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Berkeley, California

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AN IMPROVED EQUATION OF STATE

Max Jacobson
(M.S. Thesis)

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DERIVATION OF FUGACITY COEFFICIENTS FROM
AN IMPROVED EQUATION OF STATE

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May 1964

ABSTRACT

The equation of state proposed by Redlich and Kwong has been improved by addition of a deviation term containing Pitzer's acentric factor and by means of a new rule for the combination of the parameters for mixtures. Only the critical temperature, pressure, and acentric factor of the components are required in a computer program (Fortran for IBM 7090) furnishing compressibility factors, mean fugacity coefficients, and individual fugacity coefficients of the components. The equation is restricted so far to the gaseous state. Its accuracy for the compressibility factor is close to that of Pitzer's tables. The computation of fugacity coefficients does not entail any loss of formal precision.

I. INTRODUCTION

A. Previous and Present Work

In 1948, Redlich and Kwong¹ proposed an equation of state which, though still within the limits of the theorem of corresponding states, was supposed to obtain two main objectives. The first was an analytical expression which was less cumbersome than existing good equations of state and would allow the algebraic derivation of fugacity coefficients. The second objective was a good representation of the behavior of gases at high pressures. For mixtures, the assumed mixing rules for the parameters were based on general experimental and theoretical evidence. Reasonably good agreement with experimental data was obtained, despite the fact that the only parameters used were the critical temperature and pressure of the individual components.

Between 1948 and 1960, two developments suggested further work on the original equation. The increasing availability of high speed computers allowed much more complicated algebraic expressions to be handled. In addition, the need for fugacity coefficients in gaseous mixtures increased steadily. In 1960, Redlich and Dunlop² resumed the problem of the equation of state, proceeding to free the original equation from its inherent limitations by the introduction of a third parameter, namely Pitzer's acentric factor.³ In order to preserve the good behavior of the original equation at high pressure, a deviation function for the volume was constructed that decreased to zero in first or higher order with increasing pressure. The deviation function was designed to minimize the error between the new equation and a group of data for seven representative substances.

Realizing the generally satisfactory accuracy of the tables proposed by Pitzer^{4,5} and his coworkers, Ackerman⁶ attempted to develop a new deviation function, taking mainly Pitzer's tables as a guide. Ackerman's algebraic representation came fairly close to Pitzer's results and showed improvement over Dunlop's deviation function. If this accuracy could be extended to mixtures, the resultant fugacity coefficients would be of considerable value. For this reason, Gunn⁷ modified the mixing rules for the parameters, guided by observed compressibility factors for mixtures.

The object of the present work was the next and essentially final step, the derivation of individual fugacity coefficients for the components of a mixture. In addition, mean enthalpy and entropy were derived algebraically in the previous work. A computer program to calculate these quantities was developed.

II. DEVIATION AND DEVELOPMENT OF THE COMPUTER PROGRAM ES64

A. General Remarks

Previous work by Kwong, Ackerman, and Gunn has progressed to the explicit derivation of the mean fugacity coefficient ϕ from the compressibility factor Z according to the definition

$$\ln \phi = \int_0^P (Z-1) dP/P. \quad (1)$$

The derivation of individual fugacity coefficients ϕ_i from ϕ prescribed by

$$\ln \phi_i = \ln \phi + \partial \ln \phi / \partial y_i - \sum_j y_j \partial \ln \phi / \partial y_j \quad (2)$$

requires differentiation with respect to the mole fractions y_j and is somewhat complicated. It is conveniently resolved into a number of distinct steps.

The use of two operators simplifies the presentation. The first indicates the difference between derivatives resulting from the combination rules of Gunn (G) and Kwong (K). It is defined for any function F by

$$L_i(F) = \left(\frac{\partial F}{\partial y_i}\right)_G - \left(\frac{\partial F}{\partial y_i}\right)_K. \quad (3)$$

The second operates on a subscripted quantity F_i and is given by

$$K(F_i) = F_i - \sum_j y_j F_j. \quad (4)$$

Kwong's original fugacity coefficient ϕ_{K1} was derived and presented by Redlich and Kwong in 1949. Gunn's new combination rule entailed a change in the individual fugacity coefficient. The term $\ln(\phi_{KG1}/\phi_{K1})$ was derived by means of Eq. (2) with the aid of the operators L_i and K.

The necessity for the operations prescribed by the operator L_i is shown as follows: Since ϕ_K is a function of T_r and P_r (not depending explicitly on the y_j 's), we have

$$\begin{aligned} \frac{\partial \ln \phi_K}{\partial y_i} &= \left(\frac{\partial \ln \phi_K}{\partial T_r}\right)\left(\frac{\partial T_r}{\partial y_i}\right) \\ &+ \left(\frac{\partial \ln \phi_K}{\partial P_r}\right)\left(\frac{\partial P_r}{\partial y_i}\right). \end{aligned} \quad (5)$$

But since T_r and P_r are defined differently for the combinations of Kwong and Gunn, the quantities $\partial T_r/\partial y_i$ and $\partial P_r/\partial y_i$ are different for the two combination rules used.

Ackerman had devised a deviation function to improve upon Kwong's equation of state, and Gunn derived the mean deviation fugacity coefficient

ϕ_{AG} from this deviation function. In order to derive an individual deviation fugacity coefficient, Eq. (2) and operator K were applied to ϕ_{AG} yielding the quantity (ϕ_{AGi}/ϕ_{AG}) .

The final form for the individual fugacity coefficient appears as

$$\begin{aligned} \ln \phi_i &= \ln \phi_{Ki} + \ln (\phi_{KGi} / \phi_{Ki}) \\ &+ \ln \phi_{AG} + \ln (\phi_{AGi} / \phi_{AG}) \end{aligned} \quad (6)$$

The following quantities will appear frequently. They are presented here for easy reference along with their statement number location in the ES64 program. The critical quantities are denoted by TC_1 and PC_1 .

<u>Computer Symbol</u>	<u>Statement Number</u>	
BS(JS)	44	$BS_1 = 0.08667 TC_1/PC_1 = 0.08667 z_1$
AS(JS)	45	$AS_1 = 0.6540 TC_1^{1.25}/PC_1^{0.5} = 0.6541 h_1$
BR	120	$BR = 0.08667 \sum y_j z_1$
AT	119	$AT = (0.6541 \sum_j y_j h_j)^2$
AB	514	$AB_1 = BS_1/BR$
AA	513	$AA_1 = -1.3333 AS_1/(AT)^{0.5}$
Q	182	$Q = BR/(T.P)$
E	154	$E = AT/(BR \cdot T^{1.5})$
WS(JS)	input	$w_1 = \text{Pitzer's acentric factor}$
WL	121	$WL = \sum_j y_j w_j$
WN	122	$WN = 0.08667 \sum_j y_j w_j z_j$
AC	511	$AC = 1.0 - 0.5 WL$
WM	123	$WM = WN/BR$
BT	124	$BT = BR/[1.0 + 0.5(WM-WL)]$

B. Functions Based on the Equation of State of Redlich and Kwong

The individual fugacity coefficient ϕ_{Ki} is given as a function of T_r and P_r by Kwong¹ as

$$\ln \phi_{Ki} = (Z_K - 1)BS_i/BR - \ln(Z_K - Q) - E(2AS_i/AT)^{0.5} - BS_i/BR \ln(1 + Q/Z_K). \quad (7)$$

The term $\ln(\phi_{KGi}/\phi_{Ki})$ is obtained by application of Eqs. (2), (3), and (4) to the mean Kwong fugacity coefficient ϕ_K .

$$\ln(\phi_{KGi}/\phi_{Ki}) = FKG_i = \left[(\partial \ln \phi_K / \partial y_i)_G - (\partial \ln \phi_K / \partial y_i)_K \right] \quad (8)$$

$$- \sum_j y_j \left[(\partial \ln \phi_K / \partial y_j)_G - (\partial \ln \phi_K / \partial y_j)_K \right]$$

$$FKG_i = K[L_i(\phi_K)]. \quad (9)$$

Kwong's coefficient ϕ_K is a function of T_r and P_r , but not of the acentric factors w_j . Therefore, Eq. (5) furnishes

$$FKG_i = \left[(\partial \ln \phi_K / \partial T_r) L_i(T_r) + (\partial \ln \phi_K / \partial P_r) L_i(P_r) \right] - \left[(\partial \ln \phi_K / \partial T_r) \sum_j y_j L_i(T_r) + (\partial \ln \phi_K / \partial P_r) \sum_j y_j L_i(P_r) \right]. \quad (10)$$

or in terms of the operator K,

$$FKG_i = (\partial \ln \phi_K / \partial T_r) K[L_i(T_r)] + (\partial \ln \phi_K / \partial P_r) K[L_i(P_r)] \quad (11)$$

1. Temperature Derivatives

Gunn's combination for the critical temperature of a mixture is given by

$$T_M = \left(\sum_j y_j h_j \right)^{1.3333} \left[1.0 + 0.5 \left(\frac{\sum_j y_j w_j z_j}{\sum_j y_j z_j} - \sum_j y_j w_j \right) \right]^{0.6667} / \left(\sum_j y_j z_j \right)^{0.6667} \quad (12)$$

