

Liquid & Liquid-Like Roots of the Generic Cubic Equation of State

Equation (3.49) may be solved for the V in the numerator of the final fraction to give:

$$V = b + (V + \epsilon b)(V + \sigma b) \left[\frac{RT + bP - VP}{a(T)} \right] \quad (3.55)$$

This equation with a starting value of $V = b$ on the right side converges upon iteration to a liquid or liquid-like root.

An equation for Z equivalent to Eq. (3.55) is obtained when Eq. (3.52) is solved for the Z in the numerator of the final fraction:

$$Z = \beta + (Z + \epsilon\beta)(Z + \sigma\beta) \left(\frac{1 + \beta - Z}{q\beta} \right) \quad (3.56)$$

For iteration a starting value of $Z = \beta$ is substituted on the right side. Once Z is known, the volume root is $V = ZRT/P$.

Equations of state which express Z as a function of T , and P , are said to be generalized, because of their general applicability to all gases and liquids. Any equation of state can be put into this form to provide a generalized correlation for the properties of fluids. This allows the estimation of property values from very limited information. Equations of state, such as the vander Waals and Redlich/Kwong equations, which express Z as functions of T , and P , only, yield two-parameter corresponding states correlations. The SoaveRedlicWKwong (SRK) equation and the PengRobinson (PR) equation, in which the acentric factor enters through function $\alpha(T_r; \omega)$ as an additional parameter, yield three-parameter corresponding-states correlations. The numerical assignments for parameters ϵ, σ, Ω and Ψ , both for these equations and for the van der Waals and Redlich/Kwong equations, are given in Table 3.1. Expressions are also given for $a(T_r; \omega)$ for the SRK and PR equations.

Table 3.1: Parameter Assignments for Equations of State

For use with Eqs. (3.49) through (3.56)

Eq. of State	$\alpha(T_r)$	σ	ϵ	Ω	Ψ	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)	$\alpha_{\text{SRK}}(T_r; \omega)^{\dagger}$	1	0	0.08664	0.42748	1/3
PR (1976)	$\alpha_{\text{PR}}(T_r; \omega)^{\ddagger}$	$1 + \sqrt{2}$	$1 - \sqrt{2}$	0.07780	0.45724	0.30740

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

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

Iteration with an initial value $Z = 1$ converges on $Z = 0.8305$. Thus,

$$V^v = \frac{ZRT}{P} = \frac{(0.8305)(83.14)(350)}{9.4573} = 2,555 \text{ cm}^3 \text{ mol}^{-1}$$

An experimental value is $2,482 \text{ cm}^3 \text{ mol}^{-1}$.

(b) For the saturated liquid, apply Eq. (3.56) in its RK form:

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

or
$$Z = 0.026214 + Z(Z + 0.026214) \frac{(1.026214 - Z)}{(6.6048)(0.026214)}$$

The initial step is substitution of $Z = \beta$ on the right side of this equation. Iteration leads to convergence on the value $Z = 0.04331$. Whence,

$$V^l = \frac{ZRT}{P} = \frac{(0.04331)(83.14)(350)}{9.4573} = 133.3 \text{ cm}^3 \text{ mol}^{-1}$$

An experimental value is $115.0 \text{ cm}^3 \text{ mol}^{-1}$.

For comparison, values of V^v and V^l calculated for the conditions of Ex. 3.9 by all four of the cubic equations of state considered here are summarized as follows:

$V^v/\text{cm}^3 \text{ mol}^{-1}$					$V^l/\text{cm}^3 \text{ mol}^{-1}$				
Exp.	vdW	RK	SRK	PR	Exp.	vdW	RK	SRK	PR
2,482	2,667	2,555	2,520	2,486	115.0	191.0	133.3	127.8	112.6

3.6 GENERALIZED CORRELATIONS FOR GASES

Generalized correlations find widespread use. Most popular are correlations of the kind developed by Pitzer and coworkers for the compressibility factor Z and for the second virial coefficient B .

Pitzer Correlations for the Compressibility Factor

The correlation for Z takes the form:

$$Z = Z^0 + \omega Z^1 \quad (3.57)$$

where Z^0 and Z^1 are functions of both T_r and P_r

when $\omega = 0$, as is the case for the simple fluids, the second term disappears, and Z^0 becomes identical with Z .

Of the Pitzer-type correlations available, the one developed by Lee and Kesler has found greatest favour. it takes the form of tables which present values of Z^0 and Z^1 as functions of T_r and P_r . These are given in App. E as Tables E. 1 through E.4. Use of these tables often requires interpolation, which is treated at the beginning of App. F.

