THERMODYNAMIC ANALYSIS OF MULTICOMPONENT WORKING FLUIDS FOR RANKINE BOTTOMING CYCLE APPLICATIONS

by

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January 1984
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ABSTRACT

The basic equations underlying a computer code are developed to describe the thermodynamic behavior of multicomponent working fluids in Rankine cycles. The code is to be employed in the performance analysis of Rankine bottoming cycle systems. The performance of such systems depends strongly on the working fluid characteristics. The introduction of multicomponent mixtures makes available a broad spectrum of fluid properties achievable by varying the mixture composition. The code provides a tool to analytically vary the mixture composition to optimize cycle performance.

1. INTRODUCTION

Rankine bottoming cycle (RBC) systems are secondary systems that recover energy from rejected process heat or waste heat from prime movers (i.e., diesel engines, steam or gas turbines, etc.). Over the past several years RBC systems have been investigated at Argonne National Laboratory (ANL), with particular emphasis on the relative merits of various organic fluids in the lower temperature ranges (up to 700°F). In the course of this work, an RBC computer code has been developed for cost-effectiveness studies and thermodynamic performance evaluation for single-component (pure) working fluids [1,2].*

ANL's work has established that system performance depends strongly on the working fluid characteristics, and that greater flexibility in the selection and control of fluid properties is desirable. The introduction of multicomponent mixtures offers the possibility of obtaining a broader spectrum of fluid properties, continuously adjustable by varying the mixture composition to optimize cycle performance. Such a code has been developed at ANL and this report provides the analytical basis. The code is an extension of the ANL pure-fluid code [1].

When the working fluid is a multicomponent mixture, additional complexities in the thermodynamic description are introduced; four major sources of difficulties are discussed.

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*Numbers in brackets denote references.
The number of independent variables is increased to include the mixture composition. To describe the effects of composition variations, the concept of partial molar properties is introduced.

The concept of an ideal solution (or ideal mixture) is introduced to describe deviations (excess properties) of real mixtures from the ideal. This concept is analogous to the departure functions (see App. J), which describe deviations of real from ideal gas behavior for a pure fluid.

The gross mixture properties do not, in general, conform to the weighted average of the constituent properties at the mixture temperature and pressure. Deviation of the real mixture properties from the weighted average is called the property change of mixing.

For a pure fluid, the liquid/vapor phase change takes place across a single saturation line. For a binary mixture, vaporization of the liquid phase occurs at a bubble point line, and condensation of the vapor phase at the dew point line. These lines are not coincident; separation of the lines depends on composition and temperature/pressure. The concepts of fugacity and activity are introduced to predict the phase equilibrium points.

To describe the thermodynamic behavior of multicomponent organic fluids in RBC analyses, empirical equations, of which there are many types in the literature, are required to describe the working fluid properties. In general, these equations are expressed in terms of deviations from ideal gas and ideal solution behavior. Because of the lack of standardization in the selection of experimental reference bases, considerable care is required to correctly interpret and apply empirical data. For this reason, a detailed documentation of the thermodynamic theory underlying the computer code development is presented in this report. Also, if additional experimentation is required to generate input data, a concise description of the theoretical basis of the code will help guide experiment design.

2. GENERAL CONCEPTS FOR MIXTURES

2.1 INTENSIVE AND EXTENSIVE PROPERTIES

The capability to predict the properties of mixtures from known thermodynamic properties of the pure components presents a distinct advantage over experimentally determining each mixture composition. In general, a state of thermodynamic equilibrium is assumed, and any property (say, \( b_i \)) of a pure component \((i)\) is a function of only two other thermodynamic properties \((E_1,E_2)\):

\[
b_i = b_i(E_1,E_2).
\]  

(1)

If the property is proportional to its gross amount of matter, it is called an extensive property and will be designated by a capital letter. For example, the property for a gross quantity of \( N \) moles will be expressed as
\[ B_i = N b_i = B_i(E_1, E_2, N). \] (2)

Nonextensive, or intensive properties will be designated by a lower-case letter. The temperature \( t \) and pressure \( p \) are examples of intensive properties. The total volume \( V \) is an extensive property; whereas \( v \), the specific volume (per mole), is an intensive property. The subscript \( i \) ranges from 1 to \( n \) for an \( n \)-component mixture, and designates the pure component property of the \( i \)th constituent.

For an \( n \)-component mixture, a general property can be expressed analogously to (2) as a thermodynamic function.

\[ B = B(E_1, E_2, N_1, \ldots N_n) \]
\[ N = \sum N_i. \] (3)

If \( B, E_1, E_2 \) are considered to be extensive, as are the mole numbers \( N_i \), the corresponding specific intensive values are

\[ b = B/N \]
\[ e_j = E_j/N ; j = 1,2 \]
\[ y_i = N_i/N ; i = 1,n. \] (4)

The specific intensive general property then becomes the function

\[ b = b(e_1, e_2, y_1, \ldots y_{n-1}) \]
\[ l = \sum y_i. \] (5)

The number of independent variables is reduced from \((n+2)\) to \((n+1)\), because of the added constraint that the sum of the mole fractions be equal to 1.

### 2.2 PARTIAL MOLAR PROPERTIES

A useful property of an extensive function \( B \) is that it be homogeneous in its extensive arguments. For example, a general function \( F \) is homogeneous in \( Z \) when it exhibits the following property for a factor \( \alpha \):

\[ F(w, \alpha Z) = \alpha F(w, Z). \] (6)

The homogeneity property is used in the **Euler theorem**, which states that for the function (6),

\[ F = Z \frac{\partial F}{\partial Z}. \] (7)

An important application to mixtures can be made when the two independent thermodynamic properties are intensive, say \( t \) and \( p \):

\[ B = B(t, p, N_1, \ldots N_n). \] (8)

The Euler theorem then gives the summation
The derivatives are called \textit{partial molar properties} (designated by a bar over the letter)
\[ \bar{b}_i = \frac{\partial B}{\partial N_i} \bigg|_{t,p,N_j \neq 1} . \] (10)

\section*{2.3 THE GIBBS-DUHÉM EQUATION}

Dividing through (9) by \( N \) and substituting (10) shows that \( b \) is the \textit{weighted average} of the partial molar properties (at the mixture \( t \) and \( p \)) of its constituents:
\[ b = \sum y_i \bar{b}_i . \] (11)

Forming the differential of \( B \) from (8), and using the definition (10) gives
\[ dB = \frac{\partial B}{\partial t} dt + \frac{\partial B}{\partial p} dp + \sum \bar{b}_i dN_i . \] (12)

Dividing (12) by \( N \) and using the definitions of (4) gives
\[ db = \frac{\partial b}{\partial t} dt + \frac{\partial b}{\partial p} dp + \sum \bar{b}_i dy_i . \] (13)

The differential of \( b \) also can be derived from (11):
\[ db = \sum y_i db_i + \sum \bar{b}_i dy_i . \] (14)

Combining the two forms (13) and (14) gives the \textit{Gibbs-Duhem equation}, which has important applications in phase-equilibrium analysis.
\[ 0 = \frac{\partial b}{\partial t} \bigg|_{p,y} dt + \frac{\partial b}{\partial p} \bigg|_{t,y} dp - \sum y_i db_i . \] (15)

\section*{3. PROPERTY CHANGE OF MIXING}

The deviation of a general mixture property \( b \) from the weighted average of its constituent properties (at the mixture \( t \) and \( p \)) is called the \textit{property change of mixing}.
\[ \Delta b = b(t,p,y_1, \ldots, y_{n-1}) - \sum y_i b_i(t,p) . \] (16)
The property changes are thermodynamic functions that are useful because differences provide very sensitive experimental measures of the effects of variations in mixture parameters. Insight into the nature of this concept is provided by examination of the more simple behavior of an ideal gas.

3.1 MIXING OF IDEAL GASES AND DALTON'S LAW

Some properties of an ideal gas exhibit no mixing effect; others change under mixing conditions. For example, the internal energy of a mixture is the weighted sum of the pure constituent internal energies, while the resultant entropy is not. In terms of the property change of mixing,

\[ \Delta u = 0 \]
\[ \Delta s \neq 0 \]  

(17)\text{IG}

The property change of mixing (16) depends on the assumed thermodynamic conditions. For example, for a mixture in thermal equilibrium, the constituent temperatures and the mixture temperature are considered identical:

\[ t_i = t \; ; \; i = 1, n \]  

(18)

whereas, the pressure, in the special case of a mixture of ideal gases, is the sum of the partial pressure (Dalton's law). The ideal gas equations for the mixture and for the individual pure constituents at the same total volume and temperature are

\[ p = N \frac{Rt}{V} \]  \\text{and}  
\[ p_i = N_i \frac{Rt}{V} \]  

(19)\text{IG}

From the combination of these two equations, we see that the pressure ratio is equal to the mole fraction:

\[ \frac{p_1}{p} = \frac{N_1}{N} \]  
\[ = y_i \]  

(20)\text{IG}

Since the mole fraction sum (5) is unity, the mixture pressure is the sum of the partial pressures:

\[ p = \sum p_1 \]  

(21)\text{IG}

3.2 GIBBS THEOREM APPLIED TO CHANGES OF ENTHALPY, ENTROPY, AND THE GIBBS FUNCTION

A useful relationship between the extensive properties is given by the Gibbs theorem for ideal gases, which states that
"The resultant mixture property is the sum of the corresponding constituent properties that each would have at the same \( t \) and total mixture volume \( V \)."

\[
b(t,V,N_1, \ldots N_n) = \sum y_i b_i(t,V)
\]

(22)IG

This theorem is derived in Appendix A.

The left side of (22) applies to the mixture at pressure \( p \) (see Fig. A1, App. A), and the right side to the separated constituents at partial pressure \( p_i \); hence, (22) can be expressed as

\[
b(t,p,N_1, \ldots N_n) = \sum y_i b_i(t,p_i)
\]

(23)IG

Since the internal energy of an ideal gas is pressure-independent,

\[
u_i(t,p_i) = u_i(t,p)
\]

(24)IG

Upon replacing the extensive \( N \)-arguments by \( y_i \) (see Eq. 5), the internal energy equation (23) becomes

\[
u(t,p,y_1, \ldots y_{n-1}) = \sum y_i u_i(t,p)
\]

(25)IG

Comparison with the definition (16) shows that the property change of mixing (17) for the internal energy is indeed zero. The enthalpy also is pressure-independent (see A4, App. A); similarly,

\[
\Delta h = 0
\]

(26)IG

The entropy for an ideal gas, however, is not pressure-independent. For example, the entropy change for a pure \( i \)-component undergoing a reversible process with an equivalent heat exchange \( \delta Q \) is

\[
ds_i = \frac{\delta Q}{t}.
\]

Applying the 1st Law,

\[
ds_i = \frac{(du_i + pdv_i)}{t}.
\]

For an isothermal change, the internal energy change is zero, and since \( pv_i = R t \),

\[
pdv_i = v_i dp
\]

= \( R t \frac{dp}{p} \).

It follows that

\[
ds_i \bigg|_t = R \frac{dp}{p}
\]

integration gives
Substituting into (23) for the entropy gives

\[ s(t, p, y_1, \ldots, y_{n-1}) = - R \sum y_i s_i(t, p) - R \ln y_1. \]  

(28) \text{IG}

Comparison with (16) shows that the property change of mixing for the entropy is not zero:

\[ \Delta s = - R \sum y_i \ln y_i. \]  

(29) \text{IG}

The Gibbs function (see A6, App. A), in terms of \( h \) (Eq. 26) and \( s \) (Eq. 28), becomes

\[ g = \sum y_i h_i - t \left[ \sum y_i (s_i - R \ln y_i) \right] \\
= \sum y_i (h_i - t s_i) + R t \sum y_i \ln y_i \\
= \sum y_i (g_i + R t \ln y_i). \]  

(30) \text{IG}

Comparison with (16) shows that the property change of mixing for the Gibbs function is

\[ \Delta g = R t \sum y_i \ln y_i \\
= - t \Delta s. \]  

(31) \text{IG}

4. MIXTURE CHANGES OF PHASE

A major difficulty in the analysis of mixture thermodynamic properties is the occurrence of a two-phase region. Unlike a single-component fluid, the vapor/liquid saturation region is enclosed between two lines, the dew point and bubble point lines shown in Fig. 1.

A basic thermodynamic postulate says that under conditions of thermodynamic equilibrium, any property \( B \) can be expressed as a unique function of two independent properties and the composition (see Eq. 3). A mixture undergoing phase changes can be considered to be in a state of mechanical equilibrium when the pressure \( p \) is uniform, and in a state of thermal equilibrium when the temperature \( t \) is uniform. This state of mechanical/thermal equilibrium does not imply thermodynamic equilibrium, because the composition can change. However, it is generally assumed that the
mixtures in the saturated state in mechanical/thermal equilibrium is described by the thermodynamic function (3).

If heat \( \delta Q \) is supplied to the changing two-phase mixture, the heat source entropy change is \(-\delta Q/t\), while the mixture entropy change is expressed as \( dS \). By the 2nd Law, the total system entropy tends to increase:

\[
-\frac{\delta Q}{t} + dS > 0 .
\]  
(32)

The heat transfer is given by the 1st Law \( \delta Q = dU + pdV \), so that

\[
dU + pdV - tdS < 0
\]  
(33)

For constant \( t \) and \( p \),

\[
d(U + pV - tS)_{t,p} < 0
\]  
(34)

or, in terms of the Gibbs' function (see definition C11, App. C),

\[
dG_{t,p} < 0 .
\]  
(35)

As equilibrium is approached, \( G \) will diminish to a minimum, and the condition for liquid/vapor phase equilibrium is

\[
dG_{t,p} = 0 .
\]  
(36)
5. THE IDEAL SOLUTION (OR MIXTURE)

5.1 GENERALIZATION OF AN IDEAL GAS MIXTURE

The partial molar (see definition, Eq. (10)) value \( \bar{g}_1 \) for the Gibbs' function is called the \textit{chemical potential} \( \mu_1 \):

\[
\mu_1 = \bar{g}_1.
\]  

(37)

We see from (11) that the Gibbs' function is the weighted average of the constituent chemical potentials,

\[
g = \sum y_1 \mu_1.
\]  

(38)

Comparison of this expression with (30)\(_{IG}\) shows that the chemical potential for an ideal gas is

\[
\mu_{IG} = g_1 + R\tau \ln y_1.
\]  

(39)\(_{IG}\)

This equation for an ideal gas may be generalized to define an \textit{ideal solution} (or \textit{ideal mixture}).

\[
\mu_{IM} = g_1 + R\tau \ln y_1.
\]  

(40)\(_{IM}\)

5.2 VOLUMETRIC WEIGHTED AVERAGE

It should be noted that the definition of an ideal mixture does not involve conditions, such as the volumetric restrictions (see App. A) imposed in the derivation of the ideal gas relationship (39)\(_{IG}\). It follows, in fact, that an ideal gas is a special case of the more general concept of an ideal mixture.

An alternative ideal mixture definition, proved to be equivalent in Appendix B, is that the partial molar volumes be equal to the corresponding constituent specific volumes,**

\[
\bar{v}_1 = v_1.
\]  

(41)\(_{IM}\)

Comparison with (11) shows that the specific volume of an ideal mixture is the weighted average of the constituent specific volumes:

\[
v_{IM} = \sum y_1 v_1.
\]  

(42)\(_{IM}\)

\*
Note that \( \mu_{IG} = \partial g_{IG}/\partial N_1 \) and \( \mu_{IM} = \partial g_{IM}/\partial N_1 \).

** Note that \( \bar{v}_1 = \partial v_{IM}/\partial N_1 \).
6. THE FUGACITY FUNCTION

6.1 PURE SUBSTANCE FUGACITY

For a pure substance, the Gibbs' function is defined as

\[ g(t,p) = h - ts 
= u + pv - ts . \]  

(43)

The differential is

\[ dg = du + p dv + v dp - t ds - s dt . \]  

(44)

From the 1st Law, the sum of the first two terms, on the right side, for a reversible change is \( tds \), so that

\[ dg = -s dt + v dp . \]  

(45)

For an isothermal change,

\[ \left. \frac{dg}{t} \right|_t = R t \left. d \ln p \right|_t , \]  

(46)

and for an ideal gas,

\[ \left. \frac{dg}{t} \right|_t = R t \left. d \ln p \right|_t . \]  

(47)\text{IG}

Hence, we see that for an ideal gas, the pressure change provides the "driving force" for changes in the Gibbs' function. For a real gas, the same form (47)\text{IG} is assumed for the Gibbs' function change, but in place of the pressure, the driving force \( f \) is defined as the fugacity. For a pure \( i \)-substance,

\[ \left. \frac{dg_i}{t} \right|_t = R t \left. d \ln f_i \right|_t . \]  

(48)

Included in the definition is the condition that in the pressure limit \((p \to 0)\), the fugacity approaches the actual pressure:

\[ \lim_{p \to 0} f_i = p . \]  

(49)

6.2 MIXTURE FUGACITY

For a mixture, the \( i \)-constituent fugacity \( \hat{f_i} \) in the mixture is defined by a form similar to that for a pure substance.

\[ \left. \frac{dg_i}{t} \right|_t = R t \left. d \ln \hat{f_i} \right|_t . \]  

(50)
This definition also includes the condition that in the limit \((p \to 0)\) the fugacity approach the partial pressure (note that for a real gas the partial pressure has no physical significance).

\[ \lim_{p \to 0} \hat{f}_i = y_i p . \] (51)

(The roof '∧' emphasizes the distinction between the fugacity of the \(i\)-component in the mixture and the \(f_i\) value in the pure state.)

6.3 THE FUGACITY COEFFICIENT

The fugacity of a real gas deviates from the ideal gas value (i.e., the gas pressure); a measure of this deviation is provided by a fugacity coefficient, which has a value of unity for an ideal gas. For a pure \(i\)-substance, the coefficient is

\[ \phi_i = f_i / p . \] (52)

For a mixture, the \(i\)-constituent fugacity coefficient is

\[ \hat{\phi}_i = \hat{f}_i / (y_i p) . \] (53)

The fugacity coefficients can be computed from the equation of state (i.e., the \(p-v-t\) information).