Substituting the previously defined quantities, we obtain

$$T_M = \left[(AT)^{0.5} / 0.6540 \right]^{1.3333} \cdot \left[1.0 + 0.5(WM - WL) \right]^{0.6667} / (BR / 0.08667)^{0.6667} \quad (13)$$

or further

$$T_M = 0.34492 (AT/BT)^{0.6667} \quad (14)$$

(Statement number 125)

Returning to Eq. (13) and clearing the fraction in the second term yields

$$T_M = \left(\sum_j y_j h_j \right)^{1.3333} \cdot \left[\sum_j y_j z_j + 0.5 \sum_j y_j w_j z_j - 0.5 \left(\sum_j y_j w_j \right) \cdot \left(\sum_j y_j z_j \right) \right]^{0.6667} / \left(\sum_j y_j z_j \right)^{1.3333} \quad (15)$$

Since $(\partial T_r / \partial y_i) / T_r = -(\partial T_M / \partial y_i) / T_M$, differentiation of T_M yields the following equation where the subscript G refers to the fact that we are using Gunn's combination for T_M : differ-

$$\begin{aligned} (\partial T_r / \partial y_i)_G / T_r = & - \left[1.3333 h_i / \sum_j y_j h_j - 1.3333 z_i / \sum_j y_j z_j \right. \\ & + 0.6667 (z_i + 0.5 w_i z_i - 0.5 w_i \sum_j y_j z_j - 0.5 z_i \sum_j y_j w_j) / \\ & \left. \left(\sum_j y_j z_j + 0.5 \sum_j y_j w_j z_j - 0.5 \left(\sum_j y_j w_j \right) \left(\sum_j y_j z_j \right) \right) \right]. \quad (16) \end{aligned}$$

Simplifying and introducing the defined quantities, we have

$$\begin{aligned}
 (\partial T_r / \partial y_i)_G / T_r = & -1.3333 \left\{ h_i / \sum_j y_j h_j - g_i / \sum_j y_j g_j \right. \\
 & + \left[g_i (1.0 - 0.5 \sum_j y_j w_j) + 0.5 w_i (g_i - \sum_j y_j g_j) \right] / \\
 & \left. \left[2 \sum_j y_j g_j (1.0 - 0.5 \sum_j y_j w_j) + \sum_j y_j w_j g_j \right] \right\}
 \end{aligned} \tag{17}$$

$$\begin{aligned}
 (\partial T_r / \partial y_i)_G / T_r = & -1.3333 \left\{ (A S_i / 0.6540) / (A T^{0.5} / 0.6540) - \right. \\
 & (B S_i / 0.08667) / (B R / 0.08667) + \left[(B S_i / 0.08667)(1.0 - 0.5 W L) \right. \\
 & + 0.5 W S_i (B S_i / 0.08667 - B R / 0.08667) \left. \right] / \left[(2 B R / 0.08667)(1.0 - 0.5 W L) \right. \\
 & \left. + W N / 0.08667 \right]
 \end{aligned} \tag{18}$$

$$\begin{aligned}
 (\partial T_r / \partial y_i)_G / T_r = & -1.3333 \left\{ A S_i / A T^{0.5} - B S_i / B R \right. \\
 & + \left[B S_i (1.0 - 0.5 W L) + 0.5 W S_i (B S_i - B R) \right] / \\
 & \left. \left[2 B R (1.0 - 0.5 W L) + W N \right] \right\}
 \end{aligned} \tag{19}$$

$$\begin{aligned}
 (\partial T_r / \partial y_i)_G / T_r = & A A_i + 1.3333 A B_i - 1.3333 \left\{ [B S_i \cdot A C + \right. \\
 & \left. 0.5 W S_i (B S_i - B R)] / (2 B R \cdot A C + W N) \right\}
 \end{aligned} \tag{20}$$

$$\left(\frac{\partial T_r}{\partial y_i}\right)_G / T_r = AA_i + 1.3333 \left\{ AB_i - [AB_i \cdot AC + 0.5 WS_i (AB_i - 1.0)] / (2AC + WM/BR) \right\} \quad (21)$$

With the abbreviation

$$AD_i = 1.3333 \left\{ AB_i - [AB_i (AC + 0.5 WS_i) - 0.5 WS_i] / (2AC + WM) \right\} \quad (22)$$

(statement 515)

we have

$$\left(\frac{\partial T_r}{\partial y_i}\right)_G / T = (AA_i + AD_i) / T_M = UAA_i \quad (23)$$

(Statement 516)

Since Gunn's combination becomes the old Redlich-Kwong combination if the acentric factors are zero, we may obtain $(\partial T_r / \partial y_i)_K$ most readily by letting the terms involving acentric factors in Eq. (16) be equal to zero. Thus we obtain from Eq. (18)

$$\left(\frac{\partial T_r}{\partial y_i}\right)_K / T_r = -1.3333 AS_i / AT^{0.5} + 0.6667 BS_i / BR. \quad (24)$$

With the aid of Eq. (3), relations (19) and (24) may be combined as

$$L_i (\ln T_r) = \left[\left(\frac{\partial T_r}{\partial y_i}\right)_G - \left(\frac{\partial T_r}{\partial y_i}\right)_K \right] / T_r \quad (25)$$

$$L_i (\ln T_r) = -1.3333 AS_i / AT^{0.5} + 1.3333 BS_i / BR - 1.3333 \left\{ [(BS_i / BR)(1.0 - 0.5 WL + 0.5 WS_i) - 0.5 WS_i] / [2(1.0 - 0.5 WL) + WM] \right\} + 1.3333 AS_i / AT^{0.5} - 0.6667 BS_i / BR. \quad (26)$$

Simplifying we have

$$L_i(\ln T_r) = 0.3333 \left\{ - \left[(BS_i/BR)(1.0 - 0.5WL + 0.5WS_i) - 0.5WS_i \right] / [2(1.0 - 0.5WL) + WM] + 0.5 BS_i / BR \right\} \quad (27)$$

or

$$L_i(\ln T_r) = 0.3333 \left[WS_i + (BS_i/BR)(WM - WS_i) \right] / (1.0 - 0.5WL + 0.5WM). \quad (28)$$

As prescribed in (11), we need the expression $K[L_i(T_r)]$. From (28) we derive

$$\sum_j y_j L_j(T_r)/T_r = 0.3333 \left[\sum_j y_j (WS_j + BS_j \cdot WM/BR - BS_j \cdot WS_j/BR) \right] / (1.0 - 0.5WL + 0.5WM). \quad (29)$$

The definitions of WM and BS_j show that

$$\sum_j y_j L_j(T_r)/T_r = 0.3333 WL / (1.0 - 0.5WL + 0.5WM) \quad (30)$$

The operator K is defined by (4). The term $K[L_i(T_r)]$ is found from Eqs. (28) and (30) as

$$K[L_i(T_r)] = 0.3333 T_r \left[WS_i + (BS_i/BR)(WM - WS_i) - WL \right] / (1.0 - 0.5WL + 0.5WM). \quad (31)$$

To complete the temperature term in the computation of FKG_1 (Eq. 12), we need the quantity $\partial \ln \phi_K / \partial T_r$. From Redlich and Kwong,¹ we have

$$\ln \phi_K = Z - 1 - \ln(Z - BP) - (A^2/B) \ln(1 + BP/Z) \quad (32)$$

$$B = 0.08667 T_c / (P_c T) \quad (33)$$

$$A^2 = 0.4276 T_c^{2.5} / (P_c T^{2.5}) \quad (34)$$

$$h = BP/Z \quad (35)$$

$$(\partial Z / \partial T_r) = 0 \quad (36)$$

$$(\partial B / \partial T_c) / B = 1 / T_c \quad (37)$$

$$(B/A^2) [\partial(A^2/B) / \partial T_c] = 1.5 / T_c \quad (38)$$

Since $T_r \partial \ln \phi / \partial T_r = -T_c \partial \ln \phi / \partial T_c$, we have

$$T_r \partial \ln \phi_K / \partial T_r = -BP / (Z - BP) + 1.5 (A^2/B) \ln(1 + BP/Z) + (A^2/B) (BP)(1 + BP/Z) / Z \quad (39)$$

Simplifying, we obtain

$$T_r \partial \ln \phi_K / \partial T_r = -BP / Z(1 - h) + (A^2/B) [h / (1 + h)] + 1.5 (A^2/B) \ln(1 + h) \quad (40)$$

$$T_r \partial \ln \phi_K / \partial T_r = 1.0 - 1 / (1 - h) + (A^2/B) [h / (1 + h)] + 1.5 (A^2/B) \ln(1 + h) \quad (41)$$

$$T_r \partial \ln \phi_K / \partial T_r = 1.0 - Z + 1.5 (A^2/B) \ln(1 + BP/Z) \quad (42)$$

Finally, we have

$$T_r \partial \ln \phi_x / \partial T_r = -Z + 1 + 1.5 E \ln(1 + Q/Z) \quad (43)$$

$$T_r \partial \ln \phi_x / \partial T_r = FKT. \quad (44)$$

(Statement) 146)

