reversible process is too large and must be multiplied by an efficiency. If the process requires work (positive value), the value for the reversible process is too small and must be divided by an efficiency.

**Example 3.3** An ideal gas undergoes the following sequence of mechanically reversible processes in a closed system:

(a) From an initial state of 70°C and 1 bar, it is compressed adiabatically to 150 °C.

(b) It is then cooled from 150 to 70 °C at constant pressure.

(c) Finally, it is expanded isothermally to its original state.

Calculate W, Q, ΔU, and ΔH for each of the three processes and for the entire cycle. Take $C_V = (3/2)R$ and $C_P = (5/2)R$. If these processes are carried out irreversibly but so as to accomplish exactly the same changes of state (i.e. the same changes in P, T, U, and H), then different values of Q and W result. Calculate Q and W if each step is carried out with an efficiency of 80%.

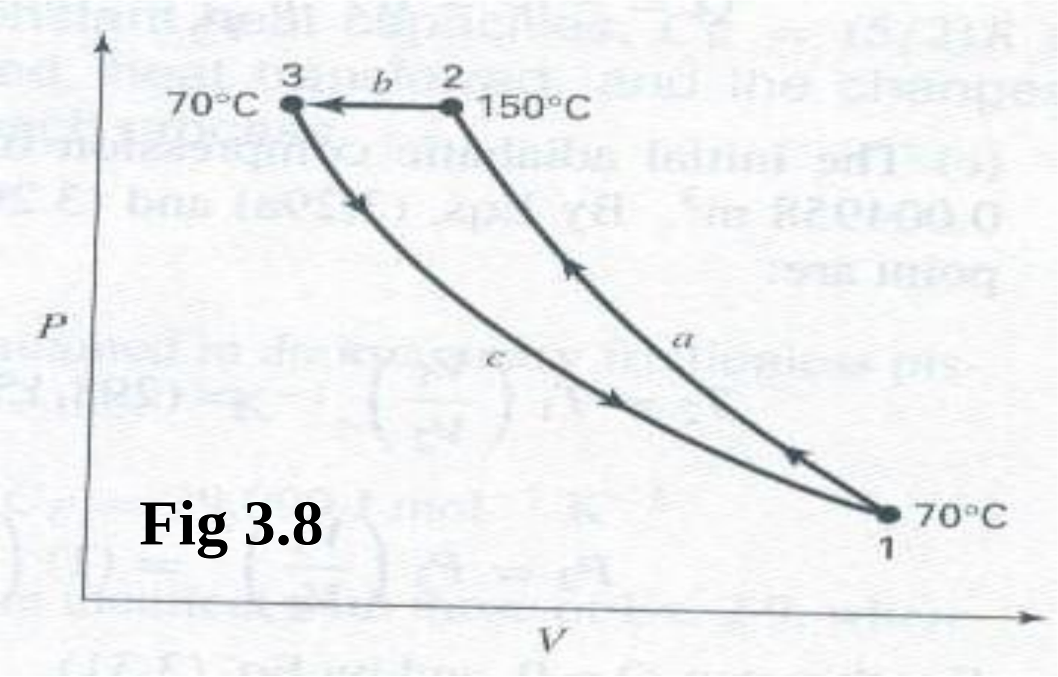


**Fig 3.8**

Choose the system as 1 mol of air, contained in an imaginary frictionless piston /cylinder arrangement. For R = 8.314 J/mol.K, $C_V$ = 12.471, $C_P$ = 20.785 J/mol.K

(a) For an ideal gas undergoing adiabatic compression, Q = 0

$\Delta U = W = C_V \Delta T = 12.471(150 - 70) = 998\ J$

$\Delta H = C_P \Delta T = 20.785(150 - 70) = 1663\ J$

$$\boxed{P_2 = P_1 \left( \frac{T_2}{T_1} \right)^{\gamma/(\gamma - 1)} = 1.689\ bar}$$

(b) For the constant-pressure process:

$Q = \Delta H = C_P \Delta T = 20.785(70 - 150) = -1663\ J$

$\Delta U = C_V \Delta T = 12.471(70 - 150) = -998\ J$

$W = \Delta U - Q = 665\ J$

(c) Isotherm process, $\Delta U$ and $\Delta H$ are zero:

$$\boxed{Q = -W = RT \ln\left( \frac{P_3}{P_1} \right) = 1495\ J}$$

Overall:

$Q = 0 - 1663 + 1495 = -168\ J$

$W = 998 + 665 - 1495 = 168\ J$

$\Delta U = 0$

$\Delta H = 0$

# Irreversible processes:

(1) For 80% efficiency:

$W(\text{irreversible}) = W(\text{reversible}) / 0.8 = 1248 \text{ J}$

$\Delta U(\text{irreversible}) = \Delta U(\text{reversible}) = 998 \text{ J}$

$Q(\text{irreversible}) = \Delta U - W = -250 \text{ J}$

(2) For 80% efficiency:

$W(\text{irreversible}) = W(\text{reversible}) / 0.8 = 831 \text{ J}$

$\Delta U = C_V \Delta T = 12.471(70 - 150) = -998 \text{ J}$

$Q = \Delta U - W = -998 - 831 = -1829 \text{ J}$

(3) Isotherm process, $\Delta U$ and $\Delta H$ are zero:

$W(\text{irreversible}) = W(\text{reversible}) \times 0.8 = -1196 \text{ J}$

$Q = \Delta U - W = 1196 \text{ J}$

(4) Overall: $Q = -250 - 1829 + 1196 = -883 \text{ J}$

$W = 1248 + 831 - 1196 = 883 \text{ J}$

$\Delta U = 0$

$\Delta H = 0$

The total work required when the cycle consists of three irreversible steps is more than 5 times the total work required when the steps are mechanically reversible, even though each irreversible step is assumed 80% efficient.

**Example.** A 400g mass of nitrogen at 27 °C is held in a vertical cylinder by a frictionless piston. The weight of the piston makes the pressure of the nitrogen 0.35 bar higher than that of the surrounding atmosphere, which is at 1 bar and 27°C. Take $C_V = (5/2)R$ and $C_P = (7/2)R$. Consider the following sequence of processes:

(a) Immersed in an ice/water bath and comes to equilibrium

(b) Compressed reversibly at the constant temperature of 0°C until the gas volume reaches one-half the value at the end of step (1) and fixed the piston by latches

(c) Removed from the ice/water bath and comes to equilibrium to thermal equilibrium with the surrounding atmosphere

(d) Remove the latches and the apparatus return to complete equilibrium with its surroundings.

Nitrogen may be considered an ideal gas. Calculate W, Q, ΔU, and ΔH for each step of the cycle.

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The steps:

$$n = \frac{m}{M} = 14.286\, mol$$

(a) $$27^\circ C, 1.35 bar \xrightarrow{constP} 0^\circ C, 1.35 bar$$

(b) $$0^\circ C, V_2 \xrightarrow{constT} 0^\circ C, V_3 = \frac{1}{2} V_2$$

(c) $$0^\circ C, V_3 \xrightarrow{constV} 27^\circ C, V_4 = V_3$$

(d) $$27^\circ C, P_4 \xrightarrow{T_4 = T_1} 27^\circ C, 1.35 bar$$

# Example 3.4 in Smith Textbook, 6th Edition.

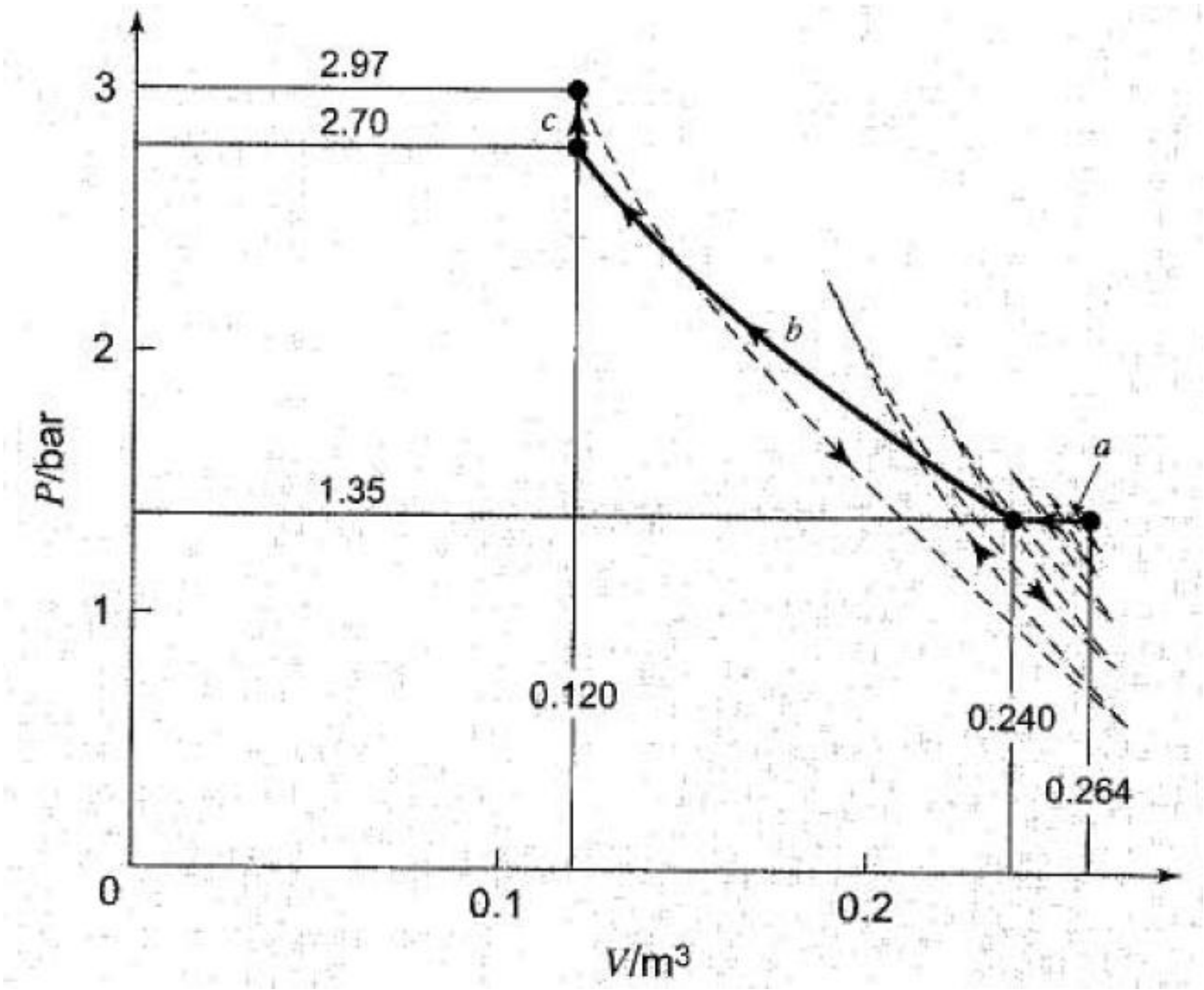

Fig 3.9

(a) $\boxed{W_1 = -n\int PdV = -nP\Delta V = -nR\Delta T = 3207\ J}$ $\boxed{Q_1 = n\Delta H_1 = nC_P\Delta T = 11224\ J}$

