
A GENERALIZED TREATMENT OF CUBIC EQUATIONS OF STATE

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Received February 8, 1989

Accepted April 10, 1989

Dedicated to late Academician Eduard Hála.

From the formula proposed for the van der Waals type equations of state, general expressions for the compressibility factor, the departure functions and the fugacity coefficient are derived. Easy construction of the formula needed is possible for any of the equations listed in the paper. The method is applicable to other equations of this type.

The equations of state (EOS) based on the van der Waals equation are often used for engineering calculations. The advantage of a generalized form of these equations has been recognized and the most thorough application can be found in the recent edition of the book by Reid et al.¹ The published cubic EOS contain up to four empirical coefficients. However, the generalized expressions given by Reid et al.¹ may be used only for the EOS with two coefficients. Therefore a more general procedure is proposed here. Equations for the compressibility factor, the thermodynamic departure functions and for the fugacity coefficient of a component in a fluid mixture are derived in terms of general parameters. Tables were prepared for a number of EOS, which give the appropriate formulae for these parameters. This enables easy construction of the required expression for each of the EOS listed. The method may be extended to further EOS of the van der Waals form.

Compressibility Factor

The cubic EOS of the van der Waals type can be represented by a general formula

$$p = \frac{RT}{v - b} - \frac{a}{w}, \quad (1)$$

where

$$w = v^2 + c_1v + c_2. \quad (2)$$

Table I summarizes various expressions for the coefficients c_1 and c_2 characterizing

different EOS. It is usually convenient to write Eq. (1) in a dimensionless form. The definitions of the compressibility factor

$$z = pv/RT, \quad (3)$$

the dimensionless coefficients

$$A = ap/(RT)^2, \quad B = bp/RT, \quad C = cp/RT, \quad D = dp/RT \quad (4)$$

and the quantities

$$W = w(p/RT)^2, \quad C_1 = c_1(p/RT), \quad C_2 = c_2(p/RT)^2 \quad (5)$$

are used to transform Eq. (1) to

$$A(z - B) + W(z - B - 1) = 0 \quad (6)$$

and Eq. (2) to

$$W = z^2 + C_1z + C_2. \quad (7)$$

TABLE I
Coefficients c_1 and c_2 , Eq. (2)

Authors	c_1	c_2	Refs
van der Waals (1873)	0	0	2
Redlich and Kwong (1949)	b	0	3
Redlich, Kwong and Soave (1972)	b	0	4
Peng and Robinson (1976)	$2b$	$-b^2$	5
Schmidt and Wenzel (1980)	$(1 + 3\omega)b$	$-3\omega b^2$	6
Yu and Lu (1987)	ub	$(u - 3)b^2$	7 ^a
Harmens and Knapp (1980)	Cb	$-(C - 1)b^2$	8 ^b
Martin (1979); Joffe (1987)	$2c$	c^2	9, 10
Adachi, Sugie and Lu (1985)	$2c$	$-c^2$	11
Patel and Teja (1982)	$b + c$	$-bc$	12
Valderrama and Cisternas (1986)	$b + c$	$-bc$	13
Adachi, Lu and Sugie (1983)	$-c + d$	$-cd$	14 ^c

^a Yu and Lu⁷ define the EOS coefficient c as $c = (u - 3)b$. The use of the dimensionless u simplifies the form of the equations and therefore u is used here instead of c . ^b The quantity c used by Harmens and Knapp⁸ is dimensionless and is written here as C . ^c The authors¹⁴ write their EOS in terms of b_1 , b_2 and b_3 which are written here as b , c and d .

The combination of Eqs (6) and (7) gives

$$z^3 + (C_1 - B - 1)z^2 + [A - (1 + B)C_1 + C_2]z - AB - (1 + B)C_2 = 0 \quad (8)$$

which is the general formula for the compressibility factor calculated from the EOS satisfying Eqs (1) and (2).

Commonly the coefficients of the EOS are calculated from the critical properties of the fluid, i.e.

$$a = A_0 \frac{(RT_c)^2}{p_c} F, \quad b = B_0 \frac{RT_c}{p_c}, \quad c = C_0 \frac{RT_c}{p_c}, \quad d = D_0 \frac{RT_c}{p_c}. \quad (9)$$

Their dimensionless form is

$$A = A_0 F \frac{p_r}{T_r^2}, \quad B = B_0 \frac{p_r}{T_r}, \quad C = C_0 \frac{p_r}{T_r}, \quad D = D_0 \frac{p_r}{T_r}. \quad (10)$$

Table II contains expressions for the coefficients A_0 , B_0 , C_0 and D_0 . The quantity F represents the temperature dependence of the coefficient a . The common formula for F is

$$F = [1 + f(1 - T_r^{1/2})]^2. \quad (11)$$

The expressions for the coefficients F and f are summarized in Table III.

