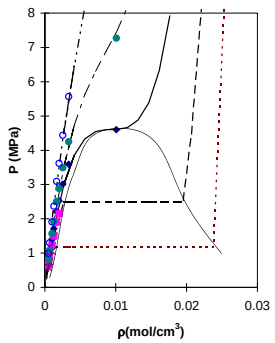
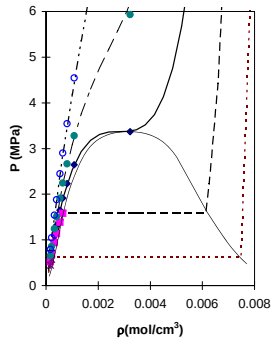
Chapter 7 EOS

Figure 7.1



Methane



Pentane

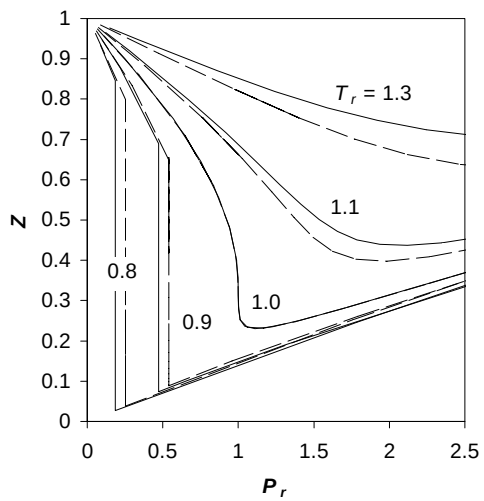
T_c - critical temperature - the temperature above which no liquid can exist. $T_r = T/T_c$

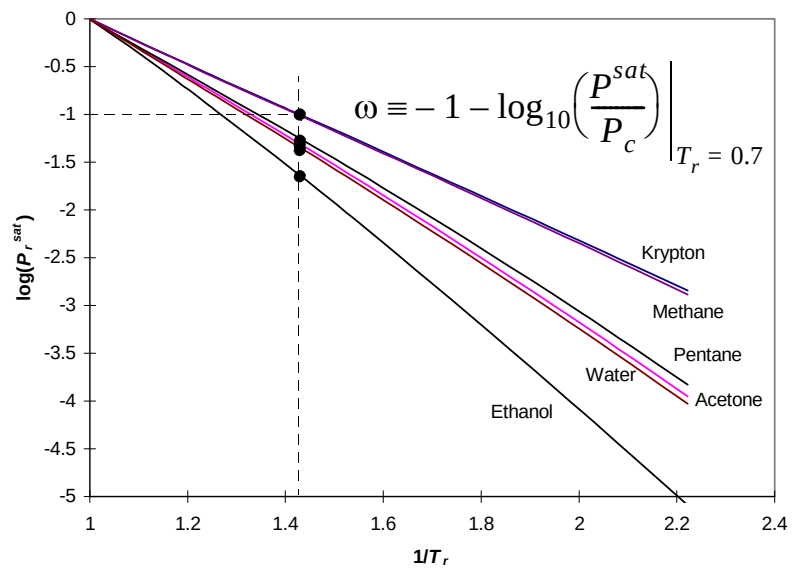
P_c - critical pressure - the pressure above which no vapor can exist. $P_r = P/P_c$

$Z = \dfrac{PV}{RT}$, compressibility factor

different than $-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$ = isothermal compressibility

Use of Tc and Pc is not sufficient for accurate Z.





Virial Equation

$$Z = 1 + B(P/RT) + C(P/RT)^2 + D(P/RT)^3 + \ \ldots$$

$$Z = 1 + BP/(RT)$$

where $B = B(T) = (B^o + \omega B^1)RT_c/P_c$

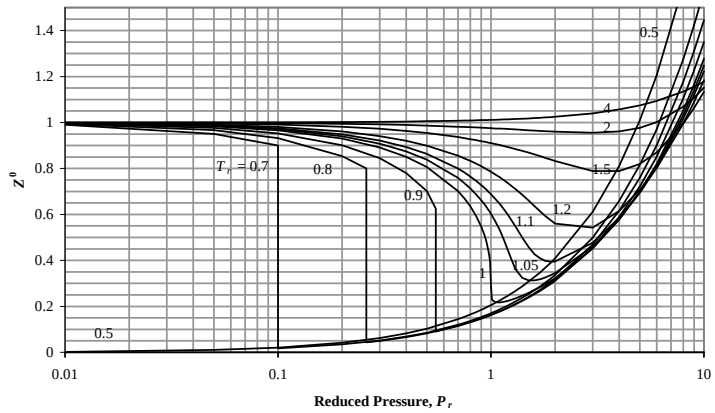
This EOS is sufficiently accurate for compression of non-ideal gases when $\boldsymbol{T_r > 0.686 + 0.439P_r}$ **or** $\mathbf{V_r > 2}$.