For a pure fluid, a \(\phi_i\)-value can be derived from an integration of the \(p-v-t\) variables. The logarithmic differentiation of (52) yields

\[ d \ln \phi_i = d \ln f_i - \frac{dp}{p} . \] (54)

Equating (46) and (48) gives

\[ d \ln f_i \bigg|_t = \frac{v_i}{R T} \text{ dp} \bigg|_t . \] (55)

Combining the above two expressions (noting that \(\phi_i = 1\) at \(p=0\)),

\[ \ln \phi_i = - \frac{1}{R T} \int_0^p \frac{R T}{p} - v_i \text{ dp} . \] (56)

For a mixture, the \(\hat{\phi}_i\)-value is derived from expressions similar to (46), (48) and (52), in which \(v_i\) is replaced by the partial molar volume \(\bar{v}_i\). In general, thermodynamic relations for partial molar properties have similar forms to those for the pure substances. Corresponding to (45), the differential \(dg_i\) for constant composition (see C19, App. C) is

\[ dg_i = - s_i \text{ dt} + \bar{v}_i \text{ dp} \] (57)

and corresponding to (46), for an isothermal change

\[ dg_i \bigg|_t = \bar{v}_i \text{ dp} . \] (58)
Combining with (50) yields

$$
\ln \hat{f}_1 - \frac{v_1}{RT} dp
$$

(59)

Logarithmic differentiation of (53) gives (note that the $y_i$ are constants for constant composition)

$$
\ln \hat{\phi}_1 = \ln \hat{f}_1 - \frac{dp}{p}
$$

(60)

Combining the above two equations and performing an integration analogous to (56),

$$
\ln \frac{\hat{\phi}_1}{\hat{f}_1} = \frac{1}{RT} \int_0^P \frac{RT}{p} - \frac{v_1}{R} dp
$$

(61)

Subtracting (56) from (61) gives

$$
\ln \frac{\phi_1}{\hat{f}_1} = \frac{1}{RT} \int_0^P (\frac{RT}{p} - \frac{v_1}{R} - \frac{v_1^i}{R}) dp
$$

(62)

For an ideal mixture, the integrand is zero, in accordance with definition (41)IM; hence, for an ideal mixture (and applying 52 and 53),

$$
\hat{\phi}_1 = \phi_1
$$

(63)IM

$$
\hat{f}_1 = y_1 \hat{f}_1
$$

7. LIQUID MIXTURES

7.1 ACTIVITY AND STANDARD STATES

For a gas mixture, the integral expression (62) involves no particular difficulties because the integration extends over a uniform phase region. An ideal gas reference base can be introduced by considering the indefinite integral of (50) (at constant t):

$$
\tilde{g}_1 = RT \ln \hat{f}_1 + \lambda_1(t)
$$

(64)

The arbitrary integration "constant" depends on t. For the ideal gas region ($p \leq p^0$),

$$
g_1^o = RT \ln(y_1 p^o) + \lambda_1(t)
$$

(65)IG

The integration constant is eliminated by subtracting (65) from (64):
\[ \tilde{g}_1 = g_1^0 + R T \ln \left( \hat{f}_1 / y_1 p^0 \right). \]  \hfill (66)

For a liquid mixture, difficulties occur because the phase changes as the integration progresses from the ideal gas reference base \( g_1^0 \). To avoid such phase changes, a new reference base at the same temperature can be defined, called a standard state; this reference base \( \{ p^*, y_1^*, ..., y_{n-1}^* \} \) may be arbitrarily chosen in the liquid state.

\[ \tilde{g}_1 = g_1^* + R T \ln \hat{a}_1. \]  \hfill (67)

The factor \( \hat{a}_1 \) is the ratio of fugacities and is called the activity:

\[ \hat{a}_1 = \frac{\hat{f}_1}{\hat{f}^*_1}. \]  \hfill (68)

Comparison of (67) with (40)_IM (recall that \( \mu_1 = \tilde{g}_1 \)) shows that

\[ \hat{a}_1^{\text{IM}} = y_1 \]  \hfill (69)_IM

and, from (68),

\[ \hat{f}_1^{\text{IM}} = y_1 \hat{f}_1^*. \]  \hfill (70)_IM

\section*{2.2 The Activity Coefficient and the Lewis-Randall Rule}

The arbitrary reference state \( \hat{f}_1^* \) may be chosen to be the fugacity \( f_1 \) for the pure \( i \)-constituent (at the mixture \( p, t \)); this reference base is called the pure solvent standard state, and is the basis for the Lewis-Randall rule (LR).

\[ \hat{f}_1^*(LR) = f_1. \]  \hfill (71)

For this reference base, it follows from (70)_IM that the Lewis-Randall ideal mixture fugacity is

\[ \hat{f}_1^{\text{IM}}(LR) = y_1 f_1. \]  \hfill (72)_IM

To provide a measure of the deviations of a real fluid mixture from the Lewis-Randall ideal mixture, an activity coefficient (ideal \( \gamma_1 = 1 \)) is defined:

\[ \gamma_1 = \frac{\hat{a}_1}{y_1} \]

\[ = \frac{\hat{f}_1}{y_1 f_1^*} \]

\[ = \frac{\hat{f}_1 / \hat{f}_1^{\text{IM}}}{\hat{f}_1 / \hat{f}_1^{\text{IM}}}. \]  \hfill (73)
8. THE VAPOR/LIQUID EQUILIBRIUM EQUATION

8.1 THE PHASE RULE

Any general intensive property $b$ for a single-phase mixture is given by (5). For a mixture containing $\pi$ phases in equilibrium (uniform $t$ and $p$), there are $\pi$ sets of composition variables: each $\alpha, \beta, \ldots$ phase has $(n-1)$ independent composition variables. Hence, (5) generalizes to

$$b = b(p, t, y_1^\alpha, \ldots, y_{n-1}^\alpha, y_1^\beta, \ldots, y_{n-1}^\beta, \ldots)$$

(74)

The Gibbs' function $G$ is a minimum when the mixture is at equilibrium (see Eqs. 35 and 36); for constant $t$ and $p$ the total differential of $G$ is zero. The expansion (C12) of the total differential then yields the equilibrium condition

$$0 = \frac{\partial G}{\partial t, p}$$

$$= \sum_{i} \nu_i \frac{dN_i}{p}$$

(75)

The value for each $i$-constituent term in the summation is the composite of all its individual phase values. For example, if interchange between any two phases, say $\alpha$ and $\beta$, is possible,

$$\sum_{i} \nu_i \frac{dN_i}{p} = \sum_{i} \nu_i^\alpha \frac{dN_i^\alpha}{p} + \sum_{i} \nu_i^\beta \frac{dN_i^\beta}{p}.$$  

(76)

As the mass interchange between each constituent must be conserved,

$$\frac{dN_i^\alpha}{p} = -\frac{dN_i^\beta}{p}.$$  

(77)

Combining (75) and (76) gives

$$0 = \sum_{i} (\nu_i^\alpha - \nu_i^\beta) \frac{dN_i^\alpha}{p}.$$  

(78)

The $dN_i^\alpha$ are independent and arbitrary, so the coefficients must be zero, leading to the $n$ constraint conditions

$$\nu_i^\alpha = \nu_i^\beta.$$  

(79)

There are $(\pi-1)$ constraint equations for $\pi$ phases in equilibrium. Also, there are $[2 + (n-1)\pi]$ "phase-rule variables" and $(\pi-1)n$ equilibrium constraint conditions in (74); consequently, the total number of independent variables (degrees of freedom) $F$ is given by the phase rule.

$$F = [2 + (n-1)\pi] - (\pi-1)n$$

$$= 2 - n + n.$$  

(80)
8.2 VAPOR/LIQUID PHASE EQUILIBRIUM (VLE)

The chemical potentials in the constraint conditions (79) are equal to the partial molar Gibbs' function $g_i$ (see Eq. 37); hence, applying (50) for the Gibbs' function differential change, the chemical potential for each constituent phase is

$$\mu_i^\alpha = RT \ln \frac{\dot{f}_i^\alpha}{f_i^\alpha} + \lambda_i(t) \quad (81)$$

Since the temperature $t$ is uniform throughout all phases, the chemical potential constraint conditions (79) are equivalent to the fugacity constraint conditions:

$$f_i^\alpha = f_i^\beta \quad (82)$$

The above conditions apply to any number of phases in equilibrium. Of particular interest is vapor/liquid equilibrium (VLE) for which the dew and bubble point lines are to be determined. The fundamental conditions (82) can be expressed in terms of the fugacity coefficient given by (53). By combining (53) and (82), and designating vapor and liquid phases by superscripts 'v' and 'l', and $y_1$ the vapor and $x_1$ the liquid composition, the fundamental equilibrium conditions become

$$\hat{y}_1^v = \hat{y}_1^l \quad (83)$$

$$\hat{\phi}_1^v = \hat{\phi}_1^l (t,p,y_1, \ldots y_{n-1})$$

$$\hat{\phi}_1^l = \hat{\phi}_1^l (t,p,x_1, \ldots x_{n-1})$$

For two phases ($n = 2$), the number of degrees of freedom given by (80) is $n$. The total number of independent variables in (83) is $2n$, so that half of these must be specified to solve the constraint equations for the remaining variables. For example, if $t$ and the vapor composition are specified, the system of equations (83) are solved for the unspecified $p$ and the liquid composition.

An alternative form of (83) can be derived from (82) by expressing the liquid fugacity in terms of the activity $y_1$ given by (73). The resulting system of constraint equations becomes

$$y_1^v \hat{\phi}_1^v p = x_1^l \gamma_1 f_1^*$$

$$\hat{\phi}_1 = \hat{\phi}_1 (t,p,y_1, \ldots y_{n-1})$$

$$\gamma_1 = \gamma_1 (t,p,x_1, \ldots x_{n-1})$$

$$f_1^* = f_1^* (t,p) \quad (84)$$
(Note that the liquid and vapor superscripts are dropped with the understanding that $\phi_i$ and $\gamma_i$ refer to the vapor and $\gamma_i$, $x_i$ and $f_i^*$ to the liquid phase.)

8.3 VLE APPROXIMATE SOLUTIONS

The fugacity and activity coefficients in (83) or (84) are complicated functions of $t$, $p$, and composition, and in practice, simplifying assumptions are introduced. Various levels of simplification are discussed below.

8.3.1 Rault's Law

The simplest approximation to VLE is Rault's Law, given by (G12) in Appendix G. The vapor phase is assumed an ideal gas, the liquid an ideal mixture, and the liquid fugacity to be independent of the pressure. The ideal mixture assumption is reasonably good when the constituents comprise similar molecular and chemical species. In other cases, Rault's Law provides a first approximation and can serve as a rough check on more complex methods.

8.3.2 Low/Moderate Pressure Approximation

An improved approximation is achieved by removing the ideal mixture restriction; however, the pressure independence assumption for the liquid-phase $\gamma_i$ and $f_i^*$ is retained. This assumption is a good approximation provided the pressure does not approach the critical value; i.e., the reduced pressure $p_r = p/p_L$ is sufficiently less than 1. The pressure independence of the liquid activity coefficient $\gamma_i$ is demonstrated in the discussion of (F44), Appendix F. The pressure independence of $f_i^*$ follows from (55), which can be expressed as

$$\ln f_i^* \frac{\partial f_i^*}{\partial p} = \frac{\gamma_i}{Rt}.$$  

The specific volume $v_i^*$ is small; consequently the derivative is small, and in the range of low/moderate pressures, the pressure differences are not excessive, so that $f_i^*$ is approximately pressure-independent. Choosing the reference base $f_i^*$ to be the pure component fugacity $f_i^*$ (at the mixture $p$, $t$), which is the Lewis-Randall rule (71), it follows that $f_i^*$ is also approximately pressure-independent, and

$$f_i(t, p, x_i, \ldots) \approx f_i(t, p_{sat}, x_i, \ldots) = f_i^{sat};$$

that is, the liquid fugacity at the system pressure is approximately equal to its fugacity value at the pure component saturation pressure $p_{sat}$, which is a function of temperature only. For the pure component, the fugacity coefficient at saturation is the same for both the liquid and vapor phases.
Combining the Lewis-Randall rule (71) with (86) and (87), the VLE condition (84) becomes

\[ Y_1 \hat{\phi}_1 p = x_1 \gamma_1 p_{1\text{sat}} \phi_{1\text{sat}}. \]  

9. SUMMARY AND CONCLUSIONS

A computer code has been developed to describe the thermodynamic behavior of multicomponent working fluids employed in Rankine bottoming cycle applications. The basic equations appearing in the code are described and derivations and detailed explanations are presented (Appendices A-J). In addition, the results of a sample computation for an ethanol/water mixture are presented (Appendix K). These results are consistent with industrial results [3]. Further work remains to incorporate the code into an overall bottoming-cycle system performance analysis.
REFERENCES


APPENDIX A. GIBBS THEOREM FOR IDEAL GASES

Gibbs theorem for ideal gases states that

"A resultant property \( b \) for a mixture is the sum of the constituent properties at the same \( t \) and total mixture volume \( V \)."

To derive this theorem, a conceptual experiment can be performed in which the constituents of a binary mixture are isothermally and reversibly separated by the process illustrated in Fig. A1 (See Ref. 4, pp. 353-355). The results can be extended to an \( n \)-component fluid by successively applying the experiment in steps. For the first-step component, \( (A) \) can be a pure constituent, and component \( (B) \) the remaining \( (n-1) \)-component mixture. In the next step the \( (n-1) \)-component mixture can be separated into another pure constituent and an \( (n-2) \)-component mixture. Repetition of these steps will separate the original mixture into the \( n \) pure constituents.

The equilibrium pressure forces in the separation process shown in Fig. A1 balance, so the mechanical work is zero. The internal energy of an ideal gas depends on only the temperature, so for an isothermal process, the change in internal energy also is zero. The heat transfer \( Q \), then, must also be zero, in accordance with the 1st Law for zero work and zero internal energy change. The conceptual process is reversible, so the entropy change is \( Q/t \) and it follows that, since \( Q \) is zero, the process is isentropic. Hence, the internal energy and entropy of the final separated gases equals the total for the initial mixture.

\[
\text{Nu}(t,V,N_1, \ldots N_n) = \sum N_i u_i(t,V) \tag{A1}_\text{IG}
\]

\[
\text{Ns}(t,V,N_1, \ldots N_n) = \sum N_i s_i(t,V). \tag{A2}_\text{IG}
\]

Dividing through by the total number of moles \( N \) gives the equations in terms of the mole fractions

\[
u(t,V,N_1, \ldots N_n) = \sum Y_i u_i(t,V) \tag{A2}_\text{IG}
\]

\[
s(t,V,N_1, \ldots N_n) = \sum Y_i s_i(t,V). \tag{A2}_\text{IG}
\]

Noting that the enthalpy is defined as

\[
h = u + pv \tag{A3}
\]

and for an ideal gas \( (pv = RT) \),

\[
h = u + RT, \tag{A4}_\text{IG}
\]

it follows that the net enthalpy change is zero for the process, and
permeable to (1) permeable to constituent (2)

ideal gas mixture
\[ p_1^0 + p_2^0 \]
\[ V = \text{volume} \]
(vacuum)
\[ V = \text{volume} \]

initial state

\[ p_1^0 \] \[ p_1^0 + p_2^0 \] \[ p_2^0 \]

constituent pressures unchanged as \( V \) and \( t \) unchanged

\[ p_2^0 A \] \[ p_2^0 A \]

net force on movable pistons = 0
\[ W = 0 \]

resultant forces

final state

constituent (1) constituent (2)

Fig. A1. Conceptual Reversible Isothermal Separation Process for Binary Mixture (Ref. 4, pp. 353-355)
Also since the Gibbs' function is defined as

\[ g = h - ts , \]  

(A6)

the same property also holds for \( g \);

\[ g(t,V,N_1, \ldots, N_n) = \sum y_i g_i(t,V) . \]  

(A7)

In fact, from just \( u \), \( s \), and \( h \), the form of the above equations can be shown (simply by applying the Legendre transformation discussed in Appendix D) to apply to any general thermodynamic function \( b \):

\[ b(t,V,N_1, \ldots, N_n) = \sum y_i b_i(t,V) , \]  

(A8)

which is the statement of the Gibbs theorem.
APPENDIX B. DEFINITIONS OF AN IDEAL MIXTURE

The equivalence of definitions (40)_{IM} and (41)_{IM} for an ideal mixture can be demonstrated by a conceptual experiment, as shown in Fig. B1 (see Ref. 5, pp. 251-256). A reversible, isothermal steady-flow mixing process is hypothesized. To a multicomponent mixture with flow rate \( N \), a small rate \( \delta N_1 \) of a pure \( i \)-constituent is added. The system inlet and outlet pressures are the same, but the mixing chamber pressure \( p^0 \) is low enough that the fluids behave as ideal gases. Work is expended in the transfer of the fluid between the inlet and outlet pressures and the lower mixing-chamber pressure. Over a small time increment, the steady-flow energy equation for the system is (for incremental enthalpy, heat, and work)

\[
\delta H = \delta Q - \delta W .
\]  

The conceptual process is assumed reversible, so that

\[
\delta Q = t\delta S .
\]  

The temperature is constant for the assumed isothermal conditions so that

\[
\delta Q = \delta(tS) .
\]  

Substitution into (B1) shows that the net flow-work between the inlet and outlet equals the change in the system Gibbs function:

\[
\delta W = \delta(H - ts) = \delta G = G_{\text{out}} - G_{\text{in}} = G(t,p,N_1,.. N_i + \delta N_1,..) - [G(t,pN_1,.. N_i,..) + g_i(t,p) \delta N_1] .
\]  

The net flow-work \( \bar{w} \), per mole of the added pure \( i \)-constituent, is obtained by dividing through by \( \delta N_1 \) and taking the limit* as \( \delta N_1 \to 0 \).

\[
-w = \bar{w}_i - g_i .
\]  

The internal flow-work rates \( \bar{W}_1 \), \( \delta W \), and \( W \), for each of the flow paths (see Fig. B1) between the mixing chamber and the system inlet and outlet boundaries are determined from the steady-flow energy equation (B1). The 1st Law applied to each of the flow paths is of the form

\[
\lim_{\delta N_1 \to 0} \left[ \frac{G(\ldots N_i + \delta N_1 \ldots) - G(\ldots N_i \ldots)}{\delta N_1} \right] = \frac{\partial G}{\partial N_1} = \bar{w}_i
\]

*Note that
\[ \delta Q = \delta U + p \delta V , \]  
\[ (B6) \]

where the internal energy increment is (recall \( H = U + pV \))

\[ \delta U = \delta H - p\delta V - V\delta p . \]  
\[ (B7) \]

Substituting into (B1), the work rate for each path involves the integral of \( V\delta p \)

\[ \dot{W}_1 = -\delta N \int_p v_1(p,t) \, dp \]  
\[ (B8) \]

\[ \dot{W}_1 = -N \int_p v(p,t,N_1, \ldots N_i, \ldots) \, dp \]  
\[ (B9) \]

\[ \dot{W}_2 = -\left( \dot{N} + \delta N \right) \int_{p_0}^p v(p,t,N_1, \ldots N_i + \delta N_i, \ldots) \, dp . \]  
\[ (B10) \]
Dividing through each of these expressions by \( \delta \dot{N}_1 \) and taking the limit as \( \delta \dot{N}_1 \to 0 \), gives the flow-works

\[
\frac{\dot{W}_1}{\delta \dot{N}_1} = \frac{W_1}{\delta N_1},
\]

\[
\frac{\dot{V}_{in}}{\delta \dot{N}_1} = \frac{V_{in}}{\delta N_1},
\]

\[
\frac{V_{out} (\dot{N} + \delta \dot{N})}{\delta \dot{N}_1} = \frac{V_{out}}{\delta N_1},
\]

where

\[
V_{in} = V(p, t, N_1, \ldots, N_i, \ldots)
\]

\[
V_{out} = V(p, t, N_1, \ldots, N_i + \delta N_i, \ldots).
\]

The flow-work (B3) for the added pure \( i \)-constituent is thus (note that \( y_i = p_i/p \))

\[
W_1' = -\int_{p}^{p_1} v_1 \, dp
\]

\[
= \int_{p_0}^{p} v_1 \, dp + \int_{p_1}^{p} v_1 \, dp
\]

\[
\text{ideal gas pressure range } \quad (v_1 = \frac{Rt}{p})
\]

\[
= \int_{p_0}^{p} v_1 \, dp - \frac{Rt}{p} \ln y_i.
\]  

The sum of the remaining flow works (B9) and (B10) becomes

\[
W_1 + W_2 = -\lim_{\delta \dot{N}_1 \to 0} \int_{p_0}^{p} \frac{V_{out} - V_{in}}{\delta N_1} \, dp
\]

\[
= -\int_{p_0}^{p_1} v_1 \, dp.
\]
The total flow-work (per mole of the added $i$-constituent) is

$$ w = w_1 + w_1' + w_2 $$

and substitution into (B5) gives

$$ \bar{g}_1 = g_1 + \ln y_1 + \int_p^{p_0} (\bar{v}_1 - v_1) \, dp \quad \text{(B13)} $$

From this equation we see that an ideal mixture is defined equivalently by the following two equations:

$$ \frac{\delta v_1^{IM}}{\delta N_1^{IM}} = v_1 \quad \text{(B14)} $$

and

$$ \frac{\delta g_1^{IM}}{\delta N_1^{IM}} = g_1 + \ln y_1 \quad \text{(B15)} $$
APPENDIX C. SOME BASIC THERMODYNAMIC IDENTITIES

Certain thermodynamic identities useful for deriving thermodynamic properties of multicomponent mixtures are collected in this Appendix. The entropy $S$, volume $V$, and constituent mole numbers $N_i$ are assumed to be independent variables. The total moles $N$ of the mixture are the summation over the $n$ constituents:

$$N = \sum_{i=1}^{n} N_i . \tag{C1}$$

The mole-fractions are defined as:

$$y_i = \frac{N_i}{N} . \tag{C2}$$

The internal energy for a uniform phase mixture in thermodynamic equilibrium is assumed to be a function of $S$, $V$, and the $N_i$:

$$U = U(S,V,N_1,\ldots,N_n) . \tag{C3}$$

For a thermodynamic function, the total differential is assumed to be exact, and the chain-rule expansion gives (partial derivatives indicated by subscripts)

$$dU = U_S dS + U_V dV + \sum_{i} U_{N_i} dN_i . \tag{C4}$$

For constant composition,

$$dU = U_S dS + U_V dV . \tag{C5}$$

The 1st Law for a closed system is (exact differentials are indicated by the prefix 'd' and inexact by 'δ')

$$dU = δQ - δW . \tag{C6}$$

For a reversible change, the heat (in) and the work (out) are

$$δQ = t \, dS$$
$$δW = p \, dV$$

and (C6) becomes

$$dU = t \, dS - p \, dV . \tag{C7}$$

Comparison with (C5) shows that for constant composition,

$$t = U_S|_{V,N} \tag{C8}$$
$$-p = U_V|_{S,N} .$$
(The notation \(( \cdot )_{V,N} \) indicates \( V \) and \( N \) held constant.)

