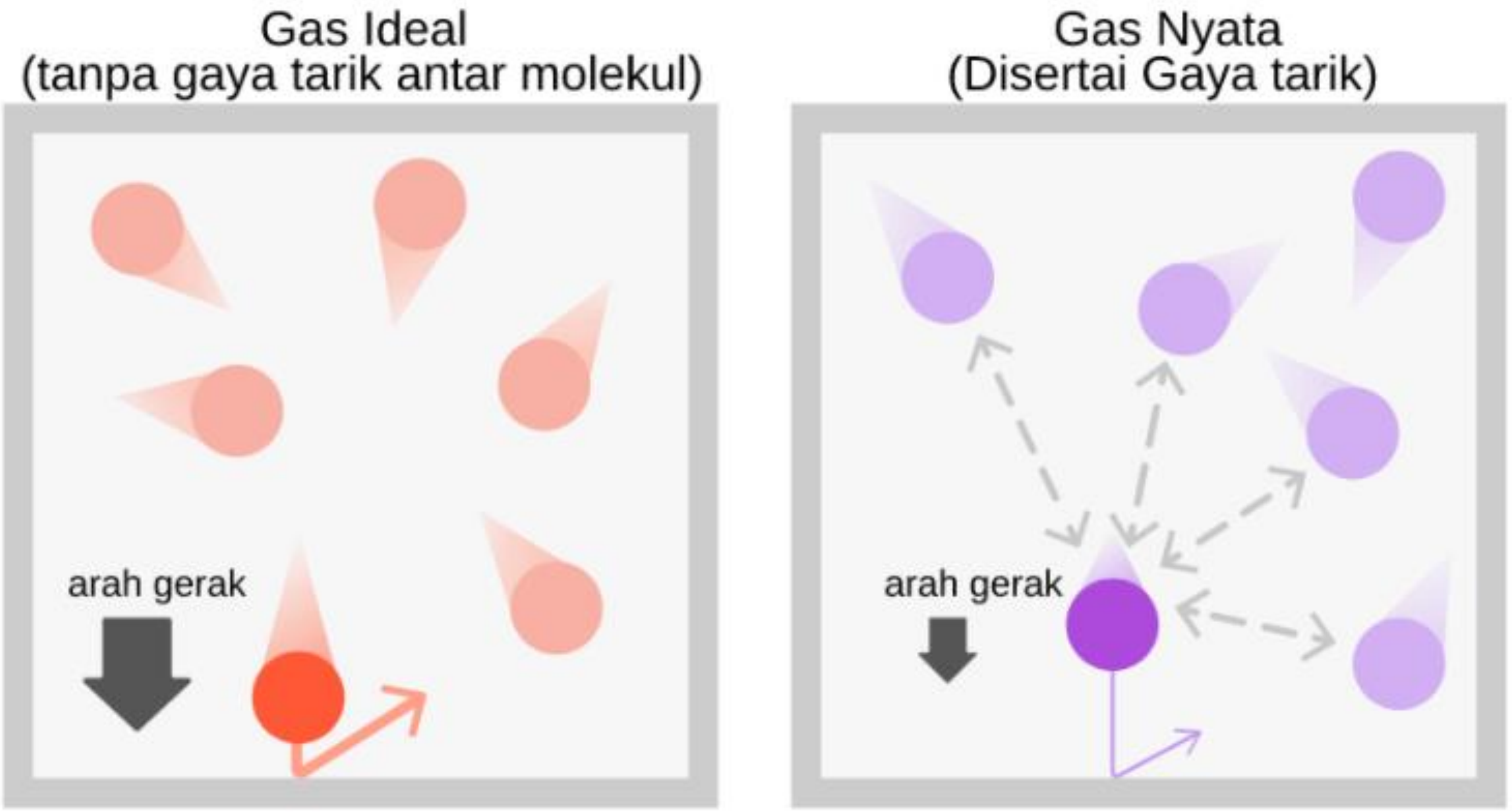
SIFAT VOLUMETRIK FLUIDA MURNI

Bagian 2

Perbedaan gas ideal dan gas nyata



Gas nyata / non ideal

$$\bar{V}_{id} = \frac{RT}{P}$$

$$Z = \frac{\bar{V}}{\bar{V}_{id}} = \frac{P\bar{V}}{RT}$$

Z = PV/RT

Z ≠ 1 (Z = faktor kompresibilitas, 0,6-2,2)

Gas nyata / non ideal

EOS untuk gas non ideal:

1. Bentuk Virial

   a. $$Z = 1 + B'P + C'P^2 + D'P^3 + \ldots$$

   b. $$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots$$

B', C', D' dst dan B, C, D dst : koefisien virial

2. Bentuk Kubik (Cubic EOS) (Pangkat Tiga)

a.l.

- Persamaan Van der Waals :

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

Dalam bentuk polinomial :

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

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

Tc = suhu kritik (App. B SVNA 8th ed.)

Pc = tekanan kritik

❑Persamaan Redlich-Kwong

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

$$a = 0,42748\,\frac{R^2 T_c^{2,5}}{P_c} \qquad\qquad b = 0,08664\,\frac{RT_c}{P_c}$$

↓ ↓

(Pada Tabel 3.1. buku SVNA merupakan parameter ψ dan Ω)

❑Persamaan Soave-Redlich-Kwong

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

$$a(T) = a_c \cdot \alpha(T)$$

$$b = 0{,}08664\,\frac{RT}{P_c}$$

$$a(T_c) = a_c = 0{,}42748\,\frac{(RT_c)^2}{P_c}$$

$$T_r = \frac{T}{T_c}$$

$$\alpha(T) = \left(1 + m\left(1 - \sqrt{T_r}\right)\right)^2$$

$$m = 0{,}480 + 1{,}574\omega - 0{,}176\omega^2$$

ω = acentric factor (lihat tabel B1 appendix SVNA) → faktor bentuk molekul seberapa dekat dengan bentuk bola

- Pers. bentuk kubik lain masih banyak lagi, tetapi cukup 3 pers. di atas sebagai contoh.
- Persamaan bentuk kubik membentuk kurva sbb:

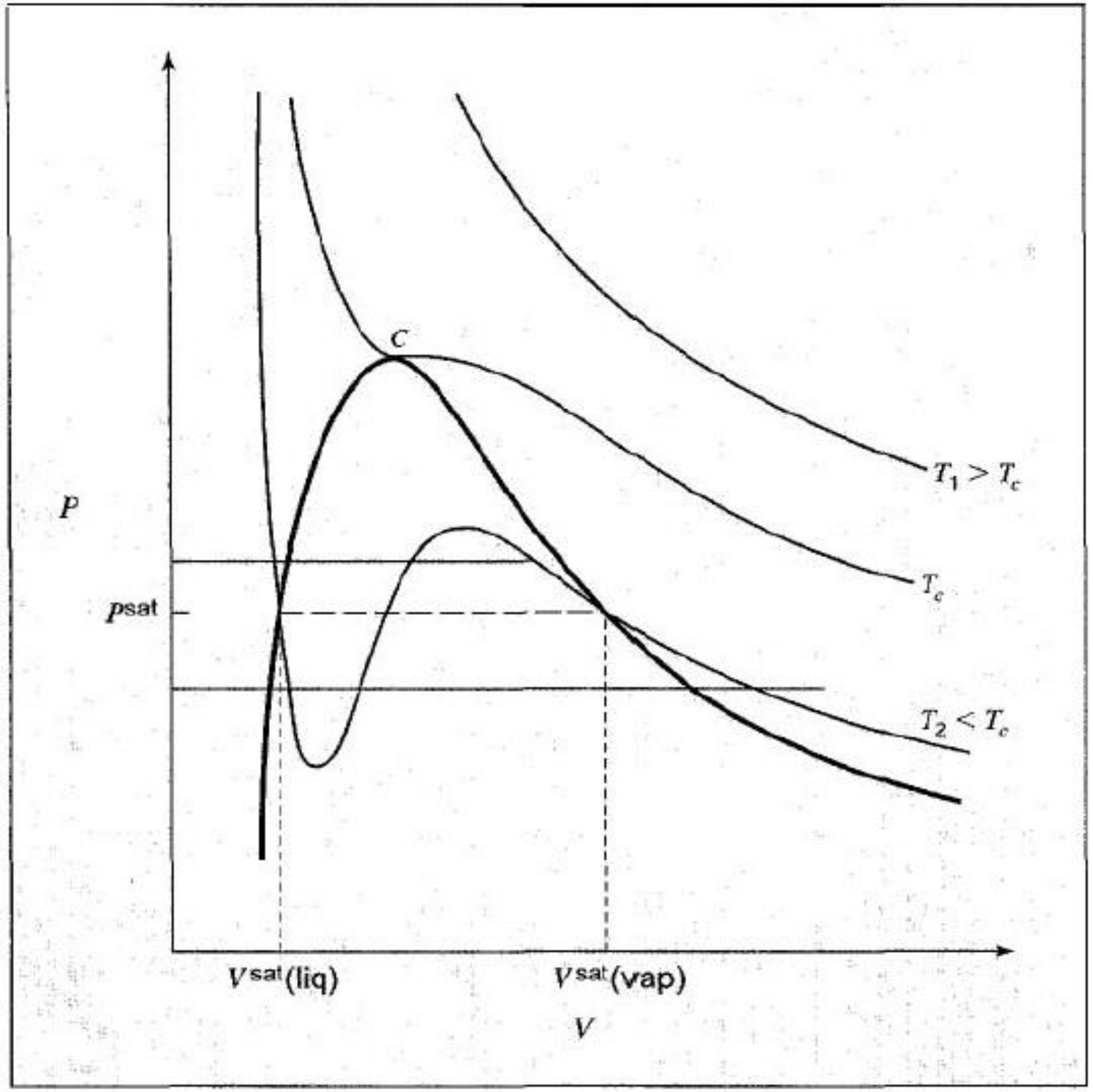
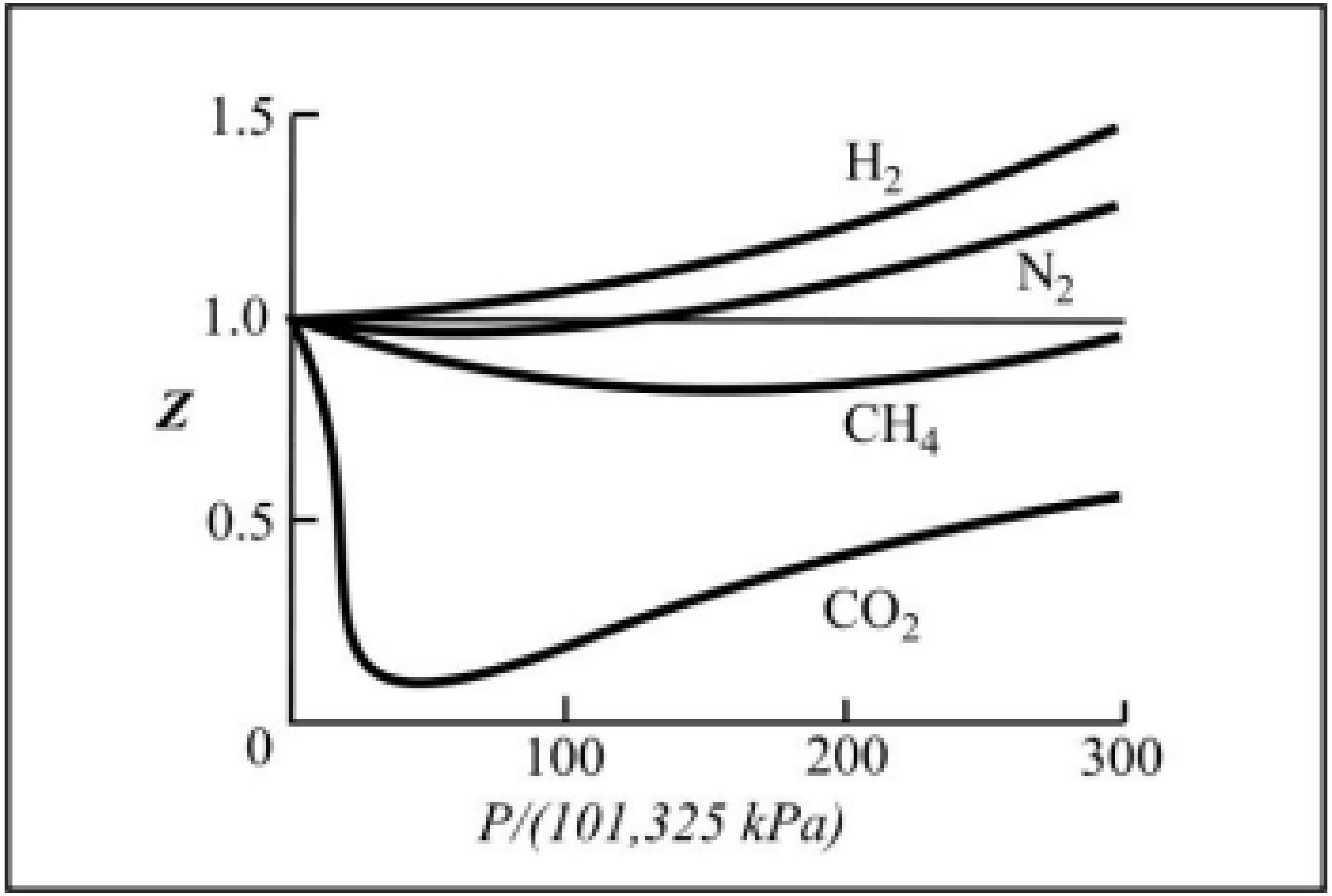