Pitzer Correlations for the Second Virial Coefficient

The basis for this is Eq. (3.37), the simplest form of the virial equation:

$$Z = 1 + \frac{BP}{RT} = 1 + \hat{B} \frac{P_r}{T_r} \quad (3.61)$$

Where \hat{B} is a reduced second virial coefficient?

$$\hat{B} = \frac{BP_c}{RT_c} \quad (3.62)$$

Thus, Pitzer and coworkers proposed a second correlation, which yields values for \hat{B}

$$\hat{B} = B^0 + \omega B^1 \quad (3.63)$$

Equation (3.63) and (3.61) together become:

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

Comparison of this equation with Eq. (3.57) provides the following identifications:

$$Z^0 = 1 + B^0 \frac{P_r}{T_r} \quad (3.64)$$

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

Second virial coefficients are functions of temperature only, and similarly B^0 and B^1 are functions of reduced temperature only. They are well represented by the following equations:

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad (3.65)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad (3.66)$$

The simplest form of the virial equation has validity only at low to moderate pressures where Z is linear in pressure. The generalized virial-coefficient correlation is therefore useful only where Z^0 and Z^1 are at least approximately linear functions of reduced pressure.

Correlations for the Third Virial Coefficient

Accurate data for third virial coefficients are far less common than for second virial coefficients. Nevertheless, generalized correlations for third virial coefficients do appear in the literature.

Equation (3.40) may be written:

$$Z = 1 + B\rho + C\rho^2 \quad (3.67)$$

where $\rho = 1/V$ is molar density. Rewritten in reduced form, this equation becomes:

$$Z = 1 + \hat{B} \frac{P_r}{T_r Z} + \hat{C} \left(\frac{P_r}{T_r Z} \right)^2 \quad (3.68)$$

where the reduced second virial coefficient \hat{B} is defined by Eq. (3.62), and the reduced third virial coefficient is defined as:

$$\hat{C} \equiv \frac{C P_c^2}{R^2 T_c^2}$$

A Pitzer-type correlation for \hat{C} is written:

$$\hat{C} = C^0 + \omega C^1 \quad (3.69)$$

An expression for C^0 as a function of reduced temperature is given by Orbey and Vera:²¹

$$C^0 = 0.01407 + \frac{0.02432}{T_r} - \frac{0.00313}{T_r^{10.5}} \quad (3.70)$$

The expression for C^1 given by Orbey and Vera is replaced here by one that is algebraically simpler, but essentially equivalent numerically:

$$C^1 = -0.02676 + \frac{0.05539}{T_r^{2.7}} - \frac{0.00242}{T_r^{10.5}} \quad (3.71)$$

Equation (3.68) is cubic in Z , and cannot be expressed in the form of Eq. (3.57). With T_r and P_r specified, solution for Z is by iteration. An initial guess of $Z = 1$ on the right side of Eq. (3.68) usually leads to rapid convergence.

Example 3.10

Determine the molar volume of *n*-butane at 510 K and 25 bar by each of the following:

- The ideal-gas equation.
- The generalized compressibility-factor correlation.
- Equation (3.61), with the generalized correlation for \hat{B} .
- Equation (3.68), with the generalized correlations for \hat{B} and \hat{C} .

Solution 3.10

(a) By the ideal-gas equation,

$$V = \frac{RT}{P} = \frac{(83.14)(510)}{25} = 1,696.1 \text{ cm}^3 \text{ mol}^{-1}$$

(b) From the values of T_c and P_c given in Table B.1 of App. B,

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

Interpolation in Tables E.1 and E.2 then provides:

$$y = y_a + (y_b - y_a) \frac{(x - x_a)}{(x_b - x_a)} \quad \text{Interpolation equation}$$