Thermodynamic Departure Functions

The thermodynamic function of a real fluid is calculated from a reference value for an ideal gas and a departure function. This is evaluated with the aid of an EOS. The cubic EOS are explicit in pressure and the departure functions are therefore derived on the basis of the Helmholtz departure function

$$A_d = \int_{\infty}^v \left(-p + \frac{RT}{v} \right) dv + RT \ln \frac{pv}{RT}. \quad (12)$$

Substitution for p from Eq. (1) and integration yields

$$\frac{A_d}{RT} = \ln \frac{RT}{p(v-b)} + \frac{a}{RT} \int_{\infty}^v \frac{dv}{w}. \quad (13)$$

For the van der Waals equation it follows

$$\frac{A_d}{RT} = \ln \frac{RT}{p(v-b)} - \frac{a}{RTv}. \quad (14)$$

The integral in Eq. (13) can be solved after substituting from Eq. (2). The result is

$$\int_{\infty}^v \frac{dv}{w} = -\frac{1}{k} \ln \frac{2v + c_1 + k}{2v + c_1 - k} = -i, \quad (15)$$

where

$$k = (c_1^2 - 4c_2)^{1/2}. \quad (16)$$

The symbols i and k are used to simplify the notation. The molar Helmholtz departure

TABLE II
Coefficients A_0 , B_0 , C_0 and D_0 , Eq. (9)

Refs	Coefficients
2	$A_0 = 27/64, B_0 = 1/8$
3	$A_0 = 0.42748, B_0 = 0.08664$
4	$A_0 = 0.42748, B_0 = 0.08664$
5	$A_0 = 0.45724, B_0 = 0.07780$
6	$A_0 = [1 - \zeta_c(1 - \beta)]^3, B_0 = \beta\zeta_c, \zeta_c = 1/[3(1 + \beta\omega)]$
7	$A_0 = 0.46863 - 0.03783\omega + 0.00752\omega^2, B_0 = 0.08928 - 0.03409\omega - 0.00518\omega^2,$ $u = 1.70083 + 0.64846\omega + 0.89593\omega^2$
8	$A_0 = 1 + 3\zeta_c[-1 + \zeta_c + \beta(1 - 2\zeta_c)] + \beta^2\zeta_c^2, B_0 = \beta\zeta_c, C = 1 + (1 - 3\zeta_c)/\beta\zeta_c,$ $\zeta_c = 0.3211 - 0.080\omega + 0.0384\omega^2, \beta = 0.10770 + 0.7640\zeta_c - 1.24282\zeta_c^2 +$ $+ 0.96210\zeta_c^3$
9, 10	$A_0 = 27/64, B_0 = 0.857z_c - 0.1674, C_0 = 1/8 - B_0$
11	$A_0 = 0.43711 + 0.02366\omega + 0.10538\omega^2 + 0.10164\omega^3,$ $B_0 = 0.08779 - 0.02181\omega - 0.06708\omega^2 + 0.10617\omega^3,$ $C_0 = 0.05060 + 0.04184\omega + 0.16413\omega^2 - 0.03975\omega^3$
12	$A_0 = 3\zeta_c^2 + B_0[3(1 - 2\zeta_c) + B_0] + C_0, B_0^3 + (1 + C_0)B_0^2 + 3\zeta_c^2B_0 - \zeta_c^3 = 0,$ $C_0 = 1 - 3\zeta_c, \zeta_c = 0.32903 - 0.07680\omega + 0.02120\omega^2$
13	$A_0 = 0.69368 - 1.06344z_c + 0.68290z_c^2 - 0.21044z_c^3 + 0.0037527z_c^4,$ $B_0 = 0.025987 + 0.18075z_c + 0.06126z_c^2, C_0 = 0.57750 - 1.89841z_c,$ $z_c = p_c v_c / RT_c$
14	$A_0 = 0.44869 + 0.04024\omega + 0.01111\omega^2 - 0.00576\omega^3,$ $B_0 = 0.08974 - 0.03452\omega + 0.00330\omega^2,$ $C_0 = 0.03686 + 0.00405\omega - 0.01073\omega^2 + 0.00157\omega^3,$ $D_0 = 0.15400 + 0.14122\omega - 0.00272\omega^2 + 0.00484\omega^3$

function is then expressed by

$$\frac{A_d}{RT} = \ln \frac{RT}{p(v-b)} - \frac{ai}{RT}. \quad (17)$$

Introducing

$$K = \frac{kp}{RT}, \quad I = \frac{1}{K} \ln \frac{2z + C_1 + K}{2z + C_1 - K} \quad (18)^*$$

we may write Eq. (17) in dimensionless parameters as

$$A_d/RT = -\ln(z - B) - AI. \quad (19)$$

TABLE III

Coefficients F and f , Eqs (9), (10) and (11). Only f is given when Eq. (11) applies