2. Pressure Derivatives

The preceding process can be repeated for the pressure derivatives

$$\partial \ln \phi_x / \partial P_r \cdot K[L_i(P_r)].$$

Gunn's combination for the critical pressure of mixture is

$$P_M = \left[\left(\sum_j y_j h_j \right)^{1.3333} / \left(\sum_j y_j \beta_j \right)^{1.6667} \right] \cdot [1.0 + 0.5(WM - WL)]^{1.6667} \quad (45)$$

or, in terms of the previously defined quantities,

$$P_M = 0.08667 T_M / BT. \quad (46)$$

(Statement) 126)

The first expression can be put in the form

$$P_M = \left[\left(\sum_j y_j h_j \right)^{1.3333} / \left(\sum_j y_j \beta_j \right)^{1.3333} \right] \cdot \left(\sum_j y_j \beta_j + 0.5 \sum_j y_j w_j \beta_j - 0.5 \sum_j y_j w_j \sum_i y_i \beta_i \right)^{1.6667}. \quad (47)$$

Since $(\partial P_r / \partial y_i)_G / P_r = -(\partial P_M / \partial y_i)_G / P_M$ we have

$$\begin{aligned}
 (\partial P_r / \partial y_i)_G / P_r &= -[1.3333 h_i / \sum_j y_j h_j - 3.3333 g_i / \sum_j y_j g_j \\
 &+ 1.6667 (g_i + 0.5 w_i g_i - 0.5 w_i \sum_j y_j g_j - 0.5 g_i \sum_j y_j w_j) / \\
 &(\sum_j y_j g_j + 0.5 \sum_j y_j w_j g_j - 0.5 \sum_j y_j w_j \sum_j y_j g_j)] .
 \end{aligned} \tag{48}$$

$$\begin{aligned}
 (\partial P_r / \partial y_i)_O / P_r &= -[1.3333 AS_i / AT^{0.5} - 3.3333 BS_i / BR \\
 &+ 1.6667 (BS_i / BR + 0.5 WS_i \cdot BS_i / BR - 0.5 WS_i \\
 &- 0.5 WL \cdot BS_i / BR) / (1.0 + 0.5 WM - 0.5 WL)]
 \end{aligned} \tag{49}$$

$$\begin{aligned}
 (\partial P_r / \partial y_i)_G / P_r &= -1.3333 AS_i / AT^{0.5} + 3.3333 \left\{ BS_i / BR \right. \\
 &- [(BS_i / BR)(1.0 + 0.5 WS_i - 0.5 WL) - 0.5 WS_i] / \\
 &\left. [2(1.0 - 0.5 WM - 0.5 WL)] \right\} .
 \end{aligned} \tag{50}$$

Finally, we have

$$(\partial P_r / \partial y_i)_G / P = (AA_i + 2.5AD_i) / P_m = UBB_i \tag{51}$$

(Statement 517)

Earlier, we found the derivative of T_r according to Kwong by letting the acentric factor w_1 be zero. Similarly, we obtain from (50)

$$(\partial P_r / \partial y_i)_K / P_r = -1.3333 AS_i / AT^{0.5} + 3.3333 (BS_i / BR - 0.5 BS_i / BR) \tag{52}$$

By subtracting Eq. (52) from Eq. (50) we have

$$L_i(\ln P_r) = [(\partial P_r / \partial y_i)_G - (\partial P_r / \partial y_i)_K] / P_r \quad (53)$$

$$L_i(\ln P_r) = 1.6667 \left\{ BS_i / BR - [(BS_i / BR)(1.0 - 0.5 WL + 0.5 WS_i) - 0.5 WS_i] / (1.0 - 0.5 WL + 0.5 WM) \right\} \quad (54)$$

$$L_i(\ln P_r) = 1.6667 \left[WS_i + (BS_i / BT)(WM - WS_i) \right] / (1.0 - 0.5 WL + 0.5 WM). \quad (55)$$

In the same manner as for the temperature function, we find

$$\left[\sum_i y_i L_i(P_r) \right] / P_r = 1.6667 WL / (1.0 - 0.5 WL + 0.5 WM) \quad (56)$$

By subtracting Eq. (56) from Eq. (55), we find

$$K[L_i(P_r)] = 1.6667 P_r \left\{ [WS_i + (BS_i / BT)(WM - WS_i) - WL] / (1.0 - 0.5 WL + 0.5 WM) \right\}. \quad (57)$$

To find the quantity $\partial \ln \phi_K / \partial P_r$, we derive from Eq. (1)

$$\partial \ln \phi_K / \partial P_r = (z_K - 1) / P_r \quad (58)$$

We now have to combine Eqs. (31), (43), (57) and (58) by substitution into Eq. (11) yielding FKG_1 or $\ln(\phi_{KGi}/\phi_{Ki})$. Thus, the correction to the original Kwong equation due to Gunn's combination is found to be

$$\begin{aligned} \ln(\phi_{KGi}/\phi_{Ki}) = & [WS_i - WL + (WM - WS_i)(BS_i/BR)] \cdot [1 - Z \\ & + 1.5E \ln(1 + Q/Z)] / [3.0(1.0 - 0.5WL + 0.5WM)] \\ & + 1.6667 [WS_i - WL + (WM - WS_i)(BS_i/BR)] \cdot (Z-1) / \\ & [1.0 - 0.5WL + 0.5WM]. \end{aligned} \quad (59)$$

Simplifying, we have

$$\begin{aligned} \ln(\phi_{KGi}/\phi_{Ki}) = & [WS_i - WL + (WM - WS_i)(BS_i/BR)] \cdot \\ & [Z - 1 + E \ln(1 + Q/Z)] / [2.0(1.0 - 0.5WL + 0.5WM)]. \end{aligned} \quad (60)$$

With the definitions

$$FKT = 1.0 - Z + 1.5E \ln(1.0 + Q/Z) \quad (61)$$

(Statement 246)

and

$$QJ = [2.0 FKT + 5.0(Z-1)] / [3.0(2.0 - WL + WM)]. \quad (62)$$

(Statement 253)

FKG_1 becomes

$$FKG_i = \ln(\phi_{KGi}/\phi_{Ki}) = QJ [WS_i - WL + (WM - WS_i)(BS_i/BR)] \quad (63)$$

(Statement 273)

We now combine Eqs. (7) and (63) and define the quantity $GNFKJ$ which

represents the natural log of Kwong's individual fugacity coefficient according to Gunn's combination,

$$GNFKJ = \ln \phi_{Ki} + \ln(\phi_{KGi} / \phi_{Ki}) \quad (64)$$

Finally we obtain

$$\begin{aligned} GNFKJ = & (z_k - 1)BS_i / BR - \ln(z_k - Q) \\ & - E(2.0 AS_i / AT^{0.5} - BS_i / BR) \ln(1 + Q/z) + FKG_i \end{aligned} \quad (65)$$

(Statement 274)

C. Deviation Functions

As shown in the "General Remarks," the contribution to the individual fugacity coefficient of the deviation function is split into the terms

$$\ln \phi_{AG} + \ln(\phi_{AGi} / \phi_{AG})$$

where $\ln \phi_{AG}$ is the log of the mean deviation fugacity and is given in subroutine FUEM designed by Gunn.⁷ The second quantity, designated by FPC_1 , is derived in this section. We define

$$FPC_i = \ln \phi_{AGi} - \ln \phi_{AG} \quad (66)$$

As noted before, $\ln \phi_1$ may be written as

$$\ln \phi_{AGi} = \ln \phi_{AG} + \partial \ln \phi_{AG} / \partial y_i - \sum_j y_j \partial \ln \phi_{AG} / \partial y_j$$

so that FPC_1 may be written as

$$FPC_i = \partial \ln \phi_{AG} / \partial y_i - \sum_j y_j \partial \ln \phi_{AG} / \partial y_j \quad (67)$$

Since $\phi_{AG} = \text{FUDEM}$ is a function of T_r , P_r , and WM , we have

$$\begin{aligned} \partial \ln \phi_{AG} / \partial y_i &= (\partial \ln \phi_{AG} / \partial T_r) (\partial T_r / \partial y_i) + (\partial \ln \phi_{AG} / \partial P_r) \cdot \\ &(\partial P_r / \partial y_i) + (\partial \ln \phi_{AG} / \partial WM) (\partial WM / \partial y_i). \end{aligned} \quad (68)$$

We have already computed $(\partial T_r / \partial y_i)$ and $(\partial P_r / \partial y_i)$ and these are designated by UAA_i and UBB_i .

$$\begin{aligned} \partial \ln \phi_{AG} / \partial y_i &= (\partial \ln \phi_{AG} / \partial T_r) (UAA_i \cdot T) + (\partial \ln \phi_{AG} / \partial P_r) \cdot \\ &(UBB_i \cdot P) + (\partial \ln \phi_{AG} / \partial WM) (\partial WM / \partial y_i). \end{aligned} \quad (69)$$

FPC_i may now be expressed by means of the operator K :

$$\begin{aligned} FPC_i &= (\partial \ln \phi_{AG} / \partial T_r) T \cdot K(UAA_i) + (\partial \ln \phi_{AG} / \partial P_r) P \cdot \\ &K(UBB_i) + (\partial \ln \phi_{AG} / \partial WM) \cdot K(\partial WM / \partial y_i). \end{aligned} \quad (70)$$

$$\text{We define } \sum_j y_j UAA_j = WA \quad \text{and} \quad \sum_j y_j UBB_j = WB.$$