$\boxed{n\Delta U_1 = Q_1 + W_1 = -11224 + 3207 = -8017\ J}$

(b) $\boxed{\Delta U_2 = \Delta H_2 = 0}$ $\boxed{Q_2 = -W_2 = nRT\ln\frac{V_3}{V_2} = -22487\ J}$

(c) $\boxed{W_3 = 0}$ $\boxed{Q_3 = n\Delta U_3 = nC_V\Delta T = 8017\ J}$ $\boxed{n\Delta H_3 = nC_P\Delta T = 11224\ J}$

(d) the oscillation of the piston

$\boxed{\Delta U_4 = \Delta H_4 = 0}$ $\boxed{Q_4 = -W_4}$

**Example 3.6.** Air flows at a steady rate through a horizontal insulated pipe which contains a partly closed valve. The conditions of the air upstream from the valve are 20°C and 6 bar, and the downstream pressure is 3 bar. The line leaving the valve is enough larger than the entrance line so that the kinetic-energy change as it flows through the valve is negligible. If air is regarded as an ideal gas, what is the temperature of the air some distance downstream from the valve?

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Flow through a partly closed valve is known as a throttling process.
For steady flow system, the first law of thermodynamics is:

$$\cancel{\frac{d(mU)_{cv}}{dt}}+\Delta\left[\left(H+\cancel{\frac{1}{2}u^2}+\cancel{zg}\right)\dot{m}\right]_{fs}=\cancel{\dot{Q}}+\cancel{\dot{W}} \longrightarrow \boxed{\Delta H=0}$$

Ideal gas: $\Delta H=\int C_P dT \longrightarrow \boxed{T_2=T_1}$

The result that ΔH = 0 is general for a throttling process.

**Example 3.7** If the flow rate of the air is 1 mol/s and if the pipe has an inner diameter of 5 cm, both upstream and downstream from the valve, what is the kinetic-energy change of the air and what is its temperature change? For air, $C_P = (7/2)R$ and the molar mass is M = 29 g/mol.

Upstream molar volume:

$$\boxed{V_1 = \frac{RT_1}{P_1} = \frac{83.14\times 293.15}{6}\times 10^{-6} = 4.062\times 10^{-3}\ {}^{m^2}\!\!/_{mol}} \quad \boxed{u_1 = \dot{n}\frac{1}{A\rho} = \dot{n}\frac{V}{A} = 2.069\ {}^{m}\!/_{s}}$$

Downstream molar volume:

$$\boxed{V_2 = 2V_1} \quad \boxed{u_2 = 2u_1 = 4.138\ {}^{m}\!/_{s}}$$

The rate of the change in kinetic energy:

$$\boxed{\dot{m}\Delta\left(\frac{1}{2}u^2\right) = \dot{n}M\left(\frac{u_2^2 - u_1^2}{2}\right) = (1\times 29\times 10^{-3})\frac{(4.138^2 - 2.069^2)}{2} = 0.186\ {}^{J}\!/_{s}}$$

$$\cancel{\frac{d(mU)_{cv}}{dt}} + \Delta\left[\left(H + \frac{1}{2}u^2 + \cancel{zg}\right)\dot{m}\right]_{fs} = \cancel{\dot{Q}} + \cancel{\dot{W}} \longrightarrow \boxed{\dot{m}\left(\frac{C_P}{M}\Delta T + \Delta\left(\frac{1}{2}u^2\right)\right) = 0}$$

$$\downarrow$$

$$\boxed{\Delta T = -0.0064\ K}$$

# Equations of State
# EOS

- **An equation of state** exists relating pressure, molar or specific volume, and temperature for any pure homogeneous fluid in equilibrium states.
- An equation of state may be solved for any one of the three quantities: P, V, or T as a function of the other two.
- Example:

$$\boxed{dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP}$$

Volume expansivity: $\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Isothermal compressibility: $\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\boxed{\frac{dV}{V} = \beta dT - \kappa dP}$$

  - For incompressible fluid (ideal situation), both β and κ are zero.
  - For liquids β is almost positive (liquid water between 0°C and 4°C is an exception), and κ is necessarily positive.
  - At conditions **not close to the critical point**, β and κ can be assumed constant: $\boxed{\ln\frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)}$

# Virial equations of state

- PV along an isotherm:
- $PV = a + bP + cP^2 = a(1 + B'P + C'P^2 + D'P^3 + \ldots)$
  - The limiting value of PV as P →0 for all the gases:
  - $(PV)^* = a = f(T)$
  - $(PV)^* = a = RT$ , with R as the proportionally constant.
  - Assign the value of 273.16 K to the temperature of the triple point of water: $(PV)_t^* = R \times 273.16$
- Ideal gas:
  - the pressure ~ 0; the molecules are separated by infinite distance; the intermolecular forces approaches zero.
  - $R = \frac{(PV)_t^*}{273.16} = 83.1447 \frac{cm^3\ bar}{mol\ K}$

# Virial equations of state

- The compressibility factor: $Z \equiv \dfrac{PV}{RT}$
- the virial expansion: $Z = 1 + B'P + C'P^2 + D'P^3 + \ldots$
- Another form: $Z = 1 + \dfrac{B}{V} + \dfrac{C}{V^2} + \dfrac{D}{V^3} + \ldots$
  - the parameters B′, C′, D′, etc. are virial coefficients, accounting of interactions between molecules.
  - the only equation of state proposed for gases having a firm basis in theory.
  - The methods of statistical mechanics allow derivation of the virial equations and provide physical significance to the virial coefficients.

# Virial equations of state

- Relationship between the two types of virial coefficients

$$\boxed{B' = \frac{B}{RT}} \qquad \boxed{C' = \frac{C - B^2}{(RT)^2}} \qquad \boxed{D' = \frac{D - 3BC + 2B^3}{(RT)^3}}$$

- The derivation of above relations:

-Get the following expression for P:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \Rightarrow P = \frac{RT}{V}\left[1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots\right]$$

- Substitute P in: $Z = 1 + B'P + C'P^2 + D'P^3 + \ldots$

- Compare the corresponding terms to get the relations between coefficients.

# Application of the virial equations

- Differentiation:

$$\boxed{\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + 3D'P^2 + \ldots} \qquad \boxed{\left(\frac{\partial Z}{\partial P}\right)_{T;P=0} = B'}$$

- The virial equation truncated to two terms satisfactorily represent the PVT behavior up to about 5 bar

$$\boxed{Z = 1 + B'P} \qquad \boxed{Z = 1 + \frac{BP}{RT} = 1 + \frac{B}{V}} \qquad \boxed{\rightarrow V = \frac{RT}{P} + B}$$

- The virial equation truncated to three terms provides good results for pressure range above 5 bar but below the critical pressure

$$\boxed{Z = 1 + B'P + C'P^2} \qquad \boxed{Z = 1 + \frac{B}{V} + \frac{C}{V^2}}$$

- Remember that the virial coefficients are function of temperature only.

**Example 3.8.** Reported values for the virial coefficients of isopropanol vapor at 200°C are:

B = -388 cm$^3$/mol and C = -26000 cm$^6$/mol$^2$. Calculate V and Z for isopropanol vapor at 200 °C and 10 bar by (1) the ideal gas equation; (2) two-term virial equation; (3) three-term virial equation.

(1) For an ideal gas, Z = 1:

$$\boxed{V=\frac{RT}{P}=\frac{83.14\times 473.15}{10}=3934\,{}^{cm^3}\!/_{mol}}$$

(2) two-term virial equation:

$$\boxed{V=\frac{RT}{P}+B=3934-388=3546\,{}^{cm^3}\!/_{mol}} \longrightarrow \boxed{Z=\frac{PV}{RT}=0.9014}$$

(3) three-term virial equation:

**Direct method:**

$$\boxed{B'=\frac{B}{RT}=\frac{-388}{(83.14)(473.15)}=-9.8633\times 10^{-3}\,bar^{-1}}$$

$$\boxed{C'=\frac{C-B^2}{(RT)^2}=\frac{-26000-(-388)^2}{[(83.14)(473.15)]^2}=-1.14087\times 10^{-4}\,bar^{-2}}$$

$$\boxed{Z=1+B'P+C'P^2=1-9.8633\times 10^{-3}(10)-1.14087\times 10^{-4}(10)^2=0.890}$$

$$\boxed{V=ZRT/P=3501\;cm^3/mol}$$

(3) three-term virial equation:

**Iterative method :**

$$\boxed{V_{i+1} = \frac{RT}{P}\left(1+\frac{B}{V_i}+\frac{C}{V_i^2}\right) = 3934\left(1+\frac{388}{3934}+\frac{-26000}{(3934)^2}\right) = 3539\,{}^{cm^3}\!/_{mol}}$$

1st iteration

Ideal gas value

…

After 5 iterations $\boxed{V_4 \sim V_5 = 3488\,{}^{cm^3}\!/_{mol}} \longrightarrow \boxed{Z = \frac{PV}{RT} = 0.89}$

# Benedict/Webb/Rubin Equation of State

$$P = \frac{RT}{V} + \frac{B_0RT - A_0 - C_0/T^2}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{V^3T^2}\left(1 + \frac{\gamma}{V^2}\right)\exp\frac{-\gamma}{V^2}$$

- where $A_0$, $B_0$, $C_0$, a, b, c, a , and $\gamma$ are all constant for a given fluid.
- It is used in the petroleum and natural-gas industries for light hydrocarbons and a few other commonly encountered gases.