Refs	Coefficients
2	$F = 1$
3	$F = T_r^{-1/2}$
4	$f = 0.480 + 1.574\omega - 0.176\omega^2$
5	$f = 0.37464 + 1.54226\omega - 0.26992\omega^2$
6	$T_r \leq 1: f = f_0 + (5T_r - 3f_0 - 1)^2/70, T_r > 1: f = f_0 + (4 - 3f_0)^2/70,$ $f_0 = 0.465 + 1.347\omega - 0.528\omega^2$
7	$T_r \leq 1: \log F = f(f_1 + f_2 T_r + f_3 T_r^2)(1 - T_r),$ $T_r > 1: \log F = f(f_1 + f_2 + f_3)(1 - T_r),$ $\omega < 0.49: f = 0.40685 + 1.87907\omega - 0.79264\omega^2 + 0.73752\omega^3,$ $f_1 = 0.53684, f_2 = -0.39244, f_3 = 0.26507,$ $0.49 < \omega < 1: f = 0.58198 - 0.17142\omega + 1.84441\omega^2 - 1.19047\omega^3,$ $f_1 = 0.79355, f_2 = -0.53409, f_3 = 0.37273$
8	$T_r \leq 1: F = [1 + f_1(1 - T_r^{1/2}) - f_2(1 - T_r^{-1})]^2,$ $T_r > 1: F = 1 - (0.6258 + 1.5227\omega) \ln T_r + (0.1533 + 0.41\omega) (\ln T_r)^2,$ $\omega \leq 0.2: f_1 = 0.50 + 0.27767\omega + 2.17225\omega^2, f_2 = -0.22 + 0.338\omega - 0.845\omega^2,$ $\omega > 0.2: f_1 = 0.41311 + 1.14657\omega, f_2 = 0.0118$
9, 10	$T_r \leq 1: f = 0.49950 + 1.5618\omega - 0.1373\omega^2 + 0.13904(T_r - 0.7) +$ $+ 0.64344(T_r - 0.7)^2$
11	$f = 0.44060 + 1.7039\omega - 1.7290\omega^2 + 0.9929\omega^3$
12	$f = 0.42241 + 1.30982\omega - 0.29594\omega^2$
13	$f = -6.608 + 70.43z_c - 159.0z_c^2$
14	$f = 0.4070 + 1.3787\omega - 0.2933\omega^2$

* Note that the formula for i or I cannot be directly applied to the van der Waals equation for which $i = 1/v$ and $I = 1/z$ (see Eq. (14)).

The molar entropy departure function is calculated from the equation

$$S_d = \int_{\infty}^v \left[\left(\frac{\partial p}{\partial T} \right)_v - \frac{R}{v} \right] dv + R \ln \frac{pv}{RT}. \quad (20)$$

Eq. (1) yields

$$\frac{1}{R} \left(\frac{\partial p}{\partial T} \right)_v = \frac{1}{v-b} - \frac{1}{Rw} \left(\frac{\partial a}{\partial T} \right)_v, \quad (21)$$

which is substituted in Eq. (20) and the integral is solved to give

$$\frac{S_d}{R} = \ln \frac{p(v-b)}{RT} + \frac{i}{R} \left(\frac{\partial a}{\partial T} \right)_v. \quad (22)$$

The temperature dependence of the coefficient a is represented by F from Eq. (9) and given in Table III. In terms of F we have at $v = \text{const.}$

$$\frac{1}{R} \frac{\partial a}{\partial T} = \frac{A_0}{R} \frac{(RT_c)^2}{p_c} \frac{\partial F}{\partial T} = \frac{a}{RF} \frac{\partial F}{\partial T} = A \frac{RT}{p} \frac{T_r}{F} \frac{\partial F}{\partial T_r}. \quad (23)$$

Therefore Eq. (22) becomes

$$\frac{S_d}{R} = \ln \frac{p(v-b)}{RT} + \frac{ai}{RF} \frac{\partial F}{\partial T} = \ln(z-B) + AI \frac{T_r}{F} \frac{\partial F}{\partial T_r} \quad (24)$$

and if Eq. (11) applies, then

$$\frac{S_d}{R} = \ln(z-B) - \frac{AI f T_r^{1/2}}{1 + f(1 - T_r^{1/2})}. \quad (25)$$

For mixtures, the expression for the derivative $\partial a/\partial T$ depends on the mixing rule used. The common mixing rule is

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad b = \sum_j x_j b_j, \quad c = \sum_j x_j c_j, \quad d = \sum_j x_j d_j, \quad (26)$$

where

$$a_{ij} = (1 - k_{ij}) (a_i a_j)^{1/2}. \quad (27)$$

When Eqs (26) and (27) hold, then using Eq. (9) the following expression, valid at

constant volume and composition, may be derived

$$\frac{\hat{c}a}{\partial T} = \sum_i \sum_j x_i x_j (1 - k_{ij}) (a_i a_j)^{1/2} \left(\frac{1}{F_i^{1/2}} \frac{\partial F_i^{1/2}}{\partial T} + \frac{1}{F_j^{1/2}} \frac{\partial F_j^{1/2}}{\partial T} \right) \quad (28)$$

and when Eq. (11) is valid, then

$$\begin{aligned} \frac{\hat{c}a}{\partial T} = & -\frac{1}{2T^{1/2}} \sum_i \sum_j x_i x_j (1 - k_{ij}) (a_i a_j)^{1/2} \left(\frac{f_i T_{ci}^{-1/2}}{1 + f_i [1 - (T/T_{ci})^{1/2}]} + \right. \\ & \left. + \frac{f_j T_{cj}^{-1/2}}{1 + f_j [1 - (T/T_{cj})^{1/2}]} \right). \quad (29) \end{aligned}$$

Other departure functions are derived from A_d and S_d and are summarized in Table IV.