We now have

$$K(UAA_i) = UAA_i - WA = UA_i \quad (71)$$

(Statement 524)

$$\text{and } K(UBB_i) = UBB_i - WB = UB_i. \quad (72)$$

(Statement 525)

$$\text{Since } WM = \frac{\sum_j y_j w_j z_j}{\sum_j y_j z_j}, \quad \text{we obtain}$$

$$\begin{aligned} \partial WM / \partial y_i &= w_i z_i / \sum_j y_j z_j - (\sum_j y_j w_j z_j) \cdot \\ &(T_{ci} / P_{ci}) / \sum_j y_j z_j. \end{aligned} \quad (73)$$

We conclude that

$$\sum_j y_j (\partial WM / \partial y_j) = 0. \quad (74)$$

Introducing the operator K, we have

$$K(\partial WM / \partial y_i) = \partial WM / \partial y_i = WS_i \cdot BS_i / BR \quad (75)$$

$$- WM \cdot BS_i / BR = (WS_i - WM) AB_i$$

$$K(\partial WM / \partial y_i) = UC_i \quad (76)$$

(Statement 520)

Now FPC_1 may be written as

$$FPC_i = (\partial \ln \phi_{AG} / \partial T_r) T \cdot UA_i + (\partial \ln \phi_{AG} / \partial P_r) P \cdot UB_i \quad (77)$$

$$+ (\partial \ln \phi_{AG} / \partial WM) \cdot UC_i$$

The derivative $\partial \ln \phi_{AG} / \partial T_r$ is obtained by means of a numerical differentiation. The subroutine FDM yields the mean deviation function $\ln \phi_{AG} = \text{FUDEM}$. We increment T_r by EE and obtain $\text{FUDEMU} = \text{FUDEM}(TR + EE)$. We obtain for the temperature derivative of $\ln \phi_{AG}$

$$\partial \ln \phi_{AG} / \partial T_r = FDT = T_m (\text{FUDEMU} - \text{FUDEM}) / EE \quad (78)$$

(Statement 195)

The quantity $\partial \ln \phi_{AG} / \partial P_r$ is obtained from Eq. (1):

$$\ln \phi = \int_0^{P_r} [(z-1)/P_r] dP_r \quad (79)$$

With $Z = Z_K + Z_{AG}$ we have

$$\ln \phi = \int_0^{P_r} [(Z_K - 1)/P_r] dP_r + \int_0^{P_r} (Z_{AG} / P_r) dP_r \quad (80)$$

Since $\ln \phi = \ln \phi_K + \ln \phi_{AG}$, we have

$$\partial \ln \phi_{AG} / \partial P_r = Z_{AG} / P_r = DV / P_r \quad (81)$$

The quantity $(\partial \ln \phi_{AG} / \partial WM) = (\partial FUDEM / \partial WM)$ is obtained from the final expression for FUDEM in Ackerman's work:

$$FUDEM = FA + FB + FC \cdot WM \quad (82)$$

$$\partial \ln \phi_{AG} / \partial WM = FC \quad (83)$$

Substituting these quantities into the expression for FPC_1 yields

$$FPC_i = FDT \cdot T \cdot UA_i + DV \cdot P_M \cdot UB_i + FC \cdot UC_i \quad (84)$$

(Statement 200)

By means of Eq. (6) the total individual fugacity coefficient may be written as

$$\ln \phi_i = GNFKJ + FUDEM + FPC_i \quad (85)$$

(Statement 276)

D. Enthalpy and Entropy

In addition to giving mean and individual fugacity coefficients for the mixture, ES64 gives the mean enthalpy and entropy for the mixture. In the following, no individual but only mean quantities will be discussed. The derivation consists of a differentiation with respect to temperature of both sides of the equation

$$(F - F^0) / T = R \ln(P\phi) \quad (86)$$

Considering the left-hand side, we have

$$[\partial(F/T) / \partial T]_p = -F/T^2 + (\partial F / \partial T) / T \quad (87)$$

$$[\partial(F/T)/\partial T]_p = -F/T^2 - S/T = -(F+TS)/T \quad (88)$$

$$[\partial(F/T)/T]_p = -H/T^2 \quad (89)$$

so that the left-hand side becomes

$$\left\{ \partial [(F-F^0)/T] / \partial T \right\}_p = -(H-H^0)/T^2. \quad (90)$$

$$-(H-H^0)/T^2 = R(\partial \ln P\phi / \partial T)_p = R(\partial \ln \phi / \partial T)_p \quad (91)$$

$$-(H-H^0)/RT^2 = (\partial \ln \phi_k / \partial T)_p + (\partial \ln \phi_{AG} / \partial T)_p \quad (92)$$

$$-(H-H^0)/RT^2 = [(\partial \ln \phi_k / \partial T_r)_p + (\partial \ln \phi_{AG} / \partial T_r)_p] / T_m \quad (93)$$

$$H-H^0 = -RT [T_r (\partial \ln \phi_k / \partial T_r)_p + T_r (\partial \ln \phi_{AG} / \partial T_r)_p] \quad (94)$$

In terms of the previously derived quantities, we have

$$H-H^0 = -RT(FKT + TR \cdot FDT). \quad (95)$$

(Statement 247)

To obtain the entropy, we derive from the preceding relations

$$S = (H-F)/T = -R \ln(P\phi) + (H-H^0)/T - (F^0-H^0)/T \quad (96)$$

$$S = -R(\ln P + \ln \phi_K + \ln \phi_{AG}) + (H - H^0)/T + S^0 \quad (97)$$

so that, in terms of the previously defined quantities, we have

$$S - S^0 = -R(\ln P + FUGAM + FUEM) + (H - H^0)/T. \quad (98)$$

(Statement 248)

The subroutine FUGAM = $\ln \phi_K$ was derived by Redlich and Kwong¹ and FUEM = $\ln \phi_{AG}$ by Gunn.⁷

III. METHODS OF CHECKING THE PROGRAM

The user of Program ES64 has not much opportunity of checking it. Comparison with observed data furnishes only spot checks. In a way he has to take the program on good faith. A systematic and thorough check is therefore an important requirement.

Ackerman checked the results of his deviation function for Z by comparison with Pitzer's tables, which had served as a guide anyway. The computation of the mean fugacity coefficient by Gunn was examined with the aid of the numerical integration of an appropriately chosen test example.

The present additions to the program required checks of the derivatives with respect to the temperature, and checks of the individual fugacity coefficients.

The differentiation of FUEM with respect to the temperature, leading to FDT, could easily be checked with the aid of the computer itself. Computations were prescribed for a set of temperatures at close intervals. The results for FUEM furnished an immediate and significant check of

the derivative FDT.

At the same time, various values of the temperature increment EE were tried out. It was concluded that $EE = 0.1^\circ\text{K}$ or $^\circ\text{R}$ is high enough so that the numerical precision of the computer is sufficient for the derivative. At the same time the value 0.1 is low enough so that deviations from linearity are not significant. The program allows arbitrary changes of EE .

A different procedure was to be chosen for the individual fugacity coefficients ϕ_{KG1} (term from the old equation), ϕ_{AG1} (term from the deviation function), and for the total values ϕ_1 . A check was considered to be necessary only for a binary mixture. The individual fugacity coefficients ϕ_1 are derived from the mean fugacity coefficients according to

$$\ln \phi_1 = \ln \phi + y_2 (d \ln \phi / dy_1) \quad (99)$$

$$\ln \phi_2 = \ln \phi - y_1 (d \ln \phi / dy_1). \quad (100)$$

It is easily seen that these relations are equivalent to

$$y_1 \ln \phi_1 + y_2 \ln \phi_2 = \ln \phi \quad (101)$$

$$\ln(\phi_1 / \phi_2) = d \ln \phi / dy_1. \quad (102)$$

The last relation may be replaced by its integral

$$\int_0^1 \ln(\phi_1 / \phi_2) dy_1 = \ln \phi_1 \Big|_{y_1=0}^{y_1=1} = \ln \phi_1^0 - \ln \phi_2^0. \quad (103)$$

The limiting values of ϕ are ϕ_1^0 and ϕ_2^0 , respectively, according to Eq. (101). Though it is theoretically possible that Eq. (103) is satisfied while Eq. (102) is not, the check of Eqs. (101) and (103) is practically sufficient.

These tests apply not only to the total fugacity coefficients ϕ_1 and ϕ_2 but also to ϕ_{KG1} and ϕ_{AG1} separately. It applies also to ϕ_{K1} , the original fugacity coefficient of Kwong, but with his corresponding combination rule.

IV. INSTRUCTIONS FOR THE USE OF ES64

A. General Remarks

The program ES64 can compute the compressibility factor, mean and individual fugacity coefficients for seven or fewer components, and the mean enthalpy and mean entropy for the mixture. Provision is made for the introduction of interaction coefficients.

If experimental compressibility factors are read into the program it will compare its values with the experimental values and compute the differences. Otherwise, the only data introduced are the critical temperature and pressure and the acentric factor for each of the components.