In general, for variable composition,

\[
dU = t \, ds - p \, dV + \sum \mu_i \, dN_i ,
\]

where \( \mu_i \) is defined as the "chemical potential".

\[
\mu_i = U_{N_i} \bigg|_{t,p,N_{j \neq i}}.
\]

The enthalpy \( H \), Helmholtz function \( A \), and Gibbs' function \( G \) are defined as

\[
H = U + pV
\]

\[
A = U - tS
\]

\[
G = H - tS .
\]

The corresponding differentials are

\[
dH = dU + p \, dV + V \, dp
\]

\[
= dV + p \, dV + \sum \mu_i \, dN_i
\]

\[
dA = dU - t \, ds - S \, dt
\]

\[
= -p \, dV - S \, dt + \sum \mu_i \, dB_i
\]

\[
dG = dH - t \, ds - S \, dt
\]

\[
= V \, dp - S \, dt + \sum \mu_i \, dN_i .
\]

The chain-rule differential expansions of \( H \), \( A \), and \( G \) are similar in form to (C4) for the internal energy \( U \). Comparison of (C9) and (C12) with the corresponding chain-rule expansions of \( dU \), \( dH \), \( dA \), and \( dG \) shows that (where \( j \neq i \)).

\[
\mu_i = H_{N_i} \bigg|_{S,p,N_{j \neq i}} = A_{N_i} \bigg|_{V,t,N_j}
\]

\[
= U_{N_i} \bigg|_{S,V,N_j} = G_{N_i} \bigg|_{p,t,N_j} .
\]
The partial derivative at constant \( p, t, \) and \( N_j \) is called the partial molar property; the Gibbs function derivative is such a partial molar property (the other derivatives in C13 are not).

\[
\frac{\partial G}{\partial N_j} = c_{N_j} \left. \frac{\partial G}{\partial c_{N_j}} \right|_{p,t} = \frac{G^{\text{Ni}}}{t}.
\] (C14)

Comparison of corresponding terms of (C9) and (C12) with the chain-rule expansion of the differentials also shows (for constant composition) that

\[
t = u = h_{s,p,y} \quad \quad -p = U_{v,s,y} = 0_{v,t,y}
\] (C15)

\[
v = h_{p,s,y} = g_{p,t,y} \quad \quad -s = a_{t,v,y} = g_{t,p,y}.
\]

For the above equations, the differential expressions (C12) are first divided by \( N \) to reduce the extensive thermodynamic properties (upper case letters) to intensive (lower case letters) properties per mole.

The conditions for exactness* of the differentials of (C9) and (C12) gives the Maxwell relations; the exactness of \( du, dh, da, \) and \( dg, \) respectively, implies the following identities:

\[
t_v|_s = -p_s|_v \quad \quad t_p|_s = v_s|_p
\] (C16)

\[
p_t|_v = s_v|_t \quad \quad v_t|_p = -s_p|_t.
\]

A useful thermodynamic identity is the Gibbs-Helmholtz equation, which relates the Gibbs function derivative at constant pressure and composition to the enthalpy.

---

*Exactness of the differential \( db(x,y) = Mdx + Ndy \) implies \( M_y = N_x.\)
\[
\frac{\partial (g/t)}{\partial t}\bigg|_{p,N} = -\left(\frac{g - t g_t}{p,N}\right)t^2
\]

\[
= -(g + ts)/t^2
\]

\[
= -h/t^2 .
\] (C17)

This last equality follows from expression (C15) for the entropy, and the Gibbs function definition (C11).

Many of the identities for the thermodynamic functions have analogous forms for partial molar properties. For example, the analogues of (C11) are easily derived:

\[
\bar{h}_i = \frac{\partial H}{\partial N_i}\bigg|_{p,t,N_j}
\]

\[
= \frac{\partial U}{\partial N_i}\bigg|_{p,t,N_j} + p \frac{\partial V}{\partial N_i}\bigg|_{p,t,N_j}
\] (C18)

\[
= \bar{u}_i + p\bar{v}_i .
\]

Similarly, it can be shown that

\[
\bar{a}_i = \bar{u}_i - ts_i .
\] (C19)

\[
\bar{g}_i = \bar{h}_i - ts_i .
\] (C20)

We see from (C15) and (C17) that v, s, and h can be expressed in terms of derivatives of g. Analogous expressions for the partial molar quantities \(\bar{v}_i, \bar{s}_i,\) and \(\bar{g}_i\) are easily derived. The exactness condition for \(dG\) yields (see Eq. C12)

\[
\frac{\partial g_i}{\partial t}\bigg|_{p,n} = \frac{\partial S}{\partial N_i}\bigg|_{t,p,N_j}
\]

\[
= -\bar{s}_i .
\] (C21)
\[ \frac{\partial \tilde{g}_1}{\partial p} \bigg|_{t,n} = \frac{\partial V}{\partial N_i} \bigg|_{t,p,N_j} \]

\[ = \bar{v}_1. \tag{C22} \]

(Note in these expressions that from Cl4, \( \bar{g}_1 \) is \( \nu_1 \)).

The analogous Gibbs-Helmholtz equation is demonstrated by the following differentiation:

\[ \frac{\partial}{\partial t} \left( \frac{\bar{g}_1}{t} \right) \bigg|_{p,n} = -\frac{1}{t^2} \left[ \bar{g}_1 - t \frac{\partial \bar{g}_1}{\partial t} \bigg|_{p,n} \right] \]

\[ = - \left( \bar{g}_1 + t\bar{s}_1 \right)/t^2 \tag{C23} \]

\[ = - \frac{\bar{h}_1}{t^2}. \]

This last equality follows from (C21) and (C22).
APPENDIX D. GENERATION OF THERMODYNAMIC FUNCTIONS BY THE LEGENDRE TRANSFORMATION

The internal energy for a single-phase, n-component mixture is assumed [see Eq. (C3), Appendix C] to be uniquely determined by specification of the entropy, volume, and composition:

$$U = U(S, V, N_1, \ldots, N_n). \quad (D1)$$

All homogeneous-phase, thermodynamic equilibrium information for the mixture is contained in this function. The introduction of other thermodynamic functions such as the enthalpy $H$, Gibbs' or Helmholtz functions $G$ and $A$, or chemical potentials does not provide any essentially new information. The value of these other functions is to facilitate the experimental acquisition of equation of state data. The equivalence of the information content in various thermodynamic functions is established by demonstrating the "one-to-one" nature of transformations between functions. The classical Legendre transformation* provides a geometric interpretation for the (1-1) relationship.

The thermodynamic function may be visualized as a surface in a three-dimensional space; the surface is described by a continuously differentiable function of two variables:

$$w = w(x, y). \quad (D2)$$

For example, $w$ may correspond to the internal energy $U$, $x$ the entropy $S$, and $y$ the volume $V$. Extension of the independent variables to include the mole numbers $N_i$, where $i$ ranges from 1 to $n$, will create a $(n+1)$-dimensional surface embedded in an $(n+2)$-dimensional space. The function $w(x, y)$ is represented by the surface shown in Fig. D1.

Tangent to the $w$-surface at any fixed point $(x, y)$ there exists a plane $w$ with running coordinates $(\hat{x}, \hat{y})$. This plane is given by the linear equations (subscript notation for partial derivatives)

$$\hat{w} - w = (\hat{x} - x)w_x + (\hat{y} - y)w_y. \quad (D3)$$

Expressing this plane in a symmetrical form is elucidating (for a duality relationship):

$$\hat{w} + w = \hat{x} \xi + \hat{y} \eta, \quad (D4)$$

where

---

$\xi = \xi(x,y) = w_x$

$\eta = \eta(x,y) = w_y$

$\omega = \omega(x,y) = x\xi + y\eta - w$.

The inverse functions of (D5) are

$x = x(\xi,\eta)$ and

$y = y(\xi,\eta)$.

If the Jacobean determinant of the transformation is not zero (i.e., the transformation is 1-1),

$$j = \begin{vmatrix} x_\xi & x_\eta \\ y_\xi & y_\eta \end{vmatrix} \neq 0$$

(D7)

$$J = \frac{1}{j} = \begin{vmatrix} \xi_x & \xi_y \\ \eta_x & \eta_y \end{vmatrix} \neq 0 .$$

Combining (D5) with (D7) shows the Jacobean to be

$$J = w_{xx} w_{yy} - w_{xy}^2 .$$

(D8)
If $J$ is zero (i.e., singular), the differential equation (D8) describes a developable surface* (except for surfaces perpendicular to the $x,y$ coordinate plane). As a developable surface is generated by the locus of a rigid straight line, it is evident that any tangent plane to such a surface will coincide with one of the straight line generators, thus intersecting the surface at an infinite set of points rather than at the single unique point $(x,y)$. For this reason, to have a (1-1) correspondence between the tangent planes $w$ and the points on the $w$-surface, it is necessary that $J \neq 0$.

To determine the inverse transformations (D6), the $w$-function of (D5) can be differentiated:

\[
\begin{align*}
\omega_\xi &= x + \xi x_\zeta + \eta y_\eta - (w x_\zeta + w y_\zeta) \\
&= x \\
\omega_\eta &= y + \xi y_\zeta + \eta y_\eta - (w x_\eta + w y_\eta) \\
&= y.
\end{align*}
\]

The duality between $(w,x,y)$ and $(\omega,\xi,\eta)$ is made apparent by collecting (D5) and (D9) into the system.

\[
\begin{align*}
w + \omega &= x \xi + y \eta \\
x &= \omega_\xi, \xi = w_x \\
y &= \omega_\eta, \eta = w_y.
\end{align*}
\]

The variables $(\omega,\xi,\eta)$ may be thought of as the "coordinates" of the tangent plane, and the transformation with $(w,x,y)$ is the "Legendre transformation" (i.e., the system D10).

Various partial transformations can be applied to generate the enthalpy $H$, and the Helmholtz and Gibbs functions $A$ and $G$. The identities (C8) of Appendix C, giving $t$ and $p$ as derivatives of $U$, can be used to construct the table presented here as Table D1.

If the energy function (D1) includes variations in the mole numbers $N_i$, the tangent plane becomes an $(n+1)$-dimensional plane with fixed slopes $w_i$. The transformation between the planes and the points on the $U$-surface becomes

\[
(U,S,V,N_1, ..., N_n) \leftrightarrow (\omega,\xi,\eta, \mu_1, ..., \mu_n).
\]

### Table D1. Duals, Transformations, and Defined Functions

<table>
<thead>
<tr>
<th>Duals</th>
<th>Transformations</th>
<th>Defined Functions</th>
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<tbody>
<tr>
<td>$U \sim \omega$, $V \sim \eta$</td>
<td>$U + \omega = \eta$</td>
<td>$-\omega = U + V\eta$</td>
</tr>
<tr>
<td></td>
<td>$\eta = U_{V} = -p$</td>
<td>$= H(S,p,N_1, \ldots N_n)$</td>
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</tr>
<tr>
<td></td>
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<td>$V \sim \eta$</td>
<td>$= St - Vp$</td>
<td>$= G(t,p,N_1, \ldots N_n)$</td>
</tr>
</tbody>
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The extended system (D10) becomes

\[
U + \omega = S\xi + V\eta + \sum N_i \mu_i
\]

\[
S = \omega_{\xi}, \quad \xi = U_{S} = t
\]

\[
V = \omega_{\eta}, \quad \eta = U_{V} = -p
\]

\[
N_i = \omega_{\mu_i}, \quad \mu_i = U_{N_i}
\]

(Note that the $\mu_i$ are consistent with C13, Appendix C.)

The above system gives

\[
-\omega = U - (St - Vp + \sum N_i \mu_i).
\]  

(D14)

Since $U$ is a homogeneous function of $S$, $V$, $N_i$, the Euler theorem (7) can be applied:

\[
U = SU_{S} + VU_{V} + \sum N_i U_{i}
\]

\[
= St - Vp + \sum N_i \mu_i.
\]  

(D15)

Comparison with the expression for $G$ given by (D11) shows that
\[ G = \sum N_1 \mu_1 ; \]  
(D16)

Comparison with (D14) shows that

\[ 0 = \omega . \]  
(D17)

The differential of \( \omega \) is

\[ 0 = d\omega \]

\[ = \omega_\xi \, d\xi + \omega_\eta \, d\eta + \sum \omega_\mu_1 \, d\mu_1 \]  
(D18)

\[ = S \, dt - V \, dp + \sum N_1 \, d\mu_1 . \]

Division by \( N \) gives the Gibbs-Duhem expression:

\[ \sum y_1 \, d\mu_1 = -s \, dt + v \, dp . \]  
(D19)

This form is consistent with (15) when the general function \( b \) is the Gibbs' function \( g \).

\[ 0 = g_\xi \, dt + g_\eta \, dp - \sum y_1 \, d\bar{g}_1 . \]  
(D20)

The derivatives of the Gibbs function are given by (C14) and (C15) in Appendix C.

\[ \bar{g}_i = \nu_1 \]

\[ g_\xi = -s \]

\[ g_\eta = v . \]  
(D21)

Upon substitution into (D20), the form (D19) is obtained.
APPENDIX E. HENRY'S LAW AND THE LEWIS-RANDALL RULE

For an ideal multicomponent mixture, the j-component fugacity \( \hat{f}_j \) varies linearly with the component mole-fraction \( y_j \) as shown by Eq. (72)_IM:

\[
\hat{f}_j^{\text{IM}}(LR) = y_j \hat{f}_j .
\]

(E1)

In this equation, the Lewis-Randall (LR) fugacity reference base is the constant pure-component fugacity \( f_1 \). The straight-line relationship (E1) is shown in Fig. E1.

![Fig. E1. Lewis-Randall Ideal Mixture Fugacity](image)

As \( j \) approaches zero, the concentration of the i-component in the mixture becomes infinitely diluted; when \( y_j \) approaches 1, the mixture approaches the pure j-component. We would expect that at these two end points, the ideal mixture and the real mixture properties become identical.

\[
\hat{f}_j \bigg|_{y_j=1} = \hat{f}_j^{\text{IM}}(LR) \bigg|_{y_j=1}
\]

(E2)

\[
\hat{f}_i \bigg|_{y_i=0} = \hat{f}_i^{\text{IM}}(LR) \bigg|_{y_i=0} .
\]

(E3)

Although the validity of the above two expressions at the limiting conditions appears to be intuitively necessary, it should be demonstrated that (E2) and (E3) are indeed consistent with previous definitions.

1. Proof of (E2), (as \( y_j \to 1 \))

From the general definition (11) of a partial molar property applied to the specific volume.

\[
v = \sum_{k} y_k \bar{v}_k .
\]

(E4)
As $y_j$ approaches unity, the mole fractions of the other components approach zero, so that (E4) becomes

$$\lim_{y_j \to 1} v = \frac{v_j}{y_j+1}.$$  \hspace{1cm} (E5)

It is also obvious that as the masses of the other components approach zero, the mixture density approaches that of the $j$-component.

$$\lim_{y_j \to 1} \frac{1}{v_j} = \frac{1}{v}.$$  \hspace{1cm} (E6)_1

This is equivalent to saying that

$$\lim_{y_j \to 1} v = v_j.$$  \hspace{1cm} (E6)_2

Comparison of the above two equations shows that

$$\lim_{y_j \to 1} (v_j - \frac{v_j}{y_j+1}) = 0.$$  \hspace{1cm} (E7)

Referring to the integral (62) for the ratio of fugacity coefficients, it is clear that the integrand approaches zero, and

$$\lim_{y_j \to 1} \left( \frac{\phi_j}{\phi_j^*} \right) = 1.$$  

From the fugacity coefficient definitions (52) and (53),

$$\lim_{y_j \to 1} \hat{f}_j = \frac{\hat{f}_j}{\hat{f}_j} y_j.$$  

Hence, from (E1), the condition (E2) is verified:

$$\lim_{y_j \to 1} \hat{f}_j = \hat{f}_j \left( LR \right) \bigg|_{y_j=1}.$$  \hspace{1cm} (E9)

The value for the activity at the limit for (E9) should be noted. The Lewis-Randall-based activity is obtained from (68) and (71).

$$a_j = \frac{\hat{f}_j / f_j}{\hat{f}_j}.$$  \hspace{1cm} (E10)

From (E9) it follows that in the limit

$$\lim_{y_j \to 1} a_j = 1.$$  \hspace{1cm} (E11)

Since the Lewis-Randall reference state is that of the pure $j$-component, the $g^{*\prime \prime}$ function reference state is

$$g_j^* = g_j.$$  \hspace{1cm} (E12)
Substituting (E11) and E12) into (67) (and applying the limit),

\[
\lim_{y_j \to 1} g_j = g_j .
\]  

(E13)

Since in the limit the mixture and pure constituent values are equal for both fugacity (see E10 and E11) and the Gibbs' function (see E13), it follows that the indefinite integrals given by (48) for the pure substance and (50) for the mixture must have the same constant \( \lambda_k(t) \) of integration independent of the pressures.

\[
g_k = R \ln f_k + \lambda_k(t) 
\]  

(E14)

Subtracting eliminates the constant:

\[
\bar{g}_k - g_k = R \ln \left( \frac{\hat{f}_k}{f_k} \right) .
\]  

(E15)

This relationship will be used in the following proof for the case of infinite dilution.

2. Proof of (E3), (as \( y_1 \to 0 \))

The limiting condition as the i-constituent becomes infinitely dilute in the mixture is somewhat more complex, and we resort to the conceptual semi-permeable membrane mechanism illustrated in Fig. E2.

![Conceptual Separation of Mixture and Pure Constituent](image)

Fig. E2. Conceptual Separation of Mixture and Pure Constituent

Initially, the mixture is contained in the Side (1) chamber, and Side (2) is either empty or contains some pure i-substance. The total number of moles of (i) is constant (superscript indicates the side):
\[ N_1^{(1)} + N_1^{(2)} = \text{constant}. \quad (E16) \]

As the system approaches equilibrium, the \( i \)-substance can migrate through the membrane and, from (E16), the changes in the mole numbers on either side of the membrane must satisfy the condition
\[ dN_1^{(1)} = -dN_1^{(2)}. \quad (E17) \]

The Gibbs function for the total system is the sum of the mixture value on Side (1) and the pure \( i \)-substance on Side (2):
\[ G = G(t,p,N_1^{(1)}, \ldots, N_1^{(1)}, \ldots) + N_1^{(2)} g_1^i(t,p_1). \quad (E18) \]

All possible system changes are subject to the constraint (E17), and at equilibrium the total Gibbs function is a minimum; in accordance with condition (36),
\[ 0 = \frac{dG}{dN_1^{(1)}} \]
\[ = \frac{\partial G}{\partial N_1^{(1)}} - g_1^i(2)(t,p_1) \]
\[ = g_1^i(1) - g_1^i(2). \quad (E19) \]

(This last equality uses the definition (10) for a partial molar property.)