Figure 3.12 Isotherms as given by a cubic equation of state

Faktor kompresibilitas (Z) untuk gas nyata



$$Z = \left(\frac{P\bar{V}}{RT} \right)_{P \to 0} = 1$$

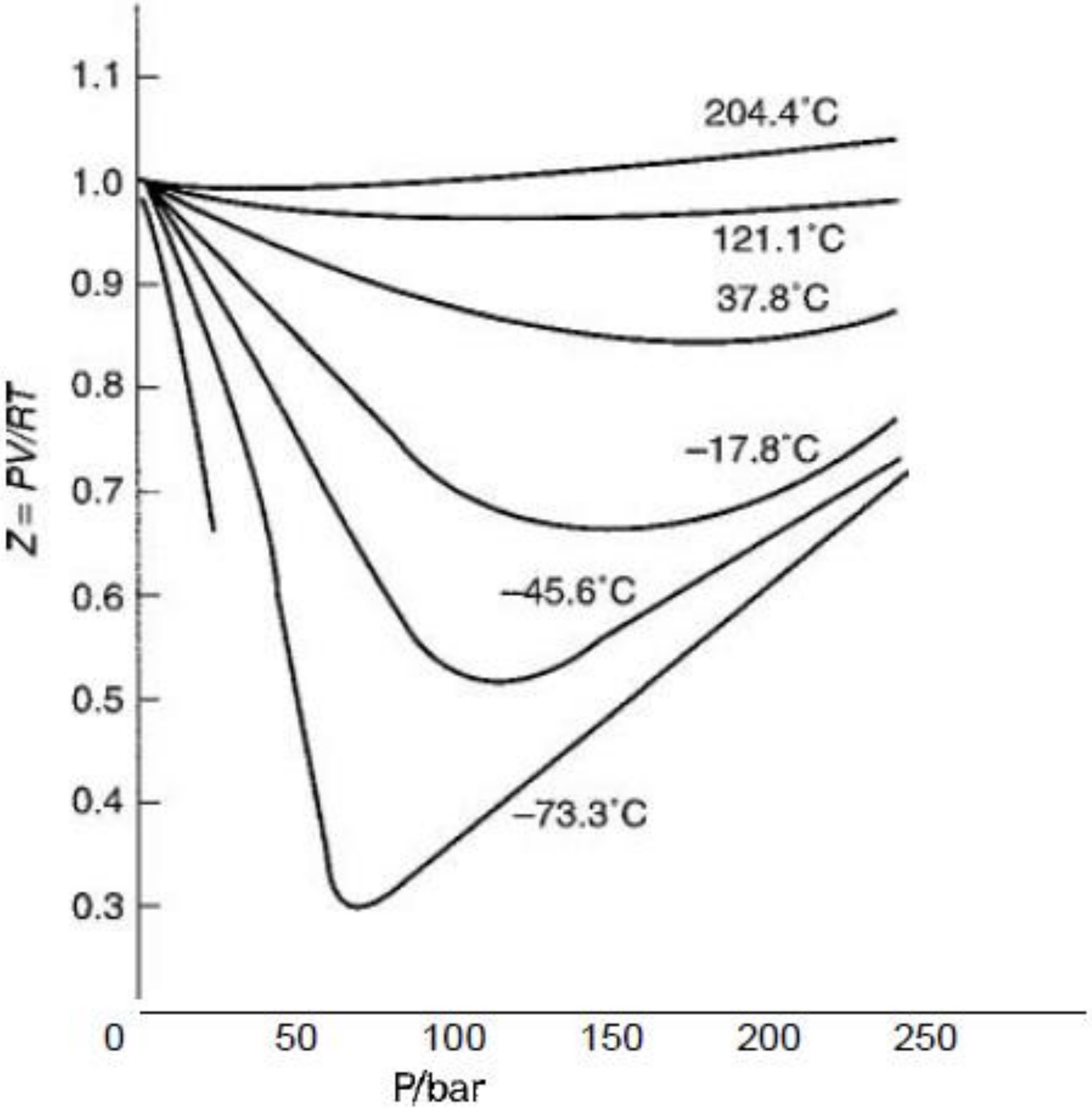


Figure 3.10 Compressibility-factor graph for methane

Application of the virial equations

- Differentiation:

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

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

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

At low pressure

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

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

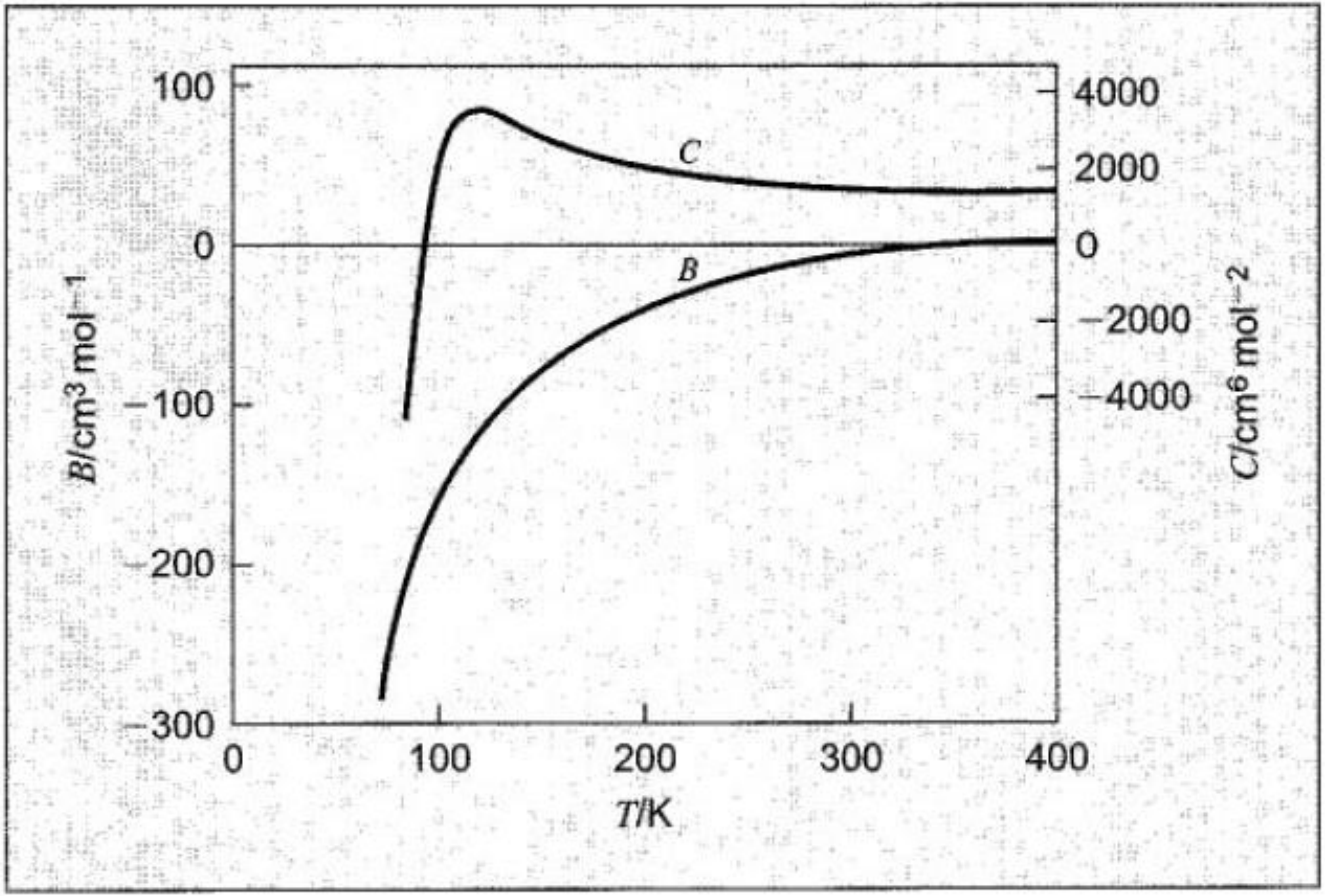


Figure 3.1 1 Density-series virial coefficients B and C for nitrogen

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:

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

(2) two-term virial equation:

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

(3) three-term virial equation:

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

1st iteration

Ideal gas value

...

After 5 iterations

$$V_4 \sim V_5 = 3488 \, {cm^3}/{mol} \rightarrow Z = \frac{PV}{RT} = 0.8866$$

Generalized correlations for gases (Korelasi Umum)

- Pitzer correlations for the compressibility factor:

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

  - $Z^0 = F^0 (T_r, P_r)$
  - 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. D, SVNA 8th ed.)).
  - Only tabular nature (disadvantage)

Simak link video berikut :
https://www.youtube.com/watch?v=WNDBxxCx0qE

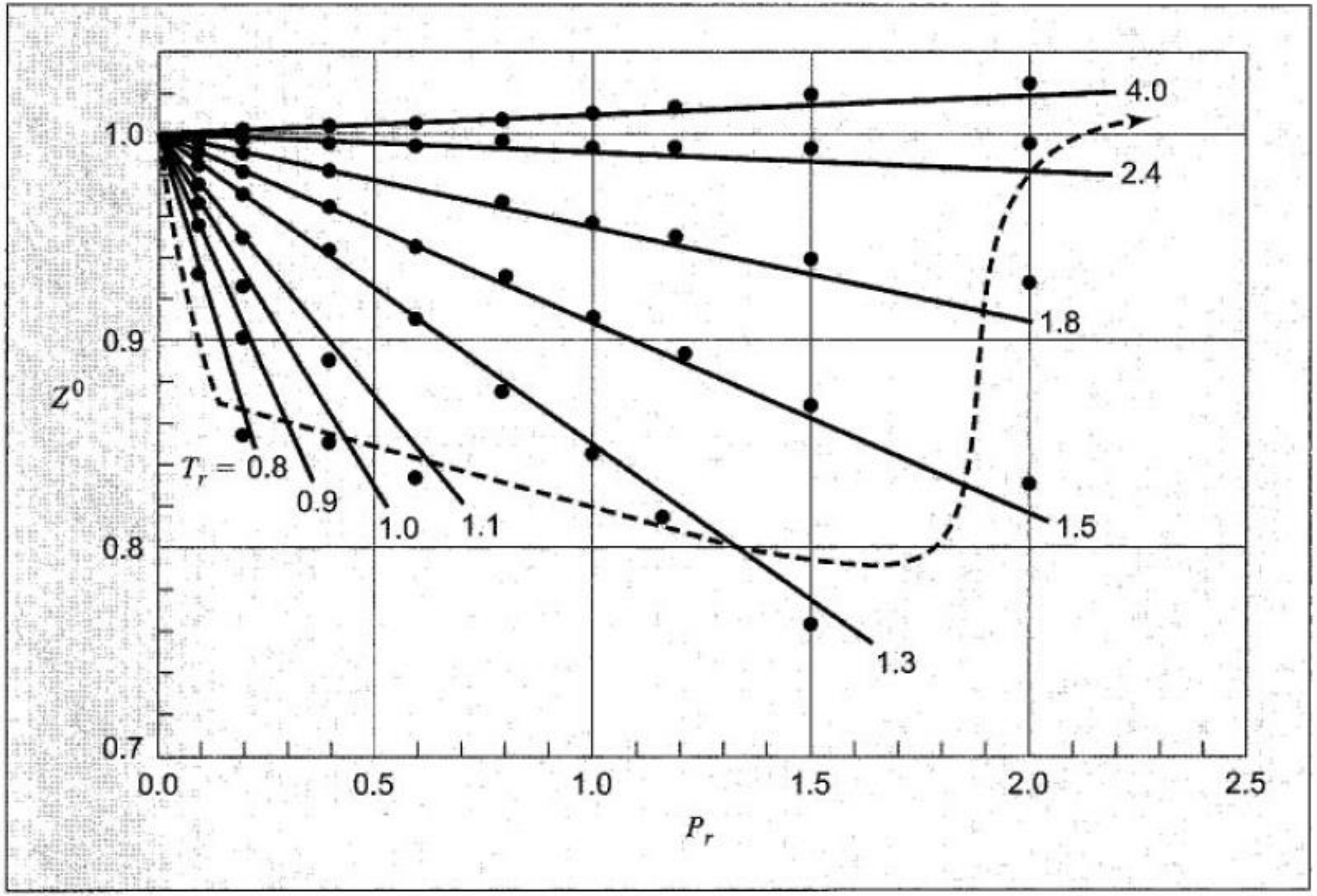


Figure 3.15 Comparison of correlations for Z^0. The virial-coefficient correlation is represented by the straight lines; the Lee/Kesler correlation, by the points. In the region above the dashed line the two correlations differ by less than 2%