To illustrate the use of the expressions suggested so far, the iteration formula for the equilibrium vapor pressure, based on a cubic EOS, will now be derived.

TABLE IV
Departure functions

$$\begin{aligned} \frac{A_d}{RT} &= -\ln(z - B) - AI \\ \frac{S_d}{R} &= \ln(z - B) + AI \frac{T_r}{F} \frac{\partial F}{\partial T_r} = \\ &= \ln(z - B) - \frac{AI f T_r^{1/2}}{1 + f(1 - T_r^{1/2})} \\ \frac{H_d}{RT} &= z - 1 + AI \left(\frac{T_r}{F} \frac{\partial F}{\partial T_r} - 1 \right) = \\ &= z - 1 - \frac{AI(1 + f)}{1 + f(1 - T_r^{1/2})} \\ \frac{G_d}{RT} &= \ln \phi = z - 1 - \ln(z - B) - AI \\ \frac{C_{pd}}{R} &= AI \frac{T_r^2}{F} \frac{\partial^2 F}{\partial T_r^2} + \frac{[(z - B)^{-1} - T_r(WF)^{-1}] \partial F / \partial T_r}{(z - B)^{-2} - AW^{-2}(2z + C_1)} - 1 \end{aligned}$$

The Newton iteration formula for the pressure is

$$p' = p - \frac{\varphi(p)}{d\varphi(p)/dp} \quad (30)$$

The pressure function $\varphi(p)$ follows from the condition of vapor-liquid equilibrium, i.e.

$$\varphi(p) = \ln \phi_v - \ln \phi_l \quad (31)$$

and its derivative is therefore

$$\frac{d\varphi(p)}{dp} = \frac{z_v - z_l}{p} \quad (32)$$

In Table IV we find

$$\ln \phi = z - 1 - \ln(z - B) - AI \quad (33)$$

The combination of Eqs (30) to (33) gives

$$p' = p \frac{\ln [(z_v - B)/(z_l - B)] + A(I_v - I_l)}{z_v - z_l} \quad (34)$$

This general expression is now applied to the EOS chosen. From Table I, the coefficients c_1 and c_2 are found. They are made dimensionless using Eq. (5) and the formulae for B , C and D are substituted from Eq. (10). The necessary values of B_0 etc. are found in Table II. The expression for the dimensionless coefficient A follows again from Eq. (10) with A_0 from Table II and the quantity F given in Table III or by Eq. (11) with the appropriate expression for f from Table III. Now the pressure is estimated, the dimensionless EOS coefficients are calculated and substituted in Eq. (8). The z_v and z_l values are then calculated, from which the I_v and I_l values are found. Then Eq. (34) yields a new estimate of the pressure etc.

Fugacity Coefficient of a Component in a Fluid Mixture

The fugacity coefficients of components are needed for calculating phase equilibrium in mixtures. The partial molar thermodynamic functions of the components are calculated from the mixture molar functions. To simplify notation the mixture molar functions will not be indexed.

For a general molar function e the following equation is valid

$$\bar{e}_i = e + \left(\frac{\partial e}{\partial x_i} \right)_{T,p,x_k \neq i} - \sum_j x_j \left(\frac{\partial e}{\partial x_j} \right)_{T,p,x_k \neq j} \quad (35)$$

This can be transformed to

$$\bar{e}_i = e + \left(\frac{\partial e}{\partial x_i} \right)_{T,v,x_{k \neq i}} - \sum_j x_j \left(\frac{\partial e}{\partial x_j} \right)_{T,v,x_{k \neq j}} - \frac{(\partial e / \partial v)_{T,x}}{(\partial p / \partial v)_{T,x}} \left[\left(\frac{\partial p}{\partial x_i} \right)_{T,v,x_{k \neq i}} - \sum_j x_j \left(\frac{\partial p}{\partial x_j} \right)_{T,v,x_{k \neq j}} \right]. \quad (36)$$

As suggested by Novák et al.^{15,16}, it is convenient to introduce an analogue to Eq. (35), which applies at constant molar volume (instead of pressure), i.e.

$$\tilde{p}_i - p = \left(\frac{\partial p}{\partial x_i} \right)_{T,v,x_{k \neq i}} - \sum_j x_j \left(\frac{\partial p}{\partial x_j} \right)_{T,v,x_{k \neq j}}. \quad (37)$$

This can be substituted in Eq. (36) to yield

$$\bar{e}_i = e + \left(\frac{\partial e}{\partial x_i} \right)_{T,v,x_{k \neq i}} - \sum_j x_j \left(\frac{\partial e}{\partial x_j} \right)_{T,v,x_{k \neq j}} - \frac{(\partial e / \partial v)_{T,x}}{(\partial p / \partial v)_{T,x}} (\tilde{p}_i - p). \quad (38)$$

This equation may be used to calculate the partial molar departure functions. For the partial molar Helmholtz departure function we get

$$\bar{A}_{di} = - \int_{\infty}^v \left(\tilde{p}_i - \frac{RT}{v} \right) dv - RT \ln \frac{pv}{RT} + \frac{p(\tilde{p}_i - p)}{(\partial p / \partial v)_{T,x}}, \quad (39)$$

from which

$$\ln \phi_i = - \frac{1}{RT} \int_{\infty}^v \left(\tilde{p}_i - \frac{RT}{v} \right) dv - \ln \frac{pv}{RT} + \frac{pv}{RT} - 1. \quad (40)$$