Since (E15) is valid independent of the pressure (the pressure corresponding to \( g_1^i \) may differ from the pressure for \( g_1^i \)), it follows from (E19) that the left side of (E15) is zero, and
\[ \ln \left( \frac{\hat{f}_i}{f_i} \right) = 0. \]

This condition implies that the argument of the log-function be unity, or
\[ \hat{f}_i^{(1)} = f_i^{(2)}. \quad (E20) \]

As \( y_i \) approaches zero, the number of moles \( N_1^{(2)} \) approaches zero, so the pressure \( p_1 \) on Side (2) must also approach zero:
\[ \lim_{y_i \to 0} p_1 = 0. \quad (E21) \]

The pure \( i \)-substance on Side (2) becomes an ideal gas as its pressure becomes sufficiently small, and, from (49), the fugacity becomes equal to the pressure. Hence, from (E21)
\[ \lim_{y_i \to 0} f_i^{(2)} = 0 \quad (E22) \]

and from (E20),
\[ \lim_{y_i \to 0} f_i^{(1)} = 0 . \quad (E23) \]

Since (E23) holds for any general mixture, the superscript can be eliminated, and
\[ \lim_{y_i \to 0} f_i = 0 . \quad (E24) \]

Note that the above derivation makes no mention of a "partial pressure" of the \( i \)-constituent in the mixture. Since the mixture pressure can have any value, the mixture cannot be considered an ideal gas, and the concept of a "partial pressure" is undefined. From (E1), we see that
\[ \lim_{y_i \to 0} f_i^{\text{TM}}(LR) = 0 . \quad (E25) \]

Comparison of the above two equations establishes the validity of (E3).

For a real mixture, the relationship of \( f_i \) to \( y_i \) deviates from the linear Lewis-Randall ideal mixture relationship shown in Fig. E1. In the neighborhood of infinite dilution \( (y_i \to 0) \), a linear approximation to the \( f_i \) versus \( y_i \) curve is represented by the tangent line at the origin (see Fig. E2).

\begin{center}
\textbf{Fig. E2. Henry's Law Approximation for Infinite Dilution}
\end{center}

The slope \( k_i \) at the origin is
If $k_i$ is chosen as the reference state fugacity in (70)$_{IM}$, rather than the Lewis-Randall pure state $f_i$,}

$$f_i^* = k_i.$$  \hspace{1cm} (E27)

The resulting linear approximation is called the Henry's law ideal mixture, and is the tangent line shown in Fig. E2.

$$f_i^{(HL)} = y_i k_i.$$  \hspace{1cm} (E28)

In the region of infinite dilution (see Fig. E2), the tangent line approximates the real solution curve, so that

$$f_i = f_i^{(HL)}.$$  \hspace{1cm} (E29)

Henry's law is thus a linear approximation to the real mixture in the infinite dilution region ($y_i \to 0$). Similarly, the Lewis-Randall rule is a linear approximation in the region ($y_j \to 1$); i.e., the straight line represented by (15) and shown in Fig. E1 is tangent to the true $f_j$ versus $y_j$ curve at $y_j = 1$.

The tangency is demonstrated as follows: The mole fraction $y_j$ is given by

$$y_j = 1 - \sum_{i \neq j} y_i.$$  \hspace{1cm} (E30)

Clearly, as $y_j$ approaches 1, the mole fractions of all other components must approach zero:

$$\lim_{y_j \to 1} y_i = 0, \text{ for all } i \neq j.$$  \hspace{1cm} (E31)

It follows that for the infinite dilution of the $i$-components, Henry's law (E29) applies for $i \neq j$.

$$f_i = y_i k_i, \text{ for all } i \neq j.$$  \hspace{1cm} (E32)

The Gibbs-Duhem equation (15) for constant $t$ and $p$ is
The differential $dg_k$ is given by (50):

$$dg_k = \frac{R}{2} \frac{d\ln f'_k}{t}.$$  \hspace{1cm} (E34)

Applying Henry's law (E32) for $i \neq j$,

$$d \ln f'_i = d \ln y'_i \quad = dy'_i/y'_i.$$  \hspace{1cm} (E35)

Hence, (E33), for $i \neq j$ may be expressed as

$$0 = y_j d \ln f'_j + \sum dy'_i.$$  \hspace{1cm} (E36)

From (E30),

$$dy_j = - \sum dy'_i,$$  \hspace{1cm} (E37)

and it follows that

$$d \ln f'_j = dy_j/y_j \quad = d \ln y_j.$$  \hspace{1cm} (E38)

This expression may be integrated, noting from (E2) that when $y_j = 1$, the mixture fugacity $f'_j = f'_j$, the pure $j$-component value.

$$\int_{\hat{f}_j}^{f_j} d \ln f'_j = \int_{\hat{y}_j}^{y_j} d \ln y_j$$

Evaluation of the definite integrals gives

$$\ln (f'_j/\hat{f}_j) = \ln (1/y_j),$$

or, under the conditions of Henry's law for the $i$-components, the Lewis-Randall approximation (E1) holds for the $j$-component:

$$\hat{f}_j = y_j f'_j = f'_j^{\text{LR}}.$$

The slope of the tangent (at $j = 1$) to the graph of the real mixture (see Fig. E2) is
This slope is identical to the slope of the Lewis-Randall straight line shown in Fig. E1. Hence, considering two components (i and j), the Lewis-Randall rule and Henry's law are dual approximations over the same region of validity, as shown in Fig. E3.
APPENDIX F. EXCESS FUNCTIONS AND THE PARTIAL MOLAR PROPERTY CHANGE OF MIXING

F1. PARTIAL MOLAR PROPERTY CHANGE OF MIXING

The reference state for the general property change of mixing defined by (16) is at the mixture temperature and pressure \((t, p)\). A more general property change of mixing can be defined for an arbitrary reference state at \((t^*, p^*)\).

\[
\Delta b = b(t, p, y_1, \ldots, y_{n-1}) - \sum y_i b_1^*(t^*, p^*) . \tag{F1}
\]

The property change of mixing for the extensive form \(B\) of the variable is obtained by multiplying (F1) by \(N\):

\[
\Delta B = B - \sum N_i b_1^* . \tag{F2}
\]

The definition (10) for a partial molar property applied to \(\Delta B\) gives (where \(j \neq 1\))

\[
\overline{\Delta b_j} = \frac{\partial \Delta B}{\partial N_j} \bigg|_{t, p, N_j} = \frac{\partial \Delta B}{\partial N_j} \bigg|_{t, p, N_j} = b_j - b_1^* . \tag{F3}
\]

The quantity \(\overline{\Delta b_j}\) is called the partial molar property change of mixing.

Substitution of the weighted average of \(b\) as defined by (11) into (F11) gives

\[
\Delta b = \sum y_i \overline{b_1} - \sum y_i b_1^* = \sum y_i \overline{b_1} - \sum y_i b_1^* = \sum y_i \overline{\Delta b_1} . \tag{F4}
\]

The weighted average for \(\Delta b\) in terms of \(\overline{\Delta b_1}\) is thus analogous to that for \(b\) in terms of \(\overline{b_1}\). Applying this weighted average form to the Gibbs function \(g\), specific volume \(v\), enthalpy \(h\), and entropy \(s\) gives the weighted average property changes of mixing:

\[
\Delta g = \sum y_i (\overline{g_1} - \overline{g_1}^*) \tag{F5}
\]

\[
\Delta v = \sum y_i (\overline{v_1} - \overline{v_1}^*)
\]

\[
\Delta h = \sum y_i (\overline{h_1} - \overline{h_1}^*)
\]

\[
\Delta s = \sum y_i (\overline{s_1} - \overline{s_1}^*) .
\]
The reference states can be expressed in terms of the Gibbs function by application of the forms (C15) to the entropy and specific volume, and (C17) to the enthalpy.

\[ v_i^* = \left. \frac{\partial g_i^*}{\partial p} \right|_t \]
\[ s_i^* = -\left. \frac{\partial g_i^*}{\partial t} \right|_p \]
\[ h_i^* = -t^2 \left. \frac{\partial (g_i^*/t)}{\partial t} \right|_p . \]

Analogous expressions for the partial molar values are obtained from (C21), (C22), and (C23).

\[ \bar{v}_i = \left. \frac{\partial g_i}{\partial p} \right|_t \]
\[ \bar{s}_i = -\left. \frac{\partial g_i}{\partial t} \right|_p \]
\[ \bar{h}_i = -t^2 \left. \frac{\partial (g_i/t)}{\partial t} \right|_p . \]

Substitution of (F6) and (F7) into (F5) and applying definition (F3) gives the property change of mixing for \( g, v, s, \) and \( h, \) in terms of \( \Delta g_1 \).

\[ \Delta g = \sum y_i \Delta g_i \]
\[ \Delta v = \sum y_i \left. \frac{\partial \Delta g_i}{\partial p} \right|_{t,y} \]
\[ = \frac{1}{p} \sum y_i \left. \frac{\partial \Delta g_i}{\partial n} \right|_{t,p} \]
\[ \Delta s = \sum y_i \left. \frac{\partial \Delta g_i}{\partial t} \right|_{p,y} \]
\[ = -\frac{1}{t} \sum y_i \left. \frac{\partial \Delta g_i}{\partial n} \right|_{p,y} \]
\[ \Delta h = -t^2 \sum y_i \left. \frac{\partial (\Delta g_i/t)}{\partial t} \right|_{p,y} \]
\[ = -t \sum y_i \left. \frac{\partial (\Delta g_i/t)}{\partial n t} \right|_{p,y} . \]
By application of (67), the Gibbs function partial molar property change of mixing $\Delta g_1$ can be expressed in terms of the activity $\hat{a}_1$:

$$\Delta g_1 = Rt \ln \hat{a}_1$$  \hspace{1cm} (F9)

$$\hat{a}_1 = \frac{f_1}{f^*_1}.$$  

Hence, the property change of mixing can be expressed in terms of the activity.

$$\frac{\Delta g}{Rt} = \sum y_1 \ln \hat{a}_1$$

$$\frac{P}{Rt} \Delta v = \sum y_1 \ln \frac{\hat{a}_1}{a_1} \ln p \Bigg|_{T,P}$$  \hspace{1cm} (F10)

$$\frac{\Delta s}{R} = - \sum y_1 \ln \hat{a}_1 - \sum y_1 \ln \frac{\hat{a}_1}{a_1} \ln t \Bigg|_{P,Y}$$

$$\frac{\Delta h}{Rt} = - \sum y_1 \ln \frac{\hat{a}_1}{a_1} \ln t \Bigg|_{P,Y}.$$  

For an ideal mixture, the activity given by (69)_{IM} is

$$\hat{a}_{1,IM} = y_1.$$  \hspace{1cm} (F11)

All derivatives in (F10) are then zero (since the mole fractions $y_1$ are held fixed), and the expressions simplify to

$$\Delta v_{IM} = 0$$

$$\Delta h_{IM} = 0$$  \hspace{1cm} (F12)

$$\frac{\Delta g_{IM}}{Rt} = \sum y_1 \ln y_1$$

$$\frac{\Delta s_{IM}}{R} = - \sum y_1 \ln y_1.$$  

These equations demonstrate that an ideal mixture undergoes no property change of mixing for the specific volume and enthalpy. This is also true for the internal energy ($u = h - pv$) and the specific heat ($c_p = \partial h/\partial t$).

$$\Delta u_{IM} = 0$$  \hspace{1cm} (F13)

$$\Delta c_p^{IM} = 0.$$
F2. EXCESS FUNCTIONS

The deviation of any intensive mixture property \( b \) from its ideal mixture value is called the excess value.

\[
b^E = b - b^{IM}.
\]  

(F14)

The corresponding extensive value is obtained by multiplication by \( N \), the total number of moles.

\[
b^E = b - b^{IM}.
\]  

(F15)

The weighted averages as defined by (11) for \( b \) and \( b^{IM} \) are

\[
b = \sum y_i b_i \quad \text{and} \quad b^{IM} = \sum y_i b_i^{IM}.
\]  

(F16)

Substitution into (F14) gives

\[
b^E = \sum y_i \left( \frac{b_i}{y_i} - b_i^{IM} \right).
\]  

(F17)

Differentiation of (F15) by \( N \) gives the partial molar value of \( b^E \) (see definition 10):

\[
\frac{\partial b^E}{\partial N} = \frac{\partial b}{\partial N} - \frac{\partial b^{IM}}{\partial N}.
\]  

(F18)

Substitution into (F17) gives the weighted average of \( b^E \).

\[
b^E = \sum y_i \frac{b_i}{y_i}.
\]  

(F19)

The property changes of mixing for \( b^E \) and \( b^{IM} \) are (see definition F1)

\[
\Delta b^E = b^E - \sum y_i b_i^{E*} \quad \text{and}
\]

\[
\Delta b^{IM} = b^{IM} - \sum y_i b_i^{IM*}.
\]  

(F20)

Combining with (F1) gives

\[
\Delta b^E - \Delta b + \Delta b^{IM} = b^E - (b - b^{IM})
\]

\[
- \sum y_i \left[ b_i^{E*} - \left( b_i^{*} - b_i^{*IM} \right) \right].
\]

The right side reduces to zero when the definition (F14) is applied to \( b \) and \( b_i \), so that
\[
\Delta b^E = \Delta b - \Delta b^{IM}.
\] (F21)

If the reference base \( b_1^{IM} \) is chosen to be the same as \( b_1^* \), then combining (F1) and (F20) gives

\[
\Delta b - \Delta b^{IM} = b - b^{IM} = b^E.
\] (F22)

Comparison of the above two equations shows that when \( b \) and \( b^{IM} \) have a common reference base

\[
\Delta b^E = b^E.
\] (F23)

For \( v, h, u, \) and \( c_p \), the ideal mixture molar change of mixing is zero \((\Delta b^{IM} = 0)\), and it follows from F22 that

\[
\begin{align*}
\frac{E}{v} &= \Delta v \\
\frac{E}{h} &= \Delta h \\
\frac{E}{u} &= \Delta u \\
\frac{E}{c_p} &= \Delta c_p.
\end{align*}
\] (F24)

The excess Gibbs function is given by the form (F22)

\[
\frac{E}{g} = \Delta g - \Delta g^{IM}.
\] (F25)

The property changes of mixing \( \Delta g \) and \( \Delta g^{IM} \) are given by the form (F10, and for the ideal mixture the activity \( \hat{a}_1^{IM} \) is \( y_1 \) (see F11); it follows that

\[
\frac{E}{g} = R_t \sum y_1 \ln (\hat{a}_1 / y_1).
\] (F26)

The ratio of the activity to \( y_1 \) is defined as the activity coefficient \( \gamma_1 \) (see 73), so that

\[
\frac{E}{g} = \frac{R_t}{\gamma_1} \sum y_1 \ln y_1,
\] (F27)

where [see (73)]

\[
\gamma_1 = \frac{\hat{a}_1}{y_1}
\] (F28)

The partial molar property change of mixing \( \Delta b_1 \) is a thermodynamic function, so the excess value is given by the form (F18)

\[
\frac{E}{\Delta b_1} = \frac{\Delta b_1}{\Delta b_1^{IM}}.
\] (F29)
Assigning the same reference base (see F3) to both terms on the right side, the reference base cancels when taking the difference and

$$\overline{\Delta b}_1^E = \overline{b}_1 - \overline{b}_1^{\text{abIM}}.$$  \hspace{1cm} (F30)

Comparison with (F18) shows that for the same reference base for $\overline{\Delta b}_1$ and $\overline{\Delta b}_1^{\text{IM}}$, a relation similar to (F23) is obtained:

$$\overline{\Delta b}_1^E = b_1^E.$$  \hspace{1cm} (F31)

The partial molar Gibbs function $g_1$ referred to the standard state $g_1^*$ is given by (67) and can be expressed as (see also F3)

$$g_1^* - g_1 = R_T \ln a_1$$

$$= \Delta g.$$  \hspace{1cm} (F32)

The ideal mixture value referred to the same standard state is

$$g_1^{\text{abIM}} - g_1^* = R_T \ln a_1^{\text{abIM}}$$

$$= \Delta g_1^{\text{abIM}}.$$  \hspace{1cm} (F33)

The activity $\hat{a}_1$ is given by (F23) in terms of the activity coefficient $\gamma_1$ and the mole fraction $y_1$:

$$\ln \hat{a}_1 = \ln \gamma_1 + \ln y_1.$$  \hspace{1cm} (F34)

and for the ideal mixture, the activity coefficient is 1, so that

$$\ln \hat{a}_1^{\text{abIM}} = \ln y_1.$$  \hspace{1cm} (F35)

Combining the above equations the activity coefficient can be expressed as

$$\ln y_1 = (g_1^* - g_1)/R_T.$$  \hspace{1cm} (F36)

In terms of the excess function relations (F30) and (F31), the activity coefficient is

$$\ln \gamma_1 = \Delta g_1^E / R_T$$

$$= g_1^E / R_T.$$  \hspace{1cm} (F37)

In general the activity coefficient is a function of temperature, pressure, and composition. For the liquid phase, if the pressure is sufficiently below the critical ("low to moderate" pressures), $\gamma_1$ is approximately independent of the pressure. The nature of this approximation is demonstrated by forming the differential of (F37) at constant composition and applying (F29).
\[ d \ln \gamma_1 = d \left( \frac{\Delta g_1}{Rt} \right) \]

\[ = d \left( \frac{\Delta g_1}{Rt} \right) + d \left( \frac{\Delta IM}{Rt} \right). \]  

From (F33) and (F35),

\[ \frac{\Delta g_1}{Rt} = \ln y. \]  

Hence, the differential of this quantity (at constant composition) is zero, and (F38) becomes

\[ d \ln \gamma_1 = d \left( \frac{\Delta g_1}{Rt} \right) \]

\[ = \frac{1}{Rt} \frac{\partial \Delta g_1}{\partial p} \bigg|_{t,y} \quad \frac{1}{R} \frac{\partial (\Delta g_1/t)}{\partial t} \bigg|_{p,y} \ dt . \]

The partial derivatives appear in the expressions for \( \Delta v \) and \( \Delta h \) given by (F8); from the form (F4),

\[ \Delta v = \sum y_i \Delta v_i \quad \text{and} \quad \Delta h = \sum y_i \Delta h_i . \]

Since the \( y_i \) are arbitrary in the expansions (F8) and (F41), the coefficients of the \( y_i \) can be equated:

\[ \Delta v_i = \frac{\partial \Delta g_1}{\partial p} \bigg|_{t,y} \]

\[ \Delta h_i = t \frac{\partial}{\partial t} \left( \frac{\Delta g_1}{t} \right) \bigg|_{p,y} . \]

and (F40) becomes

\[ d \ln \gamma_1 = \frac{\Delta v_i}{Rt} \ dp - \frac{\Delta h_i}{Rt^2} \ dt . \]
It follows that

\[ \frac{\partial \ln \gamma_i}{\partial t} \bigg|_{t, y} = \frac{\Delta v_i}{Rt} \]  

(F44)

\[ \frac{\partial \ln \gamma_i}{\partial t} \bigg|_{p, y} = -\frac{\Delta h_i}{Rt^2} \]  

(F45)

Since experiments show that \( \Delta v_i \) is small, except in the critical region, it can be assumed that the derivative in (F44) is also small, and consequently \( \gamma_i \) is approximately pressure-independent (at least over a restricted pressure range).
APPENDIX G. RAULT’S LAW APPROXIMATION FOR VAPOR/LIQUID EQUILIBRIUM

Equality of the phase fugacities is the basic condition to be satisfied for phase equilibrium (see Eq. 82). In terms of fugacity coefficients, this condition is expressed as (83)

\[ \phi_i^v y_i = \phi_i^l x_i \]  

(G1)

The fugacity coefficients, given by (53), are

\[ \phi_i^v = \hat{f}_i^v / y_i p \]  

and

\[ \phi_i^l = \hat{f}_i^l / x_i p \]  

(G2)

(G3)

In general, the fugacity coefficient is a complicated function of pressure, temperature, and mixture composition. In practice, simplifying assumptions are introduced to solve (G1). The most simple solution is obtained by assuming the vapor to be an ideal gas and the liquid to be an ideal mixture. For an ideal gas (i.e., small p), the vapor fugacity is the partial pressure, given by (51):

\[ \hat{f}_i^v = y_i p \]  

(G4)

Comparison with (G2) shows that the ideal gas, vapor fugacity coefficient is

\[ \phi_i^v = 1 \]  

(G5)

The ideal mixture liquid fugacity is given by (70)IM, and for the Lewis-Randel reference base (71), where \( f_1^l \) is the pure component value \( f_1 \),

\[ \hat{f}_i^l = x_i f_1^l \]  

(G6)

Substitution into (G3) gives

\[ \hat{\phi}_i^l = f_i^{\ell} / p \]  

(G7)

and (G1) becomes

\[ y_i = x_i f_i^{\ell} / p \]  

(G8)

At the mixture temperature \( t \), the pure component saturation pressure is \( p_i^{sat} \), and for vapor/liquid equilibrium the pure component vapor and liquid fugacities are equal:

\[ f_i^{\ell}(p_i^{sat}, t) = f_i^v(p_i^{sat}, t) = f_i^{sat} \]  

(G9)

For the vapor treated as an ideal gas, the fugacity coefficient (53) is
\[ \phi_i^\gamma(p_i, t) = 1 \]  \hspace{1cm} (G10)

\[ = f_i^{\text{sat}}/p_i^{\text{sat}}. \]

The liquid fugacity is relatively insensitive to pressure, so that

\[ f_i(p, t) = f_i(p_i^{\text{sat}}, t) \]

\hspace{1cm} (G11)

\[ = f_i^{\text{sat}}. \]

It follows from (G10) that the expression (G8) becomes **Rault's Law**:

\[ y_i = x_i p_i^{\text{sat}}/p. \] \hspace{1cm} (G12)

The value of this equation is that if the composition of one phase is known, and the pressure \( p \) and temperature \( t \) (for which the corresponding saturation pressure can be found), the composition of the other phase can be found.

