STABILITY ANALYSIS OF MULTICOMPONENT SYSTEMS

by

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ABSTRACT

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The criterion of intrinsic stability for a general m-component system is developed in terms of derivatives of U, the total internal energy. This criterion is converted to equivalent forms in terms of any Legendre Transform of U. The corresponding equations which define the critical point are derived.

Stability and critical point conditions are applied to pure and multicomponent systems. Superheat limits and critical points are calculated using the Redlich-Kwong equation-of-state and the Soave modification. The original Redlich-Kwong equation predicts that the limit of superheat for pure materials is at a reduced temperature of about .9, which agrees well with data. All other predictions show much less agreement.

Thesis Supervisor: Robert C. Reid

Title: Professor of Chemical Engineering
I am deeply grateful to Professor Robert C. Reid for his suggestions and encouragement during the work on this thesis.
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SUMMARY

The purpose of this thesis is to derive rigorously the criteria of intrinsic stability and of critical points, to examine what these criteria mean in physical terms, and to examine the accuracy of using the criteria with common equations-of-state in the prediction of limits of superheat and critical points.

In a stable equilibrium state at constant total internal energy \( U \), total volume \( V \), and mole numbers \( N_i \), the total entropy \( S \) is maximized. An equivalent statement is that at constant \( S, V \) and \( N_i \), \( U \) is minimized. Consider a homogeneous system being held at constant \( S, V \) and \( N_i \) which splits into two phases, each differing only slightly from the original. For a system to be at stable equilibrium, the energy must increase during this change.

The change in energy \( \delta U \) is expanded in a Taylor Series about the original conditions. The first derivatives of \( U \) (temperature, pressure and chemical potentials) are shown to be constant throughout a stable equilibrium system. Except at critical points, the second derivatives control the sign of \( \delta U \). Rewriting the expansion in a sum-of-squares form reveals that certain determinants of the second derivatives of \( U \) must be positive for the system to be intrinsically stable. One of these determinants is shown to become zero before or at the
same time as the others, and is thus the first criterion to be violated. This criterion of intrinsic stability is listed in Section I as Eq. (52).

The criterion of intrinsic stability is written in terms of the Helmholtz Free Energy (A) or any other Legendre Transform of \( \mathcal{U} \) using the second derivatives of Legendre Transforms derived in Appendix C. One form of this criterion is that a single second derivative be positive (Eq. (50)). At critical points, this derivative and the third derivative are zero. Using third derivatives of Legendre Transforms, these conditions are rewritten in terms of \( \mathcal{U} \) or any of its transforms, including A (Eqs. (62) and (89)).

Several stability criteria may be written in common thermodynamic terms. All stable substances satisfy the condition of thermal stability, "the heat capacity at constant volume is positive." The stability criterion which is violated when a pure material becomes unstable is the condition of mechanical stability. Equivalent forms of the mechanical stability criterion are: "the derivative of the pressure with respect to specific volume at constant temperature is negative" and "the heat capacity at constant pressure remains finite." Binary systems are stable only when the condition of diffusional stability, "the derivative of a chemical potential with respect to its mole
fraction at constant temperature and pressure is positive," is satisfied. Other equivalent forms of the conditions of thermal, mechanical and diffusional stability, and conditions of stability for ternary systems are given in Tables I through IV.

All second and higher derivatives of $A$ with respect to volume or mole numbers may be evaluated using a pressure explicit equation-of-state. Superheat limits of pure and multicomponent systems and critical points of mixtures were calculated using the original Redlich-Kwong equation-of-state and the Soave modification. The original R–K equation predicts a reduced superheat temperature of about $9/10$ for all pure materials. This is in remarkable agreement with virtually all measured compounds. The Soave equation produces much less accurate results in this instance. Both equations predict that the superheat temperature of a mixture is very close to the mole fraction average of the pure component values, which is partially reflected in the data. Calculations of mixture critical points are about equally poor using either equation. Trends are predicted correctly but actual values are significantly in error.

The apparent fault in the equations-of-state used is their poor handling of mixtures. Significantly improved mixing rules are needed to yield increased accuracy.
INTRODUCTION

Under certain conditions a liquid may be heated well above its boiling point and yet remain in the liquid state. When vaporization finally occurs, it produces a "superheat explosion" due to the sudden phase change. The explosion increases in violence as the liquid is heated further above its boiling point. All liquids at a given pressure have a temperature above which they may not be heated without spontaneously vaporizing. The degree of superheat may strongly influence the violence and/or the possibility of a superheat explosion. Thus the study of such limits of superheat is necessary in predicting the behavior of a rapidly heated liquid.

The limit of superheat is one aspect of the study of intrinsic stability, that is, the stability of a system with regard to spontaneous small changes. Systems which may undergo such changes include superheated liquids, subcooled vapors and supersaturated solutions. The central problem of this thesis is the derivation of criteria of intrinsic stability for a general m-component system. Since the study of critical points is closely related to stability phenomena, the conditions which define critical points are also developed.

The criteria of intrinsic stability are derived starting with the entropy maximization principle. A system
is assumed to split into two infinitesimally different subsystems, and equations are developed to determine whether this change proceeds spontaneously. The derivatives of Legendre Transforms are found and are used to simplify the equations obtained.

The stability and critical point conditions are examined as to their predictions about pure and multicomponent systems. They are then tested using two equations-of-state in a comparison with experimental values. Finally, this treatment is contrasted with that of several other authors.
I. DERIVATION OF STABILITY CRITERIA

The concept of intrinsic stability is not usually encountered in chemical engineering applications. For example, consider the reversible, isothermal compression of water vapor at 100°C. Normally, when the pressure reaches 1 atm, liquid water appears. Condensation begins on the vessel surfaces or on impurity motes. As the system is compressed further, more liquid phase forms. When the water is entirely liquid, the pressure rises above 1 atm.

If the vessel surfaces are not "wet" by liquid water and no other condensation surfaces are available, the water will remain entirely in the gas phase even though the pressure is raised considerably in excess of 1 atmosphere. This is because microscopic drops of liquid have a higher specific availability function than the bulk phase. (A detailed analysis of the availability is not required here—the important fact is that a potential barrier prevents nucleation). The system is then stable with regard to microscopic perturbations (intrinsic stability) even though it may be unstable with regard to a large perturbation (phase instability) i.e., the formation of two unlike phases with the transfer of mass from certain parts of the system to others. This system is termed metastable.

If the metastable vapor is compressed further it will eventually become intrinsically unstable. That is, it will
become unstable with respect even to microscopic perturbations and will spontaneously separate into two phases. The point at which a system first becomes intrinsically unstable is termed the "limit of intrinsic stability." Formulas are derived below to predict where such limits will occur. Expansions in terms of the Gibbs or the Helmholtz Free Energy are readily evaluated using volume or pressure explicit equations of state.

The criterion of intrinsic stability for an equilibrium state, first derived by Gibbs[1], is that for a stable, isolated system, the total entropy is maximized. In other words, for any possible microscopic variation at constant mole numbers, total volume and total internal energy \((N, V \text{ and } U)\),

\[ \delta S < 0 \]  

Eq. (1) is easily changed into alternate forms.

Consider a two-step reversible process starting at a stable equilibrium state holding \(V\) and \(N\) constant during both steps. The first step is any small, reversible variation at constant \(U\). By Eq. (1), \(S\) decreases. Heat may then be added reversibly until \(S\) increases to its original value. This two-step process is equivalent to a net variation at constant \(S\). In the first step \(U\) was held constant while in the second step heat was added and thus \(U\) increased. The total internal energy then increases during
all small variations around this stable state at constant \( S, V \) and \( N_i \).

A similar process may be followed starting at an unstable equilibrium state. The first step is a small variation at constant \( U \); \( S \) increases. Such a variation must exist for the state to be unstable. Heat may then be removed reversibly until \( S \) returns to its original value. \( U \) therefore decreases in this two step process. By appropriate choices, this may be shown to be equivalent to holding \( S \) constant. Thus there exists a small variation around this unstable state at constant \( S, V \) and \( N_i \) where \( U \) decreases.

An alternate criterion of intrinsic stability is that for all variations around a stable equilibrium state at constant \( S, V \) and \( N_i \),

\[
\Delta U > 0 \tag{2}
\]

Eq. (2) is equivalent to Eq. (1) since it is applicable when Eq. (1) is true and is violated when Eq. (1) is violated.

The \( V \) form of the criterion of intrinsic stability is obtained by using similar reasoning. The two-step, reversible processes are all carried out at constant \( S \) and \( N_i \). After the first small variation at constant \( V \), enough work energy is either reversibly added to or subtracted from the system (by contraction or expansion) to return \( U \).
to its original value. Assuming that the pressure is positive, the sign of $\delta V$ for the two step process is always the same as the sign of $U$ for the first step. Thus another criterion of intrinsic stability is that for all small variations around an equilibrium state at constant $U$, $S$ and $N_i$, if $P > 0$

$$\delta V > 0$$

(3)

In some metastable systems $P < 0$. The above argument holds except that the sign of $\delta V$ is changed. Therefore a general form of Eq. (3) is that for all small variations around an equilibrium state at constant $U$, $S$ and $N_i$

$$P \delta V > 0$$

(4)

Using a procedure similar to the above, the criterion of intrinsic stability for small variations around an equilibrium state at constant $U$, $S$, $V$, and $N_j \neq a$ is

$$\mu_a N_a < 0$$

(5)

Eq. (5) is not particularly useful since it requires that $S$ be held constant while $N_a$ is varied.

Eq. (2) is the form of the criterion of intrinsic stability used in this thesis. It is chosen since most of the transforms and derivatives of $U$ are common thermodynamic properties. Any other form could be used, and would yield equivalent results.

Since $N_1$, $N_2$, $N_3$ ... $N_m$, $V$ and $S$ completely specify $U$ in a single phase, the test for stability must involve the
creation of two phases, $\alpha$ and $\beta$, each differing only microscopically from the original. Differential quantities of heat, volume and mass may flow between the phases, but $S$, $V$ and all $N_i$ are held constant for the entire system. Therefore,

$$dS^\beta = -dS^\alpha$$  (6)
$$dV^\beta = -dV^\alpha$$  (7)
$$dN_i^\beta = -dN_i^\alpha$$  (8)

To simplify notation, $V$, $S$ and $N$, through $N_m$ are relabelled $x$, through $x_n$ ($n=m+2$). Since $V$, $S$ and $N_i$ are mathematically equivalent they may be relabelled in any order. For instance, the $x_i$'s could be defined (for $j>2$):

$$x_i = S$$  (9)
$$x_j = V$$  (10)
$$x_j = N_{j-2}$$  (11)

although any other ordering would be satisfactory. With any labelling, Eqs. (6), (7) and (8) summarize to

$$dx_i^\beta = -dx_i^\alpha$$  (12)

Also for convenience, partial derivatives of $U$ or any of its transforms ($A$, $G$, etc.) are indicated by subscripts:

$$U_i = \left( \frac{\delta U}{\delta x_i} \right)_{x_j \neq i}$$
$$A_v = \left. \frac{\delta A}{\delta V} \right|_{T,N_i}$$

Since each subsystem is assumed to undergo only small changes, the total internal energy may be expanded in a Taylor Series about the original conditions. Expanding through second order terms (using a superscript $^o$ to
indicate that a variable is evaluated at the original conditions)

\[ \delta U^\alpha = \sum_{i=1}^{n} U_i^\alpha \, dx_i^\alpha + \sum_{i=1}^{n} \sum_{j=1}^{n} U_{ij}^\alpha \, dx_i^\alpha \, dx_j^\alpha \]  

(13)

\[ \delta U^\beta = \sum_{i=1}^{n} U_i^\beta \, dx_i^\beta + \sum_{i=1}^{n} \sum_{j=1}^{n} U_{ij}^\beta \, dx_i^\beta \, dx_j^\beta \]  

(14)

The change in the entire system's total internal energy is the sum of the changes for the two subsystems, or

\[ \delta U = \delta U^\alpha + \delta U^\beta \]  

(15)

Combining Eqs. (12) through (15)

\[ \delta U = \sum_{i=1}^{n} (U_i^\alpha - U_i^\beta) \, dx_i^\alpha + \sum_{i=1}^{n} \sum_{j=1}^{n} (U_{ij}^\alpha + U_{ij}^\beta) \, dx_i^\alpha \, dx_j^\alpha \]  

(16)

Since all constraints on the system have been incorporated into Eq. (16), each \( dx_i^\alpha \) is independent. Eq. (16) must therefore be true for all possible sets of \( dx_i \) through \( dx_n \), including the one where \( dx_i \) is the only non-zero \( dx_j \). Thus, since \( dx_i \) may be either positive or negative, \( U_i^\alpha \) must be equal to \( U_i^\beta \) to prevent \( \delta U \) from being negative.

\[ U_i^\alpha = U_i^\beta \]  

(17)

Each \( U_i \) is an intensive variable, being either \( T \), \( P \) or a \( \mu_j \). The subsystem \( \alpha \) may be defined to be any part of the original system. Therefore Eq. (17) shows that there are no temperature, pressure or chemical potential gradients in a stable equilibrium state. Since \( m+1 \) (i.e. \( n-1 \)) intensive
variables are sufficient to define the state (but not the extent) of a single phase system, all intensive variables are constant everywhere throughout the original system.

\( U_{ij}^o \), being the derivative of an intensive variable with respect to an extensive variable, is inversely proportional to the number of moles in the subsystem under consideration. The product of \( U_{ij}^o \) and the number of moles is therefore the same for any subsystem.

\[
N^\alpha U_{ij}^o = N^\beta U_{ij}^o
\]  
(18)

Substituting Eqs. (17) and (18) into Eq. (16) and eliminating \( U_{ij}^{o\alpha} \),

\[
\delta U = N \sum_{i=1}^{n} \sum_{j=1}^{n} U_{ij}^o \delta x_i \delta x_j
\]  
(19)

The system which is being tested for stability is the original system. The subsystem \( \alpha \) may be chosen to be any part of the original system. Therefore all superscripts are dropped when substituting Eq. (19) into Eq. (2) to yield as an alternate criterion of intrinsic stability

\[
\sum_{i=1}^{n} \sum_{j=1}^{n} U_{ij} \delta x_i \delta x_j > 0
\]  
(20)

A system is intrinsically stable if Eq. (20) is satisfied for all microscopic perturbations. If the left hand side (LHS) of Eq. (20) were negative for some perturbation, the system would be unstable. If the LHS of Eq. (20) were zero, then Eqs. (13) and (14) would have to
be expanded to include third (and possibly higher) order terms. Following the above development, Eq. (20) would then include third order terms. If the signs of all the $dx_i$'s were reversed, then the sign of the second order terms would be unchanged while the sign of the third order terms would be reversed. Thus when the LHS of Eq. (20) is zero, the change in $U$ may be either positive or negative, unless the third order terms are also zero. Usually, therefore, when the LHS of Eq. (20) becomes zero, the system becomes unstable. At critical points, however, the third order terms are also zero. This special case of Eq. (20) when the LHS is zero is discussed further in Section II.

