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UNITED STATES
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INTERNAL REPORT

EQUATIONS FOR CALCULATING THE THERMODYNAMIC PROPERTIES OF
FLUIDS, INCLUDING THOSE IN THE TWO-PHASE REGION,
FROM AN EMPIRICAL EQUATION OF STATE

BY

_____Robert E. Barieau_____

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BRANCH   _____Fundamental Research_____

PROJECT NO.   _____4335_____

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Robert E. Barieau[1]

ABSTRACT

General expressions for evaluating practically all the thermo-
dynamic properties of a fluid from a single equation of state are
derived. The formulas are expressed in terms of the compressibility
factor, with this factor being an explicit function of the tempera-
ture and the molal density. Similar expressions are given using
reduced variables.

INTRODUCTION

The Helium Research Center has, as one of its long-range
objectives, the development of an equation of state for helium
that will allow all of the thermodynamic properties to be cal-
culated within the accuracy with which they are known. This
includes the calculation of the vapor pressure temperature
relationship and other thermodynamic properties in the two-phase
region.

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In this report, we derive the formulas for calculating all the thermodynamic properties of interest from a single equation of state, where the equation of state is given by the compressibility factor being an explicit function of temperature and the molal density. Similar formulas are given in terms of reduced variables.

EQUATION OF STATE

We take as our equation of state

$$P = \rho RTZ \tag{1}$$

where P is the pressure; ρ is the molal density; R is the universal gas constant; T is the absolute temperature; and Z is the compressibility factor and is actually defined by equation (1). However, we will assume that an empirical analytical expression for Z, explicit in ρ and T is available. Thus, we assume

$$Z = Z(\rho, T) \tag{2}$$

At the critical point, we have from equation (1)

$$P_c = \rho_c RT_c Z_c \tag{3}$$

where P_c is the critical pressure; ρ_c is the critical molal density; T_c is the critical absolute temperature; and Z_c is the critical compressibility factor.

Dividing equation (1) by equation (3), we have

$$\frac{P}{P_c} = \frac{\rho}{\rho_c} \frac{T}{T_c} \frac{Z}{Z_c} \tag{4}$$

We now define the reduced variables

$$\beta = P/P_c, \text{ the reduced pressure} \tag{5}$$

$$\alpha = \rho/\rho_c, \text{ the reduced molal density} \tag{6}$$

and

$$\gamma = T/T_c, \text{ the reduced absolute temperature} \tag{7}$$

Substituting equations (5), (6), and (7) into equation (4), we have as our reduced equation of state

$$\beta = \frac{\alpha\gamma Z}{Z_c} \tag{8}$$

where now

$$Z = Z(\alpha,\gamma) \tag{9}$$

USUAL CRITICAL CONDITIONS

We accept as an empirical fact that at the critical point, the following relationships hold.

$$\left(\frac{\partial P}{\partial \rho}\right)_T (\rho=\rho_c; \ T=T_c) = 0 \tag{10}$$

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T (\rho=\rho_c; \ T=T_c) = 0 \tag{11}$$

EQUIVALENT CRITICAL CONDITIONS

Differentiating equation (1) with regard to the molal density, keeping the temperature constant, we have

$$\left(\frac{\partial P}{\partial \rho}\right)_T = RTZ + \rho RT\left(\frac{\partial Z}{\partial \rho}\right)_T \tag{12}$$

Differentiating equation (12), we have

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 2RT\left(\frac{\partial Z}{\partial \rho}\right)_T + \rho RT\left(\frac{\partial^2 Z}{\partial \rho^2}\right)_T \tag{13}$$

Setting equation (12) equal to zero at the critical point, we have

$$\left(\frac{\partial Z}{\partial \rho}\right)_T (\rho=\rho_c;\ T=T_c) = \frac{-Z_c}{\rho_c} \tag{14}$$

Substituting $\rho=\alpha\rho_c$ in equation (14), we have in reduced variables

$$\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma (\alpha=1;\ \gamma=1) = -Z_c \tag{15}$$

Setting equation (13) equal to zero at the critical point, we have

$$\left(\frac{\partial^2 Z}{\partial \rho^2}\right)_T (\rho=\rho_c;\ T=T_c) = -\frac{2}{\rho_c}\left(\frac{\partial Z}{\partial \rho}\right)_T (\rho=\rho_c;\ T=T_c) \tag{16}$$

and substituting equation (14) into equation (16), we have

$$\left(\frac{\partial^2 Z}{\partial \rho^2}\right)_T (\rho=\rho_c;\ T=T_c) = \frac{2Z_c}{\rho_c^2} \tag{17}$$

In reduced variables, we have

$$\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma = \left(\frac{\partial Z}{\partial \rho}\right)_T\left(\frac{\partial \rho}{\partial \alpha}\right)_T \tag{18}$$

but

$$\left(\frac{\partial \rho}{\partial \alpha}\right)_T \;=\; \rho_c \tag{19}$$

so that

$$\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma \;=\; \rho_c \left(\frac{\partial Z}{\partial \rho}\right)_T \tag{20}$$

Then

$$\left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_\gamma \;=\; \rho_c \left(\frac{\partial^2 Z}{\partial \rho^2}\right)_T \left(\frac{\partial \rho}{\partial \alpha}\right)_T \tag{21}$$

and thus

$$\left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_\gamma \;=\; \rho_c^2 \left(\frac{\partial^2 Z}{\partial \rho^2}\right)_T \tag{22}$$

Substituting equation (17) into equation (22), we have at the critical point

$$\left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_\gamma (\alpha=1;\ \gamma=1) \;=\; 2Z_c \tag{23}$$

Equations (15) and (23) are equivalent critical conditions, but expressed in terms of reduced variables and the critical compressibility factor.