A justification for the assumption (G11) can be made as follows: Combining (46) and (48) and applying to the liquid pure \( i \)-component,

\[ \frac{d \ln f_i}{f_i} = \frac{\nu_i}{\nu_i^{\text{sat}}/p} \ln p \bigg|_t. \] \hspace{1cm} (G13)

Integration yields

\[ \ln \left( \frac{f_i/\text{sat}}{f_i^{\text{sat}}} \right) = \int_{\text{sat}}^{p} \frac{\nu_i}{\nu_i^{\text{sat}}} \frac{1}{p} \ln p \bigg|_t. \] \hspace{1cm} (G14)

The integrand is small for liquids, and as the integration range is also limited, it follows that the integral itself is small. Consequently, the argument of the logarithm is close to unity, and the approximation (G11) is validated.

Expressing \( f_i^{\text{sat}} \) in terms of the fugacity coefficient (87), the above equation can be formulated as

\[ f_i^{\text{sat}} = \phi_i^{\text{sat}} p_i^{\text{sat}} p_i \]

\hspace{1cm} (G15)

\[ p_i = \exp \left( \int_{\text{sat}}^{p} \frac{\nu_i}{\nu_i^{\text{sat}}} \bigg|_t \right). \]
The exponential $P_1$ is called the Poynting factor (see Ref. 6, p. 294).

If the fugacity base $f_1^*$ in (84) is assigned the pure liquid value $f_1^L$ in accordance with the Lewis-Randall rule (71), the VLE condition is

$$y_1 f_1^L P = x_1 y_1^L f_1^L .$$

(Substitution into this equation of the liquid fugacity value (G15) gives

$$y_1 P = x_1 y_1^L P_1.$$  \hspace{1cm} (G16)

$$F_1 = (\phi_1^{sat}/\hat{\phi}_1) P_1 .$$  \hspace{1cm} (G17)

For the vapor approximated by an ideal gas, the value of $\phi_1$ is unity (see Eq. 65). Also, for temperatures sufficiently below the critical, values of $\phi_1^{sat}$, as computed by volumetric data,* are found to be close to unity (see Ref. 5, p. 294). Hence, the correction factor $F_1$ is close to unity (since $\phi_1^{sat}$, $\hat{\phi}_1$, and $P_1$ are all close to 1), and

$$y_1 = y_1 P/x_1 P_1^{sat} .$$  \hspace{1cm} (G18)

From this equation the activity coefficient $y_1$ can be determined from measurements of the vapor and liquid composition, $y_1$ and $x_1$, the pure $i$-component saturation pressure $P_1^{sat}$, and the system pressure $P$.

*The volumetric data can be based on the B-virial coefficients (see Appendix B).
APPENDIX H. MIXTURE EQUATION OF STATE

There are numerous equations of state relating \((p, v, t)\). Two equations that will be considered for mixtures are the Redlich-Kwong equation and the Pitzer correlation.

H1. PURE-COMPONENT EQUATION OF STATE

The equation of state for a real substance can be expressed in terms of a compressibility factor \(z\) (which has a reference value of unity for an ideal gas):

\[
z = \frac{pv}{Rt}.
\] (H1)

Generalized correlations have been sought in which the equation of state can be expressed as some universal function. Introducing values at the critical point as scaling factors the thermodynamic variables can be expressed as reduced parameters:

\[
t_r = \frac{t}{t_c}
\] (H2)

\[
p_r = \frac{p}{p_c}.
\] (H3)

The assumption that \(z\) is a universal function of \(t_r\) and \(p_r\) is known as the principle of corresponding states.

\[
z = z(t_r, p_r).
\] (H4)

This equation is a "two-parameter" equation of state. An important example of such an equation is the Redlich-Kwong equation. An improved approximation is obtained by the introduction of an additional parameter for a "three-parameter" equation of state. An example is the Pitzer correlation.

H1.1 The Redlich-Kwong Equation

The Redlich-Kwong equation (Ref. 6, p. 37) is derived from the generalized van der Waals theory.

\[
p = \frac{Rt}{v - b} - \frac{a}{v(v+b)}.
\] (H5)

The constants \(a\) and \(b\) are determined from conditions at the critical point. The critical point is the peak of the saturated vapor dome curve in the \((p, v)\) state diagrams. The critical isotherm is tangent to the dome at this point, so \(dp/dv\) is zero at the critical point. Also, the curvature of the isotherm changes from concave upward for \(p\) greater than \(p_c\) to concave downward for \(p\) less than \(p_c\). Hence, the second-derivative \(d^2p/dv^2\) is zero at the critical point. These two conditions and (H5) provide three equations for the five parameters \((a, b, t_c, p_c, v_c)\). The critical volume can be eliminated and \(a\) and \(b\) expressed in terms of \(t_c\) and \(p_c\).
\[ a = \Omega_c R_t^2 \frac{R^2}{c} / p_c \]
\[ b = \Omega_b R_t c / p_c \]
\[ \Omega_a = 0.42748 \quad (H6) \]
\[ \Omega_b = 0.08664 \]

The form \((H5)\) can be solved directly for the pressure \(p\) if the temperature and specific volume \((t,v)\) are given. However, to solve for the volume \(v\) for a given \((t,p)\) requires an iterative numerical procedure. The problem is to find the root of \(F(v)\) for \((H5)\) expressed as

\[ 0 = F(v) \quad (H7) \]
\[ = \frac{Rt}{v - b} - \frac{a}{\sqrt{v(v + b)}} - p. \]

There are many numerical schemes for finding roots for systems of equations. The Newton-Raphson iterative method, which starts from a first guess, was found to converge rapidly. The concept of the iteration is illustrated schematically in Fig. H1.

**Fig. H1. Iterative Newton-Raphson Numerical Procedure**

Based on the first guess \(v_1\), the values \(y_1\) of the function \(F(v_1)\) and the derivative \(F'(v_1)\) are computed. The increment \(\Delta v\) shown in Fig. H1 is

\[ \Delta v = - \frac{y_1}{F'(v_1)} \]
The resulting second approximation is

\[ v_2 = v_1 + \Delta v, \]

and the procedure is repeated to find the third approximation \( v_3 \). The iteration is continued until the absolute value of two successive approximations is less than some preassigned \( \epsilon \).

An alternative form for an iterative solution for \( v \) is obtained by a rearrangement of the Redlich-Kwong equation \( (H5) \), which can be expressed as

\[
Z = \frac{1}{1 - h} - \frac{4.934}{1.5} \frac{h}{t_R}
\]

\[ (H8) \]

\[ h = 0.0867 \frac{p_r}{Z t_R}. \]

To solve for \( v \), the iteration is started with \( Z = 1 \) and \( h \) is computed from the second equation; a new \( Z \) is computed from the first equation and the procedure is repeated to convergence. The resulting solution for \( Z \) is used to determine \( v \) from \( (H1) \).

H1.2 The Pitzer Correlation

An improvement of the principle of corresponding states \( (H4) \) is obtained by the introduction of a third parameter, \( \omega \), the acentric factor.

\[
z = z(t_r, p_r, \omega).
\]

\[ (H9) \]

The compressibility factor can be represented by a power series in either \( p \) or \( 1/v \), in which the temperature effect is incorporated in "virial coefficients" (see Ref. 7, p. 63).

\[
z = 1 + \sum_k A_k(t)p^k
\]

\[ (H10) \]

\[
z = 1 + \sum_k B_k(t)/v^k.
\]

At low to moderate pressures, a good approximation for gases is derived by truncating the series to contain only the virial coefficients corresponding to \( k = 1 \).

\[
z = 1 + A(t)p \quad \text{and} \quad (H11)
\]

\[
z = 1 + B(t)/v. \quad (H12)
\]

Solving \( (H1) \) and \( (H12) \) for \( p \),

\[
p = \frac{Rt}{v} + \frac{B \frac{Rt}{2}}{v}. \quad (H13)
\]
Substituting this value into (H11) gives

\[ z = 1 + \frac{ARt}{v} + AB \frac{Rt}{v^2} \tag{H14} \]

Comparison of the above equations shows, incidentally, that (H11) is a higher-order approximation in 1/v than (H12). Equating coefficients of like powers of v in (H12) and (H14) shows that

\[ A = B/Rt \tag{H15} \]

Substituting into (H11) and introducing the reduced parameters (H3),

\[ z = 1 + \frac{3(t)}{R} \frac{p}{t} \tag{H16} \]


\[ = 1 + \frac{p_c}{R_c} \frac{B(t)}{R_c} \frac{p}{t} \tag{H16c} \]

To obtain the form (H9), the function of temperature B(t) must be expressed in terms of \( (t_r, p_r, \omega) \). The Pitzer correlation assumes that

\[ \frac{p_c}{R_c} B(t) = B^0(t_r) + \omega B^1(t_r) \]

\[ B^0 = 0.083 - (0.422/t_r^{1.6}) \tag{H17} \]

\[ B^1 = 0.139 - (0.172/t_r^{4.2}) \tag{H17} \]

The range of application is discussed in Ref. 7, and applies to the region above the line shown in the \( (t_r, p_r) \) diagram of Fig. H2. In this region, \( v_r \) is essentially greater than 2.

For points below the line in Fig. H2 an alternative form is proposed in Ref. 7, p. 87, where plots are given for the function \( z^0 \) and \( z^1 \):

\[ z = z^0(t_r, p_r) + \omega z^1(t_r, p_r) \tag{H18} \]

Values of the acentric factor \( \omega \) for various pure fluids are given in Appendix B of Ref. 7 (see also Ref. 6, Appendix A).

H2. MIXTURE EQUATION OF STATE

The mixture equation of state may be expressed by the two-parameter form (H4), exemplified by the Redlich-Kwong equation, or by the three-parameter form (H9) exemplified by the Pitzer correlation. In either case, critical values for the mixture must be estimated to find the reduced parameters. Estimations of the mixture critical values (called "pseudo parameters," as they have no physical significance) from the pure component critical values are called mixing rules.
Fig. H2. Region of Application of Eq. (H17) (above line). For points falling below line use Eq. (H18), where $z^0$ and $z^1$ plots are given in Ref. 7, pp. 88-90, or tables in Ref. 6, pp. 32-35.

H2.1 Mixing Rules

The critical values for a mixture must be formulated from the specified pure-component values (see Ref. 6, Appendix A for values of $T_{c1}$, $v_{c1}$, and $z_{c1}$ for a variety of fluids). Various mixing rules are proposed in Ref. 6, Chapt. 4 and in Ref. 7. A set of mixing rules applicable to the Redlich-Kwong and Pitzer equation of state formulations are given in Ref. 7, p. 272:

$$t_{c1j} = \sqrt{t_{c1}t_{cj}}$$

$$z_{c1j} = (z_{c1} + z_{cj})/2$$  \hspace{1cm} \text{(H19)}$$

$$v_{c1j} = \left[ \left( v_{c1}^{1/3} + v_{cj}^{1/3} \right)/2 \right]^3.$$  

H2.2 The Redlich-Kwong Mixture Equation of State

The Redlich-Kwong equation of state (H5) applies to a pure component; however, the same form can be assumed to apply to a mixture with the $a$ and $b$ coefficients modified by suitable mixing rules. The mixing rules proposed in Ref. 4, p. 276, based on the temperature and pressure factors given by (H19), are
\[ a_m = \sum_i \sum_j y_i y_j a_{ij} \]
\[ b_m = \sum_i y_i b_i \]
\[ a_{ij} = \Omega_i R^2 t_{ci}^{2.5} / p_{ci} \]
\[ b_i = \Omega_i R t_{ci} / p_{ci} . \]

A critical pressure factor can be computed from the form (H1):
\[ p_{ci} = z_{ci} R t_{ci} / v_{ci} \] (H21)
\[ p_{ci} = z_{ci} R t_{ci} / v_{ci} . \]

The mixture values \( a_m \) and \( b_m \) given by (H20) apply in the Redlich-Kwong equation (H5).

The "pseudo critical" mixture values can be computed directly from the form (H6):
\[ a_m = \Omega_a R^2 t_{cm}^{2.5} / p_{cm} \]
\[ b_m = \Omega_b R t_{cm} / p_{cm} . \]

Solving these two equations for \( t_{cm} \) and \( p_{cm} \) gives
\[ t_{cm} = (\Omega_b a_m / \Omega_a b_m R)^{2/3} \] (H23)
\[ p_{cm} = \left[ R(\Omega_b / b_m)^5 (a_m / \Omega_a)^2 \right]^{1/3} . \]

From these critical values in the Redlich-Kwong equation (H7), the critical volume \( v_{cm} \) can be determined, and finally the mixture "pseudo compressibility factor" is given by
\[ z_{cm} = p_{cm} v_{cm} / R t_{cm} . \] (H24)

H2.3 The Pitzer Correlation for a Vapor Mixture

The mixing rule for the B-coefficient of (H12) at a specified mixture temperature \( t \) is given in Ref. 7, p. 270, or Ref. 6, p. 83.
The $B_{ij}$ coefficient is symmetric (i.e., $B_{ii} = B_{jj}$) since the coefficient characterizes a bimolecular interaction. The critical $t_{ci}$ and $p_{ci}$ are determined from the pure component critical values by the mixing rules (H19). The mixing rule for the acentric parameter is

\[ \omega_{ij} = \frac{\omega_i + \omega_j}{2} \]  

where the pure-component values are specified (see Ref. 6, Appendix A, for $\omega_i$ for various pure fluids). With this value of $B_m$, the equation of state (H16) relating the mixture ($p, v, t$) is

\[ z_m = \frac{pv}{R_t} \]

\[ = 1 + B_m \frac{p}{R_t} \]  

This equation is valid for the reduced values ($t_r, p_r$) that fall in the region above the line shown in Fig. H2. To determine these reduced values, the pseudo critical mixture temperature and pressure are needed. These values can be estimated from the mixing rules.

\[ t_{cm} = \sum y_i t_{ci} \quad \text{and} \]

\[ p_{cm} = \sum y_i p_{ci} \]

The reduced values to be used in Fig. H2 are then

\[ t_r = t/t_{cm} \quad \text{and} \]

\[ p_r = p/p_{cm} \]

If the point ($t_r, p_r$) falls below the line, the alternate equation (H18) should be used with the functions $z^0$ and $z^1$, determined either from graphs (see Ref. 7, pp. 89, 90) or from tables (see Ref. 6, pp. 32-35). The value of the acentric factor for the mixture can be evaluated as the weighted average.

\[ \omega_m = \sum y_i \omega_i \]
APPENDIX I. APPROXIMATIONS FOR THE VLE EQUATIONS AT LOW/MODERATE PRESSURES

For pressures that can be considered to be low to moderate, compared with the critical pressure, the vapor/liquid equilibrium (VLE) is approximated by (88)

\[ y_i \hat{\phi}_i p = x_i \gamma_i p_i^{\text{sat}} \phi_i^{\text{sat}}. \] (I1)

The four functions \( \hat{\phi}_i, \gamma_i, p_i^{\text{sat}}, \) and \( \phi_i^{\text{sat}} \) can be represented by semi-empirical equations, which in general are ultimately based on temperature, pressure, and volume measurements. (The Redlich-Kwong or Pitzer equations of state discussed in Appendix H can be used for computations.) Each of the functions appearing in (I1) is discussed individually below.