The limit of intrinsic stability is reached when the LHS of Eq. (20) is zero. Since each $dx_i$ may be either positive or negative, it is desirable to express the LHS of Eq. (20) in a sum-of-squares form. Then the sign of the expression will be controlled by an appropriate combination of $U_{ij}$'s. The sum-of-squares form is derived in Appendix B. Eq. (20) may then be written as

$$\sum_{k=1}^{n} \frac{D_k}{D_{k-1}} dZ_k^2 > 0 \quad (21)$$

where

$$dZ_k = \sum_{j=k}^{n} \frac{C_{kkj}}{D_k} dx_j \quad (22)$$

$D_k$ and $C_{kkj}$ are defined as in Appendix B, with $Z_k$ of
Appendix E written as \( dZ_k \).

\[
D_k = \begin{bmatrix}
U_{11} & U_{12} & \cdots & U_{1k} \\
U_{21} & U_{22} & \cdots & U_{2k} \\
\vdots & \vdots & \ddots & \vdots \\
U_{k1} & U_{k2} & \cdots & U_{kk}
\end{bmatrix}
\]

\[
C_{kkj} = \begin{bmatrix}
U_{11} & U_{12} & \cdots & U_{1,k-1} & U_{1j} \\
U_{21} & U_{22} & \cdots & U_{2,k-1} & U_{2j} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
U_{k1} & U_{k2} & \cdots & U_{k,k-1} & U_{kj}
\end{bmatrix}
\]

Eq. (21) is the basic equation from which all other criteria of intrinsic stability will be derived. It may be simplified using the Legendre Transforms discussed in Appendix C. Following the notation of Appendix C, \( y \) is a function of \( x \) through \( x_n \) and \( \Psi \) is a partial Legendre Transform from \( x \) space to \( \xi \) space. Subscripts on \( y \) or \( \Psi \) indicate partial derivatives with respect to the corresponding variable.

\[
y = y(x_1, x_2, \ldots, x_n) \]

\[
y_i = \left( \frac{\partial y}{\partial x_i} \right)_{x_j \neq i}
\]

\[
\xi_i = \left( \frac{\partial y}{\partial x_i} \right)_{x_j \neq i} = y_i
\]

\[
\Psi = \Psi(\xi_1, x_2, \ldots, x_n) = y - \xi_1 x_1
\]

\[
\Psi_i = \left( \frac{\partial \Psi}{\partial \xi_i} \right)_{x_j \neq i}
\]
First let $y$ be the total internal energy, $U$. Rewriting $D_k$

$$D_k = \begin{vmatrix} y_{11} & y_{12} & y_{13} & \cdots & y_{1k} \\ y_{21} & y_{22} & y_{23} & \cdots & y_{2k} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ y_{k1} & y_{k2} & y_{k3} & \cdots & y_{kk} \end{vmatrix}$$

(23)

Factoring $y_{11}$ from column 1,

$$D_k = y_{11} \begin{vmatrix} 1 & y_{12} & y_{13} & \cdots & y_{1k} \\ \frac{y_{21}}{y_{11}} & \frac{y_{22}}{y_{11}} & \frac{y_{23}}{y_{11}} & \cdots & \frac{y_{2k}}{y_{11}} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{y_{k1}}{y_{11}} & \frac{y_{k2}}{y_{11}} & \frac{y_{k3}}{y_{11}} & \cdots & \frac{y_{kk}}{y_{11}} \end{vmatrix}$$

(24)

The first column of the determinant in Eq. (24) is then multiplied by $y_{12}$ and subtracted from the second column; the first column is multiplied by $y_{13}$ and subtracted from the third column; and so on. That is, for all $i>1$, the first column is multiplied by $y_{1i}$ and subtracted from the $i^{th}$ column. The end result is:
Simplifying,

\[
\begin{vmatrix}
1 & 0 & 0 & 0 \\
\frac{V_{22}}{Y_{11}} & \frac{V_{22} - V_{12} V_{13}}{Y_{11}} & \frac{V_{23} - V_{12} V_{13}}{Y_{11}} & \cdots & \frac{V_{2k} - V_{12} V_{1k}}{Y_{11}} \\
\frac{V_{31}}{Y_{11}} & \frac{V_{32} - V_{12} V_{13}}{Y_{11}} & \frac{V_{33} - V_{13} V_{13}}{Y_{11}} & \cdots & \frac{V_{3k} - V_{13} V_{1k}}{Y_{11}} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\frac{V_{k2}}{Y_{11}} & \frac{V_{k2} - V_{12} V_{13}}{Y_{11}} & \frac{V_{k3} - V_{13} V_{13}}{Y_{11}} & \cdots & \frac{V_{kk} - V_{1k} V_{1k}}{Y_{11}}
\end{vmatrix}
\]

Each term in the determinant of Eq. (26) is of the form \( y_{ij} y_{jl} y_{kl} \), where \( i \geq 2 \) and \( j \geq 2 \). By Eq. (C-25) (from Appendix C), each term is equal to \( \Psi_{ij} \), a second partial derivative of the Legendre Transform, \( \Psi \). Using this substitution, Eq. (26) becomes

\[
\begin{vmatrix}
\Psi_{22} & \Psi_{23} & \cdots & \Psi_{2k} \\
\Psi_{32} & \Psi_{33} & \cdots & \Psi_{3k} \\
\vdots & \vdots & \ddots & \vdots \\
\Psi_{k2} & \Psi_{k3} & \cdots & \Psi_{kk}
\end{vmatrix}
\]

Applying Eq. (27) to the ratio of terms found in Eq. (21)
Thus each of the determinants (except $D_o$) in Eq. (21) may be reduced by one order. The second partial derivatives of $y$ have, however, been replaced with second partial derivatives of $\Psi$. $\Psi$ is the Legendre Transform of $y$ from $x$, space to $\xi$, space. The first row and first column of the old form of the determinant, which have been eliminated in the reduced form, are the row and column which contain derivatives with respect to $x_i$, the transformed variable.

All of the determinants (except $D_o$ and $D_r$) may be reduced by another order by repeating the process used to generate Eq. (27) on each of the determinants in Eq. (28). That is, defining $\Psi^{(2)}$ as the Legendre Transform of $\Psi$ from $x_2$ space into $\xi_2$ space (also termed the second Legendre Transform of $U$ from $x$, and $x_2$ space into $\xi_1$ and $\xi_2$ space)

$$
\Psi^{(2)}(\xi_1, \xi_2, x_3 \ldots x_n)
= \Psi(\xi_1, x_2 \ldots x_n) - \xi_2 x_2 = U(x_1 \ldots x_n) - \xi_1 x_1 - \xi_2 x_2
$$

(29)
\( \xi_2 \) may be defined as a partial derivative of either \( U \) or \( \Psi \), i.e.,

\[
\xi_2 = \left| \frac{\partial \Psi}{\partial x_2} \right|_{x_1, x_i \neq x_2} = \left| \frac{\partial \Psi}{\partial x_2} \right|_{x_i \neq x_2} \tag{30}
\]

The two derivatives in Eq. (30) may be shown to be equal either by differentiating the definition of \( \Psi \), or by using Eq. (C-22) (from Appendix C).

Reducing each of the determinants in Eq. (28) and cancelling the term that was factored out, \( \Psi_{22} \), yields

\[
\begin{vmatrix}
\Psi^{(2)}_{33} & \Psi^{(2)}_{34} & \cdots & \Psi^{(2)}_{3k} \\
\Psi^{(2)}_{43} & \Psi^{(2)}_{44} & \cdots & \Psi^{(2)}_{4k} \\
\vdots & \vdots & \ddots & \vdots \\
\Psi^{(2)}_{k3} & \Psi^{(2)}_{k4} & \cdots & \Psi^{(2)}_{kk}
\end{vmatrix}
\]

\[
\frac{D_k}{D_{k-1}} = \begin{vmatrix}
\Psi^{(2)}_{33} & \Psi^{(2)}_{34} & \cdots & \Psi^{(2)}_{3k-1} \\
\Psi^{(2)}_{43} & \Psi^{(2)}_{44} & \cdots & \Psi^{(2)}_{4k-1} \\
\vdots & \vdots & \ddots & \vdots \\
\Psi^{(2)}_{k3} & \Psi^{(2)}_{k4} & \cdots & \Psi^{(2)}_{k-1,k-1}
\end{vmatrix}
\]

Thus each of the determinants (except \( D_0 \) and \( D_1 \)) in Eq. (21) has been reduced by two orders, and the second partial derivatives of \( y \) are now replaced by second partial derivatives of \( \Psi^{(2)} \).

This stepwise procedure is continued until the ratio of \( D_k \) to \( D_{k-1} \) is reduced to a single second partial derivative. In general, \( \Psi^{(p)} \) is defined as the \( p \)th Legendre Transform of \( U \) from \( x_i \) through \( x_p \) space to \( \xi_i \).
through $\xi_p$ space, that is,
\[
\psi^{(p)}(\xi_1, \xi_2 \ldots \xi_p, x_{p+1}, x_{p+2} \ldots x_n) = 
\]
\[
U(x_1, x_2 \ldots x_n) - \sum_{i=1}^p \xi_i x_i 
\]  
(32)
where
\[
\xi_i = \left. \frac{\partial U}{\partial x_i} \right|_{x_j \neq i} 
\]  
(33)
Using the notation of Eq. (32), $y$ (or $U$) is written as $\psi^{(0)}$ and $\psi$ is written as $\psi^{(1)}$. Repeating the procedure used to generate Eq. (28) on each of the determinants in Eq. (28) $k-2$ times

\[
\frac{D_{k}}{D_{k-1}} = \left| \begin{array}{c} 
\psi_{k,k}^{(k-1)} \\
\psi_{k}^{(k-1)} \\
\psi_{kk}^{(k-1)} \\
\end{array} \right| 
\]  
(34)
Eq. (34) is the final reduction of the determinants in Eq. (21). Following the identical procedure, the determinants in Eq. (22) are reduced to

\[
\frac{C_{kkj}}{D_{k}} = \frac{\psi_{k,k}^{(k-1)}}{\psi_{kk}^{(k-1)}} 
\]  
(35)
The RHS of Eq. (35) is $\psi_{k,j}^{(k-1)}/\psi_{kk}^{(k-1)}$. By Eq. (32), $\psi^{(k)}$ is the Legendre Transform of $\psi^{(k-1)}$ from $x_k$ space to $\xi_k$ space. Since $x_k$ is the transformed variable, Eq. (C-29) (from Appendix C) shows that $\psi_{k,j}^{(k-1)}/\psi_{kk}^{(k-1)}$ is equal to $\psi_{kj}^{(k)}$. Rewriting Eq. (35) (for $j>k$)

\[
\frac{C_{kkj}}{D_{k}} = \psi_{kj}^{(k)} 
\]  
(36)
From the definitions of $C_{kkj}$ and $D_k$, if $j=k$

$$
\frac{C_{kkj}}{D_k} = 1, \quad j=k
$$

(37)

Eq. (34) is substituted into Eq. (21) and Eqs. (36) and (37) are substituted into Eq. (22) to yield the reduced form of the criterion of intrinsic stability

$$
\sum_{k=1}^{n} \psi_{kk}^{(k-1)} dZ_k > 0
$$

(38)

where

$$
dZ_k = dx_k + \sum_{j=k+1}^{n} \psi_{kj}^{(k)} dx_j
$$

(39)

$\psi_{kk}^{(k-1)}$ is shown equal to $\xi_k$ either by differentiating the definition of $\Psi_{kk}^{(k-1)}$ (Eq. (32)) or by using Eq. (C-22) (from Appendix C). Therefore $\psi_{kk}^{(k-1)}$ simplifies to

$$
\psi_{kk}^{(k-1)} = \left( \frac{\partial \xi_k}{\partial x_k} \right) \xi_1 \xi_{k-1} x_{k+1} \ldots x_n
$$

(40)

Similarly, $\psi_{kJ}^{(k)}$ is shown equal to $-x_k$ either by differentiating the definition of $\Psi_{kJ}^{(k)}$ or by using Eq. (C-21) (from Appendix C). $\psi_{kJ}^{(k)}$ simplifies to

$$
\psi_{kJ}^{(k)} = \left( \frac{\partial x_k}{\partial x_j} \right) \xi_1 \xi_k x_{k+1} \ldots x_{j-1} x_{j+1} \ldots x_n
$$

(41)

For example, the system under test may contain a pure material. Then, if $x_1$, $x_2$ and $x_3$ are defined as in Eqs. (9), (10) and (11), the criterion of stability given by Eqs. (21) and (22) is:
where

\[ dZ_1 = dS + \frac{|U_{SV}|}{|U_{SS}|} dV + \frac{|U_{SN}|}{|U_{SS}|} dN \]

\[ dZ_2 = dV + \frac{|U_{SV}|}{|U_{VS}|} dS + \frac{|U_{SN}|}{|U_{VS}|} dN \]

\[ dZ_3 = dN \]

The determinants in Eqs. (42) through (45) may be reduced to single terms using the Legendre Transform methods above. This alternate form of the criterion of intrinsic stability, given by Eqs. (38) and (39), is

\[ \psi^{(0)} (dS + \psi_{12}^{(1)} dV + \psi_{13}^{(1)} dN)^2 + \psi_{22}^{(1)} (dV + \psi_{23}^{(1)} dN)^2 + \psi_{33}^{(1)} (dN)^2 > 0 \] (46)

Since \( x_1, x_2 \) and \( x_3 \) were ordered to represent \( S, V \) and \( N \) respectively, the Legendre Transforms of \( U \) as used here are

\[ \psi^{(1)} = A(T, V, N) = U - TS \]

\[ \psi^{(2)} = C(T, -P, N) = U - TS - (-P)V \]
The second derivatives in Eq. (46) are

\[ \Psi_{11}^{(0)} = U_{s s} = \left. \frac{\partial T}{\partial S} \right|_{V, N} \]

\[ \Psi_{22}^{(1)} = \Delta V = \left. \frac{\partial S}{\partial V} \right|_{T, N} \]

\[ \Psi_{12}^{(i)} = \Delta T = \left. \frac{\partial S}{\partial N} \right|_{T, V} \]

\[ \Psi_{23}^{(1)} = \Delta T = \left. \frac{\partial V}{\partial N} \right|_{T, P} \]

\[ \Psi_{33}^{(2)} = G_{NN} = \left. \frac{\partial \mu}{\partial N} \right|_{T, P} \]

Substituting the above formulas into Eq. (46) yields

\[ U_{s s}(dS + \Delta TVdV + \Delta TN dN)^2 + \Delta VV(dV + \Delta GPdN) + G_{NN}(dN)^2 > 0 \quad (47) \]

or equivalently,

\[ \left. \frac{\partial T}{\partial S} \right|_{V, N} (dS - \left. \frac{\partial S}{\partial V} \right|_{T, N} dV - \left. \frac{\partial S}{\partial N} \right|_{T, V} dN)^2 \]

\[ + \left. \frac{\partial (-P)}{\partial V} \right|_{T, N} (dV - \left. \frac{\partial V}{\partial N} \right|_{T, P} dN)^2 + \left. \frac{\partial \mu}{\partial N} \right|_{T, P} (dN)^2 > 0 \quad (48) \]

Eq. (48) may also be obtained from Eq. (46) by using Eqs. (40) and (41).

The leading coefficient of the last term in Eq. (48) is the derivative of an intensive variable (the chemical potential), evaluated while holding two other intensive variables (temperature and pressure) constant. Since two intensive variables completely specify the state of a single component system, this derivative is equal to zero. The result is generalized below to any system.
Eq. (38) is the reduced form of the criterion of intrinsic stability. The final term has $\psi^{(n-1)}_{nn}$ as a leading coefficient. Using Eq. (40), $\psi^{(n-1)}_{nn}$ is a derivative of $\xi_n$, holding all other $n-1$ $\xi_i$'s constant. Since each $\xi_i$ is either $T$, $-P$ or $\mu_i$, all $\xi_i$'s are intensive variables. Since $n-1$ (i.e. $m+1$) intensive variables completely specify the state of a system, $\psi^{(n-1)}_{nn}$ is equal to zero.

The LHS of Eq. (38) must be greater than zero for all permutations around a stable equilibrium state (except at critical points, where it may be equal to zero). There is an apparent contradiction between this fact and the preceding paragraph, since the $dx_i$'s in a variation may be selected so that all the $dZ_k$'s except $dZ_n$ are equal to zero. Since the coefficient of $dZ_n$ ($\psi^{(n-1)}_{nn}$) was shown to be equal to zero, the LHS of Eq. (38) is equal to zero for this variation. The contradiction is resolved by noting the nature of this particular variation. It is a change in mole numbers, total volume and total entropy by the same proportions, or simply a shift in the boundary between the two subsystems. There is no change in any intensive property, or in any extensive property of the entire system. Therefore this variation is actually not a variation in any measurable, physical sense.

$n-1$ independent intensive variables can always be
found for a stable single phase system. For example, the temperature, pressure and mole fractions of all but one of the components could be the independent intensive variables. Therefore the subsystem α has r-1 independent variations which do not change N^∞. If S, V and N of the entire system (α plus β) are held constant, then all of these n-1 variations cause an increase in U, since the system is stable. dZ₁ through dZₙ₋₁ correspond to linear combinations of these variations. Thus the coefficients of dZ₁ through dZₙ₋₁ (ψ⁽₀⁾ through ψ⁽ⁿ⁻²⁾ₙ₋₁) must be positive in a stable phase. The "limit of intrinsic stability" is reached when any ψ⁽ᵏ⁻¹⁾ (except ψ⁽ⁿ⁻¹⁾) becomes zero.

The ratio of Δk to Δk₋₁, if reduced k-1 times using the Legendre Transform methods discussed earlier, is shown by Eq. (34) to be equal to ψ⁽ᵏ⁻¹⁾. If the ratio of Δk to Δk₋₁ is reduced only k-2 times, it is shown equal to a form involving only derivatives of ψ⁽ᵏ⁻²⁾.

\[
ψ⁽ᵏ⁻¹⁾ = \frac{Δk}{Δk₋₁} = \frac{ψ⁽ᵏ⁻¹⁾_{ₖ₋₁} \ψ⁽ᵏ⁻²⁾_{ₖ₋₁} - ψ⁽ᵏ⁻¹⁾_{ₖ} \ψ⁽ᵏ⁻²⁾_{ₖ}}{ψ⁽ᵏ⁻²⁾_{ₖ₋₁} \ψ⁽ᵏ⁻²⁾_{ₖ₋₁} - ψ⁽ᵏ⁻²⁾_{ₖ₋₁} \ψ⁽ᵏ⁻²⁾_{ₖ₋₁}}
\]

(49)

Since both ψ⁽ᵏ⁻¹⁾ and ψ⁽ᵏ⁻²⁾ are positive in a stable phase, ψ⁽ᵏ⁻²⁾ must be positive as well. ψ⁽ᵏ⁻²⁾ would be the coefficient of dZₘ₋₁ if the ordering of xₘ₋₁ and xₖ was reversed. Therefore ψ⁽ᵏ⁻²⁾ is assumed to not increase without limit as ψ⁽ᵏ⁻²⁾ₙ₋₁ approaches zero. If ψ⁽ᵏ⁻²⁾ₙ₋₁ is
also assumed not to be zero, then Eq. (52) shows that
\( \psi_{k-k}^{(k-1)} \) becomes zero at the same time or before \( \psi_{k-k}^{(k-2)} \). Both of these assumptions are used throughout the rest of this thesis.