# Cubic equations of state

- Simple equation capable of representing both liquid and vapor behavior.
- The **van der Waals** equation of state:

$$\boxed{P = \frac{RT}{V - b} - \frac{a}{V^2}}$$

  - *a* and *b* are positive constants for a given fluid.
  - unrealistic behavior in the two-phase region. In reality, two, within the two-phase region, saturated liquid and saturated vapor coexist in varying proportions at the saturation or vapor pressure.
  - Three volume roots, of which two may be complex.
  - Physically meaningful values of V are always real, positive, and greater than constant *b*.

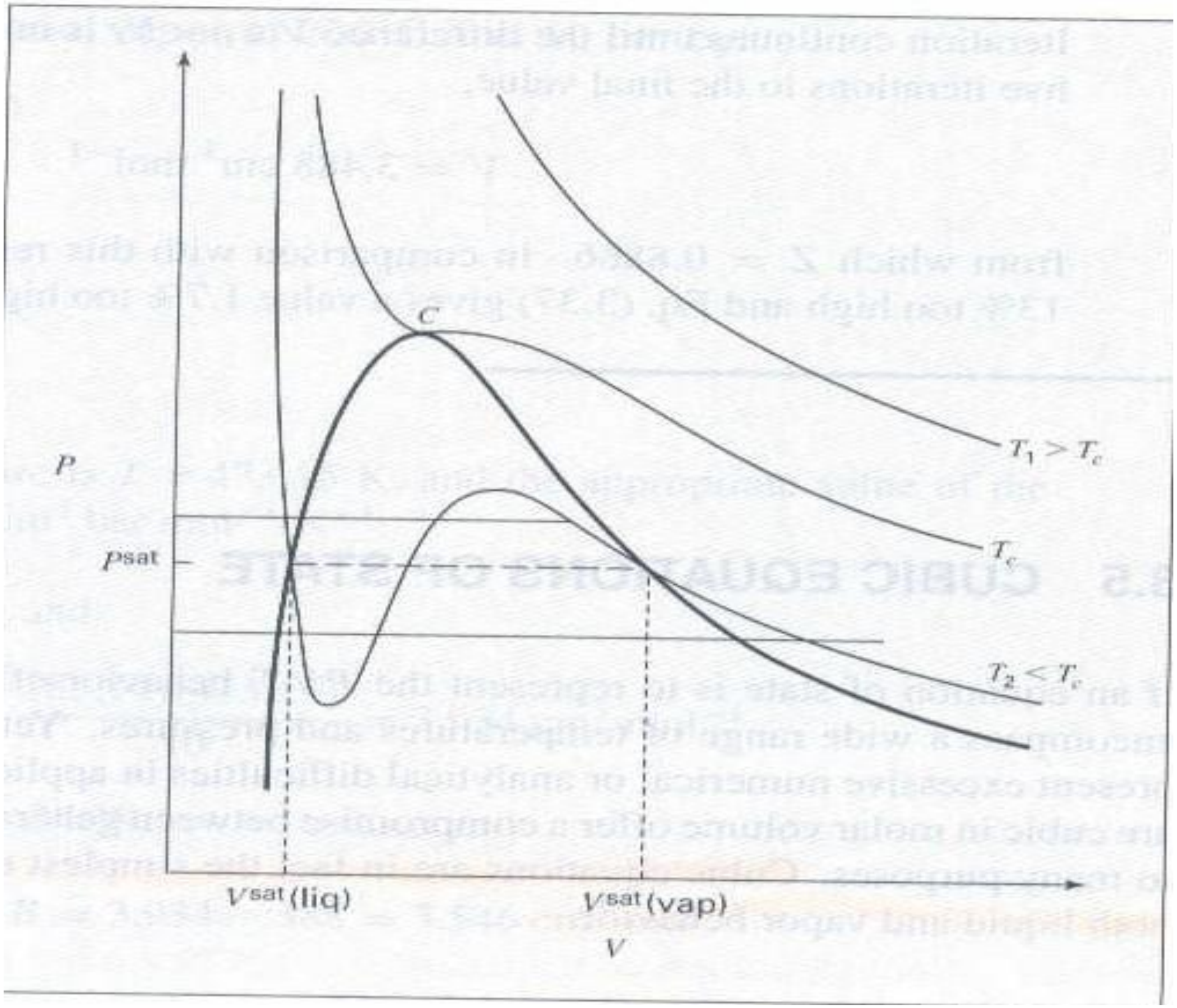


Fig 3.12

# A generic cubic equation of state

- General form:

$$\boxed{P=\frac{RT}{V-b}-\frac{\theta(V-\eta)}{(V-b)(V^2+\kappa V+\lambda)}}$$

  - where $b$, $\theta$, $\kappa$, $\lambda$ and $\eta$ are parameters depend on temperature and (mixture) composition.
  - Set $\eta = b$, $\theta = a(T)$, $\kappa = (\varepsilon+\sigma)\,b$, $\lambda = \varepsilon\sigma b^2$, we have:

$$\boxed{P=\frac{RT}{V-b}-\frac{a(T)}{(V+\varepsilon b)(V+\sigma b)}}$$

  - where $\varepsilon$ and $\sigma$ are pure numbers, the same for all substances, whereas $a(T)$ and $b$ are substance dependent.
  - Set $\varepsilon = \sigma = 0$, and a(T) = a is a substance-dependent constant to have van der Waals EOS.
  - Set $\varepsilon = 0$, $\sigma = 1$, to have Redlich/Kwong (RK) EOS:

$$\boxed{P=\frac{RT}{V-b}-\frac{a(T)}{V(V+b)}}$$

- **Determination of van der Waals parameters :**
  - The isotherm has inflection at the critical point:

$$\left(\frac{\partial P}{\partial V}\right)_{T;cr} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T;cr} = 0$$

  - Apply van der Waals at critical point: $P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c{}^2}$

    - 5 parameters ($P_c$, $V_c$, $T_c$, $a(T_c)$, $b$) with 3 equations, solve to have: $\boxed{b = \frac{1}{8}\frac{RT_c}{P_c}}$ $\boxed{a = \frac{27}{64}\frac{R^2T_c{}^2}{P_c}}$ $\boxed{V_c = \frac{3}{8}\frac{RT_c}{P_c}}$

    - $Z_c \equiv \frac{P_cV_c}{RT_c} = \frac{3}{8}$

    - Unfortunately, it does not agree with the experiment. Each chemical species has its own value of $Z_c$.

# An equivalent, but more straightforward procedure:

- Three repeated roots, V = Vc , at the critical point:

$$(V - V_c)^3 = 0$$

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \qquad (A)$$

- Rewriting van der Waals in polynomial:

$$V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0 \qquad (B)$$

- Term-by-term comparison of Eqs. (A) and (B) provides three equations:

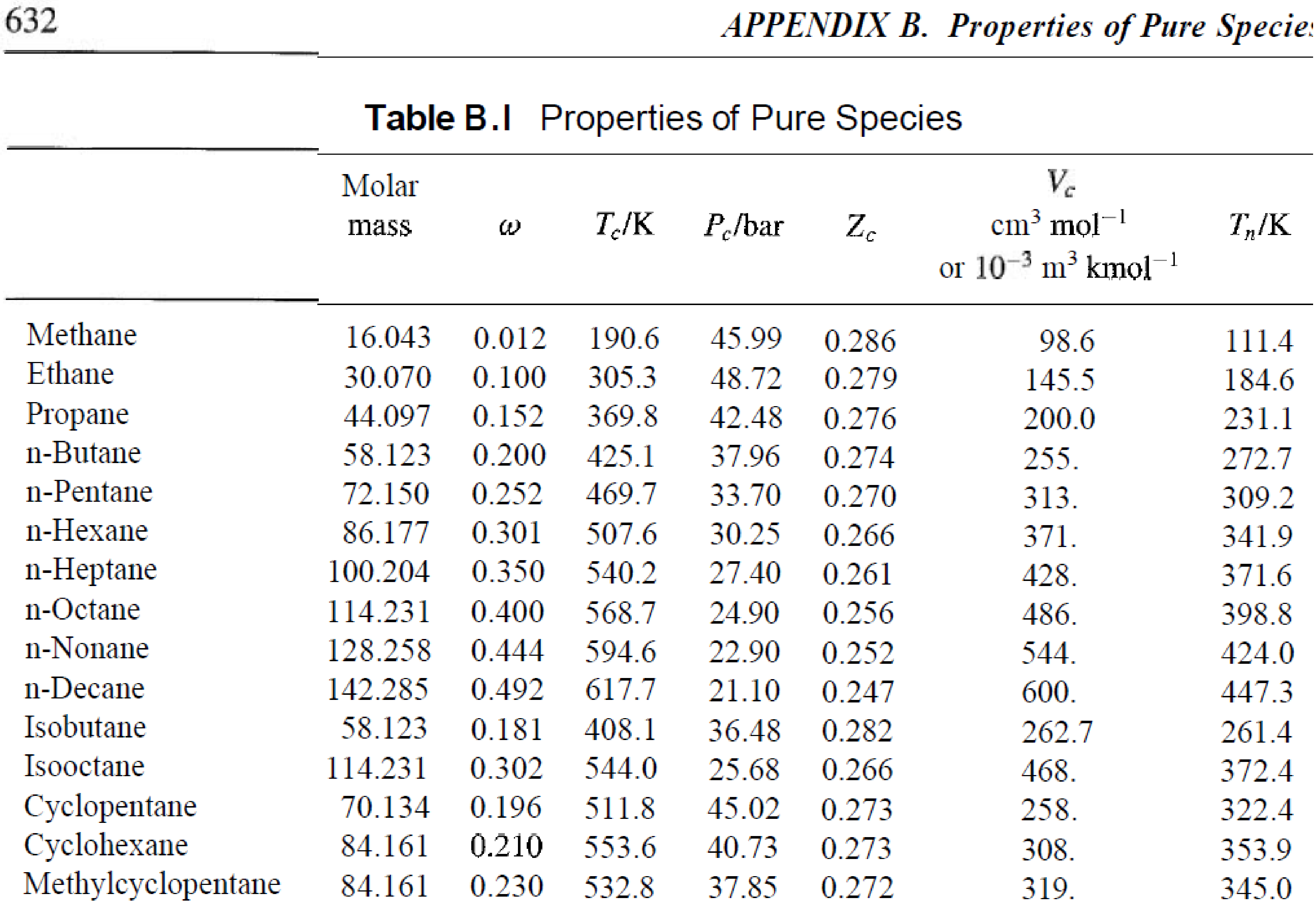
$$3V_c = b + \frac{RT_c}{P_c} \qquad (C)$$

$$3V_c^2 = \frac{a}{P_c} \qquad (D)$$

$$V_c^3 = \frac{ab}{P_c} \qquad (E)$$

- Perform elimination and substitution of Eqs. (C)-(E) to get:

$$V_c = \frac{3}{8}\frac{RT_c}{P_c} \qquad a = \frac{27}{64}\frac{R^2T_c^2}{P_c} \qquad b = \frac{1}{8}\frac{RT_c}{P_c}$$