II. THE PURE-COMPONENT VAPOR SATURATION PRESSURE \( p_i^{\text{sat}} \)

Under equilibrium conditions in a vapor/liquid two-phase system, the saturation vapor and liquid pressures balance. The pure-component saturation pressure depends only on temperature:

\[ p_v = p_l = p_i^{\text{sat}}(t). \] (I2)

A differential equation for the saturation pressure is derived from a conceptual reversible process involving a differential change in temperature and pressure (\( dt, dp \)). Under the postulated reversibility conditions, equilibrium is maintained during the process and the pressure remains at the saturation value, so that

\[ dp = dp_i^{\text{sat}}. \] (I3)

The equilibrium constraint conditions (79) apply to the chemical potential for the vapor and liquid phases and for the pure \( i \)-component substance,

\[ \mu_i^v = \mu_i^l. \] (I4)

In terms of the partial molar Gibbs function, an equivalent expression follows from (C14), where the mass exchange occurring between phases must balance (i.e., \( dN_i^l = -dN_i^v \)).

\[ -\hat{g}_i^v = \hat{g}_i^l. \] (I5)

Conforming with the limiting condition (E13), as \( y_i \rightarrow 1 \), the partial molar value becomes the pure \( i \)-component value \( g_i \), and (I5) becomes

\[ g_i^v = g_i^l. \] (I6)
Equality between the liquid and vapor Gibbs functions is maintained throughout the equilibrium pressure change, so that

\[ dg^V = dg^L. \]  \hspace{1cm} (I7)

The pressure and temperature differentials corresponding to the Gibbs function changes satisfy (CI2); in this equation the composition is constant for the pure substance.

\[ (v \, dp - s \, dt)^V = (v \, dp - s \, dt)^L. \]  \hspace{1cm} (I8)

The combination of (I3) and (I8) gives the differential equation for the change in saturation pressure with temperature:

\[ \frac{dp_{\text{sat}}}{dt} = \frac{s^v - s^l}{v^s - v^l}, \]
\[ = \frac{s^l}{v^l}/v^l. \]  \hspace{1cm} (I9)

The entropy change is related to an enthalpy change by (CI2), and noting that the composition is constant for a pure substance,

\[ dh = t \, ds + v \, dp. \]  \hspace{1cm} (I10)

This condition can be applied to a phase change process in which, for example, a differential quantity of liquid vaporizes at constant \( t \) and \( p \); integration then gives

\[ h^v - h^l = t(s^v - s^l). \]  \hspace{1cm} (I11)

The enthalpy difference is the latent heat of vaporization \( \lambda \), and (I9) becomes the familiar Clapyron equation:

\[ \frac{dp_{\text{sat}}}{d(1/t)} = \frac{\lambda}{t} \frac{v^l}{v^l}. \]  \hspace{1cm} (I12)

If the equation of state for each phase is expressed in terms of the compressibility factor \( z \), given by (H1), an alternative form of the Clapyron equation is

\[ \frac{d \ln p_{\text{sat}}}{d(1/t)} = -\frac{\lambda}{R} \frac{z^l}{z^l}. \]  \hspace{1cm} (I13)

A simplified approximation to this equation is derived from the assumption that the liquid specific volume is negligible compared with the vapor specific volume, and (dropping the vapor superscript)
\[ v_{vl} = v \quad \text{and} \]
\[ z_{vl} = z. \]  

A further simplification follows from the assumption that the vapor behaves as an ideal gas:

\[ z = 1. \]  

Under the above simplifications, (I13) is reduced to the **Clausius-Clapyron approximation**.

\[ \frac{d \ln p_{\text{sat}}}{d(1/t)} = -\frac{\lambda}{R}. \]  

If the latent heat is assumed to be constant over a range of integration, the integral of (I16) is a linear relationship between \( \ln p_{\text{sat}} \) and \( 1/t \):

\[ \ln p_{\text{sat}} = A - B/t. \]  

A similar result is obtained from the Clapyron equation (I12) if \( \lambda \) and \( v_{vl} \) are assumed to be constant over the integration. A semi-empirical modification of (I17), the **Antoine equation** gives an improved correlation with experimental data:

\[ \ln p_{\text{sat}} = A - \frac{B}{t + C}. \]  

Values of \( A, B, \) and \( C \) for many pure substances are given in Ref. 6, Appendix A.)

The saturation pressure also can be expressed by the **Pitzer correlation** [similar in form to (H14) for the B-virial coefficient, or (H15) for the compressibility factor \( z \)], relating the reduced temperature and pressure values.

\[ \ln (p_{r \text{sat}}) = f^0(t_r) + \omega f^1(t_r). \]  

The functions \( f^0 \) and \( f^1 \) are given by the **Lee-Kessler** semi-empirical expressions (see Ref. 6, p. 183).

\[ f^0 = 5.92714 - \frac{6.09648}{t_r} - 1.28862 \ln t_r + 0.169347 t_r^6 \]  

\[ f^1 = 15.2518 - \frac{15.6875}{t_r} - 13.4721 \ln t_r + 0.43577 t_r^6. \]  

The value of the acentric factor \( \omega \) can be readily deduced from a single experiment in which the boiling temperature \( t_b \) is measured at atmospheric pressure. The reduced values to be substituted into (I19) are
\[ t_r = \frac{t_b}{t_c} \]
\[ \rho_{br} = 1/p_c \].

Solving (119) for \( \omega \) gives
\[ \omega = \frac{-\ln p_c - f'(t_{br})}{f'(t_{br})} . \] (I21)

Other expressions (see Ref. 6, Chapt. 6) for the vapor pressure in terms of the temperature are obtained by the introduction of various corrections to the integration of the Claplyron equation (112). Most of these forms are based on limited data. If more data are available, curve-fitting techniques can be used to obtain the constants in the Antoine equation (118). For example, a correlation in terms of Chebyshev polynomials is

\[ \ln p_{sat} = A_0/2 + \sum A_i E_i(x) , \] (I22)

where

\[ x = \frac{2t - (t_{max} + t_{min})}{t_{max} - t_{min}} \]
\[ E_0(x) = 1 \]
\[ E_1(x) = x \]
\[ E_{i+1} - 2x E_i + E_{i-1} = 0 \].

I2. THE FUGACITY COEFFICIENT \( \hat{\phi}_1 \)

The vapor phase, i-component fugacity coefficient is a function of \( t, p, \) and the vapor composition \( (y_1, \ldots, y_n) \). An integral expression for \( \hat{\phi}_1 \) given by (61) is
\[ \ln \hat{\phi}_1 = \int_{0}^{p} \left( \frac{p v_1}{R T} - 1 \right) \frac{dp}{p} . \] (I23)

An equation of state is needed to evaluate the integral. In terms of the (extensive) compressibility factor \( Z \) and the volume \( V \), the equation of state (H1) is
\[ Z = \frac{pV}{R T} . \] (I24)
The partial molar values \( \bar{z}_1 \) and \( \bar{v}_1 \) are obtained by differentiation with respect to \( N_i \), in accordance with definition (10).

\[
\bar{z}_1 = \frac{p}{Rt} \bar{v}_1 .
\]  

(I25)

The integrand in (I23) can then be expressed as

\[
\ln \phi_1 = \int_0^p \frac{(\bar{z}_1 - 1)}{p} dp .
\]  

(I26)

The extensive form of the compressibility factor is obtained from the intensive form \( z \), by multiplication of (H13) by \( N \):

\[
Z = N + \frac{p}{Rt} NB .
\]  

(I27)

The partial molar value is (noting that \( \partial N/\partial N_i = 1 \))

\[
\bar{z}_1 = 1 + \frac{p}{Rt} \frac{\partial NB}{\partial N_1} \bigg|_{t, p, N_j \neq i} .
\]  

(I28)

Substitution into the integrand of (I26) gives

\[
\ln \phi_1 = \frac{1}{Rt} \frac{\partial NB}{\partial N_1} \int_0^p dp
\]

\[
= \frac{p}{Rt} \frac{\partial NB}{\partial N_1} .
\]  

(I29)

The derivative of the product \( NB \) is

\[
\frac{\partial NB}{\partial N_1} = B + N \frac{\partial B}{\partial N_1} .
\]  

(I30)

Since \( B \) is a function of composition,

\[
\frac{\partial B}{\partial N_1} = \sum_j \frac{\partial B}{\partial y_j} \frac{\partial y_j}{\partial N_1} .
\]  

(I31)

As the mole fraction \( y_j \) is \( N_j/N \), the derivative is

\[
\frac{\partial y_j}{\partial N_1} = \begin{cases} 
- y_j/N &; j \neq 1 \\
\frac{1}{N} (1 - y_1) &; j = 1 
\end{cases}
\]  

(I32)
Hence,
\[
\frac{3B}{3N_1} = \frac{3B}{3y_1} - \sum_j y_j \frac{3B}{3y_j}
\]
and
\[
\frac{3NB}{3N_1} = B + \frac{3B}{3y_1} - \sum_j y_j \frac{3B}{3y_j}.
\]

As an example, for a binary mixture, the mixing rule (H23) applied to \(B\) gives
\[
B = y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12}
\]
\[
\delta_{12} = 2B_{12} - B_{11} - B_{22}
\]
Then, for \(j \neq 1\), (I34) becomes
\[
\frac{3NB}{3N_1} = B_{11} + y_j^2\delta_{12}
\]
and the fugacity coefficient, from (129) is
\[
\ln \phi_i = \frac{P}{RT} (B_{11} + y_j^2\delta_{12})
\]

For a general multicomponent mixture,
\[
\ln \phi_i = \frac{P}{RT} \left[ B_{11} + \frac{1}{2} \sum_j \sum_k y_jy_k (2\delta_{j1} - \delta_{jk}) \right]
\]
\[
\delta_{jh} = 2B_{jk} - B_{jj} - B_{11}
\]
Note that \(\delta_{ii} = 0\), and, as \(B_{jk}\) is symmetric (see H20), so also is \(\delta_{jk}\).

I3. THE FUGACITY COEFFICIENT \(\phi_{i,\text{sat}}\)

The fugacity coefficient \(\phi_{i,\text{sat}}\) is for the pure substance, not in the mixture (recall that the cap-notation \(\phi_{i}\) denotes the value for the \(i\)-component in the mixture). For a pure substance, all molecular species are the same, and \(j = k\) in (I37); consequently, the \(\delta\)-terms are zero, and
\[
\ln \phi_{i,\text{sat}} = B_{11}p_{i,\text{sat}}/RT.
\]
Note that the right side of this equation depends only on \( t \), so \( \phi_{1}^{\text{sat}} \) is a function of temperature alone.

I4. THE ACTIVITY COEFFICIENT \( \gamma_{i} \)

The liquid phase activity coefficient is related by (F37) to the partial molar excess Gibbs function \( \frac{g}{E} \); the partial molar value is the derivative of \( G^{E} = N \frac{g}{E} \) with respect to \( N_{j} \) in accordance with definition (10). Noting that \( \frac{\partial N}{\partial N_{i}} = 1 \), Eq. (F37) becomes

\[
\ln \gamma_{i} = \frac{\partial \frac{g}{E}}{\partial t} \left|_{t, p, N_{j+1}} \right. \\
= \frac{\partial}{\partial N_{i}} \left( N \frac{g}{E} / R t \right) \\
= \frac{g}{E} / R t + N \frac{\partial}{\partial N_{i}} \left( \frac{g}{E} / R t \right).
\]

Letting \( \frac{g}{E} / R t \) be represented by \( b \) for notational convenience,

\[
\frac{E}{R t} = b(p, t, x_{1}, \ldots, x_{i-1}, x_{i+1}, \ldots, x_{n})
\]

\[
x_{1} = 1 - \sum_{j \neq i} x_{j}.
\]

Expanding the derivative in (139) gives

\[
\frac{\partial b}{\partial N_{i}} = \sum_{j \neq i} \frac{\partial b}{\partial x_{j}} \frac{\partial x_{j}}{\partial N_{i}}.
\]

Since \( x_{j} \) is \( N_{j}/N \), the derivative of \( x_{j} \) is

\[
\frac{\partial x_{j}}{\partial N_{i}} = - \left( \frac{N_{j}}{N^{2}} \right) \frac{\partial N}{\partial N_{j}}
\]

\[
= - \frac{x_{j}}{N}.
\]

Combining the above equations,

\[
\ln \gamma_{i} = b - \sum_{j \neq i} x_{j} \frac{\partial b}{\partial x_{j}}.
\]

The Wilson equation (see Ref. 5, p. 540) assumes \( b \) to be of the form

\[
b = \sum_{k} x_{k} \ln L_{k}.
\]
The function $L_k$ is a series summed over all constituents:

$$L_k = \sum_m x_m \Lambda_{km}.$$  \hspace{1cm} (I45)

In forming the derivative $\partial b / \partial x_j$ in (I43), it is to be noted that $j \neq i$ and that $x_i$ is a function of the other mole fractions as given by (I40); hence,

$$\frac{\partial x_m}{\partial x_j} = \begin{cases} -1 & ; m = i \\ 0 & ; m \neq i, m \neq j \\ 1 & ; m \neq i, m = j \end{cases}.$$  \hspace{1cm} (I46)

The derivative of $b$ in (I43) is computed from (I44)

$$\frac{\partial b}{\partial x_j} = - \sum_k \left[ (\ln L_k) \frac{\partial x_k}{\partial x_j} + (x_k / L_k) \frac{\partial L_k}{\partial x_j} \right].$$  \hspace{1cm} (I47)

The derivative of $L_k$ for (I45) is

$$\frac{\partial L_k}{\partial x_j} = \sum_m \Lambda_{km} \frac{\partial x_m}{\partial x_j}.$$  \hspace{1cm} (I48)

Applying (I46) to both terms in (I47),

$$\frac{\partial b}{\partial x_j} = \ln L_i - \ln L_j - \sum_k (x_k / L_k) (\Lambda_{kj} - \Lambda_{ki}).$$  \hspace{1cm} (I49)

The summation in (I43) is thus

$$\sum_k x_k \frac{\partial b}{\partial x_k} = - \ln L_i + \sum_k (x_k / L_k) \Lambda_{ki} - \sum_j x_j \sum_k (x_k / L_k) \Lambda_{kj}. \hspace{1cm} (I50)$$

The last summation can be rearranged to give

$$\sum_j x_j \sum_k (x_k / L_k) \Lambda_{kj} = \sum_k (x_k / L_k) \sum_j x_j \Lambda_{kj}$$

$$= \sum_k (x_k / L_k) L_k$$

$$= \sum_k x_k$$

$$= 1.$$  \hspace{1cm} (I51)

Substitutions into (I43) yields the equation for the liquid activity coefficient $\gamma_i$:

$$\ln \gamma_i = 1 - \ln L_i - \sum_k (x_k / L_k) \Lambda_{ki}.$$  \hspace{1cm} (I51)
where $L_i$ is the summation (I45). The $\Lambda$-parameters are semi-empirical coefficients expressed in terms of the specific (molar) volumes at temperature $t$ of the $k$- and $i$-constituents.

$$\Lambda_{ki} = \left(\frac{\nu_k}{\nu_i}\right) \exp\left(-\frac{\gamma_{ki}}{Rt}\right).$$  \hspace{1cm} (I52)

This form is based on a molecular model in which the interaction between the $k$ and $i$ molecules is represented by the constant $\gamma_{ki}$.

For a binary system (let $i,j$ be 1 or 2), the Wilson equations (I44) and (I51) reduce to

$$g^E/Rt = -x_1 \ln (x_1 + x_j \Lambda_{ij}) - x_j \ln (x_j + x_1 \Lambda_{ji})$$  \hspace{1cm} (I53)

$$\ln \gamma_i = -\ln (x_1 + x_j \Lambda_{ij}) + x_j \frac{\Lambda_{ij}}{x_1 + x_j \Lambda_{ij}} - \frac{\Lambda_{ji}}{x_j + x_1 \Lambda_{ji}}.$$  \hspace{1cm} (I54)

The values of the $\Lambda$-constants can be estimated from experimental data. For example, for a specified mixture composition, and system temperature and pressure $(t,p)$, the pure-liquid vapor pressures can be measured. The $\gamma_i$-values are approximated by (G18), and the corresponding excess Gibbs function is given by (F27).

$$g^E/Rt = \sum x_i \ln \gamma_i.$$  \hspace{1cm} (I55)

Based on test data, values of the left side of this equation can be plotted versus $x_i$ (say for $i = 1$). The $\Lambda$-coefficients in (I53) are determined by curve fitting i.e., minimizing the deviation between the function (I53) and the data points. If the points appear to be approximately linear, on a plot of $(g^E/Rt)/x_1 x_j$, a linear relationship can be assumed in place of the logarithmic form of (I53).

$$\frac{g^E/Rt}{x_1 x_j} = A_{ji} x_1 + A_{ij} x_j.$$  \hspace{1cm} (I56)

The $x_1 x_j$-factor is introduced so that the excess function will be zero for the pure substance (i.e., when either $x_i$ or $x_j$ is zero).

From (I43), where $b$ is $g^E/Rt$, the activity coefficient is given by the Margules equation:

$$\ln \gamma_i = x_i^2 \left[\Lambda_{ij} + 2(A_{ji} - A_{ij}) x_i\right].$$  \hspace{1cm} (I57)

This equation is the analogue of the Wilson equation (I54), where $g^E/Rt$ is given by (I53).

If the inverse of the left side of (I56) plots as an approximate straight line versus $x_i$, the following linear function can be devised:
\[
\frac{E}{RT} = \frac{a_{ij}}{a_{ij} x_i + a_{ij} x_j}.
\]  
(158)

From this function, the activity coefficient (given by I43) is given by the Van Laar equation:

\[
\ln \gamma_i = a_{ij} \left( \frac{1}{1 + \frac{a_{ij}}{a_{ij}} \frac{x_i}{x_j}} \right)^{-2}.
\]  
(159)

The coefficient \(a_{ij}\) can be determined experimentally from an infinite dilution of the \(i\)th component \((x_i = 0)\):

\[
a_{ij} = \ln \gamma_i^\infty.
\]  
(160)

Extensive correlations of experimental data for binary systems has led to empirical equations for \(\gamma^\infty\):

\[
\log \gamma_i^\infty = f(\alpha, \epsilon, \zeta, \eta, \theta, N_1, N_2).
\]  
(161)

Values of the parameters for classes of organic fluids are given in Ref. 6, Table 8-17, p. 334.
J1. DEPARTURE FUNCTIONS

In general, the first approximation to the properties of a real gas are based on the ideal gas equation of state. Deviations of the actual value from the ideal value are measured by a departure function (Ref. 6, p. 92). For a general intensive property \( b \), at temperature \( t \) and pressure \( p \), the departure \( D_b \) is defined as

\[
D_b(t, p) = b^0(t, p^0) - b(t, p) .
\]  

(J1)

The pressure \( p^0 \) is sufficiently low for the gas to be considered ideal. The departure function is the change in the property along an isothermal \( t \) between a pressure \( p^0 \) and the state pressure \( p \). The specific volume at \( p^0 \) is the ideal gas value.

\[
v^0 = \frac{Rt}{p^0} .
\]  

(J2)

The enthalpy departure function \( D_h \) is illustrated in Fig. J1; the ideal gas value \( h^0 \) is pressure-independent and is shown as a straight, vertical line.

An enthalpy reference base can be chosen arbitrarily at some convenient temperature \( t^0 \). The enthalpy increase along the \( p^0 \)-isobar, from the reference temperature \( t^0 \) to some desired state temperature \( t \), is

\[
h^0(t, p^0) - h^0(t^0, p^0) = \int_{t^0}^{t} C^0_p(\tilde{t}) \, d\tilde{t} .
\]  

(J3)

Along the \( p^0 \)-isobar, the gas is ideal and the specific heat is a function of \( t \) only and may be expressed as a \( t \)-power series (truncated):

\[
C^0_p(t) = A + Bt + Ct^2 + Dt^3 .
\]  

(J4)

For a specified base enthalpy value at \( (t^0, p^0) \), the value at any other gas state \( (t, p) \), with reference to the base value, is

\[
h(t, p) = h^0(t^0, p^0) + \int_{t^0}^{t} C^0_p(\tilde{t}) \, d\tilde{t} - D_h .
\]  

(J5)

This relationship is illustrated in Fig. J2.