Substitution of Eq. (1) in Eq. (37) gives

$$\tilde{p}_i = \frac{RT}{v-b} + \frac{RT}{(v-b)^2} (\tilde{b}_i - b) - \frac{\tilde{a}_i}{w} + \frac{a}{w} (\tilde{w}_2 - w), \quad (41)$$

where an analogue of Eq. (37) defines the quantities \tilde{a}_i , \tilde{b}_i and \tilde{w}_i . Substituting from Eq. (41) in Eq. (40) and integrating yields

$$\ln \phi_i = \ln \frac{RT}{p(v-b)} + \frac{\tilde{b}_i - b}{v-b} - \frac{\tilde{a}_i}{RT} i - \frac{a}{RT} \int_{\infty}^v \frac{\tilde{w}_i - w}{w^2} dv. \quad (42)$$

If a and b are defined by Eqs (26) and (27), then

$$\tilde{a}_i = 2 \sum_j x_j a_{ij} - a, \quad \tilde{b}_i = b_i \quad (43)$$

and according to Eq. (2) we have

$$\tilde{w}_i - w = v(\tilde{c}_{1i} - c_1) + \tilde{c}_{2i} - c_2 = v d_1 + d_2, \quad (44)$$

where the symbols d_1 and d_2 are introduced to simplify the form of the equations. The integral in Eq. (42) has an analytical solution. After rearrangement and re-writing the equation with the aid of the dimensionless quantities the final form of the expression for $\ln \phi_i$ is

$$\ln \phi_i = -\ln(z - B) + \frac{B_i}{B}(z - 1) - \frac{A}{K^2} \left(\frac{L}{W} - IM \right) \quad (45)$$

with

$$\begin{aligned} L &= \left[J - K^2 \left(\frac{B_i}{B} - 1 \right) \right] z + 2C_2 D_1 - C_1 D_2, \\ M &= J - (\delta_i - 1) K^2, \quad J = C_1 D_1 - 2D_2, \\ \delta_i &= 2(\sum_j x_j a_{ij})/a = 2(a_i^{1/2}/a) \sum_j x_j (1 - k_{ij}) a_j^{1/2} = \\ &= 2(\sum_j x_j A_{ij})/A = 2(A_i^{1/2}/A) \sum_j x_j (1 - k_{ij}) A_j^{1/2}. \end{aligned} \quad (46)$$

The formula for δ_i is here based on Eqs (26) and (27). The expressions for D_1 and D_2 are summarized in Table V. Eq. (45) is a general formula for all EOS, for which Eqs (1) and (2) hold.

In case the coefficients c_1 and c_2 are multiples of b , Eq. (45) can be simplified. Then the following relations are valid

$$c_1 = K_1 b, \quad c_2 = K_2 b^2. \quad (47)$$

Expressions for the dimensionless coefficients K_1 and K_2 are given in Table V. From Eqs (5), (16), (18), (44) and (47) follows

$$\begin{aligned} K &= (K_1^2 - 4K_2)^{1/2} B, \quad D_1 = K_1(B_i - B), \quad D_2 = 2K_2 B(B_i - B), \\ I &= (K_1^2 - 4K_2)^{-1/2} B^{-1} \ln \frac{2z + [K_1 + (K_1^2 - 4K_2)^{1/2}] B}{2z + [K_1 - (K_1^2 - 4K_2)^{1/2}] B} \end{aligned} \quad (48)$$

and substituting in Eqs (45) and (46) yields after rearrangement

$$\ln \phi_i = (B_i/B)(z - 1) - \ln(z - B) + AI(B_i/B - \delta_i). \quad (49)$$

This is equivalent to Eq. (5-8.12) in the book of Reid et al.¹. This equation allows to write expressions which may be simpler than those published by authors of the EOS. E.g. Yu and Lu⁷ suggest a very complicated formula for $\ln \phi_i$, which requires a considerable effort for its derivation. According to the procedure proposed here, we would find from Table V, that the coefficients K_1 and K_2 and hence Eq. (49) are applicable. The expressions for K_1 and K_2 are used in the formula for I , Eq. (48), and this gives after substituting in Eq. (49)

$$\ln \phi_i = \frac{B_i}{B}(z - 1) - \ln(z - B) + \frac{A}{K} \left(\frac{B_i}{B} - \delta_i \right) \ln \frac{2z + uB + K}{2z + uB - K},$$

with

$$K = [u^2 - 4(u - 3)]^{1/2} B, \quad u = c/b + 3$$

and δ_i defined in Eq. (46). It can be shown that the equations for $\ln \phi_i$ are equivalent.