THE PRESSURE-TEMPERATURE COEFFICIENT AT CONSTANT DENSITY

Differentiating equation (1) with regard to the temperature at constant density, we have

$$\left(\frac{\partial P}{\partial T}\right)_\rho \;=\; \rho R Z + \rho R T \left(\frac{\partial Z}{\partial T}\right)_\rho \tag{24}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\rho} = \rho RZ\left[1 + \frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\right] \tag{25}$$

Differentiating equation (8) with regard to the reduced temperature at constant reduced density, we obtain

$$\left(\frac{\partial \beta}{\partial \gamma}\right)_{\alpha} = \frac{\alpha Z}{Z_c}\left[1 + \frac{\gamma}{Z}\left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha}\right] \tag{26}$$

THE PRESSURE-DENSITY COEFFICIENT AT CONSTANT TEMPERATURE

Differentiating equation (1) with regard to the molal density at constant temperature, we find

$$\left(\frac{\partial P}{\partial \rho}\right)_{T} = RTZ + \rho RT\left(\frac{\partial Z}{\partial \rho}\right)_{T} \tag{27}$$

$$\left(\frac{\partial P}{\partial \rho}\right)_{T} = RTZ\left[1 + \frac{\rho}{Z}\left(\frac{\partial Z}{\partial \rho}\right)_{T}\right] \tag{28}$$

Differentiating equation (8) with regard to the reduced molal density at constant reduced temperature, we find

$$\left(\frac{\partial \beta}{\partial \alpha}\right)_{\gamma} = \frac{\gamma Z}{Z_c}\left[1 + \frac{\alpha}{Z}\left(\frac{\partial Z}{\partial \alpha}\right)_{\gamma}\right] \tag{29}$$

THE DENSITY-TEMPERATURE COEFFICIENT AT CONSTANT PRESSURE

We have, for any change,

$$dP = \left(\frac{\partial P}{\partial T}\right)_{\rho} dT + \left(\frac{\partial P}{\partial \rho}\right)_{T} d\rho \tag{30}$$

Then at constant pressure,

$$\left(\frac{\partial \rho}{\partial T}\right)_P = -\frac{\left(\frac{\partial P}{\partial T}\right)_\rho}{\left(\frac{\partial P}{\partial \rho}\right)_T} \tag{31}$$

Substituting equations (25) and (28) into equation (31), we have

$$\left(\frac{\partial \rho}{\partial T}\right)_P = -\frac{\rho}{T}\frac{\left[1 + \frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_\rho\right]}{\left[1 + \frac{\rho}{Z}\left(\frac{\partial Z}{\partial \rho}\right)_T\right]} \tag{32}$$

In reduced variables, we find

$$\left(\frac{\partial \alpha}{\partial \gamma}\right)_\beta = -\frac{\alpha}{\gamma}\frac{\left[1 + \frac{\gamma}{Z}\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right]}{\left[1 + \frac{\alpha}{Z}\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma\right]} \tag{33}$$

THE LOG VOLUME-PRESSURE COEFFICIENT AT CONSTANT TEMPERATURE

$$-\left(\frac{\partial \ln V}{\partial P}\right)_T = \left(\frac{\partial \ln \rho}{\partial P}\right)_T \tag{34}$$

$$= \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \tag{35}$$

$$= \frac{1}{\rho\left(\frac{\partial P}{\partial \rho}\right)_T} \tag{36}$$

Substituting equation (28) into equation (36), we have

$$-\left(\frac{\partial \ln V}{\partial P}\right)_T = \frac{1}{\rho RTZ\left[1 + \frac{\rho}{Z}\left(\frac{\partial Z}{\partial \rho}\right)_T\right]} \tag{37}$$

In reduced variables, we have

$$-P_c\left(\frac{\partial \ln V}{\partial P}\right)_T = \frac{Z_c}{\alpha \gamma Z\left[1 + \frac{\alpha}{Z}\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma\right]} \tag{38}$$

THE LOG VOLUME-TEMPERATURE COEFFICIENT AT CONSTANT PRESSURE

$$\left(\frac{\partial \ln V}{\partial T}\right)_P = -\left(\frac{\partial \ln \rho}{\partial T}\right)_P \tag{39}$$

$$= -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{40}$$

Substituting equation (32) into equation (40), we have

$$\left(\frac{\partial \ln V}{\partial T}\right)_P = \frac{\left[1 + \frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_\rho\right]}{T\left[1 + \frac{\rho}{Z}\left(\frac{\partial Z}{\partial \rho}\right)_T\right]} \tag{41}$$

In reduced variables, we have

$$T_c\left(\frac{\partial \ln V}{\partial T}\right)_P = \frac{\left[1 + \frac{\gamma}{Z}\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right]}{\gamma\left[1 + \frac{\alpha}{Z}\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma\right]} \tag{42}$$

THE SECOND DERIVATIVE OF THE PRESSURE WITH
REGARD TO THE TEMPERATURE AT CONSTANT DENSITY

Differentiating equation (24) with regard to the temperature at constant density, we have

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho = 2\rho R\left(\frac{\partial Z}{\partial T}\right)_\rho + \rho RT\left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho \tag{43}$$

Differentiating equation (26) with regard to the reduced temperature at constant reduced density, we have

$$\left(\frac{\partial^2 \beta}{\partial \gamma^2}\right)_\alpha = \frac{2\alpha}{Z_c}\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha + \frac{\alpha\gamma}{Z_c}\left(\frac{\partial^2 Z}{\partial \gamma^2}\right)_\alpha \tag{44}$$

THE FUGACITY FUNCTION

We have from the definition of fugacity

$$\ln f/P = \int_0^P (Z-1)\frac{dP}{P} \tag{45}$$

where f is the fugacity, and the integral in equation (45) is to be carried out at constant temperature. From equation (1), it follows

$$\ln P = \ln \rho + \ln R + \ln T + \ln Z \tag{46}$$

Then at constant temperature,

$$\frac{dP}{P} = \frac{d\rho}{\rho} + \frac{dZ}{Z} \tag{47}$$

Substituting equation (47) into equation (45), we have

$$\ln f/P = \int_1^Z (Z-1)\,\frac{dZ}{Z} + \int_0^\rho (Z-1)\,\frac{d\rho}{\rho} \tag{48}$$

and it follows

$$\ln f/P = (Z-1) - \ln Z + \int_0^\rho (Z-1)\,\frac{d\rho}{\rho} \tag{49}$$

In reduced variables, we have

$$\ln f/P = (Z-1) - \ln Z + \int_0^\alpha (Z-1)\,\frac{d\alpha}{\alpha} \tag{50}$$

THE RELATIVE INTERNAL ENERGY

We have from the first and second laws of thermodynamics

$$dE = TdS - PdV \tag{51}$$

where E is the internal energy, and S is the entropy.