632 *APPENDIX B. Properties of Pure Specie*

## Table B.I Properties of Pure Species

| | Molar mass | $\omega$ | $T_c$/K | $P_c$/bar | $Z_c$ | $V_c$ cm$^3$ mol$^{-1}$ or $10^{-3}$ m$^3$ kmol$^{-1}$ | $T_n$/K |
|---|---|---|---|---|---|---|---|
| Methane | 16.043 | 0.012 | 190.6 | 45.99 | 0.286 | 98.6 | 111.4 |
| Ethane | 30.070 | 0.100 | 305.3 | 48.72 | 0.279 | 145.5 | 184.6 |
| Propane | 44.097 | 0.152 | 369.8 | 42.48 | 0.276 | 200.0 | 231.1 |
| n-Butane | 58.123 | 0.200 | 425.1 | 37.96 | 0.274 | 255. | 272.7 |
| n-Pentane | 72.150 | 0.252 | 469.7 | 33.70 | 0.270 | 313. | 309.2 |
| n-Hexane | 86.177 | 0.301 | 507.6 | 30.25 | 0.266 | 371. | 341.9 |
| n-Heptane | 100.204 | 0.350 | 540.2 | 27.40 | 0.261 | 428. | 371.6 |
| n-Octane | 114.231 | 0.400 | 568.7 | 24.90 | 0.256 | 486. | 398.8 |
| n-Nonane | 128.258 | 0.444 | 594.6 | 22.90 | 0.252 | 544. | 424.0 |
| n-Decane | 142.285 | 0.492 | 617.7 | 21.10 | 0.247 | 600. | 447.3 |
| Isobutane | 58.123 | 0.181 | 408.1 | 36.48 | 0.282 | 262.7 | 261.4 |
| Isooctane | 114.231 | 0.302 | 544.0 | 25.68 | 0.266 | 468. | 372.4 |
| Cyclopentane | 70.134 | 0.196 | 511.8 | 45.02 | 0.273 | 258. | 322.4 |
| Cyclohexane | 84.161 | 0.210 | 553.6 | 40.73 | 0.273 | 308. | 353.9 |
| Methylcyclopentane | 84.161 | 0.230 | 532.8 | 37.85 | 0.272 | 319. | 345.0 |

See the Appendix B for more species…..

# Parameters of generic cubic EOS

$$\boxed{P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)}}$$

Where $\boxed{a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c}}$ $\boxed{b = \Omega \frac{RT_c}{P_c}}$

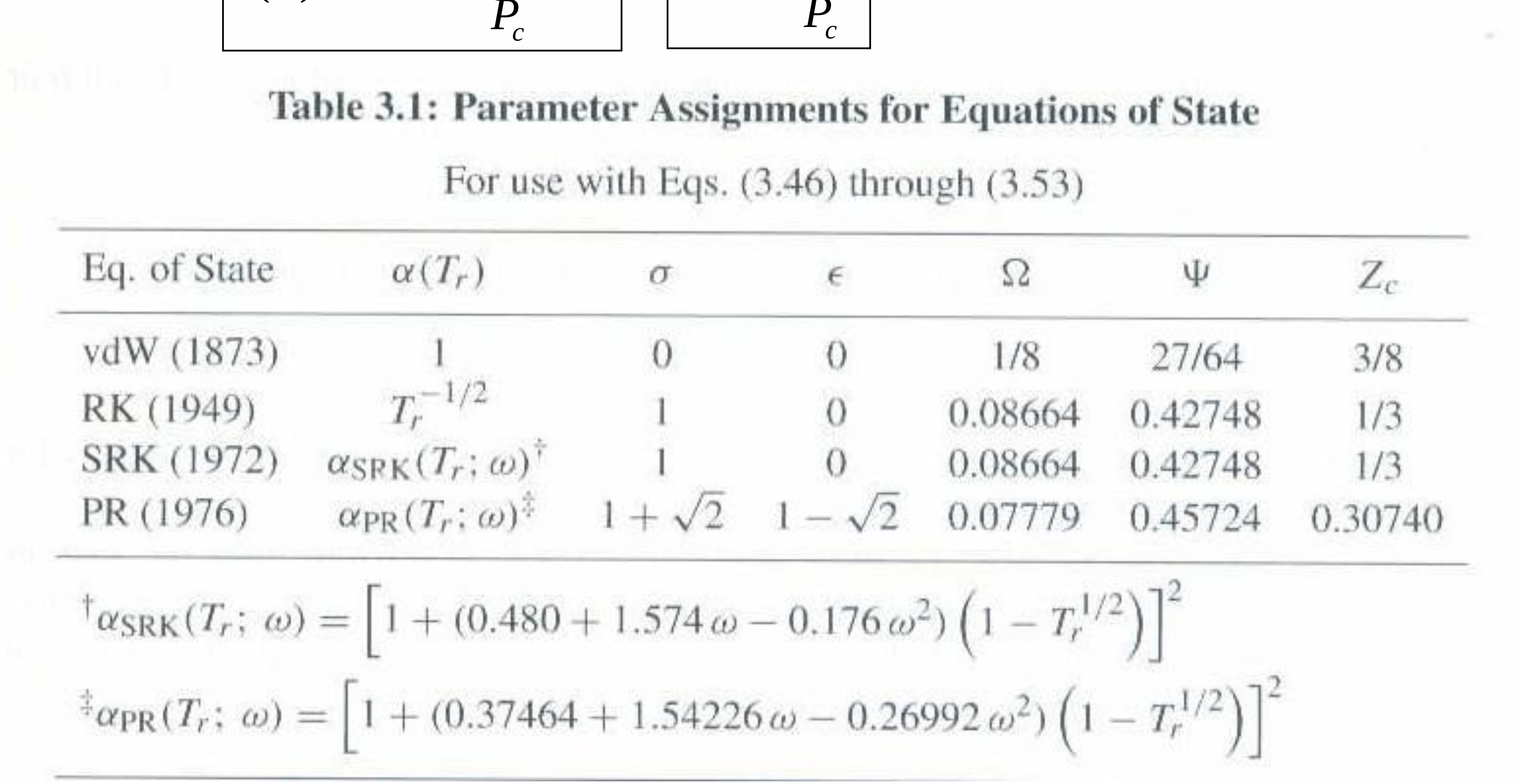


**Table 3.1: Parameter Assignments for Equations of State**

For use with Eqs. (3.46) through (3.53)

| Eq. of State | $\alpha(T_r)$ | $\sigma$ | $\epsilon$ | $\Omega$ | $\Psi$ | $Z_c$ |
|---|---|---|---|---|---|---|
| vdW (1873) | 1 | 0 | 0 | 1/8 | 27/64 | 3/8 |
| RK (1949) | $T_r^{-1/2}$ | 1 | 0 | 0.08664 | 0.42748 | 1/3 |
| SRK (1972) | $\alpha_{SRK}(T_r;\omega)^\dagger$ | 1 | 0 | 0.08664 | 0.42748 | 1/3 |
| PR (1976) | $\alpha_{PR}(T_r;\omega)^\ddagger$ | $1+\sqrt{2}$ | $1-\sqrt{2}$ | 0.07779 | 0.45724 | 0.30740 |

$^\dagger\alpha_{SRK}(T_r;\,\omega) = \left[1 + (0.480 + 1.574\,\omega - 0.176\,\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$

$^\ddagger\alpha_{PR}(T_r;\,\omega) = \left[1 + (0.37464 + 1.54226\,\omega - 0.26992\,\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$

# Parameters of generic cubic EOS

In Table 3.1

- vwd: van der Waals equation
- RK: Redlich/Kwong equation
- SRK:Soave/Redlich/Kwong (SRK) equation
- PR: Peng/Robinson (PR) equation

# Two-parameter and three-parameter theorems of corresponding states

- Two-parameter theorem: all fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree.
- Define reduced temperature and reduced pressure: $T_r \equiv \frac{T}{T_c} \qquad P_r \equiv \frac{P}{P_c}$
- Not really enough to describe the state, a third corresponding-states parameter is required.
  - The most popular such parameter is the acentric factor (K.S. Pitzer, 1995):

$$\omega \equiv -1.0 - \log\left(P_r^{sat}\right)_{T_r=0.7}$$

- Three-parameter theorem: all fluids having the same value of ω, when compared at the same reduced temperature and reduced pressure, and all deviate from ideal-gas behavior to about the same degree.