The temperature schedule provides for sets consisting of a starting temperature and higher temperatures at equal intervals. The pressure schedule may follow one of three schemes: (1) starting pressure and any

number of higher pressures at equal intervals, (2) starting pressure PL and any number of pressures of the amounts 2PL, 5PL, 10PL, etc., (3) starting pressure plus any number of additional pressures as read in as part of the data.

After a T-P schedule for a pure substance (NOS = 1) a new T-P schedule may be provided. If no other T-P schedule is desired, a blank card is inserted. Now an entirely new problem can be prescribed to the computer, beginning with a new Title-Card and the whole input as described. If no new problem is to be submitted, a second blank is inserted. The calculation will then be terminated.

After a T-P schedule for a mixture (NOS > 1) the compositions for which the computation is to be carried out must be provided for. The number of such mixtures NOM has been prescribed in the Title-Card and is fixed for a whole problem. A new T-P schedule may follow. But the same number of compositions NOM must be provided for after each T-P schedule. If no new T-P schedule is desired, a blank and a new problem (Title-Card and so on) may be put in, or two blank cards will terminate the computation.

For the various schedules, the following outputs are available:

(1) only the compressibility factor Z, (2) only the compressibility factor and the mean fugacity coefficient ϕ , (3) option (2) plus the enthalpy H and entropy S, and (4) option (3) plus individual fugacity coefficients ϕ_1 . These options are controlled by the sign of the control quantity ECL.

If the control quantity KCL = 1, the intermediate quantities FDT and $FPC_1 = \partial \ln \phi_{AG} / \partial y_1$ will be printed out. The control quantity NPC = 1 may be used to punch the normal output.

The program can also be used for computations starting from the reduced variables T_r and P_r . In this case, one sets $T_c = 1$, $P_c = 1$ and introduces T_r and P_r wherever T and P are prescribed. If heat content, entropy, and individual fugacity coefficients are desired, the absolute value of ECL in the Title Card should be 0.01 so that $EE = 0.001$. The lower numerical values of T_r necessitate a lower value of EE for the differentiation with respect to T .

The same (arbitrary) units must be used for the whole input. The output is given in the same units except for H (cal/mole) and S (cal/degree C · mole).

The various kinds of cards are described in the following in the order of the input.

B. Input

1. Title Card

Column

1-54	Title of the problem
55-56	KCL print intermediate quantities: 0 no print. 1 print.
57	MCL experimental data: 0 no 1 yes
58	NOS number of components (1-7)
59	NOM number of mixtures (1-9)
60	NPC punch normal output: 0 no punch 1 punch
61	NRC interaction coefficients: 0 no 1 yes
62-72(4 dec.)	ECL = 0: compute only Z

ECL = 99.0: compute Z and mean fugacity coefficient ϕ

ECL = < 0: compute Z, ϕ , H, S

EE = -0.1 ECL in the computation of FDT

ECL > 0 but \neq 99.0: compute Z, ϕ , H, S and ϕ_1

EE = 0.1 ECL for FDT

2. Experimental Data for Z (only if MCL = 1)

Insert any number up to 199 cards followed by one blank card

Column

1 - 10 (4 dec) ZE Experimental value

3. Substance Cards

NOS cards, one for each substance

Column

1-24 Name of substance

25-36 (6 dec) TC(JS) Critical temperature in any units.

37-48 (6 dec) PC(JS) Critical pressure in any units.

49-60 (6 dec) WS(JS) Acentric factor

4. Interaction Coefficients

NOS cards (only if NRC = 1). The input consists of a symmetric matrix of order NOS with 1.0 in the diagonal.

Column

1 - 12 (4 dec) R(1, JR) (JR = 1, 2, NOS)

13 - 22(4 dec) R(2, JR)

.....

63 - 72(4 dec) R(7, JR)

5. T-P Schedule

Column

1 - 12 (6 dec) TL lowest temperature to be introduced, in same unit as TC(JS).

- 13-24 (6 dec) PL lowest pressure to be introduced, in same units as PC(JS).
- 29-30 NOT number of temperatures to be introduced.
- 31-42 NOP number of pressures to be introduced.
- ✓ 49-60 (6 dec) DT temperature increment in same units as TL.
- 61-72 (6 dec) DP = -1: pressure schedule is PL, 2PL, 5PL, 10PL, etc., for NOP pressures.
- DP = 0: schedule given by PL and the following NOP-1 additional pressure cards.
- DP > 0: pressure increment for NOP pressures (same units as PL).

6. Additional Pressure Cards

(NOP-1 cards only if DP = 0.)

Column

13-24 (6 dec) pressure (same units as PL)

7. Composition Cards

(Only if NOS > 1, NOM cards for the preceding T-P schedule, one for each mixture)

Column

- 1-12 (4 dec) Y(1) mole fraction of first component (described in the first substance card)
- 13-22 (4 dec) Y(2) mole fraction of second component (described in the second substance card)
- 23-32 (4 dec) Y(3) mole fraction of third component (described in the third substance card)
- 33-42 (4 dec) Y(4) mole fraction of fourth component (described in the fourth substance card)

- 43-52 (4 dec) Y(5) mole fraction of fifth component (described in the fifth substance card)
- 53-62 (4 dec) Y(6) mole fraction of sixth component (described in the sixth substance card)
- 63-72 (4 dec) Y(7) mole fraction of seventh component (described in the seventh substance card)

8. New T-P schedule (insert additional pressure cards if prescribed by DP and NOP, and insert NOM composition cards if NOS > 1.)

A blank card starts a new problem (insert a full set of cards, types 1-7).

A second blank card (0 in column 58) means end of calculation.

C. Output

A typical output is shown in the Appendix. For the example the option KCL = 0, MCL = 1, NOS = 2, NRC = 0, and ECL = 1 have been chosen. For each problem, the Title Card and Substance Cards are printed out as the heading. The points are nested as follows: Each composition contains all the temperatures specified, which in turn contain each pressure specified.

After a particular composition is printed out, a heading line appears which applies to the entire composition. The symbols have the following meanings:

$$ZRK = Z_K \text{ (old equation of Redlich and Kwong)}$$

$$ZAG = Z_{AG} \text{ (improved equation)}$$

$$ZEX = \text{experimental compressibility factor}$$

$$DZ = ZEX - ZAG$$

$$\text{LOG FRK} = \log_{10} \phi_K$$

$$\text{LOG FAG} = \log_{10} \varphi_{AG}$$

FAG = φ_{AG} , final result

MZ = number of the point

Q = kind of the printed line or punched card (1 = Z
and mean values of φ , 3 = φ of components)

C = component

P = number of the phase

Immediately under the heading line the temperature (same units as the input critical data) and reduced temperature are printed. Under the temperature, the pressure, reduced pressure, enthalpy and entropy for the particular point are printed.

The MZ column has been included for easy sorting if the output is punched on cards.

Below the critical temperature, the program may give results for two different phases. The old equation, just as well as that of van der Waals, is of third degree in Z and therefore may have one or three real solutions. This is not changed by the addition of the deviation function.

For a pure substance the significance of three solutions is well known. The highest value of Z is that of the gas, the lowest that of the liquid, and the middle value represents an unstable state. Only one of the two other values must belong to a stable state. The other belongs, in general, to a metastable state. In the exceptional case of a vapor-liquid equilibrium, both phases are stable.

The computer prints out data for the gaseous and liquid state without any indication of stability. The fugacity coefficients however indicate immediately the stability for a pure substance: The fugacity coefficient of the stable phase is lower than that of the metastable phase. Vapor-liquid equilibrium exists at the given temperature and pressure only if

the two fugacity coefficients are equal.

The output does not give any indication of phase stability for mixtures. Actually the information obtained in an isolated point for a mixture is intrinsically incomplete for the decision of a question of metastability. This question can be discussed only on the basis of a set of results for a whole system at a given temperature. So far, no attempt has been made to solve the general problem of stability.

V. CONCLUSIONS

The program developed so far is believed to furnish reasonably accurate values for compressibility factors and fugacity coefficients. Its range of application is restricted to the gas phase. It will probably furnish crude approximations for the liquid phase but such results cannot be relied upon. For the gas phase the accuracy is quite close to that of Pitzer's tables. Some moderate deviations may appear in the vicinity of the critical point. For hydrogen, helium, and water, the approximation is not better than that of Pitzer's tables, i.e., not very satisfactory.

Comparison of the results for mixtures with experimental data indicated that about the same accuracy is obtained as for pure substances. No additional parameters beyond the critical temperatures, pressures and acentric factors of the components are used. Further checks will be carried out. If they are in accord with present results the proposed method may turn out to be a practically satisfactory solution of the irksome problem of the free energy of mixtures.