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \tag{52}$$

But

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{53}$$

So that

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{54}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial E}{\partial \rho}\right)_T \frac{d\rho}{dV} = -\frac{1}{V^2}\left(\frac{\partial E}{\partial \rho}\right)_T \tag{55}$$

or

$$\left(\frac{\partial E}{\partial V}\right)_T = -\rho^2\left(\frac{\partial E}{\partial \rho}\right)_T \tag{56}$$

Substituting equation (56) into equation (54), we have

$$\rho^2\left(\frac{\partial E}{\partial \rho}\right)_T = P - T\left(\frac{\partial P}{\partial T}\right)_\rho \tag{57}$$

Now substituting equation (1) and equation (24) into equation (57), we have

$$\rho^2\left(\frac{\partial E}{\partial \rho}\right)_T = -\rho RT^2\left(\frac{\partial Z}{\partial T}\right)_\rho \tag{58}$$

So that

$$\left(\frac{\partial E}{\partial \rho}\right)_T = -\frac{RT^2}{\rho}\left(\frac{\partial Z}{\partial T}\right)_\rho \tag{59}$$

We now integrate equation (59) from $\rho=0$ to $\rho=\rho$ and obtain

$$E-E^O = -RT^2 \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} \tag{60}$$

We call $E-E^O$ the reduced internal energy.

In reduced variables, we have

$$\frac{E-E^O}{RT_c} = -\gamma^2 \int_0^\alpha \left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha} \tag{61}$$

THE RELATIVE HEAT CAPACITY AT CONSTANT VOLUME

As

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V \tag{62}$$

We have on differentiating equation (60), with regard to the temperature, at constant density

$$C_V - C_V^o = -2RT \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - RT^2 \int_0^\rho \left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho \frac{d\rho}{\rho} \tag{63}$$

where C_V^o is the heat capacity at constant volume at zero density, and C_V is the heat capacity at constant volume at density, ρ. The integrals in equation (63) are to be evaluated at constant temperature. We call the quantity $C_V - C_V^o$, the relative heat capacity at constant volume.

In reduced variables, we have

$$\frac{C_V - C_V^o}{R} = -2\gamma \int_0^\alpha \left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha} - \gamma^2 \int_0^\alpha \left(\frac{\partial^2 Z}{\partial \gamma^2}\right)_\alpha \frac{d\alpha}{\alpha} \tag{64}$$

THE RELATIVE HEAT CONTENT OR RELATIVE ENTHALPY

From the definition of heat content or enthalpy, we have

$$H = E + PV \tag{65}$$

where H is the heat content or enthalpy. At zero density

$$H^o = E^o + (PV)^o \tag{66}$$

where H^O is the heat content or enthalpy at zero density. At

zero density,

$$(PV)^O = RT \tag{67}$$

So that

$$H^O = E^O + RT$$

Then

$$L = H - H^O = E - E^O + PV - RT \tag{68}$$

or

$$L = E - E^O + RT(Z-1) \tag{69}$$

We call the quantity $L = H - H^O$ the relative heat content or the

relative enthalpy.

Substituting equation (60) into equation (69), we have

$$L = RT(Z-1) - RT^2 \int_0^{\rho} \left(\frac{\partial Z}{\partial T}\right)_{\rho} \frac{d\rho}{\rho} \tag{70}$$

In reduced variables, we have

$$\frac{L}{RT_c} = \gamma(Z-1) - \gamma^2 \int_0^{\alpha} \left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha} \frac{d\alpha}{\alpha} \tag{71}$$

THE RELATIVE HEAT CAPACITY AT CONSTANT PRESSURE

As

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p \tag{72}$$

where C_p is the heat capacity at constant pressure. Then

$$\left(\frac{\partial L}{\partial T}\right)_P = C_p - C_p^o \tag{73}$$

where C_p^o is the heat capacity at constant pressure at zero density or pressure. Now

$$dL = \left(\frac{\partial L}{\partial T}\right)_\rho dT + \left(\frac{\partial L}{\partial \rho}\right)_T d\rho \tag{74}$$

So that

$$\left(\frac{\partial L}{\partial T}\right)_P = \left(\frac{\partial L}{\partial T}\right)_\rho + \left(\frac{\partial L}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_P \tag{75}$$

Differentiating equation (70) with regard to the temperature at constant density, we have

$$\left(\frac{\partial L}{\partial T}\right)_\rho = R(Z-1) + RT\left(\frac{\partial Z}{\partial T}\right)_\rho - 2RT \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - RT^2 \int_0^\rho \left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho \frac{d\rho}{\rho} \tag{76}$$

Differentiating equation (70) with regard to the density at constant temperature, we have

$$\left(\frac{\partial L}{\partial \rho}\right)_T = RT\left(\frac{\partial Z}{\partial \rho}\right)_T - \frac{RT^2}{\rho}\left(\frac{\partial Z}{\partial T}\right)_\rho \tag{77}$$

$\left(\frac{\partial \rho}{\partial T}\right)_P$ is given by equation (32). Substituting equations (32), (76), and (77) into equation (75) enables $C_p - C_p^o$ to be calculated.

In reduced variables, we have

$$\frac{C_p - C_p^o}{R} = \left(\frac{\partial \frac{L}{RT_c}}{\partial \gamma}\right)_\alpha + \left(\frac{\partial \frac{L}{RT_c}}{\partial \alpha}\right)_\gamma \left(\frac{\partial \alpha}{\partial \gamma}\right)_\beta \tag{78}$$

where from equation (71), we have

$$\left(\frac{\partial \frac{L}{RT_c}}{\partial \gamma}\right)_{\alpha} = (Z-1) + \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha} - 2\gamma\int_0^\alpha \left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha}\frac{d\alpha}{\alpha} - \gamma^2\int_0^\alpha \left(\frac{\partial^2 Z}{\partial \gamma^2}\right)_{\alpha}\frac{d\alpha}{\alpha} \quad (79)$$

and

$$\left(\frac{\partial \frac{L}{RT_c}}{\partial \alpha}\right)_{\gamma} = \gamma\left(\frac{\partial Z}{\partial \alpha}\right)_{\gamma} - \frac{\gamma^2}{\alpha}\left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha} \quad (80)$$

and where $\left(\frac{\partial \alpha}{\partial \gamma}\right)_{\beta}$ in equation (78) is given by equation (33).