# 2-parameter/3-parameter EOS

- Express Z as functions of $T_r$ and $P_r$ only, yield 2-parameter corresponding states correlations:
  - The van der Waals equation
  - The Redlich/Kwong equation
- The acentric factor enters through function $\alpha(T_r;\omega)$ as an additional paramter, yield 3-parameter corresponding state correlations:
  - The Soave/Redlich/Kwong (SRK) equation
  - The Peng/Robinson (PR) equation

- **Vapor & Vapor-Like Roots of the Generic Cubic EOS**

$$\boxed{P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)}}$$

- Multiply the Eq. by (V-b) and divide it by P:

$$V - b = \frac{RT}{P} - \frac{a(T)}{P(V+\varepsilon b)(V+\sigma b)}$$

- Rearrange the Eq. as:

$$\boxed{V = \frac{RT}{P} + b - \frac{a(T)}{P}\frac{V-b}{(V+\varepsilon b)(V+\sigma b)}}$$

**start with V(ideal-gas) and then iterate**

- The Z equation multiply by P and divide by RT is:

$$\boxed{Z = 1 + \beta - q\beta\frac{Z-\beta}{(Z+\varepsilon\beta)(Z+\sigma\beta)}}$$

$$\boxed{q \equiv \frac{a(T)}{bRT} = \frac{\Psi\alpha(T_r)}{\Omega T_r}} \qquad \boxed{\beta \equiv \frac{bP}{RT} = \Omega\frac{P_r}{T_r}}$$

**start with Z=1 and then iterate**

**Remark.** Equations of state which express Z as a function of $T_r$ and $P_r$ are said to be generalized, because of their general applicability of all gases and liquids.

## • Liquid & Liquid-Like Roots of the Generic Cubic EOS

$$\boxed{V=\frac{RT}{P}+b-\frac{a(T)}{P}\frac{V-b}{(V+\varepsilon b)(V+\sigma b)}}$$

- Rearrage the Eq. as:

$$\boxed{\frac{V-b}{(V+\varepsilon b)(V+\sigma b)}=\frac{P}{a(T)}\left[\frac{RT}{P}+b-V\right]}$$

- Rearrange the Eq. as:

$$\boxed{V=b+(V+\varepsilon b)(V+\sigma b)\frac{P}{a(T)}\left[\frac{RT}{P}+b-V\right]}$$

**start with V=b and then iterate**

- The Z equation (multiply by P and divide by RT) is:

$$\boxed{Z=\beta+(Z+\varepsilon\beta)(Z+\sigma\beta)\left(\frac{1+\beta-Z}{q\beta}\right)}$$

**start with Z=$\beta$ and then iterate**

$$\boxed{q\equiv\frac{a(T)}{bRT}=\frac{\Psi\alpha(T_r)}{\Omega T_r}} \qquad \boxed{\beta\equiv\frac{bP}{RT}=\Omega\frac{P_r}{T_r}}$$

**Example 3.9.** Given that the vapor pressure of n-butane at 350K is 9.4573 bar, find the molar volumes of (1) saturated-vapor and (2) saturated-liquid n-butane at these conditions as given by the Redlich/Kwong equation.

---

$$T_r = \frac{350}{425.1} = 0.823 \qquad P_r = \frac{9.4573}{37.96} = 0.2491$$

$$q = \frac{\Psi \alpha(T_r)}{\Omega T_r} = 6.6048 \qquad \beta = \Omega \frac{P_r}{T_r} = 0.026214$$

(1) The saturated vapor

$$\boxed{Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \varepsilon\beta)(Z + \sigma\beta)}} \rightarrow \text{Z starts at Z = 1 and converges on Z = 0.8305}$$

$$\boxed{V = \frac{ZRT}{P} = 2555 \frac{cm^3}{mol}}$$

(2) The saturated liquid

$$\boxed{Z = \beta + (Z + \varepsilon\beta)(Z + \sigma\beta)\left(\frac{1 + \beta - Z}{q\beta}\right)} \rightarrow \text{Z starts at Z = } \beta \text{ and converges on Z = 0.04331}$$

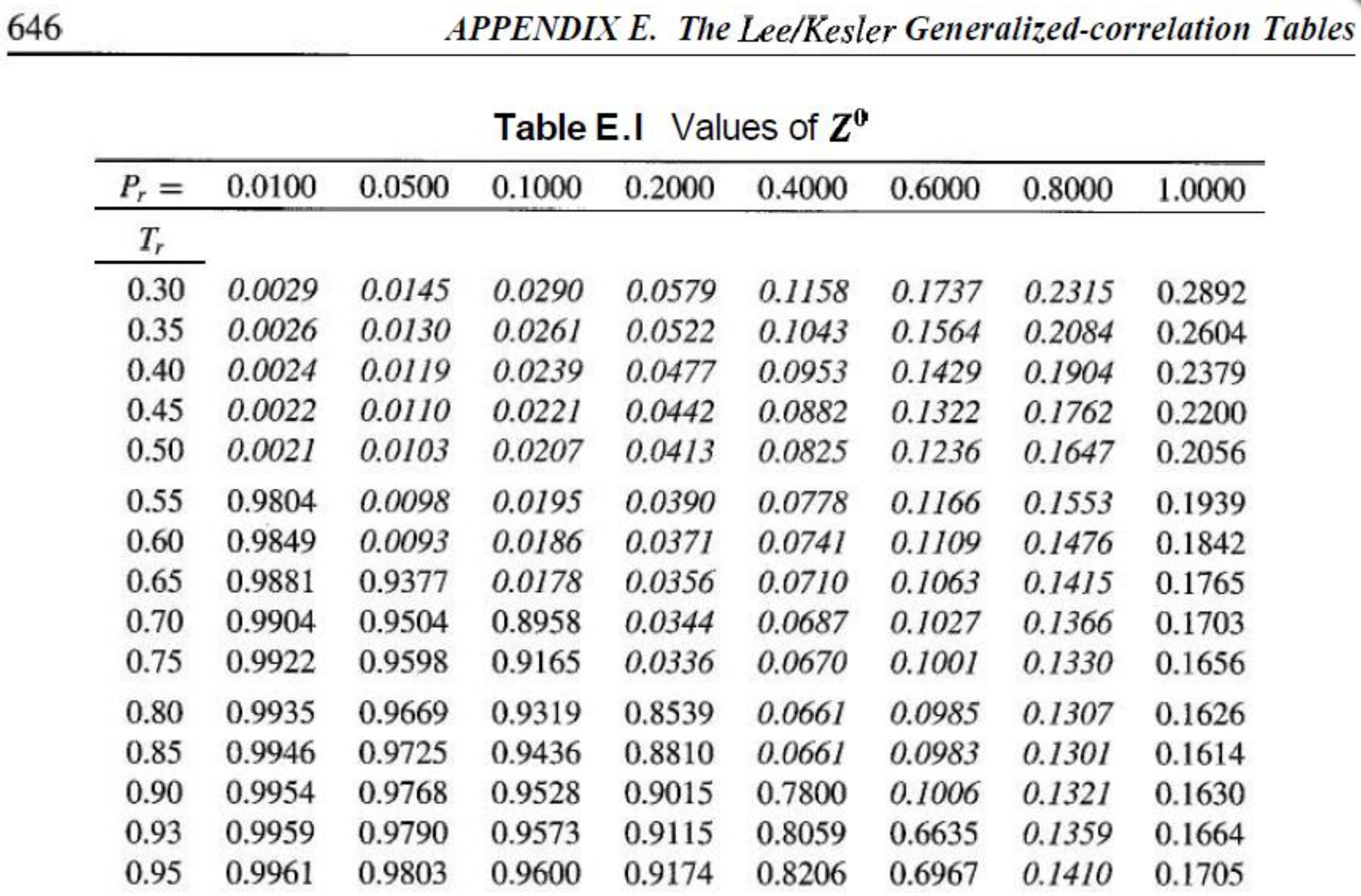
$$\boxed{V = \frac{ZRT}{P} = 133.3 \frac{cm^3}{mol}}$$

# Generalized correlations for gases

- Pitzer correlations for the compressibility factor:

$$\boxed{Z = Z^0 + \omega Z^1}$$

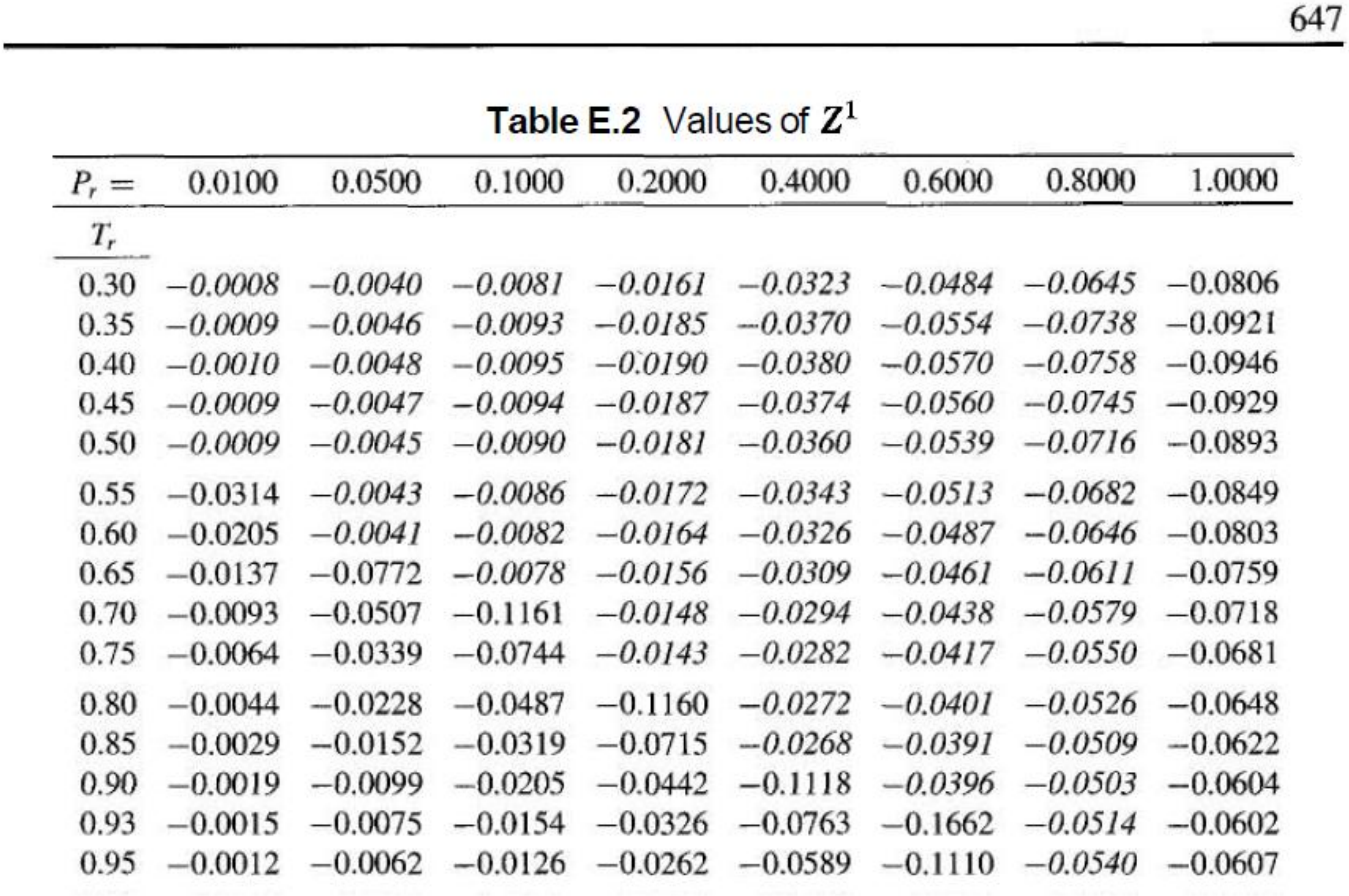
  - $Z^0 = F^0\ (T_r, P_r)$
  - Simple linear relation between Z and ω for given values of $T_r$ and $P_r$.
  - Of the Pitzer-type correlations available, the Lee/Kesler correlation provides reliable results for gases which are nonpolar or only slightly polar (App. E).
  - Only tabular nature (disadvantage)