Since \( \psi_{k-k}^{(k-1)} \) becomes zero at the same time or before \( \psi_{k-k}^{(k-2)} \), \( \psi_{n-n}^{(n-2)} \) becomes zero at the same time or before any other \( \psi_{k-k}^{(k-1)} \) (except \( \psi_{n-n}^{(n-1)} \)). Therefore the final criterion of intrinsic stability is

\[
\psi_{n-n}^{(n-2)} > 0 \tag{50}
\]

Rewriting Eq. (50) in terms of \( x_+ \)s and \( \ell_+ \)s

\[
\left( \frac{\delta \ell_{n-1}}{\delta x_{n-1}} \right) \ell_1, \ell_2, \ldots, \ell_{n-2}, x_n > 0 \tag{51}
\]

Using Eq. (34), Eq. (50) is equivalent to

\[ D_{n-1} > 0 \tag{52} \]

Using Eqs. (34) and (28), Eq. (50) is equivalent to

\[
\begin{vmatrix}
\psi_{22} & \psi_{23} & \cdots & \psi_{2,n-1} \\
\psi_{32} & \psi_{33} & \cdots & \psi_{3,n-1} \\
\vdots & \vdots & \ddots & \vdots \\
\psi_{n-1,2} & \psi_{n-1,3} & \cdots & \psi_{n-1,n-1}
\end{vmatrix} > 0 \tag{53}
\]

\( \psi_{n-n}^{(n-2)} \) (the ratio of \( D_{n-1} \) to \( D_{n-2} \)) may be expressed as the ratio of two determinants whose terms are derivatives of \( \psi^{(i)} \). Using Eq. (50)

\[ L_i > 0 \tag{54} \]

where \( L_i \) is defined for any given \( n \) and \( i \).
Eqs. (52) and (53) are Eq. (54) with i=0 and i=1, respectively.

If \((x_1, x_2 \ldots x_n) = (S, N_1, N_2 \ldots N_m, V)\) and if \(i=0\), then \(\psi^{(i)} = U\) and Eqs. (54) and (55) become

\[
\begin{vmatrix}
  U_{SS} & U_{SN_1} & U_{SN_2} & \cdots & U_{SN_m} \\
  U_{N_1S} & U_{N_1N_1} & U_{N_1N_2} & \cdots & U_{N_1N_m} \\
  U_{N_2S} & U_{N_2N_1} & U_{N_2N_2} & \cdots & U_{N_2N_m} \\
  \vdots & \vdots & \vdots & \ddots & \vdots \\
  U_{N_mS} & U_{N_mN_1} & U_{N_mN_2} & \cdots & U_{N_mN_m}
\end{vmatrix} > 0
\]

(56)

Derivatives are defined as before:

\[
U_{NiN_j} = \left( \frac{\delta U}{\delta N_i \delta N_j} \right)_{T, P, N_k \neq i, j}
\]

Eq. (56) is a criterion of intrinsic stability stated by Gibbs[2].

The example of a system containing a pure material is again employed. Values of \(x_i\) are again defined as in Eqs. (9), (10) and (11). Eqs. (52), (50) and (51) then become

\[
\begin{vmatrix}
  U_{SS} & U_{SV} \\
  U_{VS} & U_{VV}
\end{vmatrix} > 0
\]

(57)

\[
A_{VV} > 0
\]

(58)
Eqs. (57), (58) and (59) are equivalent forms of the criterion of intrinsic stability for a system containing a pure material. Forms which arise from different orderings of $x_1$, $x_2$, and $x_3$, as well as multicomponent systems are considered in Section III.
II. DERIVATION OF CRITICAL POINT CRITERIA

The "limit of intrinsic stability" is reached when Eq. (50) is first violated,  
\[ \Psi_{n-1}^{(n-2)} = 0 \]  
(60)  
or equivalently, when Eq. (51) is first violated  
\[ \left( \frac{\partial \mathcal{L}_{n-1}}{\partial x_{n-1}} \right) = 0 \]  
(61)  
or when Eq. (54) is first violated (for any i)  
\[ L_i = 0 \]  
(62)  
The locus of the points which satisfy Eq. (60), (61) or (62) is called the "spinoidal curve." In general, when a system reaches the spinoidal curve, it becomes intrinsically unstable and spontaneously separates into two (or more) phases. This is demonstrated below.

Consider a system which is being held at constant \( \xi \), through \( \xi_{n-2} \) and \( x_n \). In a stable phase, Eq. (51) (or equivalently, Eq. (50)) is true. In other words, \( U \) increases for all small variations at constant \( S, V \) and \( N_i \). For certain values of \( \xi \), through \( \xi_{n-2} \), the locus of points formed by varying \( x_{n-1} \) will intersect the spinoidal curve, where Eq. (60) becomes true.

Eq. (50) was based on the assumption that second order terms would be sufficient to determine whether \( U \) would be negative for some variation or positive for all variations. This assumption is not valid on the spinoidal curve, since
Eq. (50) predicts $U$ is non-negative for all variations and is zero for at least one variation. Therefore an equation analogous to Eq. (50), but including third (and possibly fourth) order terms is necessary to examine the stability of a system on the spinoidal curve. Such an equation is derived by examining again the two subsystems, $\alpha$ and $\beta$.

A variation possible to the system described above is holding $\xi_i$ through $\xi_{n-2}$ and $x_n$ constant in each of the two subsystems and varying the fraction of the total $x_{n-1}$ allocated to each. Assume that the subsystem $\alpha$ increases in $x_{n-1}$ and that $\beta$ decreases. If $\psi_{n-1 \ n-1 \ n-1}^{(n-2)}$ is positive then $\psi_{n-1 \ n-1}^{(n-2) \alpha}$ will become positive and $\psi_{n-1 \ n-1}^{(n-2) \beta}$ will become negative. $\alpha$ will now be in a stable region, but $\beta$ will be unstable. At this point, an additional transfer of $x_{n-1}$ from $\beta$ to $\alpha$ will take place. In effect, the subsystem $\beta$ is splitting into two smaller subsystems, one of which is becoming part of $\alpha$. Since $\beta$ is in an unstable region, this will result in a decrease in $U$, the total internal energy, as well as driving $\beta$ further into the unstable region. Thus this process is spontaneous and will continue until equilibrium is reached, with at least two distinct phases formed.

If $\psi_{n-1 \ n-1 \ n-1}^{(n-1)}$ is negative then the above argument still applies, with the roles of $\alpha$ and $\beta$ reversed. For a system to be stable and to lie on the spinoidal curve,
\( \psi_{n-1}^{(n-2)} \) must be zero

\[
\psi_{n-1}^{(n-2)} = 0 \tag{63}
\]

Rewriting Eq. (63) in terms of \( x_i \)'s and \( \xi_i \)'s

\[
\left[ \frac{\partial^n \xi_{n-1}}{\partial x_{n-1}^n} \right] \xi_1, \xi_2 \ldots \xi_{n-2}, x_n = 0 \tag{64}
\]

For a system on the spinoidal curve to be stable, in addition to Eq. (63) (or (64)), \( \psi_{n-1}^{(n-2)} \) must be positive

\[
\psi_{n-1}^{(n-2)} > 0 \tag{65}
\]

If Eq. (65) is not satisfied, then the lowest even order non vanishing derivative of \( \psi^{(n-2)} \) with respect to \( x_{n-1} \) must be positive, and all lower order derivatives must be zero. This condition is necessary to insure that after a small variation inside the entire system, all subsystems are still stable.

Varying \( x_{n-1} \) will allow a system to touch the spinoidal curve and remain stable only when particular values of \( \xi_i \) through \( \xi_{n-2} \) are held constant. If slightly different values are chosen then the system will either pass through the unstable region or else miss the spinoidal curve entirely. Thus the stable points on the spinoidal curve lie on the boundary between the unstable region (where two phases are formed) and a region where all changes are continuous. These points are called "critical points."

For example, a pure material may have \( x_1, x_2 \), and \( x_3 \),
defined as in Eqs. (9), (10) and (11). Then the conditions of the critical point (Eqs. (60) and (63)) are

\[ A_{vv} = 0 \]  \hspace{1cm} (66)
\[ A_{vvv} = 0 \]  \hspace{1cm} (67)

or equivalently, Eqs. (61) and (64)

\[ \left( \frac{\partial^2 P}{\partial V^2} \right)_{T,N} = 0 \]  \hspace{1cm} (68)
\[ \left( \frac{\partial^3 P}{\partial V^3} \right)_{T,N} = 0 \]  \hspace{1cm} (69)

Other forms of the conditions of the critical point for pure materials, as well as examples using multicomponent systems are presented in Section IV.

The section below derives a general form of Eq. (64), analogous to Eq. (57). The determinant \( M_i \) is defined as the determinant \( L_i \) (Eq. (58)) with the last row changed. The \( j^{th} \) term in the last row becomes the derivative of \( L_i \) with respect to \( x_{i+j} \).

\[
\begin{vmatrix}
\psi_{i+1}^{(i)} & \psi_{i+2}^{(i)} & \psi_{i+3}^{(i)} & \cdots & \psi_{i+n-1}^{(i)} \\
\psi_{i+2}^{(i)} & \psi_{i+3}^{(i)} & \psi_{i+4}^{(i)} & \cdots & \psi_{i+n-2}^{(i)} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\psi_{i+n-2}^{(i)} & \psi_{i+n-3}^{(i)} & \psi_{i+n-4}^{(i)} & \cdots & \psi_{i+1}^{(i)} \\
\frac{\partial L_i}{\partial x_{i+1}} & \frac{\partial L_i}{\partial x_{i+2}} & \frac{\partial L_i}{\partial x_{i+3}} & \cdots & \frac{\partial L_i}{\partial x_{n-1}}
\end{vmatrix}
\]

(70)

The first determinant considered will be \( M_0 \).
The same sequence of operations used to produce Eq. (25) is applied to $M_o$. Each element of the first column is divided by $y_{ij}$, while the entire determinant is multiplied by the same quantity. Then, for all $j$ from 2 to $n-1$, the first column is multiplied by $y_{ij}$ and subtracted from the $j^{th}$ column.

\[
M_o = \frac{\begin{vmatrix}
Y_{11} & Y_{12} & Y_{13} & \cdots & Y_{1n-1} \\
Y_{21} & Y_{22} & Y_{23} & \cdots & Y_{2n-1} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
Y_{n-1,1} & Y_{n-1,2} & Y_{n-1,3} & \cdots & Y_{n-1,n-1} \\
\frac{\partial L_o}{\partial x_1} & \frac{\partial L_o}{\partial x_2} & \frac{\partial L_o}{\partial x_3} & \cdots & \frac{\partial L_o}{\partial x_{n-1}} \\
\end{vmatrix}}{y_{11}}
\]

(71)

$\dagger_j L_o$ is defined (for $j$ between 2 and $n-1$) as the $j^{th}$ term in the last row of the determinant in Eq. (72)

\[
\dagger_j L_o = \frac{\partial L_o}{\partial x_j} \frac{\partial y_{ij}}{\partial x_1} \frac{\partial L_o}{\partial x_1}
\]

(73)

Defining $\#[\]$ as the derivative operator in brackets, below

\[
\#[\] = \left[\frac{\partial}{\partial x_j} \frac{\partial y_{ij}}{\partial x_1} \frac{\partial}{\partial x_1}\right]
\]

(74)

Eq. (73) is rewritten
Multiplying and dividing $L_0$ by $y_{11}$,
\[ t_j L_0 = [\#] \left( \frac{L_0}{y_{11}} \right) \]  
(76)

Expanding Eq. (76)
\[ t_j L_0 = y_{11}, [\#] \left( \frac{L_0}{y_{11}} \right) + \left( \frac{L_0}{y_{11}} \right) [\#] y_{11} \]  
(77)

If Eq. (77) is considered only on the spinoidal curve, $L_0$ is equal to zero
\[ t_j L_0 = y_{11}, [\#] \left( \frac{L_0}{y_{11}} \right) \]  
(78)

Repeating the procedure used above to generate Eq. (72) on $L_0$ over $y_{11}$
\[
\begin{pmatrix}
1 & 0 & \cdots & 0 \\
y_{21} & y_{22} - y_{12} y_{12} & \cdots & y_{2, n-1} - y_{12} y_{1, n-1} \\
y_{11} & y_{11} & \cdots & y_{1, n-1} \\
\vdots & \vdots & \ddots & \vdots \\
y_{n-1, 1} & y_{n-1, 2} - y_{1, n-1} y_{1, n-1} & \cdots & y_{n-1, n-1} - y_{1, n-1} y_{1, n-1} \\
y_{11} & y_{11} & \cdots & y_{1, n-1}
\end{pmatrix} \]  
(79)

A derivative operator applied to a determinant evaluates as the sum over all $k$ of the determinant with the derivative operator applied to each element of the $k^{th}$ row. Simplifying Eq. (79) and substituting it into Eq. (76)
Evaluating the $m$th element of the $k$th row in the determinant in Eq. (80)

\[
\left[ \begin{array}{cccc}
    y_{2,2} - y_{1,2} & y_{1,2} & \cdots & y_{n-1,2} - y_{1,2} \\
    \vdots & \ddots & \ddots & \vdots \\
    y_{k-1,2} - y_{1,k-1} & y_{1,k-1} & \cdots & y_{n-1,k-1} - y_{1,k-1} \\
    y_{k+1,2} - y_{1,k+1} & y_{1,k+1} & \cdots & y_{n-1,k+1} - y_{1,k+1} \\
    \vdots & \ddots & \ddots & \vdots \\
    y_{n-1,2} - y_{1,n-1} & y_{1,n-1} & \cdots & y_{n-1,n-1} - y_{1,n-1} \\
\end{array} \right] \]

\[
\mathfrak{y}_{ij} \sum_{k=2}^{n-1} \left[ \frac{\partial}{\partial x_j} \left( y_{k,2} - y_{1,k} \right) \right] \cdots \left[ \frac{\partial}{\partial x_j} \left( y_{k,n-1} - y_{1,k} \right) \right] \frac{y_{1,k}}{y_{11}} \tag{80}
\]

Rewriting Eq. (81)

\[
\left[ \frac{\partial}{\partial x_j} \left( y_{k,m} - y_{1,k} y_{1,m} \right) \right] = \frac{\delta}{\delta x_j} \left( y_{k,m} - y_{1,k} y_{1,m} \right) - y_{1,j} \frac{\delta}{\delta x_j} \left( y_{k,m} - y_{1,k} y_{1,m} \right) \frac{y_{1,k}}{y_{11}} \frac{y_{1,m}}{y_{12}} \frac{y_{1,k} y_{1,m}}{y_{13}} \frac{y_{1,j}}{y_{11}^3} \tag{81}
\]

Using Eq. (C-29) (from Appendix C), the RHS of Eq. (82) is equal to $\Psi_{km,j}^{-3}$, a third derivative of $\Psi$, the Legendre Transform of $y$ from $x$, space to $\xi$, space.

\[
\left[ \frac{\partial}{\partial x_j} \left( y_{k,m} - y_{1,k} y_{1,m} \right) \right] = \Psi_{km,j}^{-3} \frac{\delta \Psi_{km}}{\delta x_j} \tag{83}
\]
The row involving the \([\#]\) operator in each of the determinants in Eq. (80) is simplified using Eq. (83). All of the other terms in the determinants are shown equal to second derivatives of \(\Psi\), using Eq. (C-25) (from Appendix C). The simplified form of Eq. (80) is

\[
\hat{t}_j \mathcal{L}_2 = \sum_{k=2}^{n-1} \left( \frac{\partial \Psi_{k,2}}{\partial x_j} \cdots \frac{\partial \Psi_{n-1,k}}{\partial x_j} \right) \]

(Eq. 84)

The RHS of Eq. (84) is the formula for the derivative of the determinant \(\mathcal{L}_o\) with respect to \(x_j\)

\[
\frac{\hat{t}_j \mathcal{L}_2}{\mathcal{L}_o} = \frac{\partial \mathcal{L}_o}{\partial x_j}
\]

(Eq. 85)

The last row of the determinant in Eq. (72) is simplified using Eq. (85), and the rest of the terms are again simplified using Eq. (C-25). Eq. (72) becomes

\[
\mathcal{M}_o = \left| \begin{array}{cccc}
\Psi_{2,2} & \cdots & \Psi_{2,n-1} \\
\vdots & \ddots & \ddots \\
\Psi_{n-2,2} & \cdots & \Psi_{n-2,n-1} \\
\frac{\partial \mathcal{L}_o}{\partial x_1} & \cdots & \frac{\partial \mathcal{L}_o}{\partial x_{n-1}} \\
\end{array} \right|
\]

(Eq. 86)

All the terms in the determinant in Eq. (86), except for
the last row, are identical to the terms in $L_i$. For all $j$, the $j^{th}$ term in the last row is a derivative of $L_i$ with respect to $x_{l+j}$. Therefore, by Eq. (70), the RHS of Eq. (86) is equal to $M_i$. Multiplying by $y''$, 

$$M_0 = y'' M_i$$  (87)

The procedure used to derive Eq. (87), starting with $M_0$, could start with $M_L$. The result is 

$$M_i = y''_{i+1} M_{i+1}$$  (88)

Repeatedly applying Eq. (88) demonstrates that if $M_j$ is equal to zero, then $M_i$ is equal to zero, for all $i<j$. By Eq. (70), $\Psi_{n-1}^{(n-2)}$ is $M_{n-2}$. Eq. (63) shows that $\Psi_{n-1}^{(n-2)}$ is zero at critical points. Therefore an alternate form of the second equation for critical points is (for $i<n-1$)

$$M_i = 0$$  (89)

Eqs. (62) and (89) (or (60) and (63), or (61) and (64)) define the critical points of any substance.