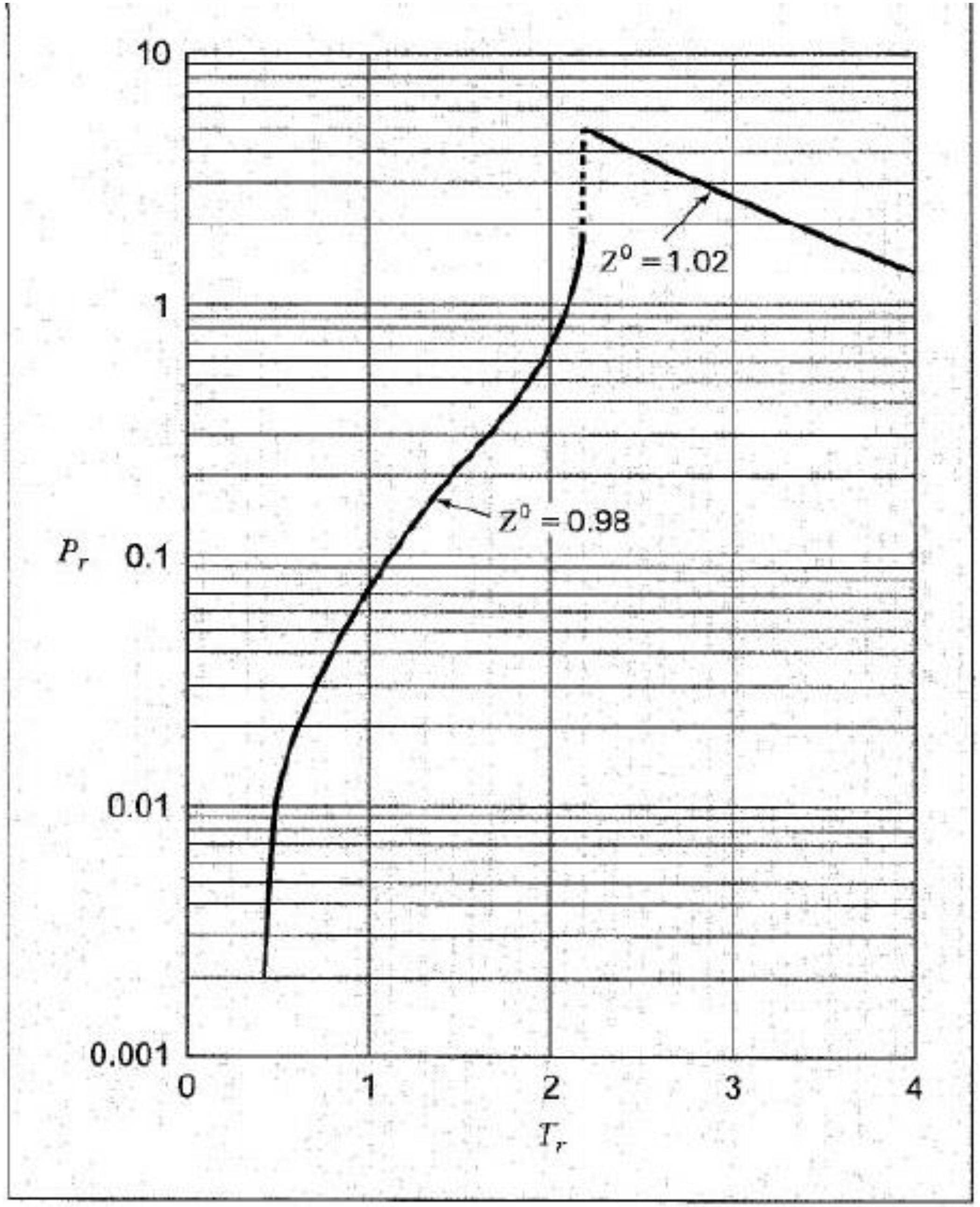


Figure 3.16 Region where Z^0 lies between 0.98 and 1.02, and the ideal-gas equation is a reasonable approximation

- Selain tersedia dalam bentuk tabel, metode Lee Kesler juga menyediakan bentuk grafik