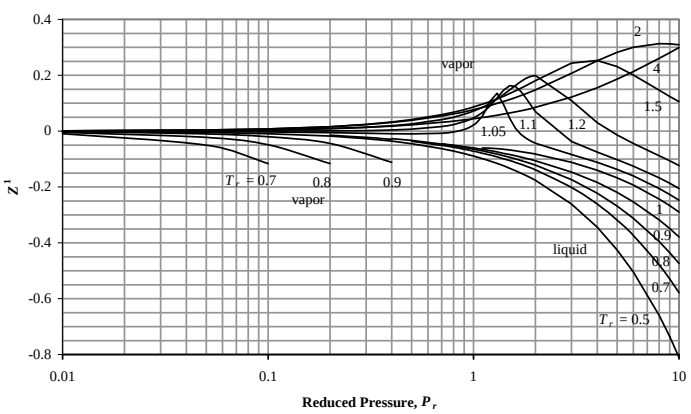
$$Z = 1 + (B^\circ + \omega B^1)P_r/T_r \qquad 7.6$$

where $B^0 = 0.083 - 0.422/T_r^{1.6}$ 7.8

$$B^1 = 0.139 - 0.172/T_r^{4.2} \qquad 7.9$$

Lee-Kesler $Z = Z^0 + \omega Z^1$





Cubic EOS -- van der Waals $P = \dfrac{RT}{(V-b)} - \dfrac{a}{V^2}$

Multiply by V/RT:

Add $1 - \dfrac{V-b}{V-b}$

Substitute $\rho = 1/V$

$$Z = 1 + \frac{b\rho}{(1-b\rho)} - \frac{a\rho}{RT} = \frac{1}{(1-b\rho)} - \frac{a\rho}{RT}$$

$$a \equiv \frac{27}{64}\frac{R^2 T_c^{\,2}}{P_c} \quad ; \qquad b \equiv 0.125 R \frac{T_c}{P_c}$$

Write as cubic in Z

Peng-Robinson EOS

$$Z = \frac{1}{(1-b\rho)} - \frac{a}{bRT}\frac{b\rho}{(1+2b\rho-b^2\rho^2)}$$

where ρ = molar density = $n/\underline{V}$

$$a \equiv a_c\alpha; \quad a_c \equiv 0.45723553\frac{R^2 T_c^{\,2}}{P_c}; \quad \alpha = [1+\kappa(1-\sqrt{T_r})]^2$$

$$b \equiv 0.07779607 R \frac{T_c}{P_c}$$

$$\kappa \equiv 0.37464 + 1.54226\omega - 0.26993\omega^2$$

and a relation that will be useful later:

$$\frac{da}{dT} = -\frac{a_C \kappa \sqrt{\alpha T_r}}{T}$$

$$Z^3 - (1-B)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0$$

Matching the critical point.

$(Z-Z_c)^3 = 0$

$= Z^3 - (3Z_c)Z^2 + (3Z_c^{\,2})Z - Z_c^{\,3} = Z^3 - a_2 Z^2 + a_1 Z - a_0.$

(See appendix B)

e.g. $(1-B) = 3Z_c$, $(A-3B^2-2B) = 3Z_c^{\,2}$

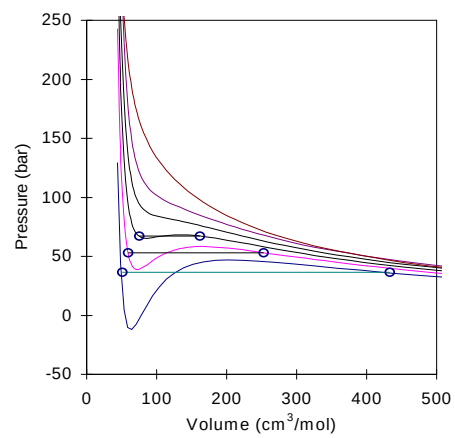


Figure 0.1 Illustration of the prediction of isotherms by the Peng-Robinson equation of state for CO_2

Cubic can be generalized. None are perfect.

vdw

$$P = \frac{RT}{V-b} - \frac{a}{V^2};$$ b - covolume, or hard sphere volume

$$b = \frac{2\pi\sigma^3 N_A}{3} = b_o;\ b_o =$$ volume of hard sphere molecules of diam σ

EOS	Z_c	
exp	0.23-0.31	most problems representing liquid V (ρ)
vdw	0.375	
PR	0.307	

Volume Translated EOS

$$\tilde{V} = V + c$$

Soave-Redlich-Kwong: $P = \dfrac{RT}{\tilde{V}-b} - \dfrac{a}{\tilde{V}(\tilde{V}+b)};$

$a = a_c\alpha;\ a_c = (0.42748R^2T_c^2)/P_c;$

$b = (0.08664RT_c)/P_c;\ \alpha = [1+\kappa(1-\sqrt{T_r})]^2;$

$\kappa = 0.480 + 1.574\omega - 0.176\omega^2$. Solve EOS for $\tilde{V}$, then find $V = \tilde{V} - c$.

Non-cubic EOS

Carnahan-Starling van der Waals

$$P = \frac{RT}{V}\left(\frac{V^3 + b_oV^2 + b_o^2V - b_o^3}{(V-b_o)^3}\right) - \frac{a}{V^2};$$

Extensions of Virial

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots$$

$$Z = 1 + \frac{BP}{RT} + C'P^2 + \ldots;\ C' = \frac{C-B^2}{(RT)^2}$$

Polymers

Sanchez-Lacombe

$$V_R^{-2} + P_R + T_R\left[\ln(1-V_R^{-1}) + \frac{(1-r^{-1})}{V_R}\right];\ V_R = \frac{V}{V^*};$$

$$P_R = \frac{P}{P^*};\ T_R = \frac{T}{T^*};$$