646 *APPENDIX E. The Lee/Kesler Generalized-correlation Tables*

### Table E.1 Values of $Z^0$

| $P_r =$<br>$T_r$ | 0.0100 | 0.0500 | 0.1000 | 0.2000 | 0.4000 | 0.6000 | 0.8000 | 1.0000 |
|---|---|---|---|---|---|---|---|---|
| 0.30 | *0.0029* | *0.0145* | *0.0290* | *0.0579* | *0.1158* | *0.1737* | *0.2315* | 0.2892 |
| 0.35 | *0.0026* | *0.0130* | *0.0261* | *0.0522* | *0.1043* | *0.1564* | *0.2084* | 0.2604 |
| 0.40 | *0.0024* | *0.0119* | *0.0239* | *0.0477* | *0.0953* | *0.1429* | *0.1904* | 0.2379 |
| 0.45 | *0.0022* | *0.0110* | *0.0221* | *0.0442* | *0.0882* | *0.1322* | *0.1762* | 0.2200 |
| 0.50 | *0.0021* | *0.0103* | *0.0207* | *0.0413* | *0.0825* | *0.1236* | *0.1647* | 0.2056 |
| 0.55 | 0.9804 | *0.0098* | *0.0195* | *0.0390* | *0.0778* | *0.1166* | *0.1553* | 0.1939 |
| 0.60 | 0.9849 | *0.0093* | *0.0186* | *0.0371* | *0.0741* | *0.1109* | *0.1476* | 0.1842 |
| 0.65 | 0.9881 | 0.9377 | *0.0178* | *0.0356* | *0.0710* | *0.1063* | *0.1415* | 0.1765 |
| 0.70 | 0.9904 | 0.9504 | 0.8958 | *0.0344* | *0.0687* | *0.1027* | *0.1366* | 0.1703 |
| 0.75 | 0.9922 | 0.9598 | 0.9165 | *0.0336* | *0.0670* | *0.1001* | *0.1330* | 0.1656 |
| 0.80 | 0.9935 | 0.9669 | 0.9319 | 0.8539 | *0.0661* | *0.0985* | *0.1307* | 0.1626 |
| 0.85 | 0.9946 | 0.9725 | 0.9436 | 0.8810 | *0.0661* | *0.0983* | *0.1301* | 0.1614 |
| 0.90 | 0.9954 | 0.9768 | 0.9528 | 0.9015 | 0.7800 | *0.1006* | *0.1321* | 0.1630 |
| 0.93 | 0.9959 | 0.9790 | 0.9573 | 0.9115 | 0.8059 | 0.6635 | *0.1359* | 0.1664 |
| 0.95 | 0.9961 | 0.9803 | 0.9600 | 0.9174 | 0.8206 | 0.6967 | *0.1410* | 0.1705 |

See the Appendix E for higher $T_r$



### Table E.2 Values of $Z^1$

| $P_r =$ <br> $T_r$ | 0.0100 | 0.0500 | 0.1000 | 0.2000 | 0.4000 | 0.6000 | 0.8000 | 1.0000 |
|---|---|---|---|---|---|---|---|---|
| 0.30 | −0.0008 | −0.0040 | −0.0081 | −0.0161 | −0.0323 | −0.0484 | −0.0645 | −0.0806 |
| 0.35 | −0.0009 | −0.0046 | −0.0093 | −0.0185 | −0.0370 | −0.0554 | −0.0738 | −0.0921 |
| 0.40 | −0.0010 | −0.0048 | −0.0095 | −0.0190 | −0.0380 | −0.0570 | −0.0758 | −0.0946 |
| 0.45 | −0.0009 | −0.0047 | −0.0094 | −0.0187 | −0.0374 | −0.0560 | −0.0745 | −0.0929 |
| 0.50 | −0.0009 | −0.0045 | −0.0090 | −0.0181 | −0.0360 | −0.0539 | −0.0716 | −0.0893 |
| 0.55 | −0.0314 | −0.0043 | −0.0086 | −0.0172 | −0.0343 | −0.0513 | −0.0682 | −0.0849 |
| 0.60 | −0.0205 | −0.0041 | −0.0082 | −0.0164 | −0.0326 | −0.0487 | −0.0646 | −0.0803 |
| 0.65 | −0.0137 | −0.0772 | −0.0078 | −0.0156 | −0.0309 | −0.0461 | −0.0611 | −0.0759 |
| 0.70 | −0.0093 | −0.0507 | −0.1161 | −0.0148 | −0.0294 | −0.0438 | −0.0579 | −0.0718 |
| 0.75 | −0.0064 | −0.0339 | −0.0744 | −0.0143 | −0.0282 | −0.0417 | −0.0550 | −0.0681 |
| 0.80 | −0.0044 | −0.0228 | −0.0487 | −0.1160 | −0.0272 | −0.0401 | −0.0526 | −0.0648 |
| 0.85 | −0.0029 | −0.0152 | −0.0319 | −0.0715 | −0.0268 | −0.0391 | −0.0509 | −0.0622 |
| 0.90 | −0.0019 | −0.0099 | −0.0205 | −0.0442 | −0.1118 | −0.0396 | −0.0503 | −0.0604 |
| 0.93 | −0.0015 | −0.0075 | −0.0154 | −0.0326 | −0.0763 | −0.1662 | −0.0514 | −0.0602 |
| 0.95 | −0.0012 | −0.0062 | −0.0126 | −0.0262 | −0.0589 | −0.1110 | −0.0540 | −0.0607 |