THE RELATIVE ENTROPY

The Gibbs free energy is defined by

$$G = H - TS \quad (81)$$

where G is the Gibbs free energy; then

$$G - G^o = H - H^o - T(S - S^o) \quad (82)$$

where G^o is the Gibbs free energy in the hypothetical standard state of unit fugacity and with the same heat content or enthalpy as the real gas at zero density.

From the definition of fugacity

$$G - G^o = RT \ln f \quad (83)$$

So that

$$S - S^o = \frac{H - H^o}{T} - R \ln f \quad (84)$$

or

$$S - S^o = \frac{L}{T} - R \ln f \qquad (85)$$

where S^o is the entropy of the gas in the hypothetical standard state of unit fugacity.

Substituting equations (49) and (70) into equation (85), we have

$$S - S^o = -RT \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - R \ln P + R \ln Z - R \int_0^\rho (Z-1) \frac{d\rho}{\rho} \qquad (86)$$

$$S - S^o = R \ln \frac{Z}{P} - RT \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - R \int_0^\rho (Z-1) \frac{d\rho}{\rho} \qquad (87)$$

Then it follows

$$S - S^o = R \ln \frac{1}{\rho RT} - R \int_0^\rho \left[\frac{\partial T(Z-1)}{\partial T}\right]_\rho \frac{d\rho}{\rho} \qquad (88)$$

and finally

$$S - S^o = -R \ln \rho RT - R \int_0^\rho \left[\frac{\partial T(Z-1)}{\partial T}\right]_\rho \frac{d\rho}{\rho} \qquad (89)$$

In reduced variables, we have

$$\frac{S - S^o + R \ln P_c}{R} = \ln \frac{Z}{\beta} - \int_0^\alpha \left[\frac{\partial \gamma(Z-1)}{\partial \gamma}\right]_\alpha \frac{d\alpha}{\alpha} \qquad (90)$$

or

$$\frac{S - S^o + R \ln P_c}{R} = -\ln \frac{\alpha \gamma}{Z_c} - \int_0^\alpha \left[\frac{\partial \gamma (Z-1)}{\partial \gamma}\right]_\alpha \frac{d\alpha}{\alpha} \tag{91}$$

THE REDUCED SECOND VIRIAL COEFFICIENT

We define the second virial coefficient, B, as

$$B = \left(\frac{\partial Z}{\partial \rho}\right)_T (\rho = 0) \tag{92}$$

Then in reduced units, we have

$$B\rho_c = \left(\frac{\partial Z}{\partial \alpha}\right)_\gamma (\alpha = 0) \tag{93}$$

We now define

$$B_r = B\rho_c \tag{94}$$

and call this quantity the reduced second virial coefficient.

Thus,

$$B_r = \left(\frac{\partial Z}{\partial \alpha}\right)_\gamma (\alpha = 0) \tag{95}$$

THE REDUCED THIRD VIRIAL COEFFICIENT

We define the third virial coefficient, C, as

$$C = \left(\frac{\partial^2 Z}{\partial \rho^2}\right)_T (\rho = 0) \tag{96}$$

Then in reduced units, we have

$$C\rho_c^2 = \left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_\gamma (\alpha = 0) \tag{97}$$

We now define

$$C_r = C\rho_c^2$$

and call this quantity the reduced third virial coefficient.

Thus

$$C_r = \left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_\gamma (\alpha=0) \tag{98}$$

THE SECOND DERIVATIVE OF THE CHEMICAL POTENTIAL OR GIBBS FREE ENERGY WITH REGARD TO THE TEMPERATURE AT CONSTANT DENSITY

From the definition of the Gibbs free energy, G, and the first and second laws of thermodynamics, we have

$$dG = -SdT + VdP \tag{99}$$

Then

$$\left(\frac{\partial G}{\partial T}\right)_\rho = -S + \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho \tag{100}$$

Differentiating equation (100) with regard to the temperature keeping the density constant, we have

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_\rho = -\left(\frac{\partial S}{\partial T}\right)_\rho + \frac{1}{\rho}\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho \tag{101}$$

Now

$$\left(\frac{\partial S}{\partial T}\right)_\rho = \frac{C_V}{T} \tag{102}$$

and thus

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_\rho = -\frac{C_V}{T} + \frac{1}{\rho}\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho \tag{103}$$

Substituting equations (43) and (63) into equation (103),
we have

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_\rho = \frac{-C_V^o}{T} + 2R \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} + RT \int_0^\rho \left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho \frac{d\rho}{\rho} + 2R\left(\frac{\partial Z}{\partial T}\right)_\rho + RT\left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho \quad (104)$$

which may be written

$$-T\left(\frac{\partial^2 G}{\partial T^2}\right)_\rho - C_V^o = -2RT \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - RT^2 \int_0^\rho \left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho \frac{d\rho}{\rho} - 2RT\left(\frac{\partial Z}{\partial T}\right)_\rho - RT^2\left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho \quad (105)$$

In reduced variables, we have

$$\frac{-T\left(\frac{\partial^2 G}{\partial T^2}\right)_\rho - C_V^o}{R} = -2\gamma \int_0^\alpha \left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha} - \gamma^2 \int_0^\alpha \left(\frac{\partial^2 Z}{\partial \gamma^2}\right)_\alpha \frac{d\alpha}{\alpha} - 2\gamma\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha - \gamma^2\left(\frac{\partial^2 Z}{\partial \gamma^2}\right)_\alpha \quad (106)$$