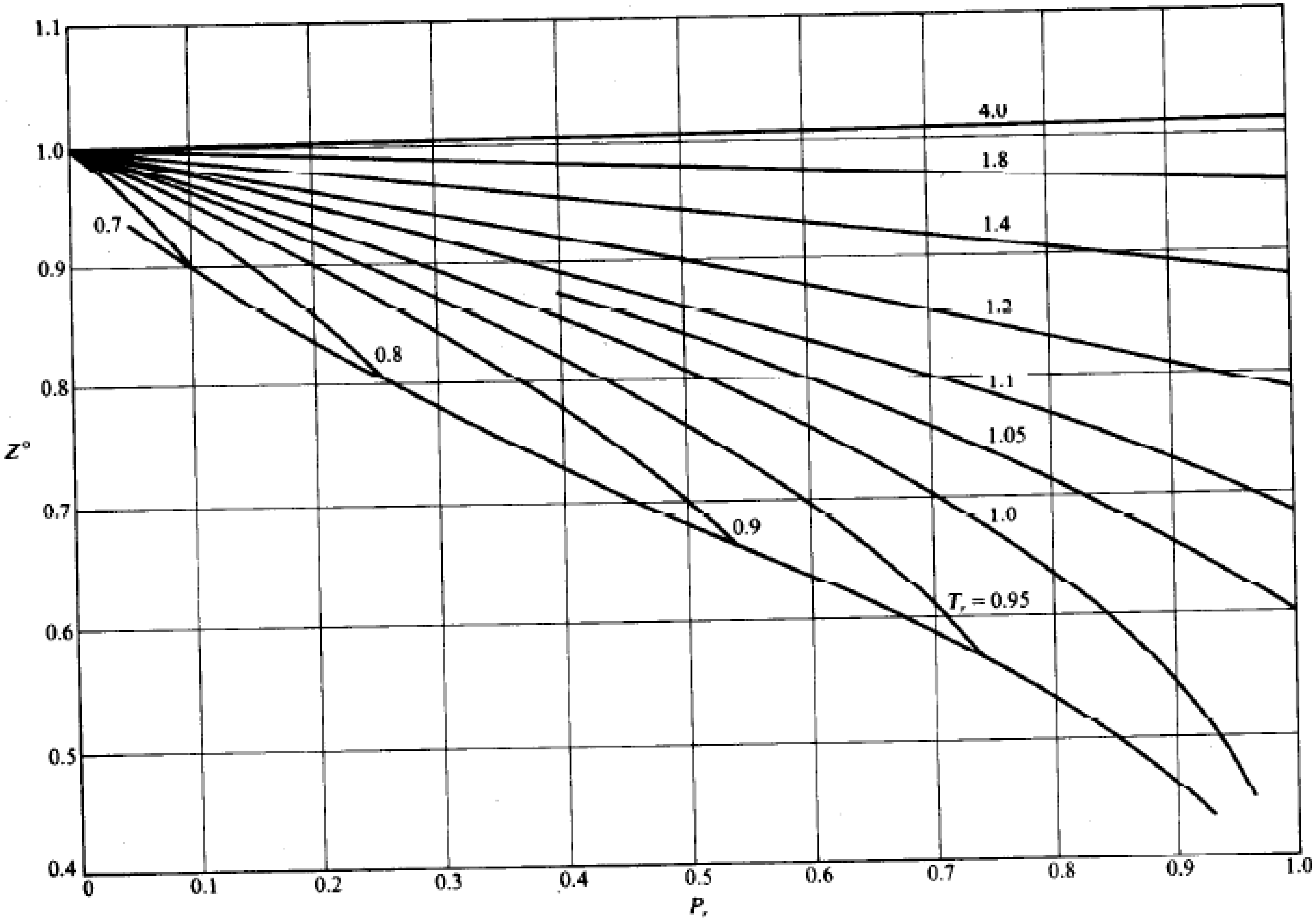


Figure 3.12 Generalized correlation for Z^0, $P_r < 1.0$. *(Based on data of B. I. Lee and M. G. Kesler, AIChE J.,* **21**: *510–527, 1975.)*

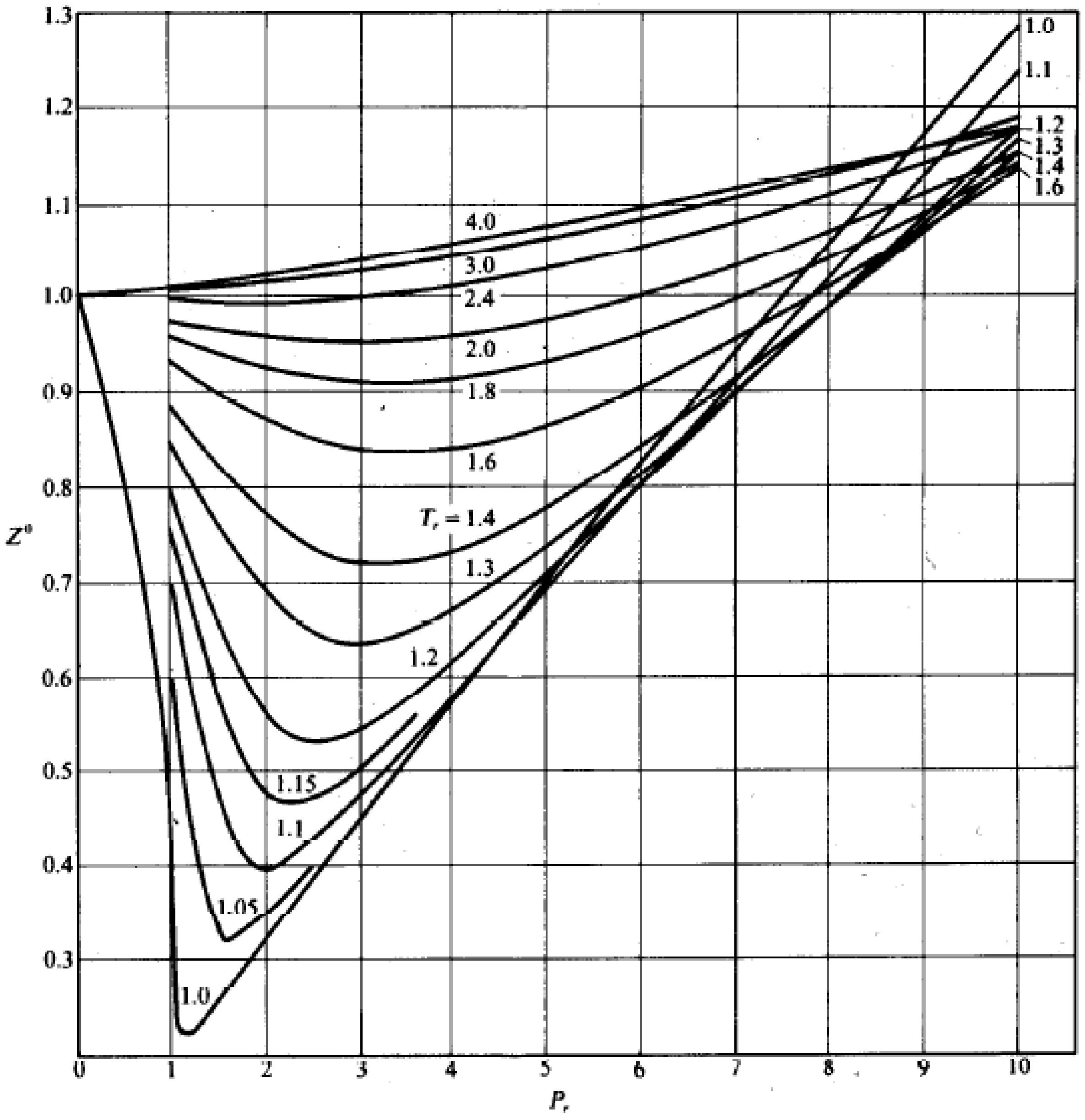


Figure 3.13 Generalized correlation for Z^0, $P_r > 1.0$. *(Based on data of B. I. Lee and M. G. Kesler,* ibid.*)*