It is convenient to employ the Helmholtz function \( a \) to derive the enthalpy and entropy departure functions. Definitions of the Helmholtz function and the enthalpy are given by (C11).
(a) Ideal Gas Isotherm for \( h^0 = C_p^0(t)(t - t_{ref}) \)

(b) Real Gas Isotherm for \( h(t,p) \)

Fig. J1. Enthalpy Departure Function \( Dh \)
The combination of these two definitions gives

\[ h = a + st - pv. \]  \hspace{1cm} (J6)

The differential along the \( t \)-isotherm is

\[ \frac{dh}{dt} = da + t \, ds + d(pv). \]

Integration along the isotherm between \( p \) and \( p^0 \) gives

\[ h^0 - h = a^0 - a + t(s^0 - s) + p^0 v^0 - pv. \]

Applying the definition (J1) of a departure function, and the ideal gas equation (J2),

\[ Dh = Da + t \, Ds + Rt - pv. \]  \hspace{1cm} (J8)

The differential of the Helmholtz function is given by (C12), and for constant composition,

\[ da = -p \, dv - s \, dt, \]

and along the \( t \)-isotherm,

\[ da \bigg|_t = -p \, dv. \]
Integration along the isotherm gives

\[
\int_{v_i}^{v} p \, dv = -a - a^0
\]

the departure function at the state point \((v, t)\) is

\[
Da(v, t) = -\int_{v_i}^{v} p \, dv - \int_{v_i}^{v^0} p \, dv.
\]  

The specific volume \(v_i\) is an arbitrary state in the ideal gas region on the \(t\)-isotherm at a pressure below \(p^0\). Adding and subtracting the integral of \(p = \frac{Rt}{v}\) between \(v_i\) and \(v\) yields

\[
Da = -\int_{v_i}^{v} p \, dv - \int_{v_i}^{v^0} \frac{Rt}{v} \, dv
\]

\[
= -\int_{v}^{v_i} \left( p - \frac{Rt}{v} \right) \, dv + \int_{v^0}^{v} \frac{Rt}{v} \, dv.
\]

From (C15), the entropy can be expressed as the derivative of the Helmholtz function; hence, in terms of the limit as \(\Delta t\) becomes infinitesimal,

\[
s(v, t) = -\lim_{\Delta t \to 0} \frac{a(v, t) - a(v, t)}{\Delta t}
\]

\[
s^0(v^0, t) = -\lim_{\Delta t \to 0} \frac{a(v^0, t + \Delta t) - a(v^0, t)}{\Delta t}.
\]

Combining these two expressions gives

\[
Dc = -\lim_{\Delta t \to 0} \frac{Da(v, t + \Delta t) - DA(v, t)}{\Delta t}
\]

\[
= -\frac{3}{8t} Da.
\]

The expression (J10) can be substituted for \(Da\), and, since the integration limits are fixed, the derivative operator can be passed under the integral sign:
The entropy and enthalpy differentials are related by (Cl2), and at constant composition,
\[ dh = t \, ds + v \, dp \, . \]

Along the \( p^0 \)-isobar, the entropy differential becomes
\[ ds = \frac{dh}{t} \]

and integration from the reference temperature \( t^0 \) to \( t \) gives an equation analogous to (J3) for the enthalpy:
\[ s^0(t, p^0) - s^0(t^0, p^0) = \int_{t^0}^{t} \left[ \frac{C_p^0(\bar{v})}{\bar{v}} \right] d\bar{v} . \] (J13)

The entropy at any gas state \( (t, p) \), with respect to the reference state \( (t^0, p^0) \), is similar to the expression (J5) for the enthalpy (see Fig. J2).
\[ s(t, p) = s(t^0, p^0) + \int_{t^0}^{t} \left[ \frac{C_p^0(\bar{v})}{\bar{v}} \right] \, \bar{v} - Ds . \] (J14)

J2. THE ENTHALPY AND ENTROPY DEPARTURE FUNCTIONS BASED ON THE REDLICH-KWONG EQUATION OF STATE

For a real gas, the enthalpy and entropy with respect to a base state \( (t^0, p^0) \) are given by (J5) and (J14). The departures \( D_h \) and \( D_s \) in these expressions are related to the Helmholtz function departure \( D_a \) in (J8). The departures \( D_a \) and \( D_s \), given by (J4) and (J12), involve integrals of the pressure, which can be expressed as a function of the temperature and the specific volume through the Redlich-Kwong equation of state. Performing the integrations and taking the limit as \( v_1 \) becomes infinite yields the expressions
\[
D_a = Rt \ln \left( 1 - \frac{b}{v} \right) + \frac{a}{b \sqrt{t}} \ln \left( 1 + \frac{b}{v} \right) + Rt \ln \frac{p^0}{Rt} . \]
(J15)

\[
D_s = -R \ln \left( 1 - \frac{b}{v} \right) + \frac{a}{2b \sqrt{t}^{1.5}} \ln \left( 1 + \frac{b}{v} \right) - R \ln \frac{p^0}{Rt} . \]
(J16)

Substitution of these values into (J8) gives the enthalpy departure
77

\[ Dh = \frac{3a}{2b \sqrt{v_t}} \ln \left( 1 + \frac{b}{v} \right) + R_t - pv. \]  

(J17)

J3. SATURATED LIQUID SPECIFIC VOLUME

Variations in the liquid specific volume are usually determined experimentally; variations with pressure are generally neglected. A number of measurement techniques are available, based in general on some form of the law of corresponding states (H4). The Gunn-Yamada method is based on the three-parameter form (H9) involving the acentric factor \( \omega \) and is applied to saturated liquids only. The semi-empirical equation (Ref. 6, p. 60) is of the form

\[ \frac{v_l}{v_{sc}} = v_r^o(t_r) \left[ 1 - \omega \Gamma(t_r) \right], \]  

(J18)

where \( v_r^o \) and \( \Gamma \) are functions of the reduced temperature \( t_r \), and \( v_{sc} \) is a "scaling parameter." The scaling parameter is defined for a value of the reduced temperature of 0.6.

\[ v_{sc} = v_{0.6} \left/ \left( 0.3862 - 0.086 \omega \right) \right. \]  

(J19)

In the event that the experimental scaling parameter is unavailable, an approximation is given by

\[ v_{sc} = \left( \frac{R_{tc}}{p_c} \right) (0.292 - 0.0967 \omega). \]  

(J20)

Expressions for \( v_r^o \) and \( \Gamma \) depend on the temperature range. In the reduced temperature range \( t_r (0.2, 1) \), the value of \( \Gamma \) is given by

\[ \Gamma = 0.29607 - 0.09045 t_r - 0.04842 t_r^2. \]  

(J21)

The function \( v_r^o \) is split into two regions:

for \( 0.2 < t_r < 0.8 \):

\[ v_r^o = 0.33593 - 0.33953 t + 1.51941 t^2 \]
\[ - 2.02512 t_r^3 + 1.11422 t_r^4 \]  

(J22)

for \( 0.8 < t_r < 1 \):

\[ v_r^o = 1 + 1.3 \sqrt{1 - t_r} \log (1 - t_r) \]
\[ - 0.50879 (1 - t_r) - 0.91534 (1 - t_r)^2. \]
An alternative procedure for determining the saturated liquid specific volume is the Benson method (Ref. 8, p. 95), based on the empirical rule of Cailletet and Mathias. The sum of the saturated liquid and vapor densities are expressed as a power series in $t$:

$$\rho_l + \rho_v = a + bt + ct^2 + \ldots$$

$$= a + bt \quad \text{(truncated)}. \quad (J23)$$

The coefficients $a$ and $b$ are determined by two imposed conditions:

- The liquid and vapor states merge at the critical point, and
- The vapor density $\rho_v$ is negligible compared to the liquid density $\rho_l$ at the normal (1 atm) boiling temperature $t_b$.

Application of these two conditions gives

$$2 \rho_c = a + bt_c$$

$$\left(\rho_l\right)_b = a + bt_b.$$  

Solving the two equations for $a$ and $b$ gives

$$a = 2 \rho_c - bt_c \quad \text{(J24)}$$

$$b = \left(\rho_l\right)_b - 2 \rho_c \right) / (t_b - t_c).$$

Substitution of these two coefficients into (J23) permits the computation of $\rho_l$.

J4. LATENT HEAT OF VAPORIZATION

Vapor enthalpies are determined from (J5), where the departure function is given by (J17) for the Redlich-Kwong equation of state. The saturated liquid enthalpy can be determined from the saturated vapor enthalpy by subtraction of the latent heat of vaporization.

A number of semi-empirical equations exist for the computation of the latent heat $\lambda$ based on the Clapyron equation (113); introducing the reduced temperature and pressure (see H2 and H3), this equation is

$$- \frac{d \ln p_r^{\text{sat}}}{d(1/t_r)} = \frac{\lambda}{R t_c z v z}. \quad (J25)$$

$$= \psi$$
The factor $\psi$ is a dimensionless latent heat. From the differentiation of the Antoine equation (118), the value of $\psi$ is

$$\psi = \frac{B}{C} \left(1 + \frac{C}{T} \right)^{\frac{1}{2}}.$$  

(J26)

An alternative expression for $\psi$ is obtained by differentiation of the Lee-Kessler expression (120) that appears in the Pitzer expansion (119).

$$\psi = 6.09648 - 1.28862 t + 1.016 t^7 + \omega (15.6875 - 13.4721 t + 2.615 t^7).$$  

(J27)

The value of $\psi$ is given by (J25) in terms of the computed $\psi$; however, the value of the factor $z_{vl}$ must also be determined. As a first approximation, a value $z_{vl} = 1$ can be assumed. A better approximation, applicable to temperatures below the boiling point, is the Haggenmacher approximation (Ref. 6, p. 186):

$$z_{vl} = \sqrt{1 - \frac{p}{T_r}}.$$  

(J28)

For greater accuracy, the value of $z_{vl}$ can be computed directly from the specific volumes of the saturated liquid and vapor.

$$z_{vl} = \frac{p_{\text{sat}}(t)}{R} (v - v_l).$$  

(J29)

The saturation pressure in this equation is given by either the Antoine equation (118) or the Pitzer correlation (119). The vapor specific volume is computed from the Redlich-Kwong equation (H7), and the liquid specific volume by the Gunn-Yamada equation (J18) or the Benson equation (J23).

After the latent heat is determined at a given temperature, say $t_1$, the latent heat $\lambda$ at any other temperature $t$ is approximated by the Watson relation (Ref. 6, p. 210):

$$\lambda = \lambda_1 \left(\frac{1 - T_r}{1 - T_{rl}}\right)^n.$$  

(J30)

where the subscript 'r' indicates the reduced temperature, and the exponent $n$ is 0.375 or 0.38.
APPENDIX K. SAMPLE COMPUTATION: ETHANOL/WATER MIXTURE

To demonstrate the performance of the fluid-property computer routine, a sample computation for an ethanol/water binary mixture is traced below. Results can be compared with computations from a Monsanto program (Ref. 4). The numerical results are presented for two fixed temperatures, 0°C and 200°F. The reference point for the enthalpy and entropy values is chosen to be the saturated liquid mixture state at 0°C. The p°-pressure for the entropy is 1 atm.

1. **Mixture Composition, y_i**

The integer subscript i = 1 for ethanol and i = 2 for water. The composition, in mole fractions, is specified as data input.

\[ y_i = 0.6, 0.4 \]  

(K1)

2. **Pure Component Acentric Factor, \( \omega_i \)**

The pure component acentric factor is given by the Pitzer correlation (I21).

\[ \omega_i = \left[ -\ln \frac{p_{ci}}{f^0(t_{bri})} \right] / f^1(t_{bri}) \]  

(K2)

The normal (1 atm) boiling temperature, and the critical temperature pressure, specific volume, and compressibility are given (from Ref. 6, App. A) as data input.

\[ t_{bi} = 351.5, 373.2 \text{ K} \]

\[ t_{ci} = 516.2, 647.3 \text{ K} \]

\[ p_{ci} = 63, 21716 \text{ atm} \]  

(K3)

\[ v_{ci} = 167, 56 \text{ cc/g mol} \]

\[ z_{ci} = 0.248, 0.229 \]

The reduced boiling temperature is

\[ t_{rbi} = t_{bri} / t_{ci} \]  

(K4)

\[ = 0.681, 0.577 \].
The Lee-Kessler functions (120) appearing in (K2) have the values*

\[ f^0 = \]

\[ f^1 = \]

The resulting acentric factors from (K2) are

\[ \omega_i = \]

(K6)

3. The Pure Component Redlich-Kwong a and b Coefficients

The coefficients in the Redlich-Kwong equation of state are given by (H6).

\[ a_i = \Omega_a R^2 t_{ci}^{2.5}/p_{ci} \]

\[ b_i = \Omega_b R^2 t_{ci}/p_{ci} \]

\[ \Omega_a = 0.4274 \]

\[ \Omega_b = 0.08664 \]

\[ R = 82.0575 \text{ cc-atm/g mol-K} \]

For the specified (K3) critical values the coefficients are

\[ a_i = \text{atm} \sqrt{K} (\text{cc/g mol})^2 \] and

\[ b_i = \text{cc/g mol}. \]

(K8)

4. The Mixture Redlich-Kwong a and b Coefficients

The mixture Redlich-Kwong coefficients are weighted averages (H20) of the component values

\[ a_m = y_1^2 a_1 + 2 y_1 y_2 a_{12} + y_2^3 a_2 \]

\[ b_m = \sum y_i b_i. \]

(K9)

*Certain intermediate values in the computation were not printed out in the original computer run. The appearance of equations in which specific numbers are missing represent suggestions for listed output if further computer runs are made.
The mixed coefficient is (H20):

\[ a_{ij} = \Omega_{ij} \frac{R^2}{c_{ij}} \frac{2-5}{p_{cij}}. \]  

(K10)

The mixing factors for temperature, compressibility, and specific volume are given by (H19), and pressure by (H21):

\[ t_{ci} = \sqrt{t_{ci} \cdot t_{cj}} \]

\[ z_{ci} = \frac{z_{ci} + z_{cj}}{2} \]  

(K11)

\[ v_{cij} = \left[ \left( v_{ci}^{1/3} + v_{cj}^{1/3} \right)^2 \right]^{3/2} \]

\[ p_{cij} = R \frac{z_{ci} \cdot t_{cij}}{v_{cij}}. \]

The mixture coefficient values from (K9) are

\[ a_m = \text{atm} \sqrt{K (cc/g mol)}^2 \]  

and

\[ b_m = \text{cc/g mol}. \]  

(K12)

5. Critical Values for the Mixture

The critical values for the mixture are computed from the Redlich-Kwong equation of state parameters. The temperature and pressure are given by (H23):

\[ t_{cm} = \left( \frac{\Omega_a b_m}{\Omega_a a_m R} \right)^{2/3} \]

\[ = \kappa \]  

(K13)

\[ p_{cm} = \left[ R \left( \frac{\Omega_b}{b_m} \right)^5 \left( a_m \right)^2 \right]^{1/3} \]

\[ = \text{atm}. \]

For the temperature and pressure values, the critical specific volume is computed by the iterative solution of (H7):

\[ v_{cm} = \text{cc/g mol}. \]  

(K14)

The compressibility factor (H1) is

\[ z_{cm} = \frac{R t_{cm}}{p_{cm} v_{cm}}. \]  

(K15)
6. Pure Component Vapor Pressure, $p_i^{\text{sat}}$

The pure component vapor pressure, as a function of the temperature, is given by the Antoine equation (I18):

$$p_i^{\text{sat}} = \exp\left(A_1 - \frac{B_1}{t + C_1}\right). \quad (K16)$$

The coefficients (Ref. 6, App. A) for pressure unit of mm/Hg and temperature °K are data input.

$$A_1 = 18.9119, \quad B_1 = 3803.98$$

$$C_1 = -41.68, \quad -46.13 \quad (K17)$$

The computed vapor pressures from (K15), converted to atm units, are

$$p_i^{\text{sat}} = \text{atm} \quad \text{for} \quad 0^\circ \text{C} \quad \text{and}$$

$$= \quad \text{atm} \quad \text{for} \quad 200 \text{ F} \quad (X18)$$

7. The Pure Component Saturation Fugacity Coefficient, $\phi_i^{\text{sat}}$

The pure component fugacity coefficient at the saturation pressure is given by (I38):

$$\phi_i^{\text{sat}} = \exp\left(B_{ii}p_i^{\text{sat}}/Rt\right). \quad (K19)$$

The virial coefficient $B_{ii}$ is given by the Pitzer correlation (H17):

$$B_{ii} = \frac{k_i^{ci}}{P_i^{ci}} \left[B^0(t_{ri}) + \omega_i B^1(t_{ri})\right]$$

$$B^0 = 0.083 - (0.422/t_{ri})^{1.6} \quad \quad (K20)$$

$$B^1 = 0.139 - (0.172/t_{ri})^{4.2}$$

$$t_{ri} = t/t_{ci}.$$  

(See Fig. H2 for region of application of these equations.)

The computed fugacity coefficient values are
\[ \phi_{i}^{\text{sat}} = \text{at } 0^0 \text{C and } \]
\[ = \text{at } 200 \text{ F}. \quad (K21) \]

8. The Pure Component Activity Coefficients, \( \gamma_i \)

The activity coefficients are given by the Van Laar equation (159):

\[ \ln \gamma_i = a_{ij} \bigg/ \left( 1 + \frac{a_{ij} x_i}{a_{ij} x_j} \right)^2. \quad (K22) \]

The Van Laar coefficients in this equation are given by (160) and (161):

\[ a_{ij} = \ln \gamma_i^\infty \quad (K23) \]
\[ = f(\alpha, \epsilon, \zeta, \theta, N_1, N_2). \]

The functional form of \( f \) and its parameters are given in Ref. 6, Table 8.17, p. 334. The ethanol \((\text{C}_2\text{H}_5\text{OH})\) has 2 carbon atoms and water none, so that

\[ N_1 = 2 \quad \text{carbon atoms in component (1)} \quad \text{and} \quad (K24) \]
\[ N_2 = 0 \quad \text{carbon atoms in component (2)}. \]

The value of \( \gamma_i^\infty \) for infinitely dilute ethanol in a water solvent, is given by the functional form (for ethanol considered to be an \( \alpha \)-primary alcohol).

\[ \gamma_i^\infty = \alpha + \epsilon N_1 + \zeta/N_1. \quad (K25) \]

The Van Laar coefficient is

\[ a_{12} = \ln \gamma_i^\infty \quad (K26) \]
\[ = 2.30258 \log \gamma_i^\infty. \]

The parameters (Ref. 5) and the computed \( a_{12} \) are

<table>
<thead>
<tr>
<th>( t ) (^{\circ} \text{C} )</th>
<th>( \alpha )</th>
<th>( \epsilon )</th>
<th>( \zeta )</th>
<th>( a_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-0.995</td>
<td>0.622</td>
<td>0.558</td>
<td>1.216</td>
</tr>
<tr>
<td>60</td>
<td>-0.755</td>
<td>0.583</td>
<td>0.460</td>
<td>1.476</td>
</tr>
<tr>
<td>100</td>
<td>-0.420</td>
<td>0.517</td>
<td>0.230</td>
<td>1.679</td>
</tr>
</tbody>
</table>
For infinitely dilute water in an ethanol solvent, the functional form (for ethanol considered to be an n-alcohol) is

$$\log \gamma_2^\infty = a + \theta/N_1$$  \hspace{1cm} (K28)

$$a_{21} = 2.30258 \log \gamma_2^\infty.$$  \hspace{1cm} (K29)

The parameters (Ref. 5) and the computed $a_{21}$ are

<table>
<thead>
<tr>
<th>$t , ^\circ C$</th>
<th>$\alpha$</th>
<th>$\theta$</th>
<th>$a_{21}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.760</td>
<td>-0.630</td>
<td>1.025</td>
</tr>
<tr>
<td>60</td>
<td>0.680</td>
<td>-0.440</td>
<td>1.059</td>
</tr>
<tr>
<td>100</td>
<td>0.617</td>
<td>-0.280</td>
<td>1.098</td>
</tr>
</tbody>
</table>

Values of the Van Laar coefficients for an arbitrary temperature must be inferred from the tabulated temperature values. For the sample computation temperatures of 0°C and 200 F, the activity coefficients given by the Van Laar equation (K21) are

$$\gamma_1 = \frac{1}{\sqrt{P_{vd}}}$$  for 0°C and

$$\gamma_1 = \frac{1}{\sqrt{P_{vd}}}$$  for 200 F.  \hspace{1cm} (K30)

9. The Dew-Point Pressure

The dew-point pressure is computed by an iterative solution of the VLE equation (II).

$$x_1 = \frac{y_1 \phi_{vd}}{\gamma_1 P_{vd}} = \frac{1}{\gamma_{vd}}.$$  \hspace{1cm} (K31)

The temperature and vapor composition $y_1$ are specified, and the pressure $p_d$ is to be determined. The dew point is shown conceptually in Fig. K1: the pressure is increased in the vapor phase, at a fixed mixture composition $y_1$, until the onset of condensation at the dew-point pressure $p_d$. The initial condensate composition is $x_1$.