If the $x_i$'s are defined as in Eqs. (9), (10) and (11), and $i$ is chosen to be 2, then the Legendre Transform in Eqs. (55) and (70) is $G$. The conditions of the critical point given by Eqs. (62) and (89) then become

$$L_2 = 0$$  (90)

$$M_2 = 0$$  (91)

where
Eqs. (90) through (93) are conditions of the critical point stated by Gibbs[3].

\[ L_2 = \begin{vmatrix}
G_{N_1 N_1} & G_{N_1 N_2} & \cdots & G_{N_1 N_{m-1}} \\
G_{N_2 N_1} & G_{N_2 N_2} & \cdots & G_{N_2 N_{m-1}} \\
\vdots & \vdots & \ddots & \vdots \\
G_{N_{m-1} N_1} & G_{N_{m-1} N_2} & \cdots & G_{N_{m-1} N_{m-1}} \\
\end{vmatrix} \tag{92} \]

\[ M_2 = \begin{vmatrix}
G_{N_1 N_1} & G_{N_1 N_2} & \cdots & G_{N_1 N_{m-1}} \\
G_{N_2 N_1} & G_{N_2 N_2} & \cdots & G_{N_2 N_{m-1}} \\
\vdots & \vdots & \ddots & \vdots \\
G_{N_{m-2} N_1} & G_{N_{m-2} N_2} & \cdots & G_{N_{m-2} N_{m-1}} \\
\end{vmatrix} \tag{93} \]

\[ \frac{\partial L_2}{\partial N_1} \quad \frac{\partial L_2}{\partial N_2} \quad \cdots \quad \frac{\partial L_2}{\partial N_{m-1}} \]
III. ONE, TWO AND THREE COMPONENT SYSTEMS

In Sections I and II formulas were derived to predict limits of intrinsic stability and critical points for a general m-component system. This section will consider the special cases of pure materials and of binary and ternary systems in more detail.

Eq. (46) gives a criterion of intrinsic stability for a pure material. The leading coefficient of the last term, $\psi_{33}^{(2)}$, was shown to be equal to zero. Therefore a pure material is stable if the leading coefficients of the first two terms are positive:

$$\psi_{11}^{(0)} > 0$$  \hspace{1cm} (94)
$$\psi_{22}^{(1)} > 0$$  \hspace{1cm} (95)

Since the leading coefficient of the second term was shown to become zero before or at the same time as that of the first, Eq. (95) is the only criterion that needs to be examined to determine the limit of stability. However, Eqs. (94) and (95) each contain useful information.

The specific form that Eq. (94) takes is dependent on the ordering of $x_1, x_2$ and $x_3$. If $x_1$ is defined as $S$, then Eq. (94) becomes

$$U_{55} > 0$$  \hspace{1cm} (96)

Since $U_5 = T$, Eq. (96) is equivalent to

$$\frac{\delta T}{\delta S} \varphi_{\text{N},N} > 0$$  \hspace{1cm} (97)
Defining $C_v$, the heat capacity at constant volume

$$C_v = T \frac{\delta S}{\delta T} \bigg|_V = \frac{T \delta S}{N \delta T} \bigg|_{V,N}$$

(98)

Substituting Eq. (98) into Eq. (97)

$$T > 0$$

(99)

Since $T$ and $N$ are always positive, Eq. (99) reduces to

$$C_v > 0$$

(100)

Eq. (94), from which Eq. (100) was derived, is valid for multicomponent systems as well as pure materials. Therefore Eq. (100) states that for an intrinsically stable substance, the heat capacity at constant volume is always positive. Eq. (100) is termed the "condition of thermal stability."

Other forms of Eq. (94) may be obtained if $x_1$, $x_2$ and $x_3$ are ordered differently. Table 1 lists all of the possible orderings of $S$, $V$ and $N$, each with the corresponding form of Eq. (94). All forms of Eq. (94) must be satisfied in any stable equilibrium state. Since the limit of intrinsic stability is reached when Eq. (95) is violated, and all forms of Eq. (94) are automatically satisfied up to that point, the label "condition of thermal stability" is herein applied to all of the forms in Table 1, not just the first.

Eq. (95) is that condition of intrinsic stability (for a pure material) which is violated first. If $(x_1, x_2, x_3)$
**TABLE I — CONDITIONS OF THERMAL STABILITY**

<table>
<thead>
<tr>
<th>ORDERING OF ((x_1, x_2, x_3))</th>
<th>(\Psi_{ii}^{(0)} &gt; 0) FORM</th>
<th>DERIVATIVE FORM</th>
</tr>
</thead>
<tbody>
<tr>
<td>((S, V, N)) or ((S, N, V))</td>
<td>(U_{ss} &gt; 0) or (U_{sv} &gt; 0)</td>
<td>(\frac{\partial T}{\partial S}</td>
</tr>
<tr>
<td>((V, S, N)) or ((V, N, S))</td>
<td>(U_{vv} &gt; 0) or (U_{vn} &gt; 0)</td>
<td>(\frac{\partial \mu}{\partial N}</td>
</tr>
<tr>
<td>((N, S, V)) or ((N, V, S))</td>
<td>(U_{nn} &gt; 0) or (U_{vn} &gt; 0)</td>
<td>(\frac{\partial P}{\partial V}</td>
</tr>
</tbody>
</table>

**TABLE II — CONDITIONS OF MECHANICAL STABILITY**

<table>
<thead>
<tr>
<th>ORDERING OF ((x_1, x_2, x_3))</th>
<th>(\Psi_{ii}^{(1)} &gt; 0) FORM</th>
<th>DERIVATIVE FORM</th>
</tr>
</thead>
<tbody>
<tr>
<td>((S, V, N))</td>
<td>(A_{VV} &gt; 0)</td>
<td>(\frac{\partial P}{\partial V}</td>
</tr>
<tr>
<td>((S, N, V))</td>
<td>(A_{NN} &gt; 0)</td>
<td>(\frac{\partial \mu}{\partial N}</td>
</tr>
<tr>
<td>((V, S, N))</td>
<td>(H_{ss} &gt; 0)</td>
<td>(\frac{\partial T}{\partial S}</td>
</tr>
<tr>
<td>((V, N, S))</td>
<td>(H_{nn} &gt; 0)</td>
<td>(\frac{\partial \mu}{\partial N}</td>
</tr>
<tr>
<td>((N, S, V))</td>
<td></td>
<td>(\frac{\partial \mu}{\partial V}</td>
</tr>
<tr>
<td>((N, V, S))</td>
<td></td>
<td>(\frac{\partial P}{\partial V}</td>
</tr>
</tbody>
</table>
are ordered \((S, V, N)\), then Eq. (95) becomes Eq. (58) (or equivalently, (59)). Multiplying each side of Eq. (59) by \(N\), the total moles, yields an expression involving only intensive properties:

\[
\frac{\delta P}{\delta V}/T < 0 \tag{101}
\]

Eq. (101) is termed the "condition of mechanical stability."

Other forms of Eq. (95) are possible, and are listed in Table 2. Since any of the forms in Table 2 is both necessary and sufficient to establish the intrinsic stability of a pure material, they must all be equivalent. Therefore the term "condition of mechanical stability" is herein used as a label for any of the forms of Eq. (95).

If \((x_1, x_2, x_3)\) are ordered as \((V, S, N)\) then

\[
\Psi'' = H = U - (-P)V
\]

and Eq. (95) becomes

\[
H_{SS} > 0 \tag{102}
\]

Since \(H = T\), Eq. (102) is equivalent to

\[
\left|\frac{\delta T}{\delta S}\right|_{P, N} > 0 \tag{103}
\]

Defining \(C_p\), the heat capacity at constant pressure

\[
C_p = T \left(\frac{\delta S}{\delta T}\right)_P = T \left(\frac{\delta S}{\delta T}\right)_{P, N} \tag{104}
\]

Substituting Eq. (104) into Eq. (103)

\[
\frac{T}{NC_p} > 0 \tag{105}
\]

Since \(T\) and \(N\) are always positive, Eq. (105) reduces to
Eq. (106) shows that the heat capacity at constant pressure is always positive for a stable equilibrium state. Eq. (105) also shows that as a pure material approaches its limit of intrinsic stability (spinoidal curve), \( C_p \) increases without limit. Eqs. (101) and (105) are equivalent forms of the criterion of mechanical stability even though one involves a heat capacity and the other uses only P-V-T properties.

Eqs. (60) and (63), which determine critical points, are easily evaluated for a pure material. Rewriting the critical point conditions for \( n=3 \)

\[ \psi_{22}^{(i)} = 0 \]  
\[ \psi_{222}^{(i)} = 0 \]

If \( (x_1, x_2, x_3) \) are again defined as \( (S, V, N) \) then Eqs. (107) and (108) become Eqs. (66) and (67), or, in the derivative form, Eqs. (68) and (69). Each side of Eqs. (68) and (69) is multiplied by \( N \), the total moles

\[ \frac{\partial P}{\partial V}/T = 0 \]  
\[ \frac{\partial^2 P}{\partial V^2}/T = 0 \]

Eq. (109) defines the spinoidal curve, the locus of points which are on the limit of stability. Eq. (109) is simply Eq. (101) with the inequality \( (<) \) changed to an equality \( (=) \). Other equations which define the spinoidal
curve are obtained from the last column of Table 2, by changing an inequality to an equality. For example, using the second entry in the last column of Table 2, the spinoidal curve is defined by

\[
\frac{\partial \mu}{\partial N_{T,V}} = 0
\]  

(111)

Critical points are defined as points on the spinoidal curve which are stable with regard to all possible small variations. Eq. (110) is an equation which must be satisfied to insure intrinsic stability for any point on the spinoidal curve. It is obtained from Eq. (109) by changing the first derivative to a second derivative. This procedure may be used on any equation which defines the spinoidal curve and is of the form of Eq. (61). For example, the first derivative in Eq. (111) is changed to a second derivative

\[
\frac{\partial^2 \mu}{\partial N^2_{T,V}} = 0
\]  

(112)

Eqs. (111) and (112) define the critical points in a pure material, and may be used in place of Eqs. (109) and (110).

The significance of Eqs. (101), (109) and (110) is apparent when examining isotherms plotted on a graph of pressure versus specific volume. Such a plot, for a hypothetical material with a critical pressure \(P_c\) of 26 atm, a critical temperature \(T_c\) of 500\(^{\circ}\)K and a critical volume \(V_c\) of .4 liters/g-mole, is presented in Figure 1.
FIGURE I — P-V PLOT OF A HYPOTHETICAL PURE MATERIAL

- ISOTHERMS
- SPINODAL CURVE
- CRITICAL POINT
- UNSTABLE REGION
- METASTABLE REGION
The material is assumed to follow the Redlich-Kwong equation-of-state, which is discussed in Section IV. The isotherms drawn inside the metastable region are valid only if no nucleation surfaces are available. If such surfaces exist, or if the substance is brought to the spinoidal curve, the material will separate into two phases, each on a boundary between the metastable and stable regions. The area below the critical temperature (500°K) and to the left of the critical point is the liquid region; the corresponding area to the right of the critical point is the vapor region.

Three isotherms are drawn on Figure 1. The isotherm at 600°K always has a negative slope. Eq. (101) is therefore always satisfied and the material remains in a stable, single phase region at all times. The 400°K isotherm reaches zero slope (the spinoidal curve) at two points. Even though the equation-of-state predicts an isotherm running through the unstable region, the slope is positive and the material cannot exist as a single phase. If the temperature is low enough, e.g. 400°K, the metastable liquid may exist under a negative pressure. The pressure of a gas is always positive. The critical isotherm (500°K) touches the spinoidal curve at one point. Since both the slope and the curvature are zero, Eqs. (109) and (110) are satisfied.
Figure 1 shows only the liquid-gas transition. Other transitions, for instance solid-liquid, will show identical effects except for not having a critical point. This thesis is mainly concerned with superheated liquids (liquids in the metastable region) and with liquid-gas critical points. These topics will be considered further in Section IV.

**BINARY SYSTEMS**

In a binary system Eqs. (94) and (95) are still satisfied by all stable equilibrium states. However, Eq. (50) is rewritten with $n=4$ to obtain the condition of intrinsic stability which is violated first:

$$\Psi_{33}^{(2)} > 0 \quad (113)$$

If $(x_1, x_2, x_3, x_4)$ are again ordered $(S, V, N_a, N_b)$ then $\Psi^{(2)} = G$ and Eq. (113) becomes

$$G_{aa} > 0 \quad (114)$$

or equivalently,

$$\left( \frac{\partial \mu_a}{\partial N_a} \right)_{T,P,N_b} > 0 \quad (115)$$

Rewriting Eq. (115) in terms of $x_a$, the mole fraction of component $a$,

$$\left( \frac{\partial \mu_a}{\partial x_a} \right)_{T,P} > 0 \quad (116)$$

Eq. (116) is termed "the condition of diffusional stability." Other orderings of $(x_1, x_2, x_3, x_4)$ will yield other forms of Eq. (113). These forms are listed in
TABLE III — CONDITIONS OF DIFFUSIONAL STABILITY

<table>
<thead>
<tr>
<th>ORDERING ($x_1, x_2, x_3, x_4$)</th>
<th>$\psi^{(2)}_{33} &gt; 0$ FORM</th>
<th>DERIVATIVE FORM</th>
</tr>
</thead>
<tbody>
<tr>
<td>or $(S, V, Na, N_b)$</td>
<td>$G_{aa} &gt; 0$</td>
<td>$\left(\frac{\partial \mu_a}{\partial Na}\right)_{T, P, N_b} &gt; 0$</td>
</tr>
<tr>
<td>or $(V, S, Na, N_b)$</td>
<td>$G_{bb} &gt; 0$</td>
<td>$\left(\frac{\partial \mu_b}{\partial Na}\right)_{T, P, N_a} &gt; 0$</td>
</tr>
<tr>
<td>or $(S, Na, V, N_b)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_b}{\partial V}\right)_{T, \mu_b, N_a} &lt; 0$</td>
</tr>
<tr>
<td>or $(N_a, S, V, N_b)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_b}{\partial V}\right)_{T, \mu_b, N_a} &gt; 0$</td>
</tr>
<tr>
<td>or $(S, N_b, V, Na)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_b}{\partial Na}\right)_{T, \mu_b, V} &gt; 0$</td>
</tr>
<tr>
<td>or $(N_b, S, V, Na)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_a}{\partial S}\right)_{P, \mu_a, N_b} &gt; 0$</td>
</tr>
<tr>
<td>or $(V, Na, S, N_b)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_a}{\partial N_b}\right)_{P, \mu_b, S} &gt; 0$</td>
</tr>
<tr>
<td>or $(N_a, V, N_b, S)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_a}{\partial N_b}\right)_{P, \mu_a, S} &gt; 0$</td>
</tr>
<tr>
<td>or $(V, Na, N_b, S)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_a}{\partial Na}\right)_{P, \mu_b, S} &gt; 0$</td>
</tr>
<tr>
<td>or $(N_a, V, N_b, S)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_a}{\partial N_b}\right)_{P, \mu_b, S} &gt; 0$</td>
</tr>
<tr>
<td>or $(V, N_b, Na, S)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_a}{\partial Na}\right)_{P, \mu_b, S} &gt; 0$</td>
</tr>
<tr>
<td>or $(N_b, V, Na, S)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_a}{\partial Na}\right)_{P, \mu_b, S} &gt; 0$</td>
</tr>
<tr>
<td>or $(Na, N_b, S, V)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_a}{\partial Na}\right)_{P, \mu_b, S} &gt; 0$</td>
</tr>
<tr>
<td>or $(N_b, Na, V, S)$</td>
<td></td>
<td>$\left(\frac{\partial \mu_a}{\partial Na}\right)_{P, \mu_b, S} &gt; 0$</td>
</tr>
</tbody>
</table>
Table 3. Since any form is both necessary and sufficient to determine the stability of a binary mixture, all forms are given the label "condition of diffusional stability."

Eq. (116) is often not the most convenient form for applications to real materials. Usually one desires to use P-V-T data. This data may be in the form of a pressure explicit equation-of-state. In this case, the Helmholtz Free Energy is particularly useful, as it is a function of temperature, total volume, and mole numbers.

Eq. (53) is of the required form. Using the same ordering as above (Eqs. (9), (10) and (11)), Eq. (53) becomes for $n=4$

$$\begin{vmatrix} A_{vv} & A_{va} \\ A_{av} & A_{aa} \end{vmatrix} > 0$$

or, in the expanded form,

$$A_{vv} A_{aa} - A_{va}^2 > 0$$

Eq. (118) may be evaluated using only a pressure explicit equation-of-state. $A_v = -P$, and thus $A_{vv}$ and $A_{va}$ are directly computable. Appendix D derives a formula for evaluating $A_{aa}$, Eq. (D-9).

The conditions of the critical point for a binary mixture are Eqs. (60) and (63), with $n=4$.

$$\psi_{33}^{(2)} = 0$$

$$\psi_{333}^{(2)} = 0$$

Eqs. (119) and (120) may be evaluated directly.
Alternately, conditions of stability may be derived from stability criteria, as was done with a pure material.

Eq. (116) is a condition of stability for a binary. Therefore the spinodal curve is defined as the locus of points where Eq. (116) is first violated.

\[ \left( \frac{\partial \mu_a}{\partial x_a} \right)_{T,P} = 0 \]  

(121)

For a binary on the spinodal curve to be stable, the second derivative of \( \mu_a \) with respect to \( x_a \) must be zero, as well as the first.

\[ \left( \frac{\partial^2 \mu_a}{\partial x_a^2} \right)_{T,P} = 0 \]  

(122)

Other forms of the conditions of the critical point may be obtained in the same fashion from the conditions of stability in Table 3, or directly from Eqs. (119) and (120).