TABLE V
Coefficients $K_{1,2}$ and the differences $D_1 = \tilde{C}_{1i} - C_1$ and $D_2 = \tilde{C}_{2i} - C_2$

Refs	K_1	K_2	D_1	D_2
2	0	0	0	0
3	1	0	$B_i - B$	0
4	1	0	$B_i - B$	0
5	2	-1	$2(B_i - B)$	$-2B(B_i - B)$
6	$1 + 3\omega$	-3ω	$(1 + 3\omega)(B_i - B)$	$-6\omega B(B_i - B)$
7	u	$u - 3$	$u(B_i - B)$	$2(u - 3)B(B_i - B)$
8	C	$1 - C$	$C(B_i - B)$	$2B(B_i - B)(1 - C)$
9, 10	—	—	$2(C_i - C)$	$2C(C_i - C)$
11	—	—	$2(C_i - C)$	$-2C(C_i - C)$
12	—	—	$B_i - B + C_i - C$	$-(B_i - B)C - B(C_i - C)$
13	—	—	$B_i - B + C_i - C$	$-(B_i - B)C - B(C_i - C)$
14	—	—	$-C_i + C + D_i - D$	$-(C_i - C)D - C(D_i - D)$

For the bubble and dew point calculations, the partial derivatives of $\ln \phi_i$ with respect to temperature and pressure, respectively, are needed at constant composition and pressure and temperature respectively. We shall represent here both the temperature and pressure by a common symbol l . Then from Eq. (45) follows

$$\frac{\partial \ln \phi_i}{\partial l} = -\frac{1}{z-B} \left(\frac{\partial z}{\partial l} - \frac{\partial B}{\partial l} \right) + \frac{B_i}{B} \frac{\partial z}{\partial l} - \left(\frac{L}{W} - IM \right) \left(\frac{1}{K^2} \frac{\partial A}{\partial l} - \frac{2A}{K^3} \frac{\partial K}{\partial l} \right) - \frac{A}{K^2} \left(\frac{1}{W} \frac{\partial L}{\partial l} - \frac{L}{W^2} \frac{\partial W}{\partial l} - I \frac{\partial M}{\partial l} - M \frac{\partial I}{\partial l} \right), \quad (50)$$

where

$$\begin{aligned} \frac{\partial J}{\partial l} &= C_1 \frac{\partial D_1}{\partial l} + D_1 \frac{\partial C_1}{\partial l} - 2 \frac{\partial D_2}{\partial l}, \\ \frac{\partial L}{\partial l} &= \left[J + K^2 \left(\frac{B_i}{B} - 1 \right) \right] \frac{\partial z}{\partial l} + z \left[\frac{\partial J}{\partial l} + 2 \left(\frac{B_i}{B} - 1 \right) K \frac{\partial K}{\partial l} \right] + \\ &+ 2 \left(C_2 \frac{\partial D_1}{\partial l} + D_1 \frac{\partial C_2}{\partial l} \right) - C_1 \frac{\partial D_2}{\partial l} - D_2 \frac{\partial C_1}{\partial l}, \\ \frac{\partial M}{\partial l} &= \frac{\partial J}{\partial l} - 2(\delta_i - 1) K \frac{\partial K}{\partial l} - K^2 \frac{\partial \delta_i}{\partial l}. \end{aligned} \quad (51)$$

The derivatives of $D_{1,2}$ can be found after substitution from Table V. The general expressions for the partial derivatives of A , B , C_1 , C_2 , K , I , z and δ_i with respect to temperature and pressure are given in Table VI.

For the more common EOS, Eq. (49) holds. At constant pressure and composition the partial derivative of $\ln \phi_i$ with respect to temperature is

$$\frac{\partial \ln \phi_i}{\partial T} = \frac{B_i}{B} \frac{\partial z}{\partial T} - \frac{1}{z-B} \left(\frac{\partial z}{\partial T} + \frac{B}{T} \right) + \left(\frac{B_i}{B} - \delta_i \right) \left(I \frac{\partial A}{\partial T} + A \frac{\partial I}{\partial T} \right) + AI \frac{\partial \delta_i}{\partial T}. \quad (52)$$

The derivatives on the righthand side of this equation are given in Table VI, but $\partial z / \partial T$ may be expressed as

$$\frac{\partial z}{\partial T} = \frac{(B-z)(a^{-1} \partial a / \partial T - 2T^{-1}) - \{z^2(1-K_1) + z[K_1 + 2B(K_1 - K_2)] + A + K_2 B(2 + 3B)\} BT^{-1}}{z\{3z + 2[B(K_1 - 1) - 1]\} + A - B[K_1(1+B) - K_2 B]} \quad (53)$$

and $\partial I/\partial T$ as

$$\frac{\partial I}{\partial T} = \frac{I}{T} - 4 \frac{z/T + \partial z/\partial T}{(2z + K_1 B)^2 - (K_1^2 - 4K_2) B^2}. \quad (54)$$

At constant composition and temperature we have

$$\frac{\partial \ln \phi_i}{\partial p} = \frac{B_i}{B} \frac{\partial z}{\partial p} - \frac{\partial z/\partial p - B/p}{z - B} + \left(\frac{B_i}{B} - \delta_i \right) \left(\frac{I}{p} + \frac{\partial I}{\partial p} \right) A, \quad (55)$$

TABLE VI

Partial derivatives of A , B , C_1 , C_2 , K , I , z and δ_i with respect to temperature and pressure