Table E.I Values of Z^0

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
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
0.97	0.9963	0.9815	0.9625	0.9227	0.8338	0.7240	0.5580	0.1779
0.98	0.9965	0.9821	0.9637	0.9253	0.8398	0.7360	0.5887	0.1844
0.99	0.9966	0.9826	0.9648	0.9277	0.8455	0.7471	0.6138	0.1959
1.00	0.9967	0.9832	0.9659	0.9300	0.8509	0.7574	0.6355	0.2901
1.01	0.9968	0.9837	0.9669	0.9322	0.8561	0.7671	0.6542	0.4648
1.02	0.9969	0.9842	0.9679	0.9343	0.8610	0.7761	0.6710	0.5146
1.05	0.9971	0.9855	0.9707	0.9401	0.8743	0.8002	0.7130	0.6026
1.10	0.9975	0.9874	0.9747	0.9485	0.8930	0.8323	0.7649	0.6880
1.15	0.9978	0.9891	0.9780	0.9554	0.9081	0.8576	0.8032	0.7443
1.20	0.9981	0.9904	0.9808	0.9611	0.9205	0.8779	0.8330	0.7858
1.30	0.9985	0.9926	0.9852	0.9702	0.9396	0.9083	0.8764	0.8438
1.40	0.9988	0.9942	0.9884	0.9768	0.9534	0.9298	0.9062	0.8827
1.50	0.9991	0.9954	0.9909	0.9818	0.9636	0.9456	0.9278	0.9103
1.60	0.9993	0.9964	0.9928	0.9856	0.9714	0.9575	0.9439	0.9308
1.70	0.9994	0.9971	0.9943	0.9886	0.9775	0.9667	0.9563	0.9463
1.80	0.9995	0.9977	0.9955	0.9910	0.9823	0.9739	0.9659	0.9583
1.90	0.9996	0.9982	0.9964	0.9929	0.9861	0.9796	0.9735	0.9678
2.00	0.9997	0.9986	0.9972	0.9944	0.9892	0.9842	0.9796	0.9754
2.20	0.9998	0.9992	0.9983	0.9967	0.9937	0.9910	0.9886	0.9865
2.40	0.9999	0.9996	0.9991	0.9983	0.9969	0.9957	0.9948	0.9941
2.60	1.0000	0.9998	0.9997	0.9994	0.9991	0.9990	0.9990	0.9993
2.80	1.0000	1.0000	1.0001	1.0002	1.0007	1.0013	1.0021	1.0031
3.00	1.0000	1.0002	1.0004	1.0008	1.0018	1.0030	1.0043	1.0057
3.50	1.0001	1.0004	1.0008	1.0017	1.0035	1.0055	1.0075	1.0097
4.00	1.0001	1.0005	1.0010	1.0021	1.0043	1.0066	1.0090	1.0115

Table E.2 Values of Z^1

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
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
0.97	-0.0010	-0.0050	-0.0101	-0.0208	-0.0450	-0.0770	-0.1647	-0.0623
0.98	-0.0009	-0.0044	-0.0090	-0.0184	-0.0390	-0.0641	-0.1100	-0.0641
0.99	-0.0008	-0.0039	-0.0079	-0.0161	-0.0335	-0.0531	-0.0796	-0.0680
1.00	-0.0007	-0.0034	-0.0069	-0.0140	-0.0285	-0.0435	-0.0588	-0.0879
1.01	-0.0006	-0.0030	-0.0060	-0.0120	-0.0240	-0.0351	-0.0429	-0.0223
1.02	-0.0005	-0.0026	-0.0051	-0.0102	-0.0198	-0.0277	-0.0303	-0.0062
1.05	-0.0003	-0.0015	-0.0029	-0.0054	-0.0092	-0.0097	-0.0032	0.0220
1.10	0.0000	0.0000	0.0001	0.0007	0.0038	0.0106	0.0236	0.0476
1.15	0.0002	0.0011	0.0023	0.0052	0.0127	0.0237	0.0396	0.0625
1.20	0.0004	0.0019	0.0039	0.0084	0.0190	0.0326	0.0499	0.0719
1.30	0.0006	0.0030	0.0061	0.0125	0.0267	0.0429	0.0612	0.0819
1.40	0.0007	0.0036	0.0072	0.0147	0.0306	0.0477	0.0661	0.0857
1.50	0.0008	0.0039	0.0078	0.0158	0.0323	0.0497	0.0677	0.0864
1.60	0.0008	0.0040	0.0080	0.0162	0.0330	0.0501	0.0677	0.0855
1.70	0.0008	0.0040	0.0081	0.0163	0.0329	0.0497	0.0667	0.0838
1.80	0.0008	0.0040	0.0081	0.0162	0.0325	0.0488	0.0652	0.0814
1.90	0.0008	0.0040	0.0079	0.0159	0.0318	0.0477	0.0635	0.0792
2.00	0.0008	0.0039	0.0078	0.0155	0.0310	0.0464	0.0617	0.0767
2.20	0.0007	0.0037	0.0074	0.0147	0.0293	0.0437	0.0579	0.0719
2.40	0.0007	0.0035	0.0070	0.0139	0.0276	0.0411	0.0544	0.0675
2.60	0.0007	0.0033	0.0066	0.0131	0.0260	0.0387	0.0512	0.0634
2.80	0.0006	0.0031	0.0062	0.0124	0.0245	0.0365	0.0483	0.0598
3.00	0.0006	0.0029	0.0059	0.0117	0.0232	0.0345	0.0456	0.0565
3.50	0.0005	0.0026	0.0052	0.0103	0.0204	0.0303	0.0401	0.0497
4.00	0.0005	0.0023	0.0046	0.0091	0.0182	0.0270	0.0357	0.0443

$$Z^0 = 0.865 \quad Z^1 = 0.038$$

Thus, by Eq. (3.57) with $\omega = 0.200$,

$$Z = Z^0 + \omega Z^1 = 0.865 + (0.200)(0.038) = 0.873$$

and
$$V = \frac{ZRT}{P} = \frac{(0.873)(83.14)(510)}{25} = 1,480.7 \text{ cm}^3 \text{ mol}^{-1}$$

If Z^1 , the secondary term, is neglected, $Z = Z^0 = 0.865$. This two-parameter corresponding-states correlation yields $V = 1,467.1 \text{ cm}^3 \text{ mol}^{-1}$, which is less than 1% lower than the value given by the three-parameter correlation.