The critical point conditions may also be expressed in Helmholtz Free Energy forms. Eqs. (62) and (89) become, for \( n=4 \) and \( i=1 \),

\[ L_i = 0 \]  

(123)

\[ M_i = 0 \]  

(124)

where

\[ L_i = \begin{vmatrix} A_{VV} & A_{VA} \\ A_{AV} & A_{AA} \end{vmatrix} \]  

(125)

\[ M_i = \begin{vmatrix} A_{VV} & A_{VA} \\ \frac{\delta L_i}{\delta V} & \frac{\delta L_i}{\delta N_a} \end{vmatrix} \]  

(126)
Expanding Eqs. (123) and (124)

\[ A_{vv} A_{aa} - A_{va}^2 = 0 \]  
(127)

\[ A_{vvv} A_{va} A_{aa} - 3 A_{vva} A_{va}^2 + 3 A_{vaa} A_{wa} A_{va} - A_{aaa} A_{iv}^2 = 0 \]  
(128)

Eqs. (127) and (128) may be evaluated using any pressure explicit equation-of-state.

The P–V–T diagram of a hypothetical binary mixture is presented in Figure 2. The binary is assumed to follow the Redlich–Kwong equation-of-state discussed in Section IV. The mixture composition is: 80% the hypothetical material in Figure 1, with \( T_c = 500^\circ K \), \( P_c = 26 \) atm and \( V_c = 0.4 \) liters/g-mole; and 20% a substance with \( T_c = 700 \) K, \( P_c = 20 \) atm and \( V_c = 0.7 \) liters/g-mole. The binary has \( T_c = 560^\circ K \), \( P_c = 30 \) atm and \( V_c = 0.45 \) liters/g-mole. The mixture values of \( T_c \) and \( V_c \) are approximately mole fraction averages of the pure component values. \( P_c \) of the mixture, however, is considerably larger than either of the pure component \( P_c \)'s.

A binary system becomes unstable more readily than a pure material. This is because for a mixture, Eq. (118) is violated before Eq. (58). The unstable region which would be calculated using Eq. (58) is contained within the unstable region indicated in Figure 2. This is verified by noting that the isotherms in Figure 2 always have a negative slope.

Different mixture compositions would produce P–V–T plots differing slightly from Figure 2. Therefore, for a
FIGURE II — P-V PLOT OF A HYPOTHETICAL BINARY MIXTURE

- ISOTHERMS
- SPINODAL CURVE
* CRITICAL POINT
UNSTABLE REGION
METASTABILE REGION
complete description of a mixture, a P-V-T-x_a plot is needed. P-V-T plots of mixtures with x_a's approaching 0 and 1 will approach the P-V-T plots of pure component b and pure component a, respectively.

TERNARY SYSTEMS

Ternary systems are analyzed by the same methods as pure and binary systems. The intrinsic stability criterion for a system with n=5 is, using Eq. (50),

$$\Psi^{(3)} > 0$$

(129)

Table 4 presents the fundamentally different derivative forms of Eq. (129). Each form involves taking a derivative while holding at least one $\mu_i$ constant. Therefore, these forms are difficult to evaluate and are not useful in calculations with real materials.

Again the $x_i$'s are defined as in Eqs. (9), (10) and (11). Then $\Psi=A$ and Eq. (54), an alternate form of the criterion of intrinsic stability becomes (for $i=1$

$$L_i > 0$$

(130)

where

$$L_i = \begin{vmatrix}
A_{vv} & A_{va} & A_{vb} \\
A_{av} & A_{aa} & A_{ab} \\
A_{bv} & A_{ba} & A_{bb}
\end{vmatrix}$$

(131)

$A_{vv}, A_{va}$ and $A_{vb}$ are evaluated directly from a pressure explicit equation-of-state. $A_{aa}, A_{bb}$ and $A_{ab}$ are evaluated using Eqs. (D-9) and (D-10), from Appendix D.
**TABLE IV — CONDITIONS OF STABILITY FOR A TERNARY SYSTEM**

<table>
<thead>
<tr>
<th>ORDERING OF ((x_1, x_2, x_3, x_4, x_5))</th>
<th>DERIVATIVE FORM</th>
</tr>
</thead>
<tbody>
<tr>
<td>((S, V, N_a, N_b, N_c))</td>
<td>(\frac{\partial \mu^b}{\partial N_b}) <em>T, P, \mu_a, N_c &gt;0</em></td>
</tr>
<tr>
<td>((S, N_a, N_b, V, N_c))</td>
<td>(\frac{\partial P}{\partial V}) <em>T, \mu_a, \mu_b, N_c &lt;0</em></td>
</tr>
<tr>
<td>((S, N_a, N_b, N_c, V))</td>
<td>(\frac{\partial \mu_c}{\partial N_c}) <em>T, \mu_a, \mu_b, V &gt;0</em></td>
</tr>
<tr>
<td>((V, N_a, N_b, S, N_c))</td>
<td>(\frac{\partial T}{\partial S}) <em>P, \mu_a, \mu_b, N_c &gt;0</em></td>
</tr>
<tr>
<td>((V, N_a, N_b, N_c, S))</td>
<td>(\frac{\partial \mu_s}{\partial N_s}) <em>P, \mu_a, \mu_b, S &gt;0</em></td>
</tr>
<tr>
<td>((N_a, N_b, N_c, S, V))</td>
<td>(\frac{\partial T}{\partial S}) <em>\mu_a, \mu_b, \mu_c, V &gt;0</em></td>
</tr>
<tr>
<td>((N_a, N_b, N_c, V, S))</td>
<td>(\frac{\partial P}{\partial V}) <em>\mu_a, \mu_b, \mu_c, S &lt;0</em></td>
</tr>
</tbody>
</table>

**NOTES:**

1. Any orderings of \(x_1, x_2, x_3, x_4\) and \(x_5\) which differ only in the arrangement of \(N_a, N_b\) and \(N_c\) and/or in the order of the first three variables are not considered different and are not listed separately above.

2. Since no third Legendre Transforms of \(U\) have common names or symbols, no condition of intrinsic stability in the \(\psi^{(3)}_{44} >0\) form is listed above.
Critical points are handled in the same way. Using the same ordering of \((x_1, x_2, x_3, x_4, x_5)\) and the same \(i(1)\), the critical point conditions of Eqs. (62) and (89) then become

\[
L_i = 0 \quad (132) \\
M_i = 0 \quad (133)
\]

where \(L_i\) is defined in Eq. (131) and

\[
M_i = \begin{vmatrix}
A_{vv} & A_{va} & A_{vb} \\
A_{av} & A_{aa} & A_{ab} \\
\frac{\delta L_i}{\delta N_a} & \frac{\delta L_i}{\delta N_a} & \frac{\delta L_i}{\delta N_b}
\end{vmatrix} \quad (134)
\]

A ternary P-V-T plot at a given \(x_a\) and \(x_b\) will appear approximately the same as Figure 2. The unstable region of a ternary is larger than that predicted by Eq. (113) (which is used in Figure 2), but is of a similar shape.

Systems with four or more components are analyzed by the same procedures used above. If the equations are always chosen to be in the Helmholtz Free Energy form, then they may be evaluated using only a pressure explicit equation-of-state. Although the number of terms in the second condition of the critical point increases considerably with an increase in the number of components, this is not a significant difficulty if a computer is used.

The equations derived above may be used to locate the spinoidal curve and critical points of any substance, given a suitable equation-of-state. Section IV demonstrates this.
using the equation of Redlich and Kwong (and also the Soave modification) with several pure materials and multicomponent systems.
IV. PREDICTING SUPERHEAT LIMITS AND CRITICAL POINTS

The equations derived in Sections I, II and III may be applied to real materials if the appropriate data is available. For example, equations involving the Gibbs Free Energy, such as Eq. (90), are readily evaluated using a volume explicit equation-of-state. Pressure explicit equations-of-state, as already noted, enable the evaluation of equations which use the Helmholtz Free Energy.

Perhaps the most used two parameter equation-of-state is that of Redlich and Kwong[4]:

$$P = \frac{RT - a'}{V - b} \left( \frac{V}{V + b} \right)$$

(135)

\(\bar{R}\) is the Gas Constant and \(a'\) and \(b\) are constants selected for each substance. Defining \(a\) as the ratio of \(a'\) to \(T^*\):

$$a = \frac{a'}{T^*}$$

(136)

Combining Eqs. (135) and (136)

$$P = \frac{RT - a}{V - b} \left( \frac{V}{V + b} \right)$$

(137)

Eq. (137) is the form of the Redlich-Kwong equation used in this thesis. The term "a" is a function of temperature. This permits modifying the equation-of-state by simply changing the temperature dependence of "a" (Eq. (136)) without changing Eq. (137).

The reduced temperature, \(T_r\), is defined as the ratio of the temperature to the critical temperature
The constant $a''$ is defined as the ratio of $a'$ to $T_c$:

$$a'' = \frac{a'}{T_c} \tag{139}$$

Combining Eqs. (136), (138) and (139):

$$a = \frac{a''}{T_r} \tag{140}$$

Substituting Eq. (140) into Eq. (137):

$$P = RT - \frac{a''}{V-b} \frac{T_c}{T_r} V(V+b) \tag{141}$$

The constants $a''$ and $b$ in Eq. (137) are evaluated using the critical point conditions for a pure material, Eqs. (109) and (110). At the critical point $T=T_c$, $T_r=1$ and $V=V_c$. Solving Eqs. (109), (110) and (137) simultaneously for $a''$, $b$ and $V_c$ yields:

$$a'' = \frac{a}{R} T_c^2 \frac{P}{P_c} \tag{142}$$

$$b = \frac{b}{RT_c} \tag{143}$$

$$V_c = \frac{RT_c}{2P_c} \tag{144}$$

where

$$@a = .427480 \tag{145}$$

$$@b = .036640 \tag{146}$$

Thus the constants in the Redlich-Kwong equation may be evaluated for any pure material, given the critical temperature and pressure. The value of $V_c$ predicted by Eq. (144) yields of value of $1/3$ for the critical compressibility. This is somewhat higher than the actual
value for all known compounds.

The reduced pressure, $P_R$, is defined as the ratio of the pressure to the critical pressure

$$\frac{P}{P_c} = P_R$$

(147)

$V'_R$, a type of reduced volume, is defined as one-third the ratio of the volume to the critical volume predicted in Eq. (144)

$$V'_R = \frac{V}{V_c}$$

(148)

Combining Eqs. (141), (142), (143) and (147)

$$P_R = \frac{T_b}{V_c} - \frac{T_b}{V} - \frac{T_b}{V_c} V_R (V + \Theta_c)$$

(149)

Eq. (149) is the completely reduced form of Eq. (135). It gives $P_R$ as a function of $T_R$ and $V'_R$. A form that is easier to use in calculations is created by expanding the last term by partial fractions, and using the identity $A_v = -P$.

$$-P_R = A_v = -\frac{T_b}{V_c} V_R (V + \Theta_c)$$

(150)

$$\Theta_c = \frac{\Theta_a}{\Theta_b T_R^a}$$

(151)

$\Theta_c$ is a function of temperature.

Using Eq. (148), the definition of $V'_R$, and taking all derivatives at constant $T$ and $N$

$$A_{VV} = \frac{\partial A_v}{\partial V} = \frac{1}{N} \frac{\partial A_v}{\partial V} = \frac{P_c}{NRT_c} \frac{\partial A_v}{\partial V}$$

(152)
Combining Eqs. (150) and (152)

\[ \frac{NRT_c \Delta_{vv}}{P_c^2} = \frac{T_R}{(V_R-\Theta_b)^2} \frac{\Theta_c}{V_R^2} \left( \frac{\Theta_c}{V_R+\Theta_b} \right)^2 \]  

(153)

Eq. (153) is used with Eq. (58) to determine the stability of any pure material, given \( T_R \) and \( V_R' \).

**SUPERHEAT LIMITS**

A liquid at 1 atm pressure will vaporize when the temperature is raised above its normal boiling point, assuming that nucleation surfaces exist. If the liquid is not in contact with any nucleation surfaces, the temperature may be raised to the limit of intrinsic stability (spinoidal curve) before it vaporizes. Liquids heated above the normal boiling point are termed "superheated" liquids, and the temperature at which the liquid reaches the spinoidal curve is termed the "limit of superheat." Eq. (66) gives a defining equation of the spinoidal curve for a pure material.

Combining Eqs. (66) and (153) yields a criterion of the spinoidal curve in terms of \( T_R \) and \( V_R' \)

\[ \frac{T_R}{(V_R-\Theta_b)^2} \frac{\Theta_c}{V_R^2} \left( \frac{\Theta_c}{V_R+\Theta_b} \right)^2 = 0 \]  

(154)

A liquid at the limit of superheat will satisfy Eq. (154). In addition, if the pressure is 1 atm,

\[ P_R = 1 \text{ atm} \]  

(155)

Solving Eqs. (154) and (155) simultaneously for \( V_R \) and \( T_R \) yields the limit of superheat for any material, in terms of
FIGURE III — LIMIT OF SUPERHEAT OF A PURE MATERIAL

LIMIT OF SUPERHEAT

$T_R = c W$

$P_c (atm)$

--- ORIGINAL REDLICH-KWONG

--- SOAVE MODIFICATION
the reduced temperature. Figure 3 is a graph of the limit of superheat (as $T_a$) as a function of $P_R$ (or $P_c$). For materials with critical pressures above 10 atm, the reduced temperature at the limit of superheat predicted by the original Redlich-Kwong equation is between .894 and .904.

Limits of superheat for ten hydrocarbons, as calculated using Eqs. (154) and (155), are listed in Table 5 under the columns labelled R-K. Also listed in Table 5 are experimental values obtained from Eberhart, Kremsner and Blander[5]. The calculated values are in good agreement with the experimental data, the average absolute deviation being 2°K. Since the Redlich-Kwong equation always predicts a reduced limit of superheat of about .9, a good rule-of-thumb for pure materials is that the limit of superheat is nine-tenths of the critical temperature.

A modification of the Redlich-Kwong equation is used in this thesis. Soave proposed[6] retaining Eq. (137), but changing the definition of "a". Instead of Eq. (140), "a" is defined by

$$a = a''\left[1 + (0.480 + 1.57\omega - 0.176\omega^2)(1 - T_a^{5})\right]^2$$  \hspace{1cm} (156)

where $\omega$ is the acentric factor and $a''$ and $b$ are still defined by Eqs. (142) and (143). If the definition of $\Theta_c$ is changed to

$$\Theta_c = \frac{\Theta_a}{\Theta_b} \left[1 + (0.480 + 1.57\omega - 0.176\omega^2)(1 - T_a^{5})\right]^2$$  \hspace{1cm} (157)
### TABLE V — LIMITS OF SUPERHEAT OF PURE HYDROCARBONS

<table>
<thead>
<tr>
<th>HYDROCARBON</th>
<th>SUPERHEAT LIMIT (DEGREES K)</th>
<th>REDUCED SUPERHEAT LIMIT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R-K</td>
<td>SRK</td>
</tr>
<tr>
<td>n-butane</td>
<td>381</td>
<td>368</td>
</tr>
<tr>
<td>n-pentane</td>
<td>421</td>
<td>430</td>
</tr>
<tr>
<td>n-hexane</td>
<td>455</td>
<td>466</td>
</tr>
<tr>
<td>n-heptane</td>
<td>485</td>
<td>498</td>
</tr>
<tr>
<td>n-octane</td>
<td>511</td>
<td>525</td>
</tr>
<tr>
<td>n-nonane</td>
<td>534</td>
<td>551</td>
</tr>
<tr>
<td>2,3-dimethylpropane</td>
<td>389</td>
<td>395</td>
</tr>
<tr>
<td>2,2,4-trimethylpentane</td>
<td>488</td>
<td>500</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>496</td>
<td>505</td>
</tr>
<tr>
<td>1-pentene</td>
<td>417</td>
<td>426</td>
</tr>
</tbody>
</table>

**AVERAGE ABSOLUTE ERROR**

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.004</td>
<td>.020</td>
</tr>
</tbody>
</table>

**Notes:**

- R-K=Calculated using the Redlich-Kwong equation-of-state
- SRK=Calculated using the Soave modification to the R-K
- EXP=Experimental values[5]
then Eqs. (152), (153) and (154) are usable with the Soave modification.

Figure 3 and Table 5 also have calculations using the Soave-Redlich-Kwong equation. In Figure 3, the Soave equation predicts that the limit of superheat is a function of critical pressure and acentric factor. The predicted values span a much larger range ($T_R$ from .89 to .94) than do those of the original Redlich-Kwong. The experimental limits of superheat in Table 5 are much closer to the original Redlich-Kwong prediction of $T_R=.9$. Therefore, the Soave modification is not recommended for superheat limit calculations.