THE DIFFERENCE BETWEEN THE HEAT
CAPACITIES AT CONSTANT PRESSURE AND AT CONSTANT VOLUME

We have

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p \quad (72)$$

and

$$\left(\frac{\partial E}{\partial T}\right)_\rho = C_V \quad (62)$$

So that

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_\rho \quad (107)$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_\rho + \left(\frac{\partial H}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_P \tag{108}$$

and it follows

$$C_p - C_V = \left[\frac{\partial (H-E)}{\partial T}\right]_\rho + \left(\frac{\partial H}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_P \tag{109}$$

From equation (65), we have

$$H-E = PV = RTZ \tag{110}$$

Then

$$\left[\frac{\partial (H-E)}{\partial T}\right]_\rho = RZ + RT\left(\frac{\partial Z}{\partial T}\right)_\rho \tag{111}$$

$$\left[\frac{\partial (H-E)}{\partial T}\right]_\rho = R\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right] \tag{112}$$

Now

$$\left(\frac{\partial H}{\partial \rho}\right)_T = \left(\frac{\partial L}{\partial \rho}\right)_T \tag{113}$$

and we thus have from equation (77)

$$\left(\frac{\partial H}{\partial \rho}\right)_T = RT\left(\frac{\partial Z}{\partial \rho}\right)_T - \frac{RT^2}{\rho}\left(\frac{\partial Z}{\partial T}\right)_\rho \tag{114}$$

Multiplying equation (114) by equation (32), we have

$$\left(\frac{\partial H}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_P = \frac{-R\left[\rho\left(\frac{\partial Z}{\partial \rho}\right)_T - T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]\left[1 + \frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_\rho\right]}{\left[1 + \frac{\rho}{Z}\left(\frac{\partial Z}{\partial \rho}\right)_T\right]} \tag{115}$$

$$\left(\frac{\partial H}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_P = - \frac{R\left[\rho\left(\frac{\partial Z}{\partial \rho}\right)_T - T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]}{\left[Z + \rho\left(\frac{\partial Z}{\partial \rho}\right)_T\right]} \tag{116}$$

Adding equations (112) and (116), we have

$$C_p - C_V = R\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]\left\{1 - \frac{\left[\rho\left(\frac{\partial Z}{\partial \rho}\right)_T - T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]}{\left[Z + \rho\left(\frac{\partial Z}{\partial \rho}\right)_T\right]}\right\} \tag{117}$$

and thus

$$C_p - C_V = \frac{R\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]^2}{\left[Z + \rho\left(\frac{\partial Z}{\partial \rho}\right)_T\right]} \tag{118}$$

In reduced variables, we have

$$\frac{C_p - C_V}{R} = \frac{\left[Z + \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right]^2}{\left[Z + \alpha\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma\right]} \tag{119}$$

THE RATIO OF THE HEAT CAPACITIES AT
CONSTANT PRESSURE AND AT CONSTANT VOLUME

We have

$$\frac{C_p}{C_V} = \frac{(C_p - C_V) + C_V}{C_V} \tag{120}$$

C_V should be calculated from equation (63) and $C_p - C_V$ from

equation (118). The substitution of these quantities into

equation (120) enables C_p/C_V to be calculated. In reduced variables, we have

$$\frac{C_p}{C_V} = \frac{\dfrac{C_p - C_V}{R} + \dfrac{C_V}{R}}{\dfrac{C_V}{R}} \qquad (121)$$

Then $\dfrac{C_V}{R}$ is to be calculated from equation (64) and $\dfrac{C_p - C_V}{R}$ from equation (119) and when these two quantities are substituted in equation (121), C_p/C_V can be calculated.

THE VELOCITY OF SOUND

If the propagation of a sound wave in a gas is reversible and adiabatic, then the equation for the velocity of sound is given by (1)[2/]

[2/] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

$$Ma^2 = \frac{C_p}{C_V}\left(\frac{\partial P}{\partial \rho}\right)_T \qquad (122)$$

where M is the molecular weight, and a is the velocity of sound.

Equation (122) may be written

$$Ma^2 = \frac{C_p - C_V}{C_V}\left(\frac{\partial P}{\partial \rho}\right)_T + \left(\frac{\partial P}{\partial \rho}\right)_T \qquad (123)$$

From equations (28) and (118), we have

$$(C_p - C_V)\left(\frac{\partial P}{\partial \rho}\right)_T = R\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]^2 RT \tag{124}$$

$$= R^2 T\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]^2 \tag{125}$$

Substituting equations (28) and (125) into equation (123), we have

$$Ma^2 = \frac{R^2 T\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]^2}{C_V} + RT\left[Z + \rho\left(\frac{\partial Z}{\partial \rho}\right)_T\right] \tag{126}$$

C_V is to be calculated from equation (63). In reduced variables,

we have

$$\frac{Ma^2}{RT_c} = \frac{R\gamma\left[Z + \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right]^2}{C_V} + \gamma\left[Z + \alpha\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma\right] \tag{127}$$

C_V/R is now to be calculated from equation (64).

THE TEMPERATURE-PRESSURE COEFFICIENT AT CONSTANT ENTHALPY OR THE JOULE-THOMSON COEFFICIENT

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \tag{128}$$

where μ is the Joule-Thomson coefficient.

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{129}$$

$$dH = C_p dT + \left(\frac{\partial L}{\partial P}\right)_T dP \tag{130}$$

Then with dH = 0,

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu = -\frac{1}{C_p}\left(\frac{\partial L}{\partial P}\right)_T \qquad (131)$$

$$\mu = -\frac{1}{C_p}\left(\frac{\partial L}{\partial \rho}\right)_T\left(\frac{\partial \rho}{\partial P}\right)_T \qquad (132)$$

$$\mu = -\frac{\left(\frac{\partial L}{\partial \rho}\right)_T}{C_p\left(\frac{\partial P}{\partial \rho}\right)_T} \qquad (133)$$

Now

$$\left(\frac{\partial L}{\partial T}\right)_P = C_p - C_p^o \qquad (73)$$

so that

$$C_p = C_p^o + \left(\frac{\partial L}{\partial T}\right)_P \qquad (134)$$

Substituting equation (75) into equation (134), we have

$$C_p = C_p^o + \left(\frac{\partial L}{\partial T}\right)_\rho + \left(\frac{\partial L}{\partial \rho}\right)_T\left(\frac{\partial \rho}{\partial T}\right)_P \qquad (135)$$