(c) Values of B^0 and B^1 are given by Eqs. (3.65) and (3.66):

$$B^0 = -0.232 \quad B^1 = 0.059$$

Equations (3.63) and (3.61) then yield:

$$\hat{B} = B^0 + \omega B^1 = -0.232 + (0.200)(0.059) = -0.220$$

$$Z = 1 + (-0.220) \frac{0.659}{1.200} = 0.879$$

from which $V = 1,489.1 \text{ cm}^3 \text{ mol}^{-1}$, a value less than 1% higher than that given by the compressibility-factor correlation.

(d) Values of C^0 and C^1 are given by Eqs. (3.70) and (3.71):

$$C^0 = 0.0339 \quad C^1 = 0.0067$$

Equation (3.69) then yields:

$$\hat{C} = C^0 + \omega C^1 = 0.0339 + (0.200)(0.0067) = 0.0352$$

With this value of \hat{C} and the value of \hat{B} from part (c), Eq. (3.68) becomes,

$$Z = 1 + (-0.220) \left(\frac{0.659}{1.200Z} \right) + (0.0352) \left(\frac{0.659}{1.200Z} \right)^2$$

or
$$Z = 1 - \frac{0.121}{Z} + \frac{0.0106}{Z^2}$$

Whence,
$$Z = 0.876 \quad \text{and} \quad V = 1,485.8 \text{ cm}^3 \text{ mol}^{-1}$$

The value of V differs from that of part (c) by about 0.2%. An experimental value for V is $1,480.7 \text{ cm}^3 \text{ mol}^{-1}$. Significantly, the results of parts (b), (c), and (d) are in excellent agreement. Mutual agreement at these conditions is suggested

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)? Base calculations on each of the following:

- (a) The ideal-gas equation.
- (b) The Redlich/Kwong equation.
- (c) A generalized correlation.

Solution 3.11

(a) By the ideal-gas equation,

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

(b) The pressure as given by the Redlich/Kwong equation is:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \quad (3.47)$$

Values of $a(T)$ and b come from Eqs. (3.45) and (3.46), where $\alpha(T_r) = T_r^{-1/2}$ in Eq. (3.45). With values of T_c and P_c from Table B.1 converted to (R) and (atm),

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

$$a = 0.42748 \frac{(1.695)^{-1/2} (0.7302)^2 (343.1)^2}{45.4} = 453.94(\text{atm})(\text{ft})^6$$

$$b = 0.08664 \frac{(0.7302)(343.1)}{45.4} = 0.4781(\text{ft})^3$$

Substitution of numerical values into the Redlich/Kwong equation now yields:

$$P = \frac{(0.7302)(581.67)}{2 - 0.4781} - \frac{453.94}{(2)(2 + 0.4781)} = 187.49(\text{atm})$$

(c) Because the pressure here is high, the generalized compressibility-factor correlation is the proper choice. In the absence of a known value for P_r , an iterative procedure is based on the following equation:

$$P = \frac{ZRT}{V} = \frac{Z(0.7302)(581.67)}{2} = 212.4 Z$$

Because $P = P_c P_r = 45.4 P_r$, this equation becomes:

$$Z = \frac{45.4 P_r}{212.4} = 0.2138 P_r \quad \text{or} \quad P_r = \frac{Z}{0.2138}$$

One now assumes a starting value for Z , say $Z = 1$. This gives $P_r = 4.68$, and allows a new value of Z to be calculated by Eq. (3.57) from values interpolated in Tables E.3 and E.4 at the reduced temperature of $T_r = 1.695$. With this new value of Z , a new value of P_r is calculated, and the procedure continues until no significant change occurs from one step to the next. The final value of Z so found is 0.890 at $P_r = 4.14$. This may be confirmed by substitution into Eq. (3.57) of values for Z^0 and Z^1 from Tables E.3 and E.4 interpolated at $P_r = 4.14$ and $T_r = 1.695$. With $\omega = 0.012$,

$$Z = Z^0 + \omega Z^1 = 0.887 + (0.012)(0.258) = 0.890$$

$$P = \frac{ZRT}{V} = \frac{(0.890)(0.7302)(581.67)}{2} = 189.0(\text{atm})$$

Because the acentric factor is small, the two- and three-parameter compressibility-factor correlations are little different. Both the Redlich/Kwong equation and the generalized compressibility-factor correlation give answers close to the experimental value of 185(atm). The ideal-gas equation yields a result that is high by 14.6%.