The pure-component saturation $p_{vd}$ and $\phi_{vd}$ are given by (K18) and (K21). The condensate composition $x_1$ depends on the undetermined pressure, as does the fugacity and activity coefficients $\phi_{vd}$ and $\gamma_{vd}$. The iteration begins by setting $\gamma_1 = 1$, and an approximate pressure:

$$p_m = \frac{1}{\gamma_1 P_{vd}}.$$  \hspace{1cm} (K32)
With this pressure, the $\hat{\phi}_i$ are computed from (I37):

$$\ln \hat{\phi}_i = \frac{P}{Rt} \left[ B_{ii} + \frac{1}{2} \sum_j \sum_k y_j y_k (2 \delta_{ji} - \delta_{jk}) \right]$$  \hspace{1cm} (K33)

$$\delta_{jk} = 2 B_{kk} - B_{jj} - B_{ii} .$$

The $B_{ij}$ coefficients are given by (H25) and the acentric factor by (H26).

$$B_{ij} = \frac{R t c_{ij}}{p_{cij}} \left[ B^0(t_{rij}) + \omega_{ij} B^1(t_{rij}) \right]$$  \hspace{1cm} (K34)

$$t_{rij} = t/t_{cij}$$

$$\omega_{ij} = (\omega_i + \omega_j)/2 .$$

The Pitzer correlation functions $B^0$ and $B^1$ are given by (H17).

$$B^0(t_r) = 0.083 - (0.422/t_r^{1.0})$$  \hspace{1cm} (K35)

$$B^1(t_r) = 0.139 - (0.172/t_r^{4.2}) .$$

From the first-approximation $\hat{\phi}_i$, the $x_i$ are computed from (K31). The $x_i$ are normalized to make
\[ \sum x_i = 1 \]  \hspace{1cm} \text{(K36)}

The normalized \( x_i \) are then used in the Van Laar equation (K21) to compute the \( \gamma_i \). With these new \( \gamma_i \), the \( x_i \) are recomputed from (K31) and tested against (K36). If (K35) is not satisfied within a preassigned small \( \epsilon \), the pressure is adjusted in accordance with

\[ \sum x_i > 1 : \text{reduce } p_d \]  \hspace{1cm} \text{(K37)}
\[ \sum x_i < 1 : \text{increase } p_d \]

The computations are repeated to convergence.

The computed dew-point pressures (for \( \epsilon = \) ) at the two specified temperatures are

\[ p_d = \begin{cases} \text{atm}, & \text{at } 0^\circ\text{C} \end{cases} \]  \hspace{1cm} \text{(K38)}
\[ = \begin{cases} \text{atm}, & \text{at } 200 \text{ F} \end{cases} \]

10. The Bubble-Point Pressure

The bubble point is shown conceptually in Fig. K2 (compare with Fig. K1 for dew point). The pressure, at constant mixture composition \( x_i \) in the liquid-phase region is slowly reduced until the onset of vaporization at the bubble-pressure \( p_b \). The composition of the initial vapor is \( y_i \).

The bubble-point pressure is computed by an iterative solution of the VLE (I1):

\[ y_i \sat = x_i \gamma_i p_i \sat \phi_i / \phi_i \sat p_b \]  \hspace{1cm} \text{(K39)}

The vapor composition \( y_i \) and the fugacity and activity coefficients depend on the undetermined pressure. For the first approximation, the pressure is \( p_m \) from (K32). For this pressure, the \( \gamma_i \) are computed from the Van Laar equation (K21), and \( y_i \) is computed from (K39). For the first approximation, set \( \phi_i = 1 \); the values of \( x_i \), \( p_i \sat \) and \( \phi_i \sat \) are known. The \( y_i \) are normalized to satisfy

\[ \sum y_i = 1 \]  \hspace{1cm} \text{(K40)}

The \( \phi_i \) are computed from (K33) and the \( y_i \) are recomputed from (K39), and tested against (K40). If (K40) is not satisfied within a preassigned \( \epsilon \), the pressure is adjusted in accordance with the criterion

\[ \sum y_i > 1 : \text{increase } p_b \]  \hspace{1cm} \text{(K41)}
\[ \sum y_i < 1 : \text{decrease } p_b \]
Fig. K2. Constant Temperature Diagram of Bubble-Point and Dew-Point Lines (decreasing pressure at mixture composition \( x_i \) to bubble-point)

The computations are repeated to convergence.

The computed bubble-point pressures (for \( e = \ldots \) ) are

\[
P_b = \begin{cases} 
\text{atm} & , \text{at } 0^\circ C \\
\text{atm} & , \text{at } 200 \text{ F} 
\end{cases}
\]  \quad (K42)

11. The Pure Component Saturation Vapor and Liqu'd Specific Volumes

The pure component saturated vapor specific volume is obtained by the iterative solution of the Redlich-Kwong equation (H7). The iteration starts from the ideal gas value \( \frac{Rt}{p_i} \) sat as the first approximation:

\[
0 = F(v_i) = \frac{Rt}{v_i - b_i} - \frac{a_i}{\sqrt{v_i(v_i + b_i)}} - p_i \text{ sat}.
\]  \quad (K43)

The computed values are

\[
v_{v_i} = \begin{cases} 
\text{cc/g mol} & , \text{at } 0^\circ C \\
\text{cc/g mol} & , \text{at } 200 \text{ F} 
\end{cases}
\]  \quad (K44)
The pure component saturated liquid specific volume can be computed from the Benson equations (J23) and (J24).

\[
\rho_{li} = \frac{2}{v_{ci}} + \left(\rho_{li}^b - \frac{2}{v_{ci}}\right) \frac{t_{ci} - t}{t_{ci} - t_{bi}} - \frac{1}{v_{vi}}. \tag{K45}
\]

Experimental saturation densities measured at a boiling temperature of 243 K are given in Ref. 6, Appendix A.

\[
\text{LIQDEN} = 0.780, \ 0.998 \ \text{g/cc} \tag{K46}
\]

\[
\text{MOLWT} = 46.069, \ 18.015 \ \text{g/g mol}. \tag{K47}
\]

The mole-density is

\[
(\rho_{li})_b = \text{LIQDEN}/\text{MOLWT} \tag{K48}
\]

\[
= 0.01713 \ , \ 0.0554 \ \text{g mol/cc}. \tag{K49}
\]

The densities computed from (K45) are

\[
\rho_{li} = \ \text{g mol/cc at 0^\circ C} \quad \text{and} \tag{K50}
\]

\[
= \ \text{g mol/cc at 200 F}. \tag{K51}
\]

The corresponding specific volumes \((1/\nu_i)\) are

\[
\nu_{li} = \ \text{cc/g mol at 0^\circ C} \quad \text{and} \tag{K52}
\]

\[
= \ \text{cc/g mol at 200 F}. \tag{K53}
\]

12. The Latent Heat of Vaporization

At moderate pressures the mixture latent heat of vaporization can be approximated by the ideal mixing average of the pure component latent heats (see Ref. 8, p. 337):

\[
\lambda_m = \sum y_i \lambda_i. \tag{K54}
\]

The latent heat for each component is given by (J18).

\[
\lambda_i = R \frac{t_{ci}}{z_{vi}} \psi_i. \tag{K55}
\]

The value of \(z_{v_i}\) is approximated by (J29).

\[
z_{v_i} = \frac{p_{i}^{\text{sat}}(t)}{R} (v_{vi} - \nu_{li}). \tag{K56}
\]
For the saturation pressures (K18) and vapor and liquid specific volumes (K44), (K49), the \( z_{v_{ki}} \) values are

\[ z_{v_{ki}} = \ldots \] (K52)

The \( \psi \)-factor is given by (J26), based on the Antoine equation:

\[ \psi = B_i / t_{ci} (1 + C_i / t_{ci} - t_i)^2 \] (K53)

Values of the Antoine coefficients \( B_i \) and \( C_i \) are given by (K17) and \( t_{ci} \) by (K3); the computed \( \psi_i \) values are

\[ \psi_i = \text{at } 0^\circ C \quad \text{and} \]
\[ = \text{at } 200^\circ F. \] (K54)

The corresponding latent heat values from (K51) are

\[ \lambda_i = \text{at } 0^\circ C \quad \text{and} \]
\[ = \text{at } 200^\circ F. \] (K55)

The mixture latent heat values from (K50) are

\[ \lambda_m = \text{at } 0^\circ C \quad \text{and} \]
\[ = \text{at } 200^\circ F. \] (K56)

13. The Dew-Point Vapor Properties

13.1 The Vapor Specific Volume

The saturated vapor mixture specific volume \( v_d \) at the specified temperature \( t \) and dew-point pressure \( p_d \) is computed from the Redlich-Kwong equation (K43), starting from the ideal gas first-approximation value \( R_t / p_d \). The coefficients \( a_m \) and \( b_m \) are given by (K12). The computed values are

\[ v_d = \text{cc/g mol at } 0^\circ C \quad \text{and} \]
\[ = \text{cc/g mol at } 200^\circ F. \] (K57)

13.2 The Vapor Enthalpy

With reference to Fig. J5, the values for \( t^0 \) and \( h^0(t^0,p^0) \) are chosen to be

\[ t^0 = 0^\circ K \]
\[ h^0(t^0,p^0) = 0. \] (K58)

The pressure \( p^0 \) is not specified other than that its value be sufficiently low for the gas at state \( (t^0,p^0) \) to be ideal. Hence, the enthalpy at any \( (t,p) \) vapor state given by (J5) becomes
\[ h_v = \int_0^t C_p^0 \, dt - Dh. \]  \quad (K59)

Integration of the polynomial (J4) for the integrand \( C_p^0 \) gives
\[ h_v = At + \frac{B}{2} t^2 + \frac{C}{3} t^3 + \frac{D}{4} t^4 - Dh. \]  \quad (K60)

The mixture specific heat coefficients, \( A, B, C, D \) are assumed to be approximated by the weighted average of the pure component values given in Ref. 6, Appendix A.

<table>
<thead>
<tr>
<th>( A_i )</th>
<th>( B_i )</th>
<th>( C_i )</th>
<th>( D_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>2.153</td>
<td>0.05113</td>
<td>-20.04E-6</td>
</tr>
<tr>
<td>Water</td>
<td>7.701</td>
<td>4.544E-4</td>
<td>2.521E-6</td>
</tr>
</tbody>
</table>

The weighted averages (\( \sum y_i A_i \), etc.) are
\[ A = \]
\[ B = \]  \quad (K62)
\[ C = \]
\[ D = \]

The departure \( Dh \), in terms of the Redlich-Kwong equation of state, is given by (J17).
\[ Dh = \frac{3 a_m}{2 b_m \sqrt{v}} \ln \left( 1 + \frac{b_m}{v_d} \right) + Rt - p_d v_d. \]  \quad (K63)

The computed values are
\[ Dh = \] at 0°C and
\[ = \] at 200°F.

The dew-point vapor enthalpy values computed from (K60) are
\[ (h_v)_d = \] at 0°C and
\[ = \] at 200°F.

It is convenient to refer enthalpy values to a reference base of the liquid mixture at a temperature of 0°C (273.16 K), rather than at the absolute zero temperature. The reference pressure at this temperature is the bubble-point value.
\[ t_{\text{ref}} = 273.16 \, \text{K} \quad \text{(K66)} \]

\[ P_{\text{ref}} = P_b \]

\[ h_{\text{ref}} = h_v(t_{\text{ref}}, P_d) - \lambda_m. \]

The value \( h_v \) is the saturated vapor enthalpy given by (K60), referred to the absolute-zero temperature, and \( \lambda_m \) is the mixture latent heat of vaporization. The dew-point vapor enthalpy with respect to \( h_{\text{ref}} \) is

\[ h_d = (h_v)_d - h_{\text{ref}}. \quad \text{(K67)} \]

The reference vapor enthalpy value at 0°C is given by (K65), and the latent heat by (K56); the reference enthalpy is thus

\[ h_{\text{ref}} = \ldots \quad \text{(K68)} \]

and the dew-point enthalpies with respect to this reference are

\[ h_d = \begin{cases} \text{at 0°C} & \text{and} \\ \text{at 200 F} & \end{cases} \quad \text{(K69)} \]

An alternative procedure may be followed in which the approximation (K50) for \( \lambda_m \) is avoided. The reference saturated liquid enthalpy at the bubble-point pressure is given by the non-ideal mixing (16) of the pure component enthalpies at the mixture temperature and pressure.

\[ h_{\text{ref}} = \sum x_i h_i(t, p_b) + \Delta h. \quad \text{(K70)} \]

The property change of mixing (F41) is

\[ \Delta h = \sum x_i \overline{\Delta h}_i, \quad \text{(K71)} \]

where the partial molar property change of mixing (T45) is given by

\[ \overline{\Delta h}_i = -R \alpha \ln \gamma_i / \Delta t. \quad \text{(K72)} \]

The derivative is evaluated by solving the Van Laar equation (K22) at the temperatures \((t + \delta t)\) and \((t - \delta t)\) for a small temperature increment \(\delta t\), and approximating the derivative by the finite-difference expression:

\[ \frac{\partial \ln \gamma_i}{\partial t} = \frac{\ln \gamma_i(t + \delta t) - \ln \gamma_i(t - \delta t)}{2 \delta t}. \quad \text{(K73)} \]

The value of the component enthalpy at the bubble-point pressure \( p_b \) will be relatively close to the saturated liquid enthalpy at \( p_b \text{sat} \). From (C12), for constant composition,

\[ dh = t \, ds + v \, dp. \]
For an isentropic pressure change, the differential enthalpy change is
\[ dh = v \, dp \, . \]

It follows that, to a first-order approximation,
\[ h_i(t, p_b) = h_i(t, p_{sat}) + (p_b - p_{sat}) - v_i(t, p_{sat}) \, . \]  

The saturated liquid enthalpy is obtained from the saturated vapor enthalpy,
\[ h_{li} = h_{vi} - \lambda_i \, . \]  

The computed enthalpy values at 0°C are summarized below.

<table>
<thead>
<tr>
<th>Enthalpy</th>
<th>Equation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( h_{vi} )</td>
<td>K60</td>
<td></td>
</tr>
<tr>
<td>( h_{ref} )</td>
<td>K70</td>
<td></td>
</tr>
<tr>
<td>( \Delta h )</td>
<td>K71</td>
<td></td>
</tr>
<tr>
<td>( \overline{\Delta h_i} )</td>
<td>K72,73</td>
<td>(K77)</td>
</tr>
<tr>
<td>( h_i(t, p_b) )</td>
<td>K74</td>
<td></td>
</tr>
<tr>
<td>( h_{li} )</td>
<td>K75</td>
<td></td>
</tr>
</tbody>
</table>

13.3 The Vapor Entropy

For a Rankine cycle analysis only differences in enthalpy and entropy are required. Selection of reference points for the expression of "absolute values" is a matter of convenience. For example, it is convenient to let \( t^0 \) be zero in the enthalpy computation from (K29). However, for the entropy computation from (J14), a zero temperature will produce a singularity. It should be noted also that the enthalpy is independent of the choice of \( p^0 \), provided only that \( p^0 \) is sufficiently small, whereas the entropy value depends on \( p^0 \). The expression (J16) for the entropy departure \( Ds \) involves \( p^0 \). To avoid the singularity for a zero absolute temperature, entropy values are referred to the saturated liquid mixture at 273.16 K (corresponding to 0°C). The enthalpy values also are referred to this point, so that both the enthalpy and entropy will have a common reference point.

The enthalpy values referred to the \( t^0 \)-isotherm are shown in Fig. J2. These values are then shifted by (K66) to the saturated liquid reference at 273.16 K. The figure will then have the general appearance of Fig. K3 shown for the entropy. In this figure, the saturation pressure is given by (K66), and is the reference pressure; the reference entropy is zero.
The saturated vapor entropy value is thus

\[ s_v(t_{\text{ref}}, p_{\text{ref}}) = \frac{\lambda_m}{t_{\text{ref}}} \]  

(K79)

where \( \lambda_m \) is given by (K50). With reference to the figure and the entropy expressions (J14) and (J16), the absolute entropy at any \((t,p)\) is

\[
s(t,p) = \frac{\lambda_m}{t_{\text{ref}}} + D_{sref} + \left[ A \ln t + B \frac{t^2}{2} + C \frac{t^3}{3} \right]_{t_{\text{ref}}}^{t} - Ds
\]

(K80)
\[ D_s = -R \ln \left[ \frac{D_c}{R} (v - b_m) + \frac{a_m}{2 b_m} \ln \left( 1 + \frac{b_m}{v} \right) \right]. \] 

(K81)

The computed values are

\[ D_s^{\text{ref}} = \text{for } 0^\circ \text{C} \]
\[ = \text{for } 0^\circ \text{C} \]
\[ = \text{for } 200 \text{ F} \]

(K82)

\[ (s_v)^{\text{ref}} = \text{for } 0^\circ \text{C} \]
\[ s = \text{for } 200 \text{ F}. \]

14. The Bubble-Point Properties

14.1 The Liquid Specific Volume

At relatively moderate pressures, the saturated liquid density is given by Amagat's law (Ref. 8, p. 321), which corresponds to the ideal mixture value.

\[ \rho_{lm} = \sum x_i \rho_i. \]  

(K83)

For the pure component density values given by (K48), the mixture values are

\[ \rho_{lm} = \text{g mol/cc at } 0^\circ \text{C} \text{ and } \]  
\[ = \text{g mol/cc at } 200 \text{ F}. \]  

(K84)

14.2 The Liquid Enthalpy

The saturated liquid enthalpy is the saturated vapor value (K69) minus the latent heat of vaporization (K56).

\[ h_l = 0 \text{ at } 0^\circ \text{C} \text{ and } \]  
\[ = \text{at } 200 \text{ F}. \]  

(K85)

14.3 The Liquid Entropy

The saturated liquid entropy (K66), is the saturated vapor value minus \( \lambda_m / t \).
15. Non-Saturation Mixture Properties

The basic mixture properties involved in the Rankine cycle analysis are the enthalpy, entropy, and specific volume. These properties can be displayed as functions of \((t,p)\), either as graphs or tables. The procedure for the sample computation is to select a set of pressures, and for each pressure to tabulate the properties for a range of incremental temperatures.

15.1 The Vapor Region

When the pressure is below the dew-point value \(p_d\), the mixture is in the vapor region. The vapor specific volume, enthalpy, and entropy are based on the Redlich-Kwong equation of state: the specific volume from \((K43)\); the enthalpy from \((K59)\), \((K60)\), and \((K63)\), expressed with respect to \(h_{\text{ref}}\) by \((K67)\); and the entropy from \((K81)\) and \((K82)\).

15.2 The Liquid Region

When the pressure is above the bubble-point value \(p_b\), the mixture is in the liquid region. The liquid specific volume, being weakly dependent on the pressure, is assumed to equal approximately the saturation value \(v_b\). Greater accuracy could be achieved by the Yen-Woods procedure (Ref. 6, p. 62, and p. 86 for mixtures).

The enthalpy and entropy values are extrapolated linearly from the bubble-point values, at constant temperature, for the pressure increase above \(p_b\):

\[
h = h_b + \left. \frac{\partial h}{\partial p} \right|_t (p - p_b)
\]

\[
s = s_b + \left. \frac{\partial s}{\partial p} \right|_t (p - p_b).
\]

The partial derivatives can be computed from the volume expansivity, defined as

\[
\beta = \frac{1}{v} \left. \frac{\partial v}{\partial t} \right|_p,
\]

where \(\left. \frac{\partial v}{\partial t} \right|_p\) is approximated by the change in the saturated specific volumes with temperature determined from \((K8)\). The entropy derivative is related directly to \(\beta\) through the Maxwell relation \((C16)\):
\[
\frac{\partial s}{\partial p} = - \frac{\partial v}{\partial t} \bigg|_p = \beta v \quad \text{(K89)}
\]

The enthalpy derivative follows from (C12) for constant composition

\[
\frac{\partial h}{\partial p} = v + t \frac{\partial s}{\partial p} \bigg|_t
\]

\[
= v - t \frac{\partial v}{\partial t} \bigg|_p = (1 - \beta t)v \quad \text{(K90)}
\]
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