Then

$$C_p\left(\frac{\partial P}{\partial \rho}\right)_T = \left[C_p^o + \left(\frac{\partial L}{\partial T}\right)_\rho\right]\left(\frac{\partial P}{\partial \rho}\right)_T + \left(\frac{\partial L}{\partial \rho}\right)_T\left(\frac{\partial \rho}{\partial T}\right)_P\left(\frac{\partial P}{\partial \rho}\right)_T \qquad (136)$$

Now

$$d\rho = \left(\frac{\partial \rho}{\partial T}\right)_P dT + \left(\frac{\partial \rho}{\partial P}\right)_T dP \qquad (137)$$

Then with $d\rho = 0$,

$$\left(\frac{\partial P}{\partial T}\right)_\rho = \frac{-\left(\frac{\partial \rho}{\partial T}\right)_P}{\left(\frac{\partial \rho}{\partial P}\right)_T} = -\left(\frac{\partial \rho}{\partial T}\right)_P \left(\frac{\partial P}{\partial \rho}\right)_T \tag{138}$$

Substituting equation (138) into equation (136), we have

$$C_p\left(\frac{\partial P}{\partial \rho}\right)_T = -\left(\frac{\partial L}{\partial \rho}\right)_T\left(\frac{\partial P}{\partial T}\right)_\rho + \left[C_p^O + \left(\frac{\partial L}{\partial T}\right)_\rho\right]\left(\frac{\partial P}{\partial \rho}\right)_T \tag{139}$$

From equation (69), we have

$$L = E - E^O + RT(Z-1) \tag{69}$$

Then

$$\left(\frac{\partial L}{\partial T}\right)_\rho = \left[\frac{\partial(E - E^O)}{\partial T}\right]_\rho + R(Z-1) + RT\left(\frac{\partial Z}{\partial T}\right)_\rho \tag{140}$$

$$= C_V - C_V^O - R + R\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right] \tag{141}$$

Substituting equation (25) into equation (141), we have

$$\left(\frac{\partial L}{\partial T}\right)_\rho = C_V - C_V^O - R + \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho \tag{142}$$

Adding C_p^O to each side of equation (142), we have

$$C_p^O + \left(\frac{\partial L}{\partial T}\right)_\rho = C_V + C_p^O - C_V^O - R + \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho \tag{143}$$

From equation (118), we see that at zero density

$$C_p^O - C_V^O = R \tag{144}$$

So that

$$c_p^o + \left(\frac{\partial L}{\partial T}\right)_\rho = c_V + \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho \tag{145}$$

Substituting equation (145) into equation (139), we have

$$c_p\left(\frac{\partial P}{\partial \rho}\right)_T = -\left(\frac{\partial L}{\partial \rho}\right)_T\left(\frac{\partial P}{\partial T}\right)_\rho + \left[c_V + \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho\right]\left(\frac{\partial P}{\partial \rho}\right)_T \tag{146}$$

Now substituting equation (146) into equation (133), we have

$$\mu = \frac{\left(\frac{\partial L}{\partial \rho}\right)_T}{\left(\frac{\partial L}{\partial \rho}\right)_T\left(\frac{\partial P}{\partial T}\right)_\rho - \left[c_V + \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho\right]\left(\frac{\partial P}{\partial \rho}\right)_T} \tag{147}$$

For substitution in equation (147): $\left(\frac{\partial L}{\partial \rho}\right)_T$ is to be calculated

from equations (113) and (114); $\left(\frac{\partial P}{\partial T}\right)_\rho$ is to be calculated from

equation (25); $\left(\frac{\partial P}{\partial \rho}\right)_T$ is to be calculated from equation (28); and

c_V is to be calculated from equation (63). In reduced variables,

equation (147) can be written

$$\frac{\mu P_c}{T_c} = \frac{\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma - \frac{\gamma}{\alpha}\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha}{\left[\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma - \frac{\gamma}{\alpha}\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right]\left(\frac{\partial \beta}{\partial \gamma}\right)_\alpha - \frac{1}{\gamma}\left[\frac{c_V}{R} + Z + \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right]\left(\frac{\partial \beta}{\partial \alpha}\right)_\gamma} \tag{148}$$

THE JOULE-THOMSON INVERSION CURVE

The Joule-Thomson inversion curve is defined as the curve for which

$$\mu = 0 \tag{149}$$

We see from equation (147) that μ will equal zero, if

$$\left(\frac{\partial L}{\partial \rho}\right)_T = 0 \tag{150}$$

and if $\left[C_V + \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho\right]\left(\frac{\partial P}{\partial \rho}\right)_T$ is not equal to zero. Then equations (113) and (114) lead to

$$\left(\frac{\partial Z}{\partial \rho}\right)_T = \frac{T}{\rho}\left(\frac{\partial Z}{\partial T}\right)_\rho \tag{151}$$

or

$$\rho\left(\frac{\partial Z}{\partial \rho}\right)_T = T\left(\frac{\partial Z}{\partial T}\right)_\rho \tag{152}$$

In reduced variables, we have

$$\alpha\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma = \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \tag{153}$$

THE PRESSURE-TEMPERATURE COEFFICIENT AT CONSTANT ENTROPY

We have from the elementary laws of differentiation

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{154}$$

Now from the first and second laws of thermodynamics

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \tag{155}$$

and

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{\rho^2}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{156}$$

Substituting equations (155) and (156) into equation (154), we have

$$dS = \frac{C_p}{T} dT + \frac{1}{\rho^2}\left(\frac{\partial \rho}{\partial T}\right)_P dP \tag{157}$$

Then with $dS = 0$, it follows

$$\left(\frac{\partial P}{\partial T}\right)_S = -\frac{C_p \rho^2}{T\left(\frac{\partial \rho}{\partial T}\right)_P} \tag{158}$$

$$\left(\frac{\partial P}{\partial T}\right)_S = -\frac{\rho^2 C_p \left(\frac{\partial T}{\partial \rho}\right)_P}{T} \tag{159}$$