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APPENDICES

A. ESG4

B. Sample Calculation

ES64. EQUATION OF STATE 1964

C SUBROUTINES REQUIRED - VIETA MOD 3, FDM, ANGLE, FTEM, FUGAM, DEV, FFC
1 DIMENSION TI(9), ZE(200), A(4), SUR(4), TC(7), PC(7), AS(7), BS(7), CS(7)
2, WS(7), R(7,7), P(99), Y(7), U(53), HHS(7), X(3), UA(7), UR(7),
3UC(7), BAU(7), UU(53), FPC(7), BA(7)
6 FORMAT (9A6, I2, 5I1, F11.4)
7 FORMAT (1H1, 9A6, I2, 5I1, F7.3)
8 FORMAT (F10.4)
9 FORMAT (4A6, 3F12.6)
10 FORMAT (1H0, 4A6, 3F12.6)
11 FORMAT (F12.4, 6F10.4)
12 FORMAT (//)
13 FORMAT (2F12.6, 4X12, 10X12, 6X2F12.6)
14 FORMAT (12HOCOMPOSITION)
15 FORMAT (12XF12.6)
16 FORMAT (73HO ZRK ZAG ZEX DZ LOG FRK LOG FA
2G FAG MZQCP/)
17 FORMAT (2HOT, F12.4, 4H TR, F10.5)
18 FORMAT (1HT, F12.4, 4H TR, F10.5)
19 FORMAT (2HOP, F17.4, 6H PR, F12.4, 7H H, F10.1, 3H S, F9.4)
20 FORMAT (1HP, F17.4, 6H PR, F12.4, 7H H, F10.1, 3H S, F9.4, 3X, 14)
21 FORMAT (4F9.4, F11.4, 2F9.4, 15, 2H1, I1)
24 FORMAT (37X, F11.4, 2F9.4, 14, 1H3, 2I1)
25 FORMAT (4HOFDT, F19.6, 9H FUDEM, F15.6, 6H FC, F18.6/3H EE, F20.6,
210H FUDEMU, F14.6, 7H FCU, F17.6)
26 FORMAT (4H FPC, F12.6)
27 FORMAT (15HOCRITICAL POINT)
28 FORMAT (1H, 4F9.4, F11.4, 2F9.4, 14, 2H1, I1)
29 FORMAT (4H FKT, F19.6, 9H Q, F15.6, 6H OJ, F18.6)

C INPUT AND INDEPENDENT INTERMEDIATES
C
31 READ INPUT TAPE 2, 6, (TI(M), M=1, 9), KCL, MCL, NOS, NOM, NPC, NRC, ECL
32 WRITE OUTPUT TAPE 3, 7, (TI(M), M=1, 9), KCL, MCL, NOS, NUM, NPC, NRC, ECL
33 IF (MCL) 39, 39, 34
34 READ INPUT TAPE 2, 8, ZE(MCL)
35 IF (ZE(MCL)) 38, 38, 36
36 MCL=MCL+1
37 GO TO 34
38 MCL=MCL-1
39 IF (NOS) 40, 40, 41
40 NOS=1
41 DO 45 JS=1, NOS
42 READ INPUT TAPE 2, 9, (SUB(M), M=1, 4), TC(JS), PC(JS), WS(JS)
43 WRITE OUTPUT TAPE 3, 10, (SUB(M), M=1, 4), TC(JS), PC(JS), WS(JS)
44 BS(JS)=0.08667*TC(JS)/PC(JS)
45 AS(JS)=0.6540*TC(JS)**1.25/SQRTF(PC(JS))
46 IF (NRC) 50, 50, 47
47 DO 49 JR=1, NOS
48 READ INPUT TAPE 2, 11, (R(JS, JK), JS=1, NOS)
49 WRITE OUTPUT TAPE 3, 11, (R(JS, JR), JS=1, NOS)

ES64 EQUATION OF STATE 1964

50 WRITE OUTPUT TAPE 3,12

C

C PRESSURE SCHEDULE

51 READ INPUT TAPE 2,13,TL,PL,NOT,NOP,DT,DP

52 P(1)=PL

53 JP=2

54 IF(DP)55,66,69

55 P(JP)=P(JP-1)*2.0

56 JP=JP+1

57 IF(JP-NOP)58,58,74

58 P(JP)=P(JP-1)*2.5

59 JP=JP+1

60 IF(JP-NOP)61,61,74

61 P(JP)=P(JP-1)*2.0

62 JP=JP+1

63 IF(JP-NOP)55,55,74

64 READ INPUT TAPE 2,15,P(JP)

65 JP=JP+1

66 IF(JP-NOP)64,64,74

67 P(JP)=P(JP-1)+DP

68 JP=JP+1

69 IF(JP-NOP)67,67,74

C

C CONTROL SCHEDULE

74 A(1)=1.0

75 A(2)=-1.0

76 IF (NOM) 77,77,78

77 NOM=1

78 EE=0.1*ECL

79 IF (ECL) 87,80,82

80 MISS=0

81 GO TO 88

82 IF (ECL-99.0) 85,83,85

83 MISS=1

84 GO TO 88

85 MISS=3

86 GO TO 88

87 MISS=2

88 MZ=0

C

Y-CYCLE

101 DU 293 JM=1,NOM

102 IF (NUS-1) 130,130,103

C

MIXTURES

103 READ INPUT TAPE 2,11,(Y(JS),JS=1,NOS)

104 WRITE OUTPUT TAPE 3,14

105 WRITE OUTPUT TAPE 3,11,(Y(JS),JS=1,NOS)

106 WRITE OUTPUT TAPE 3,12

107 BR=0.0

108 AT=0.0

109 WL=0.0

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```
110 WN=0.0
111 DO 122 JS=1,NOS
112 HHS(JS)=0.0
113 IF (NRC) 117,117,114
114 DO 115 JR=1,NOS
115 HHS(JS)=HHS(JS)+Y(JR)*R(JS,JR)*AS(JR)
116 GO TO 119
117 DO 118 JR=1,NOS
118 HHS(JS)=HHS(JS)+Y(JR)*AS(JR)
119 AT=AT+Y(JS)*AS(JS)*HHS(JS)
120 BR=BR+Y(JS)*BS(JS)
121 WL=WL+Y(JS)*WS(JS)
122 WN=WN+Y(JS)*BS(JS)*WS(JS)
123 WM=WN/BR
124 BT=BR/(1.0 + 0.5*(WM-WL))
125 TM=0.34492*(AT/BT)**0.666667
126 PM=0.08667*TM/BT
127 IF (MISS-2) 136,136,128
128 CALL FFC(AS,BS,WS,Y,TM,PM,WL,WM,UA,UB,UC,KCL,BR,NOS,AT)
129 GO TO 136
C PURE SUBSTANCE
130 PM=PC(1)
131 AT=AS(1)**2
132 BR=BS(1)
133 BT=BS(1)
134 WM=WS(1)
135 TM=TC(1)
C GENERAL
136 WRITE OUTPUT TAPE 3,16
137 IF (NPC-2) 139,139,138
138 WRITE OUTPUT TAPE 14,16
139 T=TL
C T-CYCLE
151 DO 292 JT=1,NOT
152 TR=T/TM
153 B=BT/T
154 E=AT/(BT*T**1.5)
155 IF (MISS) 168,168,156
156 IF (NOS-1) 159,159,157
157 DO 158 JS=1,NOS
158 BA(JS)=T*UA(JS)
159 CALL FTEM(U,TR)
160 IF (MISS-1) 168,168,161
161 TU=T+EE
162 TRU=TU/TM
163 BU=BT/TU
164 EU=AT/(BT*TU**1.5)
165 DO 166 JS=1,NOS
166 BAU(JS)=TU*UA(JS)
167 CALL FTEM(UU,TRU)
```

ES64 EQUATION OF STATE 1964

```
168 WRITE OUTPUT TAPE 3,17,T,TR
169 IF (NPC) 171,171,170
170 WRITE OUTPUT TAPE 14,18,T,TR
171 CONTINUE
C P-CYCLE
180 DU 290 JP=1,NOP
181 MZ=MZ+1
182 Q=B*P(JP)
183 A(3)=Q*(E-1.0-Q)
184 A(4)=-E*Q**2
996 IF (KCL) 185,185,997
997 WRITE OUTPUT TAPE 3,11,AT,BT,B,E,Q,A(3),A(4)
185 CALL VIETA(A,X,MTYPE)
998 IF (KCL) 186,186,999
999 WRITE OUTPUT TAPE 3,11,(A(M),M=1,4),(X(K),K=1,3)
186 PR=P(JP)/PM
187 DV=DEV(TR,PR,TM,PM,WM)
191 IF (MISS) 198,198,192
192 CALL FDM(U,TR,PR,WM,FC,FUEM)
193 IF (MISS-1) 198,198,194
194 CALL FDM(UU,TRU,PR,WM,FCU,FUEMU)
195 FDT=(FUEMU-FUEM)*TM/EE
198 IF (MISS-2) 219,219,199
199 DU 203 JS=1,NOS
200 FPC(JS)=FDT*UA(JS)*T +DV*UB(JS)*PM +FC*UC(JS)
201 IF (KCL) 203,203,202
202 WRITE OUTPUT TAPE 3,26,FPC(JS)
203 CONTINUE
C PHASE CALCULATION
219 IF (ABSF(TR-1.0)-0.0003) 220,221,221
220 IF (ABSF(PR-1.0)-0.0003) 222,221,221
221 IF (MTYPE) 225,222,223
222 WRITE OUTPUT TAPE 3,27
223 LP=1
224 GO TO 230
225 LP=2
226 XMAX=MAX1F(X(1),X(2),X(3))
227 XMIN=MIN1F(X(1),X(2),X(3))
228 X(1)=XMAX
229 X(2)=XMIN
230 DO 284 MP=1,LP
231 IF (MISS-1) 236,232,232
232 GNFK=FUGAM(Q,E,X(MP))
233 GFK=0.434294*GNFK
234 GFA=GFK+0.434294*FUEM
235 FAG=EXPF(FUEM+GNFK)
236 IF (MCL) 237,237,240
237 ZE(MZ)=0.0
238 DZ=0.0
239 GO TO 241
```

ES64 EQUATION OF STATE 1964