**BINARY SYSTEMS**

The original Redlich-Kwong equation-of-state and the Soave modification are used for multicomponent systems, by making $a'$ and $b$ functions of composition. The definitions of the mixture constants, in terms of pure component constants, are termed "mixing rules." In the original mixing rules, still widely used, the mixture values of $b$ and the square root of $a'$ are each computed as a mole fraction average of the pure component values. Writing these rules for a binary system,

$$
a'^{1/2} = x_a a'_a + x_b a'_b \quad (158)
$$

$$
b = x_a b_a + x_b b_b \quad (159)
$$

where $a'_a$, $a'_b$, $b_a$ and $b_b$ are the pure component values and
x_a and x_b are mole fractions. Rewriting Eqs. (158) and (159) in terms of mole numbers, using Eq. (136) to note that the mixing rules for "a" are the same as those for a',

\[ a = \frac{1}{N} \left( N_a a_a^s + N_b a_b^s \right)^2 \]  
\[ b = 1 \left( N_a b_a + N_b b_b \right) \]  

Eq. (137), in either the original or the Soave form, is applicable to binary mixtures using Eqs. (160) and (161).

The most convenient equations which define the spinodonal curve and critical points of a binary mixture are expressed in terms of \( \Delta G \), the Helmholtz Free Energy. To make Eq. (137) compatible with \( \Delta G \), it is rewritten in terms of the total volume, \( V \)

\[ -A_v = P = NRT - \frac{\Theta_d}{V} + \frac{\Theta}{V + \Theta} \]  

where

\[ \Theta = \frac{N_a a_a^s + N_b a_b^s}{N_a b_a + N_b b_b} \]  

\[ \Theta_d = N \frac{a}{b} \frac{N_a a_a^s + N_b a_b^s}{N_a b_a + N_b b_b} \]  

\( \Theta_d \) and \( \Theta \) are functions of composition, and \( \Theta_d \) is a function of temperature.

Eq. (127) defines the spinodonal curve of a binary mixture. The terms \( A_{vv}, A_{va} \) and \( A_{aa} \) are evaluated (for the Redlich-Kwong equation) using Eqs. (E-1), (E-2) and (E-6) (from Appendix E). Solving Eqs. (127) and (155) simultaneously yields the limit of superheat for a binary material. The required data are the critical temperature,
pressure and mole fraction of each component (plus the acentric factor, for the Soave equation). Figures 4 and 5 give the calculated and experimental [5] limits of superheat for the systems n-octane in n-pentane and cyclohexane in n-pentane, as a function of composition.

The calculated limits of superheat, for both the original Redlich-Kwong equation and the Soave modification, are almost exactly mole fraction averages of the superheat limits of the pure compounds. This does not agree well with the data, as the experimental values in Figures 4 and 5 deviate somewhat from a straight-line plot. The original Redlich-Kwong matches the data much better than the Soave modification. This is to be expected, since the original equation is also better with pure materials.

The reason that the theoretical treatment produces disappointing results may lie in the term $A_{aa}$. $A_{aa}$ is calculated using Eq. (D-9) (from Appendix D), which involves an integration across the unstable region of the second derivative of pressure with respect to a mole number. Since substances cannot exist in the unstable region, any equation-of-state in that region must be based on extrapolations. Taking the second derivative of the pressure with respect to a mole number is a severe test of the mixing rules (Eqs. (158) and (159)). Most thermodynamic calculations take at most the first
FIGURE IV — LIMIT OF SUPERHEAT OF N-OCtANE IN N-PENTANE

SUPERHEAT LIMIT (°K)

--- CALCULATED USING THE REDLICH-KWONG EQUATION

--- CALCULATED USING THE SOAVE MODIFICATION

△ EXPERIMENTAL DATA[5]
FIGURE V — LIMIT OF SUPERHEAT OF CYCLOHEXANE IN N-PENTANE

SUPERHEAT LIMIT (°K)

MOLE FRACTION CYCLOHEXANE

--- --- CALCULATED USING THE REDLICH–KWONG EQUATION

--- --- CALCULATED USING THE SOAVE MODIFICATION

Δ EXPERIMENTAL DATA[5]
derivative. Much more refined mixing rules are required to produce accurate predictions of the limit of superheat.

**CRITICAL POINTS**

Eq. (128), the second condition of the critical point for a binary material, is also evaluated using Eqs. (E-1) through (E-7) (from Appendix E). Even though the term $A_{aaa}$ involves a third derivative of $P$ with respect to $N_a$, the integration does not extend across the unstable region. Therefore the critical point calculations may be expected to produce more accurate results than those of the limit of superheat.

The critical point conditions, Eqs. (127) and (128), are solved simultaneously for the critical temperature and volume, and the equation-of-state is used to obtain the critical pressure. Figures 6 and 7 give the calculated critical temperatures for the systems n-heptane in ethane and n-butane in carbon dioxide, as a function of composition. Figures 8 and 9 do the same for the critical pressures. The results of both the original Redlich-Kwong equation and the Soave modification are plotted, together with experimental data collected by Spear, Robinson and Chao[7].

Both equations-of-state yield values in fair agreement with the experimental data. As in the limit of superheat calculations, the mixing rules are suspected of causing
FIGURE VI — N-HEPTANE-ETHANE CRITICAL TEMPERATURES

CRITICAL TEMPERATURE (°K)

MOLE FRACTION N-HEPTANE

--- CALCULATED USING THE REDLICH-KWONG EQUATION

--- CALCULATED USING THE SOAVE MODIFICATION

△ EXPERIMENTAL DATA[7]
FIGURE VII — N-BUTANE-CARBON DIOXIDE CRITICAL TEMPERATURES

CRITICAL TEMPERATURE (°K)

MOLE FRACTION N-BUTANE

— — CALCULATED USING THE REDLICH-KWONG EQUATION

— — CALCULATED USING THE SOAVE MODIFICATION

Δ EXPERIMENTAL DATA[7]
FIGURE VIII — N-HEPTANE-ETHANE CRITICAL PRESSURES

Critical Pressure (atm)

Mole Fraction N-Heptane

— — — Calculated using the Redlich-Kwong equation

— — — Calculated using the Soave modification

Δ Experimental data[7]
FIGURE IX — N-BUTANE—CARBON DIOXIDE CRITICAL PRESSURES

CRITICAL PRESSURE (ATM)

MOLE FRACTION N-BUTANE

--- CALCULATED USING THE REDLICH—KWONG EQUATION
--- CALCULATED USING THE SOAVE MODIFICATION
△ EXPERIMENTAL DATA[7]
most of the inaccuracy. The use of interaction parameters in the mixing rules would undoubtably improve the predictions. These parameters are usually empirical, being determined from data already available. Therefore, the use of interaction parameters is more a correlative than a predictive technique.

The results obtained using the original Redlich–Kwong equation and the Soave modification to predict superheat limits and critical points are somewhat disappointing. Their moderate success, however, leads to hope that improved equations-of-state or more likely, improved mixing rules will yield significantly higher accuracy.
V. DISCUSSION

The study of intrinsic stability, as well as virtually every other branch of thermodynamics, got its start and first major developments from J. Willard Gibbs. In his article "On the Equilibrium of Heterogeneous Substances"[83], Gibbs introduces the entropy maximization principle and shows its equivalence to the energy minimization principle. Then the fundamental equation $U = U(S, V, N, \ldots N_m)$ is developed, as well as the forms in terms of $A$, $G$ and $H$.

Working with only the fundamental equations, the uniformity of temperature, pressure and chemical potential in a system at equilibrium is deduced. The stability equations $D_k > 0$ for all $k<n$, in the form where $(x, \ldots x_n) = (S, N, \ldots N_m, V)$ are then found. The equation which is violated first is listed as Eq. (56). These criteria are transformed into a single equation in the form of Eq. (51), with the same ordering of $x_i$ through $x_n$.

The corresponding conditions of the critical point, Eqs. (60) and (63), are developed by considering the intensive properties of coexistent phases near a critical point. A consideration of the stability of the coexistent phases yields the alternate criteria of Eqs. (62) and (89), with $i=0$ and the same ordering of $x_i$ through $x_n$ as above. The forms with $i=2$ are also stated, and are listed as
Eqs. (90) through (93).

The above paragraphs demonstrate that Gibbs developed every significant area of stability. The major problem in his work is its extreme lack of readability. Often the step-by-step logic is not apparent. Much of later authors' work can be considered a clarification rather than an extension of Gibbs.

The separation of one phase into two separate phases is used by Prigogine and Defay[9] as a basis for the calculation of the stability of a system. This treatment is much more intuitive, as it models the actual physical process which occurs when a system becomes unstable. The stability of a pure component is determined by directly studying the entropy increase in the formation of a microscopic new phase differing only slightly from the original. Multicomponent systems are considered only at constant temperature and pressure.

Prigogine and Defay derive the conditions of thermal, mechanical and diffusional stability. The question of which conditions are violated first is not discussed, except that the condition of diffusional stability is shown to be the violated before mechanical for a binary mixture. The critical point conditions are stated without proof; however, a fairly extensive treatment of critical behavior in solutions is presented.
In deriving the conditions of stability, Gibbs uses $\psi^{(n)}$, the $n^{th}$ Legendre Transform of $U$ (transformed with respect to all of its variables), as well as the transforms $A, G$ and $H$. Although he discusses the relationships between these functions, the general nature of Legendre Transforms is not developed.

Callen presents the use of Legendre Transforms in thermodynamics[10]. $A, G, H$ and $\psi^{(p)}$, the $p^{th}$ transform of $U$, are defined and analyzed in terms of a general theory of Legendre Transforms. For instance, the various first derivatives of transforms are derived.

The sum-of-squares form of the expansion of the change in $U$ is obtained directly in the reduced notation of Eqs. (38) and (39). In an appendix, the alternative formulation in terms of determinants is developed. The significance of the criteria of stability is not explained, however. Callen's treatment, although general and highly mathematical, is easy to follow. This is due to his use of Legendre Transforms, a very important development.

Munster covers Legendre Transforms and fundamental equations in somewhat more detail[11]. The derivation of the stability criteria is also extensive and presented in several different ways. Otherwise, the treatment is similar to Callen's.
The idea of a subsystem which is enclosed by a diathermal, non-rigid and totally permiable membrane is introduced by Modell and Reid[12]. This permits all possible variations between the subsystem and the main system, and insures complete generality.

Second derivatives of Legendre Transforms are obtained using a Taylor Expansion. This permits the conversion of the U form of the stability criteria to the A form, the A form to the G form, and so on until one derives the $\Psi_{n-1}^{(k-2)}$ form. Thus the stability criteria of Eqs. (54) and (55) are deduced, with $x_i$ through $x_n$ defined as in Eqs. (9), (10) and (11).

Other authors present derivations of stability or critical point conditions which are either similar to previous works[13] or are unclear[14]. The last reference suffers from not having defined the change which occurs when a system becomes unstable.

This thesis considers the formation of two phases of any size, not necessarily one large and one small, from an original homogeneous phase. Thus this model of intrinsic instability corresponds more closely to the actual physical processes.

The third derivatives of Legendre Transforms were found in order to show the equivalence of the various forms of the second condition of the critical point. This, plus
the general representation of variables used, enables the expression of the criteria of stability and of the critical point in terms of any Legendre Transform of $U$.

Redlich and Kister derive critical point criteria for a binary system, usable with an equation-of-state[15]. Some of their derivatives are in terms of volume, some in terms of pressure. Although formulas are given to convert to the form most suitable for any equation-of-state, this treatment is awkward and unnecessary.

Given a pressure explicit equation-of-state, the forms of the stability and critical point criteria in terms of $A$ are the most convenient, $A$ being a function of $T$, $V$ and $N_i$. They are derived in this thesis for an arbitrary $m$-component system.

The results obtained by using the condition of stability and the Redlich-Kwong equation-of-state to predict superheat limits are good for pure materials and fairly poor for mixtures. For this and other reasons discussed in Section IV, the mixing rules are thought to be causing most of the error. The Soave modification produces quite poor superheat limit predictions.

Critical points of binary mixtures are not predicted well using either equation-of-state. Again mixing rules are suspect. The calculation of superheat limits and critical points involves taking second or third derivatives
of the pressure with respect to a mole number. This is an extreme test of mixing rules, and it is not surprising that the results are poor.

The accurate prediction of superheat limits and critical points may only be obtained if equations-of-state and associated mixing rules are greatly improved. In fact, obtaining this accuracy may be regarded as an advanced test of an equation-of-state, probably not satisfied by any now in common use.
This appendix proves a formula which relates any determinant to determinants of one order and two orders smaller. The relation is used in Appendix B in deriving the sum-of-squares form for a general quadratic expression. The formula is presented here as a separate appendix since it may have other uses. For example, it could have been used to prove which of the conditions of stability were violated first, except that other methods were easier.

The desired formula is: if $i<k$ and $j<m$ then

$$B_{ijkl}=B_{ij}B_{km}-B_{im}B_{kj} \quad (A-1)$$

$B$ is defined as an $n$ by $n$ determinant, $B_{ij}$ as $B$ with the $i^{th}$ row and $j^{th}$ column removed (the minor of $U_{ij}$), $B_{ijkm}$ as $B$ with the $i^{th}$ and $k^{th}$ rows and the $j^{th}$ and $m^{th}$ columns removed, etc.
In the first step of the proof Eq. (A-1) is assumed true for a particular \( n \) with \((i, j, k, m)=(1, 1, 2, 2)\) and is then shown true for any set of \( i, j, k, \) and \( m \). \( B' \) is defined identical to \( B \) but with the second and \( m \text{th} \) columns interchanged (\( m>2 \)).

\[
B_{11221} = B_{1221} = B_{2112} = B_{2211} =
\begin{vmatrix}
U_{33} & U_{34} & \cdots & U_{3n} \\
U_{43} & U_{44} & \cdots & U_{4n} \\
\vdots & \vdots & \ddots & \vdots \\
U_{n3} & U_{n4} & \cdots & U_{nn}
\end{vmatrix}
\]

Relabeling 2 as \( m' \) and \( m \) as \( 2' \) in the second and \( m \text{th} \) columns Eq. (A-1), if true for \((i, j, k, m)=(1, 1, 2, 2)\), applied to \( B' \) (which appears identical to \( B \) except that certain subscripts are primed) yields

\[
B'B'_{11221} = B'_{11} B'_{22',1} - B'_{12',2} B'_{21}
\]

From determinant column exchange rules,

\[
B' = -B
\]

\[
B'_{11} = -B_{11} \quad ; \quad B'_{22} = -B_{22}
\]
Combining Eqs. (A-2) through (A-6) and factoring yields

\[ B_{1/2} = (-1)^{m+1} B_{1/m} \]
\[ B_{1/2} = (-1)^{m+1} B_{2/m} \]

Equation (A-7) is Eq. (A-1) with \((i, j, k) = (1, 1, 2)\), but with \(m\) arbitrary. The same proof applies if \(i, j,\) or \(k\) instead of \(m\) were changed to a different value. Therefore, if Eq. (A-1) were true for \((i, j, k, m) = (1, 1, 2, 2)\) it must be true for any \((i, j, k, m)\).

The second step of the proof involves showing Eq. (A-1) to be true for \(n=2\). Since \(B_{1/2} \), as a 0 by 0 determinant, is defined equal to 1,

\[ B = U_{11} U_{22} - U_{12} U_{21} = U_{22} U_{11} - U_{21} U_{12} \]

transforms to

\[ B_{1/2} B_{2/2} = B_{1/2} B_{2/2} \]

Thus Eq. (A-1) holds for \(n=2\).

In the third step of the proof Eq. (A-1) is assumed true for an \(n-1\) by \(n-1\) determinant, \(B_{1/1}\), and is then shown true for \(B\), the \(n\) by \(n\) determinant.

By the above assumption, if \(k>2\) and \(i>2\) then

\[ B_{1/1} B_{1/2} k i = B_{1/2} B_{1/2} k i - B_{1/2} B_{1/2} i k \]

Each term is multiplied by \((-1)^k U_{k1}\), summed from \(k=3\) to \(n\) and rearranged, giving
\[ B_{11} \sum_{k=3}^{n} (-1)^{k} U_{k1} B_{1k2} k1 = \]

\[ B_{11} 22 \sum_{k=3}^{n} (-1)^{k} U_{k1} B_{1k1} - B_{112} \sum_{k=3}^{n} (-1)^{k} U_{k1} B_{12k1} \quad (A-11) \]

Expanding \( B_{12} \), \( B_{1\iota} \) and \( B_{1\iota 2} \) by minors along the first column

\[ B_{12} = U_{21} B_{121} + \sum_{k=3}^{n} (-1)^{k} U_{k1} B_{1k2} \quad (A-12) \]

\[ B_{1\iota} = U_{21} B_{1\iota 2} + \sum_{k=3}^{n} (-1)^{k} U_{k1} B_{1k1} \quad (A-13) \]

\[ B_{1\iota 2} = \sum_{k=3}^{n} (-1)^{k} U_{k1} B_{1\iota 2k1} \quad (A-14) \]

Combining eqs. (A-11) through (A-14) and simplifying

\[ -B_{11} B_{1\iota 22} = B_{112} B_{1\iota} - B_{112 \iota} B_{12} \quad (A-15) \]

Each term is then multiplied by \((-1)^{i} U_{i\iota}\), summed from \( i=3 \) to \( n \), and rearranged, giving

\[ -B_{11} \sum_{i=3}^{n} (-1)^{i} U_{i\iota} B_{221i} = \]

\[ B_{1122} \sum_{i=3}^{n} (-1)^{i} U_{i\iota} B_{1i\iota} - B_{12} \sum_{i=3}^{n} (-1)^{i} U_{i\iota} B_{2i1i} \quad (A-16) \]

Expanding \( B_{1}, B_{11}, \) and \( B_{22} \) by minors along the first row

\[ B = U_{11} B_{11} - U_{12} B_{13} - \sum_{i=3}^{n} (-1)^{i} U_{i\iota} B_{1i\iota} \quad (A-17) \]

\[ B_{21} = U_{12} B_{2112} + \sum_{i=3}^{n} (-1)^{i} U_{i\iota} B_{211i} \quad (A-18) \]
Combining Eqs. (A-16) through (A-19) and simplifying

\[ E_{22} = U_{22} B_{2211} + \sum_{i=3}^{n} (-1)^i U_{1i} B_{221i} \]  \hspace{1cm} (A-19)

By the first part of this appendix, Eq. (A-20) implies Eq. (A-1). Thus, if Eq. (A-1) is true for determinants of order \( n-1 \), it is true for determinants of order \( n \). Since Eq. (A-1) is true for determinants of order 2, we have shown by induction that Eq. (A-1) is true for all \( n \geq 2 \).
This appendix derives the sum-of-squares form for a general quadratic expression. The form is used to show when the differential in energy goes negative and the system in question therefore becomes unstable.