We have

$$dP = \left(\frac{\partial P}{\partial T}\right)_\rho dT + \left(\frac{\partial P}{\partial \rho}\right)_T d\rho \tag{160}$$

Then with $dP = 0$

$$\left(\frac{\partial T}{\partial \rho}\right)_P = -\frac{\left(\frac{\partial P}{\partial \rho}\right)_T}{\left(\frac{\partial P}{\partial T}\right)_\rho} \tag{161}$$

So that

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{\rho^2 C_p \left(\frac{\partial P}{\partial \rho}\right)_T}{T\left(\frac{\partial P}{\partial T}\right)_\rho} \tag{162}$$

Substituting for $C_p\left(\frac{\partial P}{\partial \rho}\right)_T$ from equation (146) in equation (162), we have

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{\rho^2\left\{-\left(\frac{\partial L}{\partial \rho}\right)_T\left(\frac{\partial P}{\partial T}\right)_\rho + \left[C_V + \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho\right]\left(\frac{\partial P}{\partial \rho}\right)_T\right\}}{T\left(\frac{\partial P}{\partial T}\right)_\rho} \tag{163}$$

and it follows

$$\left(\frac{\partial P}{\partial T}\right)_S = -\frac{\rho^2\left(\frac{\partial L}{\partial \rho}\right)_T}{T} + \frac{\rho^2\left[C_V + \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho\right]\left(\frac{\partial P}{\partial \rho}\right)_T}{T\left(\frac{\partial P}{\partial T}\right)_\rho} \tag{164}$$

For substitution in equation (164): $\left(\frac{\partial L}{\partial \rho}\right)_T$ is to be calculated from equations (113) and (114); $\left(\frac{\partial P}{\partial T}\right)_\rho$ is to be calculated from equation (25); $\left(\frac{\partial P}{\partial \rho}\right)_T$ is to be calculated from equation (28); and C_V is to be calculated from equation (63). In reduced variables, equation (164) may be written

$$\left(\frac{\partial P}{\partial T}\right)_S = -R\rho_c\alpha\left[\alpha\left(\frac{\partial Z}{\partial \alpha}\right)_T - \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right] + \frac{R\rho_c\alpha^2\left[\frac{C_V}{R} + \frac{Z_c}{\alpha}\left(\frac{\partial \beta}{\partial \gamma}\right)_\alpha\right]\left(\frac{\partial \beta}{\partial \alpha}\right)_\gamma}{\gamma\left(\frac{\partial \beta}{\partial \gamma}\right)_\alpha} \tag{165}$$

But

$$R\rho_c = \frac{P_c}{T_c Z_c}$$

(166)

So that

$$\frac{T_c}{P_c}\left(\frac{\partial P}{\partial T}\right)_S = \left(\frac{\partial \beta}{\partial \gamma}\right)_S = -\frac{\alpha}{Z_c}\left[\alpha\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma - \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right] + \frac{\alpha^2\left[\dfrac{C_V}{R} + \dfrac{Z_c}{\alpha}\left(\dfrac{\partial \beta}{\partial \gamma}\right)_\alpha\right]\left(\dfrac{\partial \beta}{\partial \alpha}\right)_\gamma}{Z_c\gamma\left(\dfrac{\partial \beta}{\partial \gamma}\right)_\alpha}$$

(167)

EQUATIONS FOR TWO-PHASE EQUILIBRIUM

The equations derived so far apply to any state of a gas or

fluid. We will now derive equations that are applicable only when

two phases are present in thermodynamic equilibrium. In these

derivations, we will neglect the effect of a gravitational field

on the thermodynamic properties. The resulting equations are thus

only strictly applicable to the interface region between the two

phases, which may be considered at the same level in a gravitational

field. We thus take as our conditions for thermodynamic equilibrium:

1. The two phases must be under the same temperature;

2. The two phases must be under the same pressure; and

3. The two phases must have the same chemical potential or

Gibbs free energy.

EQUALITY OF PRESSURE AND TEMPERATURE

We have from equation (1)

$$P = \rho RTZ \tag{1}$$

For phase 1, which we think of as the gas phase, we can then write

$$P_1 = \rho_1 RT_1 Z_1 \tag{168}$$

For the second phase, which we think of as the liquid phase, we can write

$$P_3 = \rho_3 RT_3 Z_3 \tag{169}$$

Equality of pressure gives

$$P_1 = P_3 = P \tag{170}$$

and equality of temperature gives

$$T_1 = T_3 = T \tag{171}$$

It then follows that equality of pressure and temperature leads to

$$\rho_1 Z_1 = \rho_3 Z_3 \tag{172}$$

Since we have assumed Z is an explicit function of ρ and T, equation (172) establishes T as a function of ρ_1 and ρ_3, the saturated vapor and liquid densities. Once ρ_1 and ρ_3 are known, equation (172) may be solved for T. This value of T may then be substituted in the equation

$$P = \rho_1 RTZ_1 \tag{173}$$

and the equilibrium pressure calculated.

In terms of reduced variables, we have

$$\alpha_1 Z_1 = \alpha_3 Z_3 \tag{174}$$

and

$$\beta = \frac{\alpha_1 \gamma Z_1}{Z_c} \tag{175}$$

EQUALITY OF CHEMICAL POTENTIAL OR GIBBS FREE ENERGY

Equality of the chemical potential or Gibbs free energy requires

$$G_1 = G_3 \tag{176}$$

where G_1 is the Gibbs free energy of the saturated vapor, and G_3 is the Gibbs free energy of the saturated liquid, or

$$G_3 - G_1 = 0 = \int_{P_1}^{P_3} \left(\frac{\partial G}{\partial P}\right)_T dP \tag{177}$$

From the definition of G and the first and second law of thermodynamics, it can be shown