```
240 DZ=ZE(MZ)-X(MP)-DV
241 ZAG=X(MP)+DV
245 IF (MISS-1) 254,254,246
246 FKT=-X(MP)+1.0+1.5*E*LOGF(1.0+Q/X(MP))
247 H=-1.98726*T*(FKT+TR*FDT)
252 CONTINUE
248 S=-1.98726*(LOGF(P)+FUDEM+GNFKJ)+H/T
253 QJ=(2.0*FKT+5.0*(X(MP)-1.0))/(3.0*(2.0-WL+WM))
254 CONTINUE
255 WRITE OUTPUT TAPE 3,19,P(JP),PR,H,S
256 IF (NPC) 258,258,257
257 WRITE OUTPUT TAPE 14,20,P(JP),PR,H,S,MZ
258 IF (KCL)260,260,259
259 WRITE OUTPUT TAPE 3,29,FKT,Q,QJ
260 CONTINUE
261 IF(KCL) 263,263,262
262 WRITE OUTPUT TAPE 3,25,FDT,FUDEM,FC,EE,FUDEMU,FCU
263 WRITE OUTPUT TAPE 3,28,X(MP),ZAG,ZE(MZ),DZ,GFK,GFA,FAG,MZ,MP
264 IF (NPC) 271,271,265
265 WRITE OUTPUT TAPE 14,21,X(MP),ZAG,ZE(MZ),DZ,GFK,GFA,FAG,MZ,MP
C INDIVIDUAL FUGACITY COEFFICIENTS
271 IF (MISS-2) 283,283,272
272 DO 282 JS=1,NOS
273 FKG=QJ*(WS(JS)-WL+(WM-WS(JS))*PS(JS)/RR)
274 GNFKJ =(X(MP)-1.0)*PS(JS)/RR-LOGF(X(MP)-Q)-E*(2.0*AS(JS)/
2SQRT(AT)-BS(JS)/RR)*LOGF(1.0+Q/X(MP)) +FKG
275 GFKJ=0.434294*GNFKJ
276 GNFLAGJ=GNFKJ+FPC(JS)+FUDEM
277 GFAGJ=0.434294*GNFLAGJ
278 FAGJ=EXP(GNFLAGJ)
279 WRITE OUTPUT TAPE 3,24, GFKJ,GFAGJ,FAGJ,MZ,JS,MP
280 IF (NPC) 282,282,281
281 WRITE OUTPUT TAPE 14,24, GFKJ,GFAGJ,FAGJ,MZ,JS,MP
282 CONTINUE
283 CONTINUE
284 CONTINUE
290 CONTINUE
291 T=T+DT
292 CONTINUE
293 CONTINUE
294 READ INPUT TAPE 2,13 ,TL,PL,NOT,NOP,DT,DP
295 IF (TL) 297,297,52
297 READ INPUT TAPE 2,6,(TI(M),M=1,9),KCL,MCL,NOS,NOM,NPC,NRC,ECL
298 IF (NOS) 299,299,32
299 CALL EXIT
END(1,0,0,0,0,0,1,0,0,1,0,0,0,0,0)
```

FTEM SUBROUTINE (P-INDEPENDENT INTERMEDIATES FOR FUEM)

```
SUBROUTINE FTEM(U,TR)
DIMENSION U(53),V(52)
401 SQ = 1.414214
402 TT = TR
403 V(1) = ((1.0+14137.6*(TT-1.0)**2)/1397.12)**0.25
404 V(2) = -13.44*TT+12.41
405 V(3) = -0.035/(1.0+14137.6*(TT-1.0)**2)
406 V(4) = 0.00260913*(TT-3.19325)
407 V(5) = 0.00113345*(TT**2-4.08560)
408 V(6) = 0.00704758*TT-0.144392
409 V(7) = 4.98358*(TT-1.00122)
410 V(8) = (-0.246973)*(TT+0.226285)
411 V(9) = TT-1.0
412 V(10) = (0.825714+0.00115729*TT)/TT**3
413 V(11) = (0.00736587-0.00255204*TT)/TT**3
414 V(12) = 0.564037*(TT-2.46596)/TT
415 V(13) = 0.00913531*(TT-13.6087)/TT
416 V(18) = V(2)/V(1)
417 V(19) = 0.176777*V(1)*V(3)*(V(2)**2-V(1)**2)
418 V(20) = 0.353554*V(1)*V(3)*(V(2)**2+V(1)**2)
419 V(21) = (-V(1)**2*V(2)*V(3))
420 V(22) = V(4)/V(8)-V(7)*(V(5)+V(4)*V(6))/V(8)**2+V(5)*V(6)*V(7)
1 /V(8)**3
421 V(23) = 0.5*((V(5)+V(4)*V(6))/V(8)**2-2.0*V(5)*V(6)*V(7)/V(8)
422 V(24) = V(5)*V(6)/V(8)**3
423 V(25) = 0.176777*(V(22)-V(24))
424 V(26) = 0.353554*(V(22)+V(24))
425 V(27) = (-0.000643158*TT**2)
426 V(28) = V(9)*V(10)/V(13)-V(12)*(V(9)*V(11)-0.049*V(10))/V(13)
1 -0.049*V(11)*V(12)**2/V(13)**3
427 V(29) = (V(9)*V(11)-0.049*V(10))/V(13)**2+0.098*V(11)*V(12)/V
1 **3
428 V(30) = 0.049*V(11)/V(13)**3
429 V(31) = 0.176777*(V(28)+V(30))
430 V(32) = 0.353554*(V(28)-V(30))
431 V(43) = LOGF((V(18)**2+SQ*V(18)+1.0)/(V(18)**2-SQ*V(18)+1.0)
432 V(44)=0
433 V(45) = ATANF(V(18)**2)
434 V(46) = LOGF((V(7)**2+SQ*V(7)+1.0)/(V(7)**2-SQ*V(7)+1.0))
435 V(47)=0
436 V(48) = ATANF(V(7)**2)
437 V(49) = 0
438 V(50) = LOGF((V(12)**2+SQ*V(12)+1.0)/(V(12)**2-SQ*V(12)+1.0)
439 V(51)=0
440 V(52) = ATANF(V(12)**2)
441 DO 442 I=1,13
442 U(I) = V(I)
443 DO 444 J=18,32
444 U(J) = V(J)
```

FTEM SUBROUTINE (P-INDEPENDENT INTERMEDIATES FOR FUEM)

445 DU 446 K=43,52

446 U(X) = V(K)

447 RETURN

END(1,0,0,0,0,0,1,0,0,1,0,0,0,0,0)

FFC SUBROUTINE FFC (P,T-INDEPENDENT QUANTITIES)

```
      SUBROUTINE FFC(AS,BS,WS,Y,TM,PM,WL,WM,UA,UB,UC,KCL,BR,NOS,AT)
501 DIMENSION AS(7),BS(7),WS(7),Y(7),UA(7),UB(7),UC(7),UAA(7),UBB(7)
502 FORMAT (4H0FFC, 3F18.12)
511 AC = 1.0 - 0.5WL
512 WA=0.0
513 WB=0.0
514 DO 522 JS=1,NOS
515 AA=-1.33333*AS(JS)/SORTF(AT)
516 AB=BS(JS)/BR
517 AD=1.33333*(AB-((AB*(AC+0.5*WS(JS))-0.5*WS(JS))/(2.0*AC+WM)))
518 UAA(JS)=(AA+AD)/TM
519 UBH(JS)=(AA+2.5*AD)/PM
520 UC(JS)=AB*(WS(JS)-WM)
521 WA=WA+UAA(JS)*Y(JS)
522 WB=WB+UBB(JS)*Y(JS)
523 DO 528 JS=1,NOS
524 UA(JS)=UAA(JS)-WA
525 UB(JS)=UBH(JS)-WB
526 IF (KCL) 528,528,527
527 WRITE OUTPUT TAPE 3,502,UA(JS),UB(JS),UC(JS)
528 CONTINUE
      RETURN
      END(1,0,0,0,0,0,1,0,0,1,0,0,0,0,0)
```

FDM FUG COEFF GUNN2 FROM DEV ACKERMAN MOD 2 JACOBSON