Assuming that $U_{kj}=U_{jk}$ and that all denominators are non-zero, the desired result is

$$
\sum_{k=1}^{n} \sum_{j=1}^{n} U_{kj} x_k x_j = \sum_{k=1}^{n} \frac{D_k}{D_{k-1}} Z_k^2
$$

where

$$Z_k = \sum_{j=k}^{n} \frac{C_{kkj} x_j}{D_k}$$

$D_k$ is the $k$ by $k$ principle sub-determinant of the matrix of the coefficients of the quadratic. $C_{kij}$ is $D_k$ with all $U_{km}$ in the $k^{th}$ row replaced with $U_{jm}$ and all $U_{mk}$ in the $k^{th}$ column replaced with $U_{jm}$.

$$
D_k = \begin{vmatrix}
U_{11} & U_{12} & \cdots & U_{1k} \\
U_{21} & U_{22} & \cdots & U_{2k} \\
& \vdots & \ddots & \vdots \\
U_{k1} & U_{k2} & \cdots & U_{kk}
\end{vmatrix}
$$

$$
C_{kkj} = \begin{vmatrix}
U_{11} & U_{12} & \cdots & U_{1,k-1} & U_{1j} \\
U_{21} & U_{22} & \cdots & U_{2,k-1} & U_{2j} \\
& \vdots & \ddots & \vdots & \vdots \\
U_{k1} & U_{k2} & \cdots & U_{k,k-1} & U_{kj}
\end{vmatrix}
$$
The derivation comes from working with the expression $E_m$ defined

$$E_m = \sum_{k=m}^{n} \sum_{j=m}^{n} C_{mikh} x_k x_j$$

Since $C_{mnn} = D_m$

$$E_m = \frac{D_m}{D_{m-1}} \left( x_m^2 + 2x_m \sum_{j=m+1}^{n} \frac{C_{mni} x_j}{D_m} \right) + \sum_{k=m+1}^{n} \sum_{j=m+1}^{n} \frac{C_{mkj} x_k x_j}{D_{m-1}}$$

Adding and subtracting terms to "complete-the-square"

$$E_m = \frac{D_m}{D_{m-1}} \left[ x_m^2 + 2x_m \sum_{j=m+1}^{n} \frac{C_{mni} x_j}{D_m} + \left( \sum_{j=m+1}^{n} \frac{C_{mni} x_j}{D_m} \right)^2 \right]$$

$$- \frac{D_m}{D_{m-1}} \sum_{k=m+1}^{n} \frac{C_{mkn} x_k}{D_m} \sum_{j=m+1}^{n} \frac{C_{mni} x_j}{D_m} + \sum_{k=m+1}^{n} \sum_{j=m+1}^{n} \frac{C_{mkj} x_k x_j}{D_{m-1}}$$

Simplifying

$$E_m = \frac{D_m}{D_{m-1}} \left( x_m + \sum_{j=m+1}^{n} \frac{C_{mni} x_j}{D_m} \right)^2$$

$$+ \sum_{k=m+1}^{n} \sum_{j=m+1}^{n} \frac{C_{mkj} C_{mni} - C_{mkm} C_{mnj}}{D_m D_{m-1}}$$

If $B$ (of Appendix A) is defined as $C_{m+njk}$, then the determinant reduction formula shows that

$$C_{m+njk} D_{m-1} = C_{mkj} C_{mnm} - C_{mkn} C_{mnj}$$
Substituting Eq. (B-7) into Eq. (B-6)

\[ E_m = \frac{D_m}{D_{m-1}} \left( \sum_{j=m}^{n} C_{m,m,j} x_j \right)^2 + \sum_{k=m+1}^{n} \sum_{j=m+1}^{n} \frac{C_{m+1,k,j}}{D_{m}} \]  

(B-8)

Substituting Eqs. (B-2) and (B-3) into Eq. (B-8)

\[ E_m = \frac{D_m}{D_{m-1}} Z_m^2 + E_{m+1} \]  

(B-9)

Applying Eq. (B-9) to \( E_i \) \( n-1 \) times

\[ E_i = \sum_{k=1}^{n-1} \frac{D_m}{D_{m-1}} Z_k^2 + E_{n} \]  

(B-10)

From Eq. (B-3)

\[ E_n = \sum_{k=n}^{n} \sum_{j=n}^{n} \frac{C_{n,k,j} x_k x_j}{D_{n-1}} \]  

(B-11)

Using Eq. (B-2)

\[ E_n = \frac{D_n}{D_{n-1}} Z_n^2 \]  

(B-12)

Substituting Eq. (B-12) into Eq. (B-10)

\[ E_i = \sum_{k=1}^{n} \frac{D_k}{D_{k-1}} Z_k^2 \]  

(B-13)

Since \( U_{k,j} = C_{1,k,j} \) and \( D_0 = 1 \), Eq. (B-3) shows that

\[ E_i = \sum_{k=i}^{n} \sum_{j=i}^{n} U_{k,j} x_k x_j \]  

(B-14)

Combining Eqs. (B-13) and (B-14), one obtains Eq. (B-1), the desired result.
In this appendix the first, second and third partial derivatives of $\Psi$, the Legendre Transform of $y$, are expressed in terms of derivatives of $y$. These formulas enable the rapid interconversion of $U$ and any of its transforms ($A$, $G$, etc.). In particular, the determinants arising from the stability and critical point conditions are easily simplified.

Throughout this derivation, all terms that will appear only in fourth or higher order derivatives are dropped. Subscripts on $y$ and $\Psi$ indicate corresponding partial derivatives.

$y$ is the given

$$y=y(x_1, x_2, x_3 \ldots x_n)$$

$\Psi$, the Legendre Transform of $y$, is defined

$$\delta y = \frac{\partial y}{\partial x_i}$$

$$\Psi = \Psi(\delta_{x_1}, x_2, x_3 \ldots x_n) = -\varepsilon_i x_i$$

Defining $\delta \varepsilon_i$ and $\delta x_i$

$$\delta \varepsilon_i = \varepsilon_i - \varepsilon^o$$

$$\delta x_i = x_i - x_i^o$$

Using Eqs. (C-3) and (C-4) in Eq. (C-2)

$$\Psi = -\varepsilon_i x_i^o - \varepsilon_i^o \delta x_i - x_i^o \varepsilon_i - \delta \varepsilon_i x_i$$

Expanding $y$ around $y^o$ using a Taylor Series
\[
y = y^o + \sum_{i=1}^{n} y_i^o \delta x_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} y_{ij}^o \delta x_i \delta x_j + \frac{1}{6} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} y_{ijk}^o \delta x_i \delta x_j \delta x_k \quad (C-6)
\]

DO, D1 and D2 are defined independent of \( x \),

\[
DO = \sum_{i=2}^{n} y_i^o \delta x_i + \frac{1}{2} \sum_{i=2}^{n} \sum_{j=2}^{n} y_{ij}^o \delta x_i \delta x_j + \frac{1}{6} \sum_{i=2}^{n} \sum_{j=2}^{n} \sum_{k=2}^{n} y_{ijk}^o \delta x_i \delta x_j \delta x_k \quad (C-7)
\]

\[
D1 = \sum_{i=2}^{n} y_{i}^o \delta x_i + \frac{1}{2} \sum_{i=2}^{n} \sum_{j=2}^{n} y_{ij}^o \delta x_i \delta x_j \quad (C-8)
\]

\[
D2 = \sum_{i=2}^{n} y_{i}^o \delta x_i \quad (C-9)
\]

Combining Eqs. (C-6) through (C-9)

\[
y = y^o + DO + (y^o + D1) \delta x_i + \frac{1}{2} (y^o + D2) \delta x_i^2 + \frac{1}{6} y_{i}^o \delta x_i^3 \quad (C-10)
\]

From Eq. (C-4)
\[
d(\delta x_i) = dx_i \quad (C-11)
\]

Using Eq. (C-11) to differentiate Eq. (C-10) with respect to \( x \),

\[
y_i = y_i^o + D1 + (y_i^o + D2) \delta x_i + \frac{1}{2} y_{i}^o \delta x_i^2 \quad (C-12)
\]

Substituting Eqs. (C-1) and (C-3) into Eq. (C-12)

\[
\delta \xi = D1 + (y_i^o + D2) \delta x_i + \frac{1}{2} y_{i}^o \delta x_i^2 \quad (C-13)
\]

Solving for \( \delta x_i \) and choosing the positive root of the quadratic

\[
\delta x_i = \{-y_i^o - D2 + [(y_i^o + D2)^2 - 2y_{i}^o (D1 - \delta \xi_i)]^{1/2}\} y_{i}^o \quad (C-14)
\]

Using the binomial expansion

\[
\delta x_i = (y_i^o + D2)^{-1} (D1 - \delta \xi_i) - \frac{1}{2} y_{i}^o (y_i^o + D2)^{-3} (D1 - \delta \xi_i)^2 \quad (C-15)
\]

Using the geometric series
\[ y_{i}^{o} \delta x_{t} = -(1-y_{i}^{o,-1} D_{2})(D_{1}-\delta \xi_{t}) - \frac{1}{2} y_{i}^{o} y_{i}^{o,-2}(D_{1}-\delta \xi_{t})^{2} \quad (C-16) \]

Substituting Eq. (C-10) into Eq. (C-5) and Eq. (C-16) into both yields

\[ \Psi = y_{i}^{o} - \xi_{i}^{o} x_{t} - x_{t} \delta \xi_{t} + D_{2} y_{i}^{o,-2}(D_{1}-\delta \xi_{t})(D_{1}-\delta \xi_{t})^{2} \]

\[ - \frac{1}{2} y_{i}^{o} y_{i}^{o,-3}(D_{1}-\delta \xi_{t})^{3} \quad (C-17) \]

Substituting Eqs. (C-2), (C-7), (C-8) and (C-9) into Eq. (C-17)

\[ \Psi = y_{i}^{o} - x_{t} \delta \xi_{t} + \sum_{i=2}^{n} y_{i}^{0} \delta x_{i} - \frac{1}{2} y_{i}^{0,-1} \delta \xi_{t}^{2} + y_{i}^{0} \delta \xi_{t} \sum_{j=2}^{n} y_{j,i}^{0} \delta x_{i} + \frac{1}{2} y_{i}^{0,-2} y_{i}^{0} \delta \xi_{t}^{3} \]

\[ + \frac{1}{2} \sum_{i=2}^{n} \sum_{j=2}^{n} (y_{i,j}^{0} - y_{i}^{0,-1} y_{i,j}^{0}) \delta x_{i} \delta x_{j} + \frac{1}{2} y_{i}^{0,-2} y_{i}^{0} \delta \xi_{t}^{3} \]

\[ + \frac{1}{2} \sum_{i=2}^{n} \sum_{j=2}^{n} (y_{i,j}^{0} - y_{i}^{0,-1} y_{i,j}^{0}) \delta x_{i} \delta x_{j} + \frac{1}{2} y_{i}^{0,-2} y_{i}^{0} \delta \xi_{t}^{3} \]

\[ + \frac{1}{2} \sum_{i=2}^{n} \sum_{j=2}^{n} (y_{i,j}^{0} - y_{i}^{0,-1} y_{i,j}^{0}) \delta x_{i} \delta x_{j} + \frac{1}{2} y_{i}^{0,-2} y_{i}^{0} \delta \xi_{t}^{3} \]

Rearranging Eq. (C-18) so the terms which are summed are symmetrical with respect to the summation indices
Expanding $\Psi$ around $\Psi^0$ using a Taylor Series

\[
\Psi = \Psi^0 - x_i \delta \xi^i + \sum_{i=2}^{n} y^0_i \delta x_i - \frac{1}{2} y^0_{ii} \delta \xi^2_i + \sum_{i=2}^{n} y^0_{ii} \delta \xi^i \delta x_i \\
+ \frac{1}{2} \sum_{i=2}^{n} \sum_{j=2}^{n} (y^0_{ij} - y^0_{ii} y^0_{ij} y^0_{ij} - y^0_{ii} y^0_{ij} y^0_{ij}) \delta x_i \delta x_j + \frac{1}{6} y^0_{ii} y^0_{ii} y^0_{ij} \delta \xi^3_i \\
+ \frac{1}{2} \sum_{i=2}^{n} (y^0_{ii} - y^0_{ii} y^0_{ii} y^0_{ii} y^0_{ii}) \delta \xi^2_i \delta x_i \\
+ \frac{1}{2} \sum_{i=2}^{n} \sum_{j=2}^{n} (y^0_{ij} - y^0_{ij} - y^0_{ij} y^0_{ij} - y^0_{ij} y^0_{ij}) \delta x_i \delta x_j \\
+ \frac{1}{6} \sum_{i=2}^{n} \sum_{j=2}^{n} \sum_{k=2}^{n} (y^0_{ijk} - y^0_{ij} y^0_{ij} y^0_{ij} y^0_{ij} + y^0_{ij} y^0_{ij} y^0_{ij} + y^0_{ij} y^0_{ij} y^0_{ij}) \delta x_i \delta x_j \delta x_k \\
(C-19)
\]

Comparing Eqs. (C-19) and (C-20) term-by-term yields (for $i \geq 2, j \geq 2$ and $k \geq 2$)

\[
\Psi_i = -x_i \\
\Psi_j = y_{ij} \\
\Psi_{ii} = -y_{ii} \\
\Psi_{ij} = y_{ij} - y_{ii} y_{ij} y_{ij} \\
\Psi_{ij} = y_{ij} - y_{ii} y_{ij} y_{ij} \\
\Psi_{ij} = y_{ij} - y_{ii} y_{ij} y_{ij} \\
\Psi_{ij} = y_{ij} - y_{ii} y_{ij} y_{ij} \\
\Psi_{ij} = y_{ij} - y_{ii} y_{ij} y_{ij} \\
\Psi_{ij} = y_{ij} - y_{ii} y_{ij} y_{ij} \\
\Psi_{ij} = y_{ij} - y_{ii} y_{ij} y_{ij} \\
(C-21)
(C-22)
(C-23)
(C-24)
(C-25)
\[
\psi_{11} = \psi_{111} \quad \psi_{11}^{-3} \\
\psi_{111} = \psi_{1111} \quad \psi_{111}^{-3}
\]

\[
\psi_{i;j} = \psi_{11} \psi_{111}^{-3} - (\psi_{11} \psi_{1111} + \psi_{11} \psi_{11111}) \psi_{11}^{-3} + \psi_{11} \psi_{11} \psi_{111} \psi_{111}^{-3}
\]

\[
\psi_{i;jk} = \psi_{11} \psi_{1111}^{-3} - (\psi_{11} \psi_{11111} + \psi_{11} \psi_{111111}) \psi_{11}^{-3} + \psi_{11} \psi_{11} \psi_{111} \psi_{1111} \psi_{11111} \psi_{111111}^{-3}
\]

Eqs. (C-21) through (C-29) are the desired first, second and third derivatives of the Legendre Transform.

For example, let

\[
y(x_1, x_2, x_3) = u(S, V, N)
\]

\[
\psi(x_1, x_2, x_3) = a(T, V, N) = u - TS
\]

\[
dy = \frac{\partial}{\partial V} (u - TS) = \frac{\partial}{\partial T} S - \frac{\partial}{\partial V} V + \frac{\partial}{\partial N} N
\]

Derivatives are defined as before:

\[
A_v = \left( \frac{\partial A}{\partial v} \right)_{T, N}
\]

In this example all derivatives are taken holding \(N\) constant.

\[
\psi_1 = A_T = -S = -x_1 = -S
\]

\[
\psi_2 = A_V = -P = y_2 = u_2 = -P
\]

\[
\psi_{12} = A_{TV} = \left( \frac{\partial T}{\partial V} \right)_T S = \frac{\partial y_{12}}{\partial y_{111}} = u_{55} u_{55}^{-1} = \left( \frac{\partial T}{\partial V} \right)_T S \left( \frac{\partial T}{\partial S} \right)_V ^{-1}
\]

\[
\psi_{111} = A_{TVV} = \left( \frac{\partial^3 T}{\partial V^2} \right)_V = y_{111} \quad y_{111}^{-3} = u_{555} u_{555}^{-3} = \left( \frac{\partial^3 T}{\partial V^2} \right)_V \left( \frac{\partial T}{\partial S} \right)_V ^{-3}.
\]
\[ \Psi_{122} = A_{TVV} = \left( \frac{\partial^2 S}{\partial V^2} \right)_T \]

\[ = y_{122} \psi + 2y_{12} y_{112} \psi^2 + y_{112} y_{1} + y_{11} \psi^3 \]

\[ = U_{5VV} U_{33} - 2U_{5V} U_{5SV} U_{5S} + U_{3V} U_{5SS} U_{5S}^2 U_{5S}^3 \]

\[ \left( \frac{\partial^2 T}{\partial V^2} \right)_S \left( \frac{\partial T}{\partial S} \right)_V - 2 \left( \frac{\partial T}{\partial V} \right)_S \left( \frac{\partial^2 T}{\partial S^2} \right)_V + \left( \frac{\partial T}{\partial V} \right)_S \left( \frac{\partial^2 T}{\partial S^2} \right)_V \]

**Note:**

In this appendix only the first Legendre Transform of \( y \) from \( x \), space to \( \xi \), space was considered. Eq. (32) defines \( \Psi^{(p)} \), the \( p \)-th Legendre Transform of \( y \) from \( x \) through \( x_p \) space to \( \xi \), through \( \xi_p \) space. \( \Psi^{(p)} (\xi, \ldots \xi_p, x_{p+1}, \ldots x_n) \) may be defined recursively as the Legendre Transform of \( \Psi^{(p-1)} (\xi, \ldots \xi_{p-1}, x_p \ldots x_n) \) from \( x_p \) space to \( \xi_p \) space, since \( \Psi^{(1)} \) is defined as \( y \).