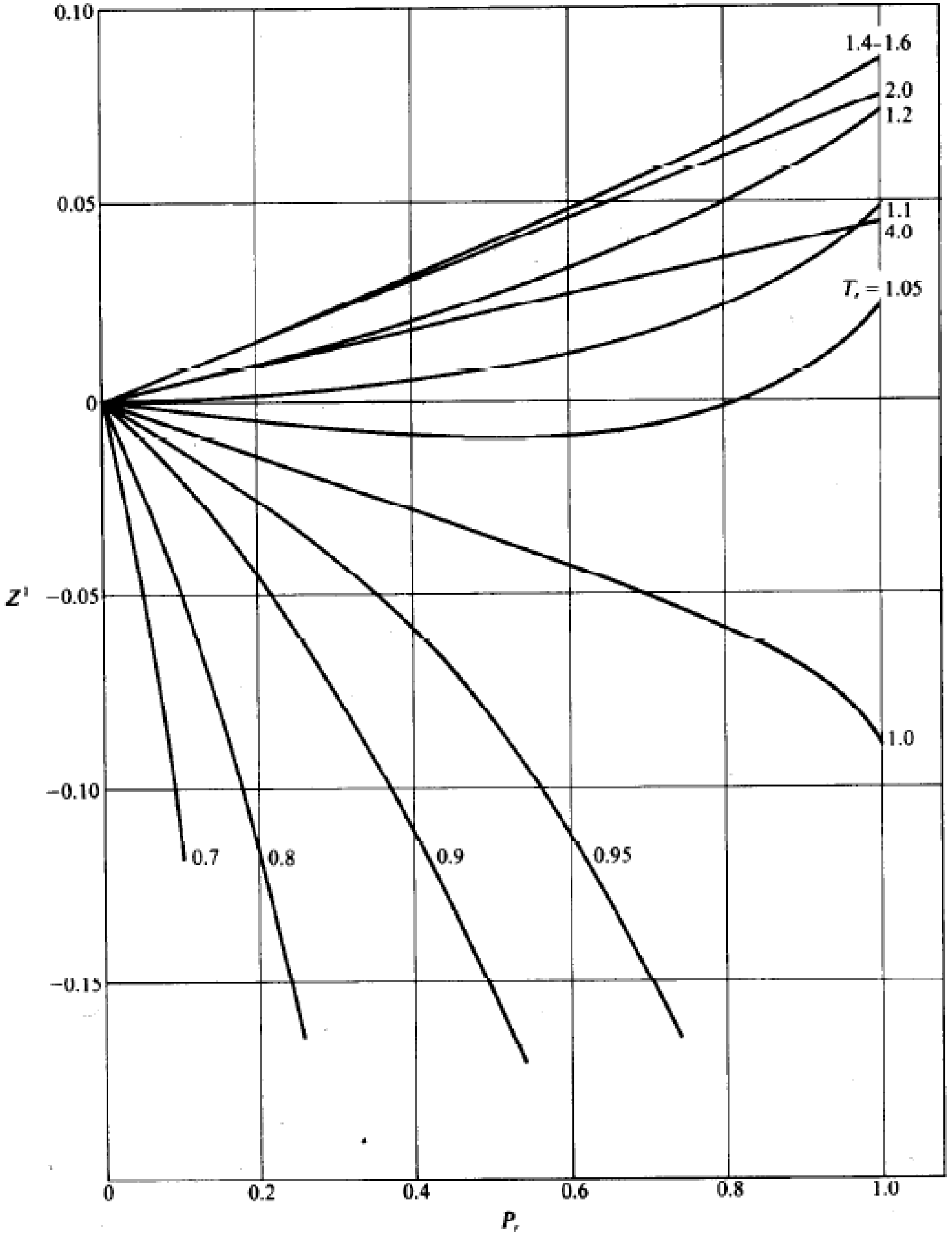


Figure 3.14 Generalized correlation for Z^1, $P_r < 1.0$. *(Based on data of B. I. Lee and M. G. Kesler,* ibid.*)*

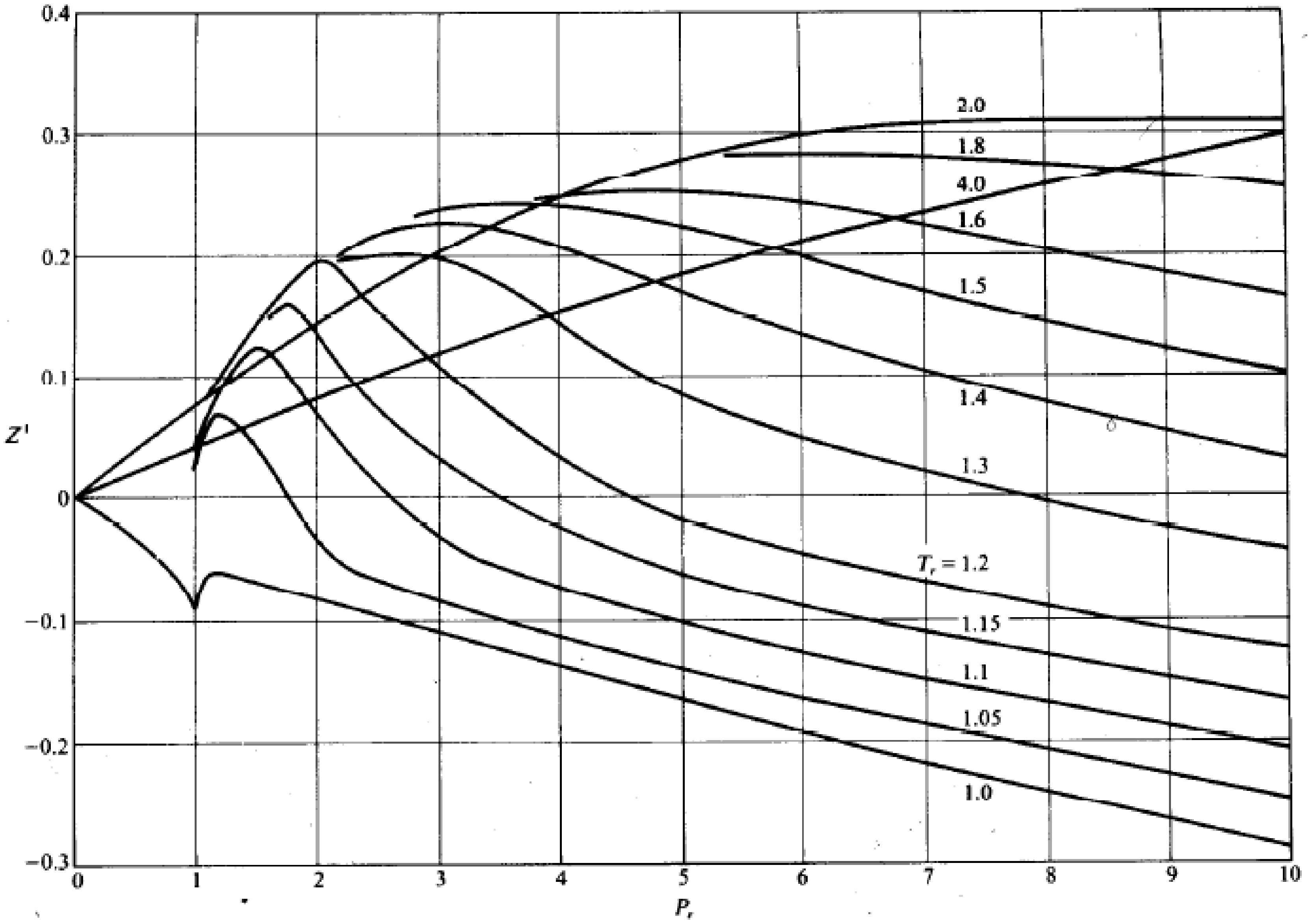


Figure 3.15 Generalized correlation for Z^1, $P_r > 1.0$. *(Based on data of B. I. Lee and M. G. Kesler,* ibid.*)*

Pitzer correlations for the 2nd virial coefficient

- Correlation:

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

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

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

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

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

  - 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.