Constant pressure and composition

$$\frac{\partial A}{\partial T} = A \left(\frac{1}{a} \frac{\partial a}{\partial T} - \frac{2}{T} \right)$$

$$\frac{1}{a} \frac{\partial a}{\partial T} = \frac{1}{a} \sum_i \sum_j x_i x_j (1 - k_{ij}) (a_i a_j)^{1/2} \left(F_i^{-1/2} \frac{\partial F_i^{1/2}}{\partial T} + F_j^{-1/2} \frac{\partial F_j^{1/2}}{\partial T} \right) =$$

$$= \frac{1}{2a} \sum_i \sum_j x_i x_j (1 - k_{ij}) (a_i a_j)^{1/2} \left(F_i^{-1} \frac{\partial F_i}{\partial T} + F_j^{-1} \frac{\partial F_j}{\partial T} \right) =$$

$$= -(2AT^{1/2})^{-1} \sum_i \sum_j x_i x_j (1 - k_{ij}) (A_i A_j)^{1/2} \cdot$$

$$\cdot \left(\frac{f_i T_{ci}^{-1/2}}{1 + f_i [1 - (T/T_{ci})^{1/2}]} + \frac{f_j T_{cj}^{-1/2}}{1 + f_j [1 - (T/T_{cj})^{1/2}]} \right)$$

$$\frac{\partial B}{\partial T} = -\frac{B}{T}, \quad \frac{\partial C_1}{\partial T} = -\frac{C_1}{T}, \quad \frac{\partial C_2}{\partial T} = -2 \frac{C_2}{T}, \quad \frac{\partial K}{\partial T} = -\frac{K}{T}$$

$$\frac{\partial I}{\partial T} = \frac{I}{T} - 4 \frac{z/T + \partial z/\partial T}{(2z + C_1)^2 - K^2}$$

$$\frac{\partial z}{\partial T} = \frac{(B - z) \partial A/\partial T - [z(z + C_1) + A + C_2] B/T - (z - B - 1)(zC_1 + 2C_2)/T}{z[3z + 2(C_1 - B - 1)] + A - (1 + B)C_1 + C_2}$$

$$\frac{\partial \delta_i}{\partial T} = \left(a_i^{-1/2} \frac{\partial a_i^{1/2}}{\partial T} - a_i^{-1} \frac{\partial a_i}{\partial T} \right) \delta_i + 2 \frac{a_i^{1/2}}{a} \sum_j x_j (1 - k_{ij}) \frac{\partial a_j^{1/2}}{\partial T}$$

$$\frac{\partial a_i^{1/2}}{\partial T} = \left(\frac{a_i}{F_i} \right)^{1/2} \frac{\partial F_i^{1/2}}{\partial T} = - \left(\frac{a_i}{T} \right)^{1/2} \frac{f_i T_{ci}^{1/2}}{1 + f_i [1 - (T/T_{ci})^{1/2}]}$$

TABLE VI
(Continued)

Constant temperature and composition

$$\frac{\partial A}{\partial p} = \frac{A}{p}, \quad \frac{\partial B}{\partial p} = \frac{B}{p}, \quad \frac{\partial C_1}{\partial p} = \frac{C_1}{p}, \quad \frac{\partial C_2}{\partial p} = 2 \frac{C_2}{p}, \quad \frac{\partial K}{\partial p} = \frac{K}{p}$$

$$\frac{\partial I}{\partial p} = -\frac{I}{p} + 4 \frac{z/p - \partial z/\partial p}{(2z + C_1)^2 - K^2}$$

$$\frac{\partial z}{\partial p} = \frac{1}{p} \frac{A(B - z) + B[z(z + C_1) + A + C_2] + (1 + B - z)(zC_1 + 2C_2)}{z[3z + 2(C_1 - B - 1)] + A - (1 + B)C_1 + C_2}$$

$$\frac{\partial \delta_i}{\partial p} = 0$$

with

$$\frac{\partial z}{\partial p} = \frac{1}{p} \frac{A(B - z) + B\{z^2(1 - K_1) + z[K_1 + 2B(K_1 - K_2)] + A + K_2B(2 + 3B)\}}{z\{3z + 2[B(K_1 - 1) - 1]\} + A - B[(1 + B)K_1 - K_2B]} \quad (56)$$

and

$$\frac{\partial I}{\partial p} = -\frac{I}{p} + 4 \frac{z/p - \partial z/\partial p}{(2z + K_1B)^2 - (K_1^2 - 4K_2)B^2} \quad (57)$$

The equations given in this paper facilitate the treatment and comparison of different cubic EOS. E.g. Patel and Teja¹⁴ suggest this formula for the fugacity coefficient

$$\ln \phi = z - 1 - \ln(z - B) - \frac{a}{2RTN} \ln \frac{z + M}{z + Q}$$

where

$$B = \frac{bp_c}{RT_c}, \quad M = \left(\frac{b+c}{2} - N\right) \frac{p}{RT}, \quad N = \left[bc + \frac{(b+c)^2}{2}\right]^{-1/2},$$

$$Q = \left(\frac{b+c}{2} + N\right) \frac{p}{RT}$$

and a , b , c are the EOS coefficients. In our treatment, the Eq. (33) applies

$$\ln \phi = z - 1 - \ln(z - B) - AI$$

The quantity A is defined in Eq. (4) and I in Eq. (18). We find the formula for K from Eqs (16) and (18). The necessary expressions for c_1 and c_2 are given in Table I. Then

$$K = [(B + C)^2 + 4BC]^{1/2} \quad \text{and} \quad I = \frac{1}{K} \ln \frac{2z + B + C + K}{2z + B + C - K}.$$