Eqs. (C-21) through (C-29) give first, second and third derivatives of \( \Psi \) in terms of derivatives of \( y \). They may also be used to give the derivatives of \( \Psi^{(p)} \) in terms of derivatives of \( \Psi^{(p-1)} \), if \( y \) is changed to \( \Psi^{(p-1)} \), \( \Psi \) is changed to \( \Psi^{(p)} \) and all subscript 1's are changed to subscript \( p \)'s. In other words, Eqs. (C-21) through (C-29) are usable with any Legendre Transform, as long as the subscript "1" means a derivative with respect to the transformed variable.
APPENDIX D
CHEMICAL POTENTIAL DERIVATIVES

In this appendix a formula for $A_{ab}$, a second derivative of the Helmholtz Free Energy with respect to mole numbers, is derived. $A_{ab}$ is the derivative of a chemical potential with respect to a mole number at constant temperature, total volume and other mole numbers. The formula requires pressure to be given as a function of temperature, total volume and mole numbers, and is therefore usable with any pressure explicit equation-of-state. These derivatives are used in finding the limits of intrinsic stability, given such an equation of state.

The derivation begins with the Maxwell Relation

$$\left( \frac{\partial \mu_a}{\partial V} \right)_{T,N} = -\left( \frac{\partial P}{\partial N_a} \right)_{T,V,N_i \neq a} \quad (D-1)$$

Taking the derivative of each side with respect to $N_b$, holding $T$, $V$ and other $N_i$ constant

$$\left( \frac{\partial^2 \mu_a}{\partial V \partial N_b} \right)_{T,N_i \neq b} = -\left( \frac{\gamma^2 P}{\partial N_a \partial N_b} \right)_{T,V,N_i \neq a,b} \quad (D-2)$$

Multiplying each side by $dV$ and integrating from $V=\infty$ to $V$ (with superscript *'s indicating that the variable is evaluated in the limit of infinite total volume)

$$\left( \frac{\partial \mu_a}{\partial N_b} \right)_{T,V,N_i \neq b} - \left( \frac{\partial \mu_a}{\partial N_b} \right)_{T,V,N_i \neq b}^{*} = \int_{\infty}^{V} \gamma^2 P \left( \frac{\partial^2 \mu_a}{\partial N_a \partial N_b} \right)_{T,V,N_i \neq a,b} dV \quad (D-3)$$
All materials (at a given temperature) behave as ideal gases if the specific volume is sufficiently large. That is, if $N$ and $T$ are held constant, then a substance will approach ideal gas behavior in the limit of infinite total volume. Since the fugacity of an ideal gas is equal to the partial pressure, the chemical potential of an ideal gas (using the definition of fugacity with $\lambda_a(T)$ being a function of temperature only) is

$$\mu_a = RT \ln \left( \frac{PN_a}{N} \right) + \lambda_a(T) = RT \ln \left( \frac{N_aRT}{V} \right) + \lambda_a(T) \quad (D-4)$$

Taking the derivative of each side with respect to $N_a$ (holding $T$, $V$ and all other $N_i$ constant) and evaluating at the limit of infinite total volume

$$\left( \frac{\partial \mu_a}{\partial N_a} \right)_{T,V,N_i \neq a} = RT \quad (D-5)$$

Repeating the last step but taking the derivatives with respect to $N_b$ instead of $N_a$ (valid only for $a \neq b$)

$$\left( \frac{\partial \mu_a}{\partial N_b} \right)_{T,V,N_i \neq b} = 0 \quad (D-6)$$

Substituting Eq. (D-5) into Eq. (D-3)

$$\left( \frac{\partial \mu_a}{\partial N_a} \right)_{T,V,N_i \neq a} = -\int_0^V \left( \frac{\lambda_a^2 P}{3N_a^2} \right)_{T,V,N_i \neq a} \frac{dV}{N_a} + RT \quad (D-7)$$

Substituting Eq. (D-6) into Eq. (D-3) (valid for $a \neq b$)

$$\left( \frac{\partial \mu_a}{\partial N_b} \right)_{T,V,N_i \neq b} = -\int_0^V \left( \frac{\lambda_a^2 P N_a^2}{3N_b^2} \right)_{T,V,N_i \neq a,b} \frac{dV}{N_a} \quad (D-8)$$

To simplify the notation of Eqs. (D-7) and (D-8), subscripts on $A$ are again defined as partial derivatives.
\[ A_v = \left( \frac{\partial A}{\partial V} \right)_{T,N} \quad ; \quad A_a = \left( \frac{\partial A}{\partial N_a} \right)_{T,V,N_i \neq a} \]

Eq. (D-7) simplifies to

\[ A_{aa} = \int_{-\infty}^{V} A_{vaa} \, dV + RT \frac{V}{N_a} \quad \text{(D-9)} \]

Eq. (D-8) becomes (for \( a \neq b \))

\[ A_{ab} = \int_{-\infty}^{V} A_{vab} \, dV \quad \text{(D-10)} \]

Eqs. (D-7) and (D-8) (or (D-9) and (D-10)) may be used to find the second derivative of the Helmholtz Free Energy with respect to mole numbers, given pressure as a function of temperature, total volume and mole numbers.
APPENDIX E

REDLICH–KWONG DERIVATIVES

This appendix derives the derivatives of the Redlich–Kwong equation-of-state used in evaluating the stability and critical point conditions of a binary mixture. The required derivatives in terms of \( A \), the Helmholtz Free Energy, are \( A_{vv}, A_{va}, A_{aa}, A_{vvv}, A_{vva}, A_{vaa} \) and \( A_{aaa} \).

Eq. (162) gives \( A_v \) in terms of \( V, T, N_a \) and \( N_b \). The derivatives \( A_{vv}, A_{va}, A_{vvv}, A_{vva} \) and \( A_{vaa} \) are thus evaluated directly:

\[
A_{vv} = \frac{NRT}{(V-E_f)^2} \frac{-\Theta_d + \Theta_d}{V^2 (V+E_f)^2}
\]  
(E-1)

\[
A_{va} = \frac{RT}{V-E_f} \left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{NRT}{V} + \left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{1}{V} + \left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{1}{V+E_f} \frac{\Theta_d}{(V+E_f)^2}
\]  
(E-2)

\[
A_{vvv} = \frac{2NRT}{(V-E_f)^3} \frac{2\Theta_d}{V^3 (V+E_f)^3}
\]  
(E-3)

\[
A_{vva} = \frac{RT}{(V-E_f)^2} + \frac{2(\partial \Theta_f)}{(\partial N_a)} \frac{NRT}{V} - \frac{2(\partial \Theta_f)}{(\partial N_a)} \frac{1}{V} \]

\[ \frac{1}{(V+E_f)^2} \frac{\Theta_d}{(V+E_f)^2} \]

\[
A_{vaa} = \left[ \frac{\partial^2 \Theta_f}{\partial N_a^2} \right] \frac{NRT + 2(\partial \Theta_f) \frac{RT}{(V-E_f)^2}}{\left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{1}{V} - 2 \left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{1}{(V+E_f)^2} \frac{\Theta_d}{(V+E_f)^2} \]

\[ - \left( \frac{\partial \Theta_d}{\partial N_a} \right) \frac{1}{V+E_f} + \left[ \frac{\partial^2 \Theta_f}{\partial N_a^2} \right] \frac{\Theta_d + 2 \frac{\partial \Theta_f}{\partial N_a \frac{1}{(V+E_f)^2}} \left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{1}{(V+E_f)^2} \]

\[ - 2 \left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{2 \Theta_d}{(V+E_f)^3} \]  
(E-5)
Eq. (D-9) (from Appendix D) gives a formula for $A_{aa}$ in terms of $A_{vaa}$. $A_{aa}$ and $A_{aaa}$ are calculated using Eqs. (D-9) and (I-5)

$$A_{aa} = \left( \frac{\partial^2 \Theta_f}{\partial N_a^2} \right) \ln \left( \frac{V}{V + \Theta_f} \right) + \left[ \frac{\partial^2 \Theta_f}{\partial N_a^2} \right] NRT + 2 \left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{1}{V - \Theta_f} \left( \frac{\partial \Theta_f}{\partial N_a} \right) \left( \frac{\partial \Theta_f}{\partial N_a} \right) RT \left( \frac{\partial \Theta_f}{\partial N_a} \right)^2$$

$$-\left[ \frac{\partial^2 \Theta_f}{\partial N_a^2} \right] \Theta_d + 2 \left( \frac{\partial \Theta_f}{\partial N_a} \right) \left( \frac{\partial \Theta_f}{\partial N_a} \right) \left( \frac{\partial \Theta_f}{\partial N_a} \right) + \left( \frac{\partial \Theta_f}{\partial N_a} \right)^2 \frac{\Theta_d}{\Theta_f} + \frac{RT}{N_a}$$

$$\text{(E-6)}$$

$$A_{aaa} = \left( \frac{\partial^3 \Theta_f}{\partial N_a^3} \right) \ln \left( \frac{V}{V + \Theta_f} \right) + \left[ \frac{\partial^3 \Theta_f}{\partial N_a^3} \right] NRT + 3 \left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{1}{V - \Theta_f} \left( \frac{\partial \Theta_f}{\partial N_a} \right)^3 \left( \frac{\partial \Theta_f}{\partial N_a} \right)^3$$

$$-\left[ \frac{\partial^3 \Theta_f}{\partial N_a^3} \right] \Theta_d + 3 \left( \frac{\partial \Theta_f}{\partial N_a} \right) \left( \frac{\partial \Theta_f}{\partial N_a} \right) \left( \frac{\partial \Theta_f}{\partial N_a} \right) + 3 \left( \frac{\partial \Theta_f}{\partial N_a} \right) \left( \frac{\partial \Theta_f}{\partial N_a} \right) \left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{1}{V - \Theta_f}$$

$$+ \left( \frac{\partial \Theta_f}{\partial N_a} \right)^2 \left( \frac{\partial \Theta_f}{\partial N_a} \right) \left( \frac{\partial \Theta_f}{\partial N_a} \right) + \left( \frac{\partial \Theta_f}{\partial N_a} \right)^2 \left( \frac{\partial \Theta_f}{\partial N_a} \right) \frac{1}{V - \Theta_f}$$

$$-2 \left( \frac{\partial \Theta_f}{\partial N_a} \right)^3 \Theta_d \frac{\Theta_d}{\Theta_f} - \frac{RT}{N_a}$$

$$\text{(E-7)}$$

$\Theta_d$ and $\Theta_f$ are expressed in terms of mole numbers in Eqs. (163) and (164). Using Eqs. (163) and (164) to evaluate the derivatives of $\Theta_d$ and $\Theta_f$

$$\left( \frac{\partial \Theta_d}{\partial N_a} \right) = 2a^5 \left( \frac{N_a a^5 + N_b a^5}{N_a b + N_b b} - b_a (N_a a^5 + N_b a^5)^2 \right)$$

$$\text{(E-8)}$$

$$\left( \frac{\partial^2 \Theta_d}{\partial N_a^2} \right) = \frac{2a^5}{N_a b + N_b b} - 4a^5 \frac{b_a N_a a^5 + N_b a^5}{(N_a b + N_b b)^2} + 2b^2_a (N_a a^5 + N_b a^5)^2$$

$$\text{(E-9)}$$

$$\left( \frac{\partial^3 \Theta_d}{\partial N_a^3} \right) = -6a^5 b_a + 12a^5 \frac{b_a N_a a^5 + N_b a^5}{(N_a b + N_b b)^2} - 6b^2_a (N_a a^5 + N_b a^5)^2$$

$$\text{(E-10)}$$

$$\left( \frac{\partial \Theta_f}{\partial N_a} \right) = \frac{b_a}{N_a}$$

$$\text{(E-11)}$$
Eqs. (E-1) through (E-7), which use Eqs. (E-8) through (E-13), are the desired formulas.
APPENDIX F

NOMENCLATURE

LETTERS

A — Helmholtz Free Energy = U - TS
a — a' / T^\gamma
a' — constant in the Redlich-Kwong equation-of-state
a'' — a' / T_c^\gamma
B — n by n determinant
Bi — B with the i^{th} row and j^{th} column removed
Bi_j km — Bi with the k^{th} row and m^{th} column removed
B' — B with the second and m^{th} columns interchanged
b — constant in the Redlich-Kwong equation-of-state
C_{kij} — D_k with all U_{km} in the k^{th} row changed to U_{im} and all U_{mk} in the k^{th} column changed to U_{mj}
C_p — heat capacity at constant pressure = T \frac{\delta S}{\delta T}/P
C_v — heat capacity at constant volume = T \frac{\delta S}{\delta T}/V
D_k — k by k determinant with U_{ij}; the i^{th} by j^{th} term
E_m — \sum_{k=m}^{n} \sum_{j=m}^{n} C_{m,k} \Xi_{m,k} \Xi_{j} \Xi_{k} x_k x_j
G — Gibbs Free Energy = U - TS + PV
H — total enthalpy = U + PV
L_i — the determinant

\begin{vmatrix}
\psi_{i+1,i+1}^{(1)} & \cdots & \psi_{i+1,n-1}^{(1)} \\
\vdots & \ddots & \vdots \\
\psi_{n-1,i+1}^{(1)} & \cdots & \psi_{n-1,n-1}^{(1)}
\end{vmatrix}
$M_{ij}$ — $L_i$ with the $j^{th}$ term in the last row replaced with the derivative of $L_i$ with respect to $x_{i+j}$

$m$ — the number of components in the system

$N$ — the total number of moles

$n$ — the number of independent variables = $m+2$

$P$ — pressure

$P_c$ — critical pressure

$P_R$ — reduced pressure = $P/P_c$

$R$ — Gas constant

$S$ — total entropy

$T$ — temperature

$T_c$ — critical temperature

$T_R$ — reduced temperature = $T/T_c$

$U$ — total internal energy

$V$ — total volume

$V$ — specific volume

$V_c$ — critical volume

$V_{c_R}$ — $V_R / R T_c$

$x_a$ — (letter subscript) mole fraction of component $a$

$x_i$ — (number subscript) $i^{th}$ fundamental variable (either $S, V$ or $N_j$)

$y$ — function of $x$, through $x_n=U$

$Z_k = \sum_{j=k}^{n} \frac{C_{kk} x_j}{D_k}$
OTHER SYMBOLS

\( \mu \) — chemical potential

\( \lambda(T) \) — purely temperature dependent part of the fugacity

\( \omega \) — acentric factor

\( \Psi \) — Legendre Transform of \( y \) from \( x_i \) to \( \xi_i \), space = \( y - \xi_i x_i \)

\( \Psi^{(p)} \) — \( p \)th Legendre Transform of \( y \) from \( x_i \) through \( x_r \) to \( \xi_i \), through \( \xi_p \), space = \( y - \sum_{i=1}^{p} \xi_i x_i \)

\( \xi_i \) — conjugate variable of \( x_i \) = \( \frac{\partial y}{\partial x_i} \)

\( \mathcal{L}_o \) — \([\#]\mathcal{L}_o\)

\([\#]\) — the derivative operator \( [\frac{\partial}{\partial x_j} - \frac{\partial \psi}{\partial y_{ij}} \frac{\partial}{\partial x_i}] \)

\( \epsilon_a \) — 0.427480

\( \epsilon_b \) — 0.086640

\( \epsilon_c \) — \( \sigma_a/(\epsilon_b T R^5) \)

\( \epsilon_d \) — \( -Na/b \)

\( \epsilon_f \) — \( Nb \)

OTHER SUBSCRIPTS

Subscripts on \( U, A, G \) and \( H \), and numerical subscripts on \( y, \Psi \) and \( \Psi^{(p)} \) indicate partial derivatives with respect to the corresponding variable. Otherwise, subscripts indicate that the value is of the corresponding component.

\( U_S \) — derivative of \( U \) with respect to \( S \)

\( N_a \) — number of moles of component \( a \)
SUPERSCRIP'TS

* —evaluated at the limit of infinite total volume

* —value around which an expansion is being made
APPENDIX G

LITERATURE CITATIONS