```

SUBROUTINE FDM(U,TR,PR,WM,FC,FUDEM)
DIMENSION U(53)
SQ=1.414214
638 U(14) = (PR+U(2))/U(1)
639 U(15) = U(8)*PR+U(7)
640 U(16) = 0.495493*PR/TR
641 U(17) = U(13)*PR+U(12)
6420U(33) = LOGF((U(14)**2+      SQ*U(14)+1.0)/(U(14)**2-      SQ*U(14)
1 +1.0))
643 AZ = U(2)/U(1)
644 AY = 1.0/U(1)
645 U(34) = ANGLE(AZ,AY,PR)
646 U(35) = ATANF(U(14)**2)
6470U(36) = LOGF((U(15)**2+      SQ*U(15)+1.0)/(U(15)**2-      SQ*U(15)
1 +1.0))
648 U(37) = ANGLE(U(7),U(8),PR)
649 U(38) = ATANF(U(15)**2)
6500U(39) = LOGF((U(16)**2+      SQ*U(16)+1.0)/(U(16)**2-      SQ*U(16)
1 +1.0)) -2.0*ATANF(      SQ*U(16)/(1.0-U(16)**2))
6510U(40) = LOGF((U(17)**2+      SQ*U(17)+1.0)/(U(17)**2-      SQ*U(17)
1 +1.0))
652 U(41) = ANGLE(U(12),U(13),PR)
653 U(42) = ATANF(U(17)**2)
654 FA = U(19)*(U(33)-U(43)) + U(20)*U(34) + U(21)*(U(35)-U(45))
6550FB = U(25)*(U(36)-U(46)) + U(26)*U(37) + U(23)*(U(38)-U(48))
1 + U(27)*U(39)
656 FC = U(31)*(U(40)-U(50)) + U(32)*U(41) + U(29)*(U(42)-U(52))*0.50
657 FUDEM = FA+FB+WM*FC
661 RETURN
END(1,0,0,0,0,0,1,0,0,1,0,0,0,0,0)
```


DEV DEVIATION D-8 + DZC + ACENT 123

```
FUNCTION DEV(TR,PR,TC,PC,W)
C            ***** PARAMETERS FROM            PITZER            *****
701 D8=.00260913*PR*(TR-3.19325 -1.774864 *PR+.434418 *PR*TR**2)*
1 (1.0-.1443918 *PR+ .00704758 *TR*PR) / (1.0+ 616.8304 *(TR-
2 1.001216 - .01121414 *PR- .0495574 *PR*TR )**4 )
3 + .000442593 *TR**3*PR**3 / (TR**4+ .0602768 *PR**4 )
702 ACENT = TR*PR*(TR-1.0-0.049*PR)*( .8257143 + .00736587 *PR
1 +(-.00255204)*TR*PR+ .001157295 *TR )/ (TR**4+ .1012124 *(TR
2 - 2.46596 - .220411 *PR+ .01619634 *TR*PR)**4 )
C            ***** CRITICAL CORRECTION            *****
703 DZC = -0.035 * PR**3 / ( 1.0 + 14137.6 * (TR - 1.0)**2 +
1 1397.124 * (PR - 1.03 - 13.44 * (TR - 1.0))**4 )
704 DEV = D8 + DZC + ACENT = W
RETURN
END(1,0,0,0,0,0,1,0,0,1,0,0,0,0,0)
```

ANG FUNCTION ANGLE

```
FUNCTION ANGLE(AZ,AY,PR)
801 OAX=ATANF(0.1414214*AY*(1.0+AZ**2+0.1*AY*AZ)/((AZ**2+0.1*AY*AZ)**2+
1 1.0-(0.1*AY)**2))
802 DEN=(AZ**2+AY*AZ*PR)**2+1.0-(AY*PR)**2
803 DNU=1.414214*AY*PR*(1.0+AZ*(AZ+AY*PR))
804 IF (ABSF(DEN)-1.0E-20) 805,805,808
805 IF (ABSF(DNU)-1.0E-15) 808,808,806
806 ANGLE= 1.5707963
807 GO TO 815
808 ANGLE=ATANF(DNU/DEN)
809 AW = AX*ANGLE
810 IF(AW)811,811,815
811 IF(ANGLE) 812,812,814
812 ANGLE = 3.1415926+ANGLE
813 GO TO 815
814 ANGLE = ANGLE-3.1415926
815 RETURN
END(1,0,0,0,0,0,1,0,0,1,0,0,0,0,0)
```

FUGAM MEAN FUGACITY COEFFICIENT KWONG

```
FUNCTION FUGAM(Q,E,Z)
900 FUGAM = (Z-1.0 - LOGF(Z-Q) - E*LUGF(1.0+Q/Z))
901 RETURN
END(1,0,0,0,0,0,1,0,0,1,0,0,0,0,0)
```

VMOD3 SOLUTION OF THE GENERAL CUBIC EQUATION MOD 3

```
C WITHOUT CUBERTF, ASINF, ACOSF, FOR GENERAL USE
SUBROUTINE VIETA (A, Y, MTYPE)
DIMENSION A(4), B(3), Y(3)
  B(1) = A(2)/A(1)
  B1OV3 = B(1)/3.0
  B(2) = A(3)/A(1)
  B(3) = A(4)/A(1)
  ALF = B(2) - B(1)*B1OV3
  BET = 2.0*B1OV3**3 - B(2)*B1OV3 + B(3)
  BETOV2 = BET/2.0
  ALFOV3 = ALF/3.0
  CUAOV3 = ALFOV3**3
  SQBOV2 = BETOV2**2
  DEL = SQBOV2 + CUAOV3
  IF (DEL) 40,20,30
20 MTYPE = 0
  GAM = SQRTF(-ALFOV3)
  IF (BET) 22,22,21
21 Y(1) = -2.0*GAM - B1OV3
  Y(2) = GAM - B1OV3
  Y(3) = Y(2)
  GO TO 50
22 Y(1) = 2.0*GAM - B1OV3
  Y(2) = -GAM - B1OV3
  Y(3) = Y(2)
  GO TO 50
30 MTYPE = 1
  EPS = SQRTF(DEL)
  TAU = -BETJV2
  RCU=TAU+EPS
  SCU=TAU-EPS
  SIR=1.0
  SIS=1.0
  IF (RCU) 31,32,32
31 SIR=-1.0
32 IF (SCU) 33,34,34
33 SIS=-1.0
34 R=SIR*(SIR*RCU)**0.33333333
  S=SIS*(SIS*SCU)**0.33333333
  Y(1) = R + S - B1OV3
  Y(2) = -(R+S)/2.0 - B1OV3
  Y(3) = 0.86602540*(R-S)
  GO TO 50
40 MTYPE = -1
  QUOT = SQBOV2/CUAOV3
  ROOT = SQRTF(-QUOT)
  IF (BET) 42,41,41
41 PHI = (1.5707963 + ATANF(ROOT / SQRTF(1.0 - ROOT**2))) / 3.0
  GO TO 43
```

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VMDD3 SOLUTION OF THE GENERAL CUBIC EQUATION MOD 3

```
42 PHI = ATANF(SQRTF(1.0 - ROOT**2) / ROOT) / 3.0      00010042
43 FACT = 2.0*SQRTF(-ALFOV3)                          00010043
   Y(1) = FACT*COSEF(PHI) - B1OV3                    00010044
   Y(2) = FACT*COSEF(PHI + 2.0943951) - B1OV3       00010045
   Y(3) = FACT*COSEF(PHI + 4.1887902) - B1OV3       00010046
50 RETURN                                             00010047
   END(1,0,0,0,0,0,1,0,0,1,0,0,0,0,0)
```

PROPANE-ISOPENTANE SYSTEM

	$T_c, ^\circ K$	$P_c, atm.$	ω
PROPANE	369.999998	42.011000	0.152000
ISOPENTANE	460.799999	32.900000	0.212000

-002100 1.000

acentric factor

COMPOSITION

0.5090 0.4910

	ZRK	ZAG	ZEX	DZ	LOG FRK	LOG FAG	FAG	MZQCP
T	348.2000	TR	0.86779					
P	0.7262	15.0000 0.7176	PR 0.	0.4232 0.	H -0.1038 -0.0530 -0.1566	-565.0 S -0.1075 -0.0547 -0.1623	-6.5124 0.7807 0.8817 0.6882	11 1 1311 1321
P	0.0758	15.0000 0.0572	PR 0.	0.4232 0.	H -0.1014 0.1775 -0.3905	-3464.6 S -0.1051 0.1759 -0.3963	-14.8510 0.7851 1.4993 0.4015	11 2 1312 1322

COMPOSITION

0.4140 0.5860

	ZRK	ZAG	ZEX	DZ	LOG FRK	LOG FAG	FAG	MZQCP
T	373.2000	TR	0.91138					
P	0.6515	20.0000 0.6412	PR 0.	0.5771 0.	H -0.1262 -0.0502 -0.1799	-803.4 S -0.1305 -0.0509 -0.1867	-7.5091 0.7405 0.8894 0.6506	11 1 1311 1321
P	0.1097	20.0000 0.0994	PR 0.	0.5771 0.	H -0.1245 0.1601 -0.3256	-3253.0 S -0.1288 0.1594 -0.3324	-14.0807 0.7434 1.4436 0.4652	11 2 1312 1322

COMPOSITION

0.9090 0.0910

	ZRK	ZAG	ZEX	DZ	LOG FRK	LOG FAG	FAG	MZQCP
T	373.2000	TR	1.02227					
P	0.5453	39.0000 0.5347	PR 0.	0.9900 0.	H -0.1583 -0.1380 -0.3603	-1171.9 S -0.1612 -0.1399 -0.3747	-9.6827 0.6899 0.7247 0.4220	11 1 1311 1321

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