It can be seen that there is an error in the definition of the coefficient B (see Eq. (4)). The quantity N should correspond to our $k/2$, i.e.

$$\frac{k}{2} = \left[\left(\frac{b+c}{2} \right)^2 + bc \right]^{1/2}.$$

Therefore, the sign of the exponent in the definition of N is wrong and the denominator 2 should be 4. Patel and Teja¹⁴ define another quantity d as

$$d = \left[bc + \frac{(b+c)^2}{4} \right]^{1/2}$$

which is again $k/2$ and, therefore, the correct expression for N . The comparison of their expression for the molar entropy departure function with our Eq. (24) shows the incorrect inclusion of pressure in their formula.

This was another example of the utility of the unified treatment, which is also useful for computer programming.

LIST OF SYMBOLS

A	dimensionless coefficient, Eq. (4)
A	molar Helmholtz function, J mol^{-1}
A_0	dimensionless coefficient, Eq. (9) or Table II
a	EOS coefficient, $\text{Pa m}^6 \text{ mol}^{-2}$
a_{ij}	binary coefficient, Eqs (26) and (27), $\text{Pa m}^6 \text{ mol}^{-2}$
B	dimensionless coefficient, Eq. (4)
B_0	dimensionless coefficient, Eq. (9) or Table II
b	EOS coefficient, $\text{m}^3 \text{ mol}^{-1}$
C	dimensionless coefficient, Eq. (4) or Table I
C_0	dimensionless coefficient, Eq. (9) or Table II
C_p	molar heat capacity at constant pressure, $\text{J mol}^{-1} \text{ K}^{-1}$
$C_{1,2}$	dimensionless coefficients, Eq. (5)

<i>c</i>	EOS coefficient, $\text{m}^3 \text{mol}^{-1}$
<i>c</i> ₁	coefficient, Eq. (2) or Table I, $\text{m}^3 \text{mol}^{-1}$
<i>c</i> ₂	coefficient, Eq. (2) or Table I, $\text{m}^6 \text{mol}^{-2}$
<i>D</i>	dimensionless coefficient, Eq. (4)
<i>D</i> ₀	dimensionless coefficient, Eq. (9) or Table II
<i>D</i> _{1,2}	dimensionless form of the differences from Eq. (44), see also Eq. (48) or Table V
<i>d</i>	EOS coefficient, $\text{m}^3 \text{mol}^{-1}$
<i>d</i> ₁	difference, Eq. (44), $\text{m}^3 \text{mol}^{-1}$
<i>d</i> ₂	difference, Eq. (44), $\text{m}^6 \text{mol}^{-2}$
<i>e</i>	general molar function, J mol^{-1}
<i>F</i>	dimensionless coefficient, Eq. (10) or Table III
<i>f</i>	dimensionless coefficient, Eq. (11) or Table III
<i>G</i>	molar Gibbs function, J mol^{-1}
<i>H</i>	molar enthalpy, J mol^{-1}
<i>I</i>	dimensionless parameter, Eq. (18)
<i>i</i>	parameter, Eq. (15), mol m^{-3}
<i>J</i>	dimensionless parameter, Eq. (46)
<i>K</i>	dimensionless parameter, Eq. (18)
<i>K</i> _{1,2}	dimensionless coefficients, Eq. (47) or Table V
<i>k</i>	parameter, Eq. (16)
<i>k</i> _{ij}	dimensionless binary interaction coefficient
<i>L</i>	dimensionless parameter, Eq. (46)
<i>l</i>	temperature or pressure
<i>M</i>	dimensionless parameter, Eq. (46)
<i>p</i>	pressure, Pa
<i>R</i>	universal gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
<i>S</i>	molar entropy, $\text{J mol}^{-1} \text{K}^{-1}$
<i>T</i>	temperature, K
<i>v</i>	molar volume, $\text{m}^3 \text{mol}^{-1}$
<i>W</i>	dimensionless quantity, Eq. (5)
<i>w</i>	quantity defined by Eq. (2), $\text{m}^6 \text{mol}^{-2}$
<i>x</i>	mole fraction
<i>z</i>	compressibility factor
<i>δ</i> _i	quantity defined by Eq. (46)
<i>φ</i>	fugacity coefficient
<i>ω</i>	acentric factor

Subscripts

<i>c</i>	critical property
<i>d</i>	departure function
<i>i, j, k</i>	components
<i>l</i>	liquid phase
<i>r</i>	reduced property
<i>v</i>	vapor phase

Superscripts

—	partial molar quantity
~	quantity defined by an equation having the form of Eq. (37)

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Translated by the author.