See the Appendix E for higher $T_r$

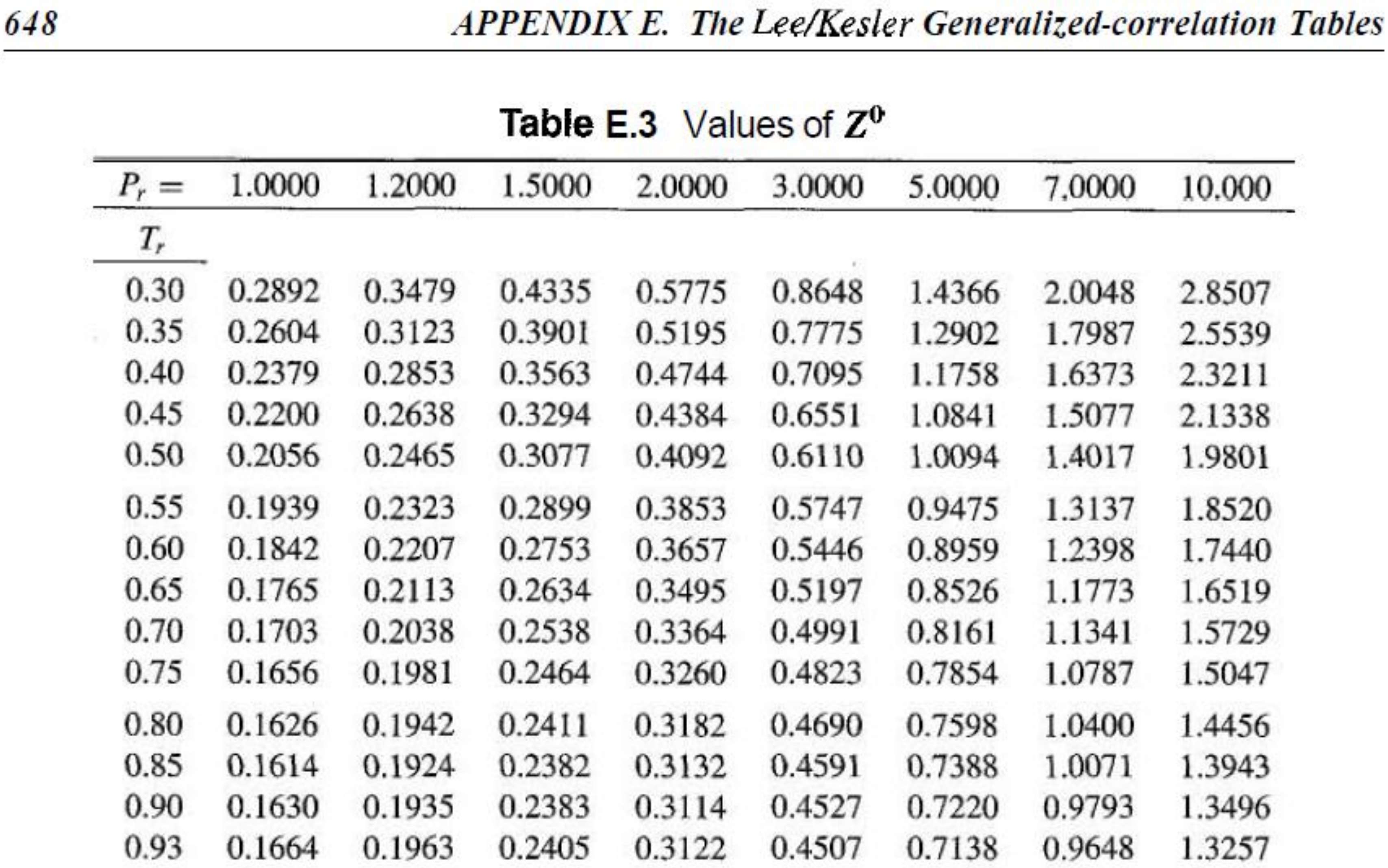


**Table E.3** Values of $Z^0$

| $P_r =$ <br> $T_r$ | 1.0000 | 1.2000 | 1.5000 | 2.0000 | 3.0000 | 5.0000 | 7.0000 | 10.000 |
|---|---|---|---|---|---|---|---|---|
| 0.30 | 0.2892 | 0.3479 | 0.4335 | 0.5775 | 0.8648 | 1.4366 | 2.0048 | 2.8507 |
| 0.35 | 0.2604 | 0.3123 | 0.3901 | 0.5195 | 0.7775 | 1.2902 | 1.7987 | 2.5539 |
| 0.40 | 0.2379 | 0.2853 | 0.3563 | 0.4744 | 0.7095 | 1.1758 | 1.6373 | 2.3211 |
| 0.45 | 0.2200 | 0.2638 | 0.3294 | 0.4384 | 0.6551 | 1.0841 | 1.5077 | 2.1338 |
| 0.50 | 0.2056 | 0.2465 | 0.3077 | 0.4092 | 0.6110 | 1.0094 | 1.4017 | 1.9801 |
| 0.55 | 0.1939 | 0.2323 | 0.2899 | 0.3853 | 0.5747 | 0.9475 | 1.3137 | 1.8520 |
| 0.60 | 0.1842 | 0.2207 | 0.2753 | 0.3657 | 0.5446 | 0.8959 | 1.2398 | 1.7440 |
| 0.65 | 0.1765 | 0.2113 | 0.2634 | 0.3495 | 0.5197 | 0.8526 | 1.1773 | 1.6519 |
| 0.70 | 0.1703 | 0.2038 | 0.2538 | 0.3364 | 0.4991 | 0.8161 | 1.1341 | 1.5729 |
| 0.75 | 0.1656 | 0.1981 | 0.2464 | 0.3260 | 0.4823 | 0.7854 | 1.0787 | 1.5047 |
| 0.80 | 0.1626 | 0.1942 | 0.2411 | 0.3182 | 0.4690 | 0.7598 | 1.0400 | 1.4456 |
| 0.85 | 0.1614 | 0.1924 | 0.2382 | 0.3132 | 0.4591 | 0.7388 | 1.0071 | 1.3943 |
| 0.90 | 0.1630 | 0.1935 | 0.2383 | 0.3114 | 0.4527 | 0.7220 | 0.9793 | 1.3496 |
| 0.93 | 0.1664 | 0.1963 | 0.2405 | 0.3122 | 0.4507 | 0.7138 | 0.9648 | 1.3257 |

See the Appendix E for higher $T_r$

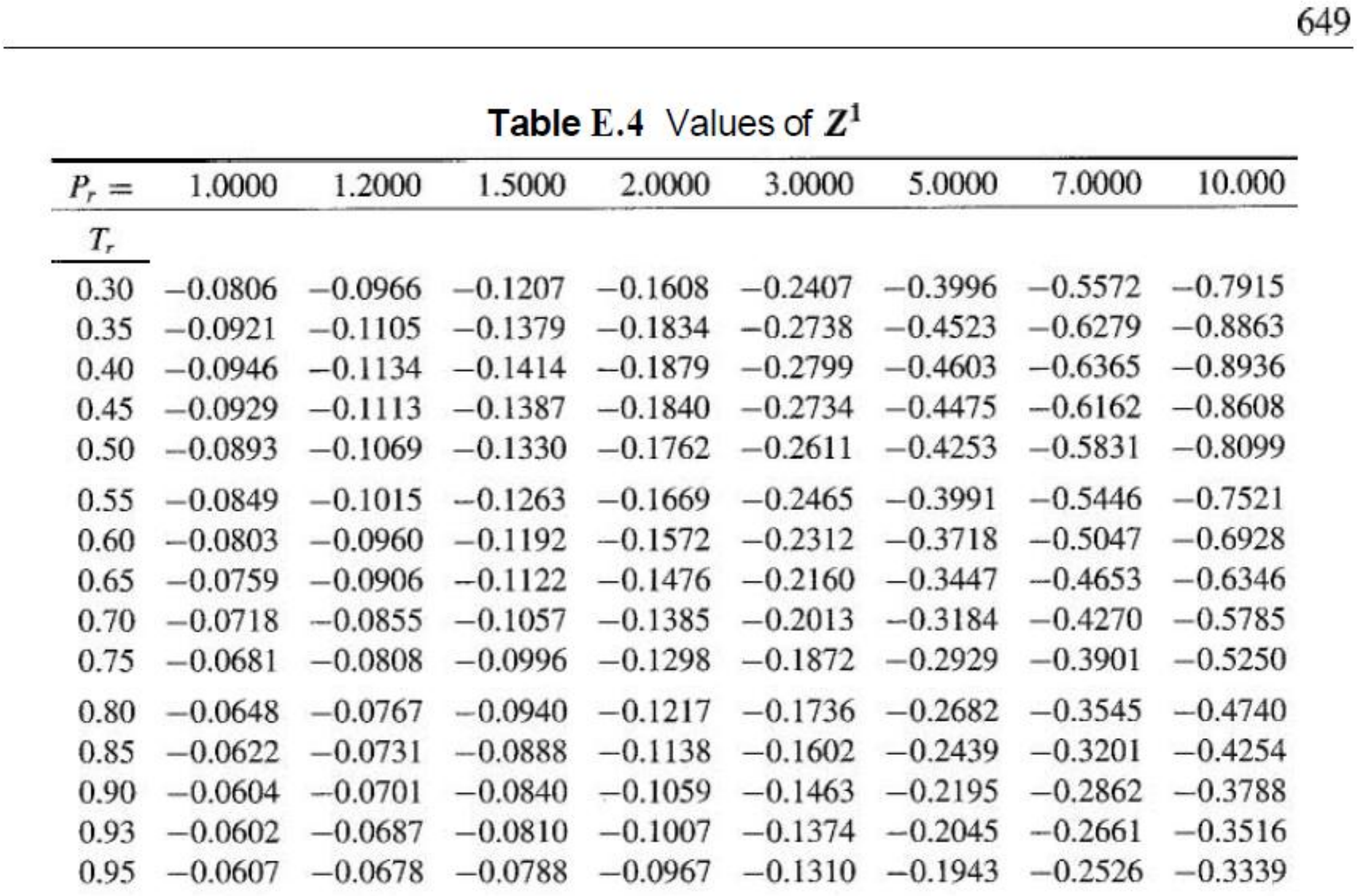


Table E.4 Values of $Z^1$

| $P_r =$ <br> $T_r$ | 1.0000 | 1.2000 | 1.5000 | 2.0000 | 3.0000 | 5.0000 | 7.0000 | 10.000 |
|---|---|---|---|---|---|---|---|---|
| 0.30 | −0.0806 | −0.0966 | −0.1207 | −0.1608 | −0.2407 | −0.3996 | −0.5572 | −0.7915 |
| 0.35 | −0.0921 | −0.1105 | −0.1379 | −0.1834 | −0.2738 | −0.4523 | −0.6279 | −0.8863 |
| 0.40 | −0.0946 | −0.1134 | −0.1414 | −0.1879 | −0.2799 | −0.4603 | −0.6365 | −0.8936 |
| 0.45 | −0.0929 | −0.1113 | −0.1387 | −0.1840 | −0.2734 | −0.4475 | −0.6162 | −0.8608 |
| 0.50 | −0.0893 | −0.1069 | −0.1330 | −0.1762 | −0.2611 | −0.4253 | −0.5831 | −0.8099 |
| 0.55 | −0.0849 | −0.1015 | −0.1263 | −0.1669 | −0.2465 | −0.3991 | −0.5446 | −0.7521 |
| 0.60 | −0.0803 | −0.0960 | −0.1192 | −0.1572 | −0.2312 | −0.3718 | −0.5047 | −0.6928 |
| 0.65 | −0.0759 | −0.0906 | −0.1122 | −0.1476 | −0.2160 | −0.3447 | −0.4653 | −0.6346 |
| 0.70 | −0.0718 | −0.0855 | −0.1057 | −0.1385 | −0.2013 | −0.3184 | −0.4270 | −0.5785 |
| 0.75 | −0.0681 | −0.0808 | −0.0996 | −0.1298 | −0.1872 | −0.2929 | −0.3901 | −0.5250 |
| 0.80 | −0.0648 | −0.0767 | −0.0940 | −0.1217 | −0.1736 | −0.2682 | −0.3545 | −0.4740 |
| 0.85 | −0.0622 | −0.0731 | −0.0888 | −0.1138 | −0.1602 | −0.2439 | −0.3201 | −0.4254 |
| 0.90 | −0.0604 | −0.0701 | −0.0840 | −0.1059 | −0.1463 | −0.2195 | −0.2862 | −0.3788 |
| 0.93 | −0.0602 | −0.0687 | −0.0810 | −0.1007 | −0.1374 | −0.2045 | −0.2661 | −0.3516 |
| 0.95 | −0.0607 | −0.0678 | −0.0788 | −0.0967 | −0.1310 | −0.1943 | −0.2526 | −0.3339 |

See the Appendix E for higher $T_r$

# Pitzer correlations for the 2nd virial coefficient

- Correlation: $Z = 1 + \frac{BP}{RT} = 1 + B^0 \frac{P_r}{T_r} + \omega B^1 \frac{P_r}{T_r}$

$$Z = Z^0 + \omega Z^1$$

$$Z^0 = 1 + B^0 \frac{P_r}{T_r}$$

$$Z^1 = B^1 \frac{P_r}{T_r}$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

  - Validity at low to moderate pressures
  - For reduced temperatures greater than $T_r \sim 3$, there appears to be no limitation on the pressure.
  - Simple and recommended.
  - Most accurate for nonpolar species.