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

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

(2) The generalized compressibility-factor correlation

$$T_r = \frac{510}{425.1} = 1.200 \qquad P_r = \frac{25}{37.96} = 0.659$$

the acentric factor → $\omega = 0.200$

the Lee/Kesler correlation

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

(3) The generalized virial-coefficient correlation

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

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

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

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

(2) The RK equation

$$T_r = \frac{581.67}{343.1} = 1.695$$

$$a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c} = 453.94\ \frac{atm}{ft^6}$$

$$b = \Omega \frac{RT_c}{P_c} = 0.4781\ ft^3$$

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

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

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

$$P_r = \frac{P}{45.4} = \frac{Z}{0.2138}$$

$$T_r = \frac{581.67}{343.1} = 1.695$$

→ Z starts at Z = 1 and converges on Z = 0.890

$$P = 189.0\ atm$$

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 .

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

(1) The ideal-gas equation

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

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

$$T_r = \frac{338.15}{405.7} = 0.834$$

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

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

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

the acentric factor

$$\omega = 0.253$$

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

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

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:

$$V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}$$

- Generalized density correlation for liquid (Lydersen, Greenkorn, and Hougen, 1955):

$$\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V}$$

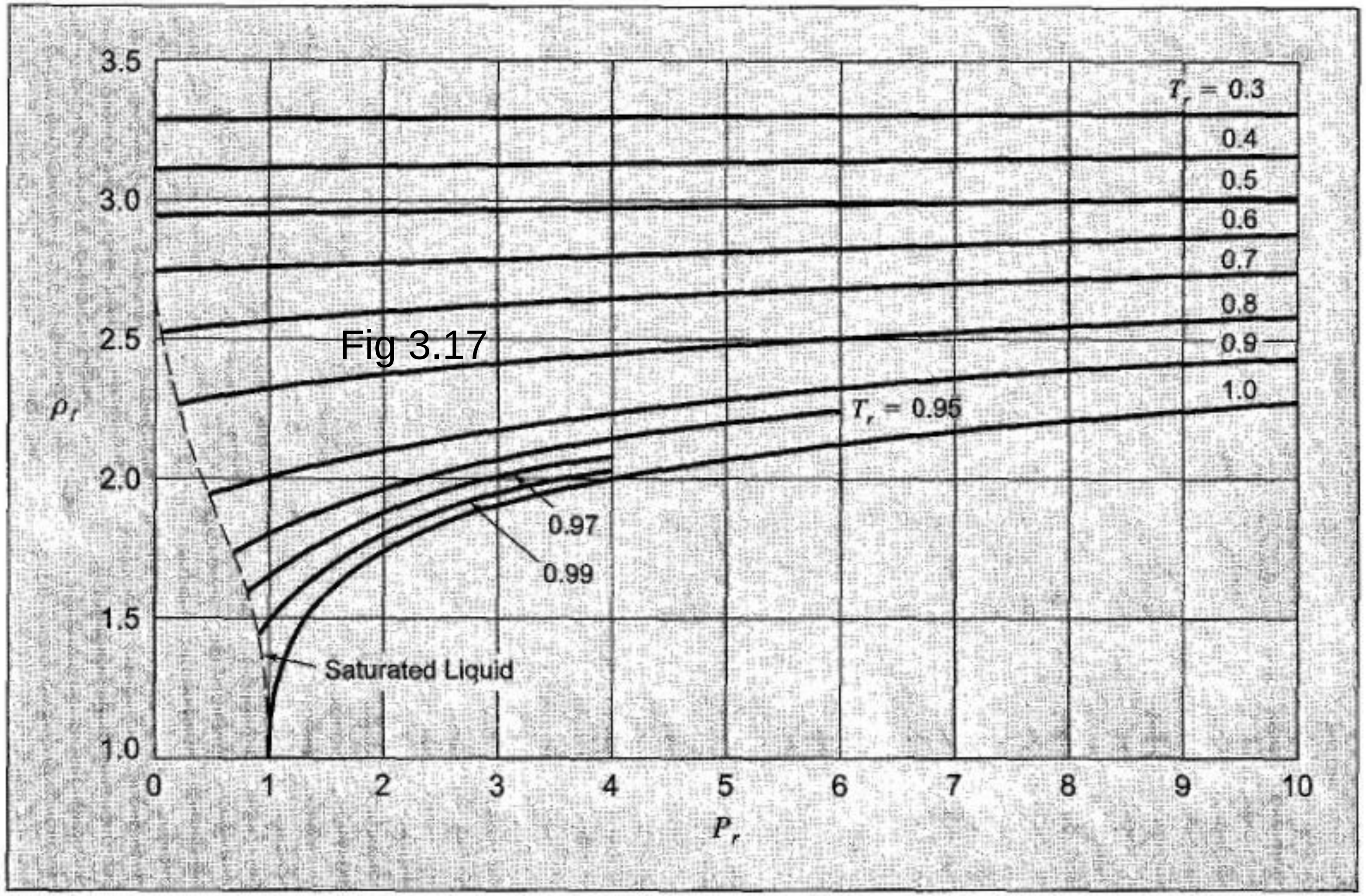


Figure 3.17 Generalized density correlation for liquids

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

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

(1) Apply the Rackett equation at the reduced temperature

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

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

(2) At 100 bar

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

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

Fig 3.17 →

$$\rho_r = 2.38 \qquad V = \frac{V_c}{\rho_r} = 30.45 \frac{cm^3}{mol}$$

$$V_2 = V_1 \frac{\rho_{r1}}{\rho_{r2}} = V^{310K} \frac{\rho_{r1,310K,saturated\,liquid}}{\rho_{r2,100bar}} = 29.14 \frac{2.34}{2.38} = 28.65 \frac{cm^3}{mol}$$