**Example 3.10**. Determine the molar volume of n-butane at 510K and 25 bar by, (1) the ideal-gas equation; (2) the generalized compressibility-factor correlation; (3) the generalized virial-coefficient correlation.

---

(1) The ideal-gas equation

$$\boxed{V = \frac{RT}{P} = 1696.1\,\frac{cm^3}{mol}}$$

(2) The generalized compressibility-factor correlation

$$\boxed{T_r = \frac{510}{425.1} = 1.200} \quad \boxed{P_r = \frac{25}{37.96} = 0.659} \quad \xrightarrow[\textbf{Table B1}]{\text{the acentric factor}} \quad \boxed{\omega = 0.200}$$

the Lee/Kesler correlation ↓ Tables E1 and E2:

$$\boxed{Z^0 = 0.865} \quad \boxed{Z^1 = 0.038} \rightarrow \boxed{Z = Z^0 + \omega Z^1 = 0.873} \boxed{V = \frac{ZRT}{P} = 1480.7\,\frac{cm^3}{mol}}$$

(3) The generalized virial-coefficient correlation

$$\boxed{T_r = \frac{510}{425.1} = 1.200} \boxed{B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}} \boxed{B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}}$$

$$\boxed{Z = 1 + B^0 \frac{P_r}{T_r} + \omega B^1 \frac{P_r}{T_r} = 0.879} \quad \boxed{V = \frac{ZRT}{P} = 1489.1\,\frac{cm^3}{mol}}$$

**Example 3.11.** What pressure is generated when 1 (lb mol) of methane is stored in a volume of 2 (ft)$^3$ at 122°F using (1) the ideal-gas equation; (2) the Redlish/Kwong equation; (3) a generalized correlation .

(1) The ideal-gas equation

$$\boxed{P=\frac{RT}{V}=\frac{0.7302(122+459.67)}{2}=212.4\ atm}$$

(2) The RK equation

$$\boxed{T_r=\frac{581.67}{343.1}=1.695} \quad \boxed{a(T)=\Psi\frac{\alpha(T_r)R^2T_c^2}{P_c}=453.94\ \frac{atm}{ft^6}} \quad \boxed{b=\Omega\frac{RT_c}{P_c}=0.4781\ ft^3}$$

$$\boxed{P=\frac{RT}{V-b}-\frac{a(T)}{V(V+b)}=187.49\ atm}$$

(3) The generalized compressibility-factor correlation is chosen (high pressure)

$$\boxed{P=\frac{ZRT}{V}=\frac{Z(0.7302)(122+459.67)}{2}=212.4Z\ atm}$$

$$\boxed{P_r=\frac{P}{45.4}=\frac{Z}{0.2138}} \quad \boxed{T_r=\frac{581.67}{343.1}=1.695} \longrightarrow$$

Initial guess: Z = 1 and iterate to converge to Z = 0.890

$$\boxed{P=189.0\ atm}$$

the Lee/Kesler correlation

**Tables E1 and E2:**

**Example 3.12.** A mass of 500 g of gases ammonia is contained in a 30000 $cm^3$ vessel immersed in a constant-temperature bath at 65°C. Calculate the pressure of the gas by (1) the ideal-gas equation; (2) a generalized correlation .

$$\boxed{V=\frac{V^t}{n}=1021.2\,\frac{cm^3}{mol}}$$

(1) The ideal-gas equation

$$\boxed{P=\frac{RT}{V}=27.53\,bar}$$

(2) The generalized virial-coefficient correlation is chosen (low pressure, $P_r \sim 3$ )

$$\boxed{T_r=\frac{338.15}{405.7}=0.834} \longrightarrow \boxed{B^0=0.083-\frac{0.422}{T_r^{1.6}}} \quad \boxed{B^1=0.139-\frac{0.172}{T_r^{4.2}}}$$

$$\boxed{P_r\sim\frac{27.53}{112.8}=0.244}$$

the acentric factor

$$\boxed{\omega=0.253}$$

$$\boxed{Z=1+\left(B^0+\omega B^1\right)\frac{P_r}{T_r}=1-0.541\frac{P_r}{T_r}}$$

$$\boxed{P=\frac{ZRT}{V}=23.76\,bar}$$

# Generalized correlations for liquids

- The generalized cubic equation of state (low accuracy)
- The Lee/Kesler correlation includes data for subcooled liquids
  - Suitable for nonpolar and slightly polar fluids
- Estimation of molar volumes of saturated liquids
  - Rackett, 1970: $\boxed{V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}}$
- Generalized density correlation for liquid (Lydersen, Greenkorn, and Hougen, 1955): $\boxed{\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V}}$

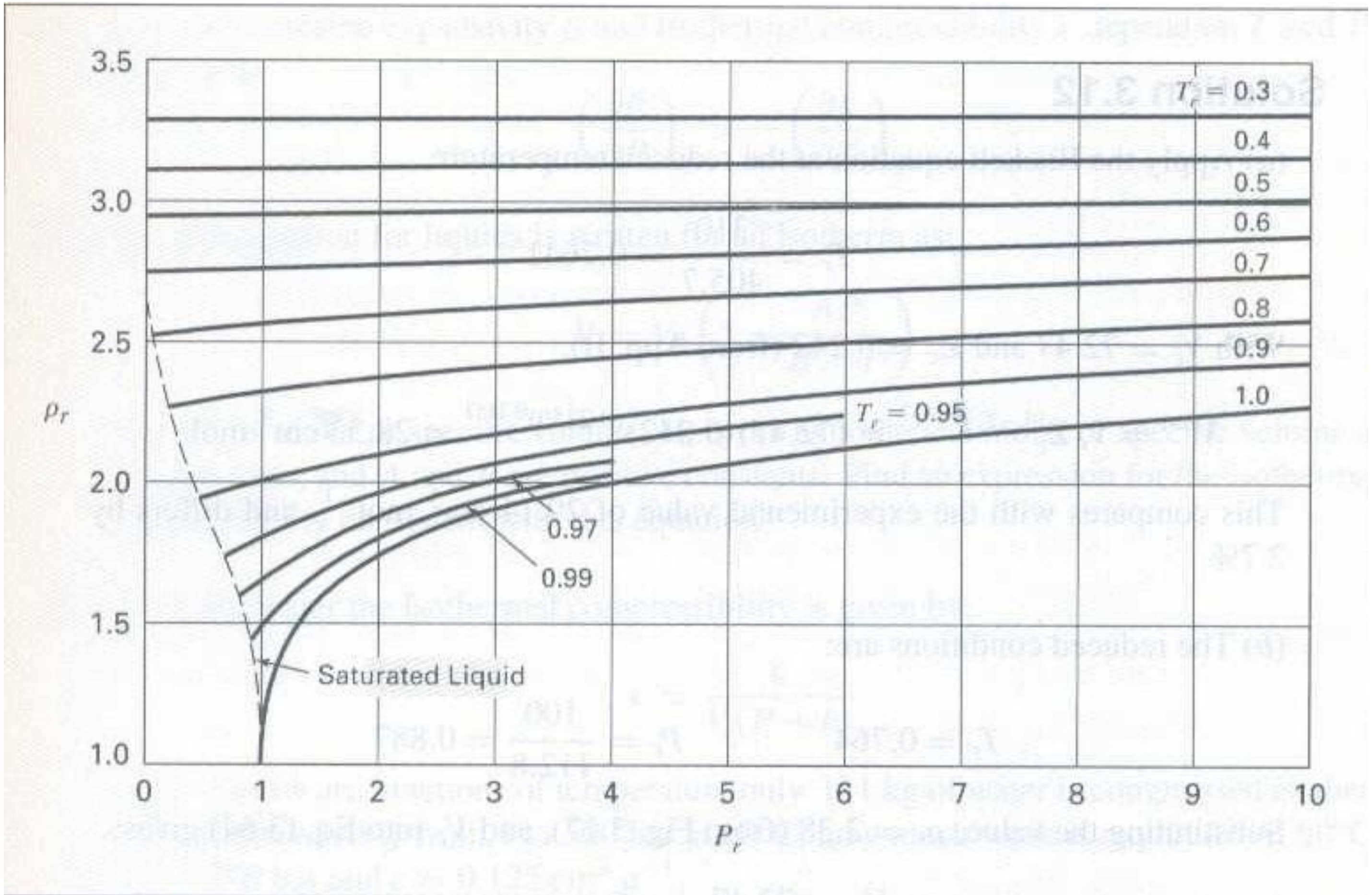


Fig 3.17

$$\boxed{V_2 = V_1 \frac{\rho_{r1}}{\rho_{r2}}}$$

**Example 3.13.** For ammonia at 310 K, estimate the density of (1) the saturated liquid; (2) the liquid at 100 bar

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(1) Apply the Rackett equation at the reduced temperature

$$\boxed{T_r = \frac{310}{405.7} = 0.7641} \quad \boxed{V_c = 72.47} \quad \boxed{Z_c = 0.242}$$

$$\boxed{V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}} = 28.33 \frac{cm^3}{mol}}$$

the experimental value is 29.14 cm$^3$ mol$^{-1}$

(2) At 100 bar

$$\boxed{P_r = \frac{100}{112.8} = 0.887}$$

$$\boxed{T_r = \frac{310}{405.7} = 0.7641}$$

$$\xrightarrow{\text{Fig 3.17}} \quad \boxed{\rho_r = 2.38} \quad \boxed{V = \frac{V_c}{\rho_r} = 30.45 \frac{cm^3}{mol}}$$

the experimental value of 28.6 cm$^3$ mol$^{-1}$,