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{178}$$

Then the equality of the Gibbs free energy requires

$$\int_{P_1}^{P_3} V dP = 0 \tag{178}$$

but

$$V dP = d(PV) - P dV \tag{179}$$

Substituting equation (179) into equation (178), we have

$$\int_{P_1 V_1}^{P_3 V_3} d(PV) - \int_{V_1}^{V_3} PdV = 0 \tag{180}$$

or

$$P_3 V_3 - P_1 V_1 = \int_{V_1}^{V_3} PdV \tag{181}$$

Dividing by RT, we have

$$\frac{P_3 V_3}{RT} - \frac{P_1 V_1}{RT} = \int_{V_1}^{V_3} \frac{PV}{RT} \frac{dV}{V} \tag{182}$$

From the definition of the compressibility factor, we then have

$$Z_3 - Z_1 = \int_{V_1}^{V_3} Z \frac{dV}{V} \tag{183}$$

now

$$\frac{dV}{V} = - \frac{d\rho}{\rho} \tag{184}$$

So that

$$Z_3 - Z_1 = - \int_{\rho_1}^{\rho_3} Z \frac{d\rho}{\rho} \tag{185}$$

or finally

$$Z_1 - Z_3 = \int_{\rho_1}^{\rho_3} Z \frac{d\rho}{\rho} \tag{186}$$

Equations (172) and (186) determine the equilibrium densities, ρ_1 and ρ_3 as a function of temperature. These two equations must be solved for ρ_1 and ρ_3 as a function of T before any of the other two-phase thermodynamic properties can be calculated.

In terms of reduced variables, we have as a condition for the equality of the Gibbs free energy

$$Z_1 - Z_3 = \int_{\alpha_1}^{\alpha_3} Z \frac{d\alpha}{\alpha} \tag{187}$$

THE TEMPERATURE COEFFICIENT OF THE VAPOR PRESSURE CURVE

The expression for the temperature coefficient of the vapor pressure curve may be derived very simply from equation (181). We have, since $P_1 = P_3 = P$,

$$P(V_3 - V_1) = \int_{V_1}^{V_3} P dV \tag{188}$$

Differentiating totally with regard to the temperature, we have

$$\frac{dP}{dT}(V_3 - V_1) + P(V_3' - V_1') = \int_{V_1}^{V_3} \left(\frac{\partial P}{\partial T}\right)_V dV + P(V_3' - V_1') \tag{189}$$

or

$$\frac{dP}{dT} = \frac{1}{V_3 - V_1} \int_{V_1}^{V_3} \left(\frac{\partial P}{\partial T}\right)_V dV \tag{190}$$

Since the right-hand side of equation (190) is the average

value of $\left(\dfrac{\partial P}{\partial T}\right)_V$ over the interval V_1 to V_3, we see that as the

critical point is approached, where $V_1 = V_3$, that

$$\left(\frac{dP}{dT}\right)_{c.p.} = \left(\frac{\partial P}{\partial T}\right)_{V \atop c.p.} \tag{191}$$

and we see that the slope of the vapor pressure curve at the

critical point is continuous with the slope of the critical iso-

metric at the critical point.

Substituting for $V_3 - V_1$ from equation (188) into equation (190),

we have

$$\frac{dP}{dT} = \frac{P \displaystyle\int_{V_1}^{V_3} \left(\frac{\partial P}{\partial T}\right)_V dV}{\displaystyle\int_{V_1}^{V_3} P\,dV} \tag{192}$$

or

$$\frac{dP}{dT} = \frac{P \displaystyle\int_{\rho_1}^{\rho_3} \left(\frac{\partial P}{\partial T}\right)_\rho \frac{d\rho}{\rho^2}}{\displaystyle\int_{\rho_1}^{\rho_3} P\,\frac{d\rho}{\rho^2}} \tag{193}$$

In terms of the compressibility, this equation becomes

$$\frac{dP}{dT} \; = \; \frac{P \displaystyle\int_{\rho_1}^{\rho_3} \left[\frac{\partial(TZ)}{\partial T}\right]_\rho \frac{d\rho}{\rho}}{T \displaystyle\int_{\rho_1}^{\rho_3} Z \, \frac{d\rho}{\rho}} \tag{194}$$

which may be written

$$\frac{d \ln P}{d \ln T} \; = \; \frac{\displaystyle\int_{\rho_1}^{\rho_3} \left[\frac{\partial(TZ)}{\partial T}\right]_\rho \frac{d\rho}{\rho}}{\displaystyle\int_{\rho_1}^{\rho_3} Z \, \frac{d\rho}{\rho}} \tag{195}$$

$$\frac{d \ln P}{d \ln T} \; = \; \frac{\displaystyle\int_{\rho_1}^{\rho_3} Z \, \frac{\partial\rho}{\rho} + T \int_{\rho_1}^{\rho_3} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho}}{\displaystyle\int_{\rho_1}^{\rho_3} Z \, \frac{\partial\rho}{\rho}} \tag{196}$$

$$\frac{d \ln P}{d \ln T} \; = \; 1 + \frac{T \displaystyle\int_{\rho_1}^{\rho_3} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho}}{\displaystyle\int_{\rho_1}^{\rho_3} Z \, \frac{d\rho}{\rho}} \tag{197}$$

We then have from equation (186)

$$\frac{d \ln P}{d \ln T} = 1 + \frac{T}{Z_1 - Z_3} \int_{\rho_1}^{\rho_3} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} \tag{198}$$

In terms of reduced variables, we have

$$\frac{d \ln \beta}{d \ln \gamma} = 1 + \frac{\gamma}{Z_1 - Z_3} \int_{\alpha_1}^{\alpha_3} \left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha} \tag{199}$$

Then

$$\frac{d\beta}{d\gamma} = \beta' = \frac{\beta}{\gamma} + \frac{\beta}{Z_1 - Z_3} \int_{\alpha_1}^{\alpha_3} \left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha} \tag{200}$$

THE TEMPERATURE COEFFICIENTS OF THE SATURATED LIQUID AND VAPOR DENSITIES

We have

$$\frac{dP}{dT} = \left(\frac{\partial P}{\partial T}\right)_{\rho_1} + \left(\frac{\partial P}{\partial \rho_1}\right)_T \frac{d\rho_1}{dT} \tag{201}$$

Thus

$$\frac{d\rho_1}{dT} = \rho_1' = \frac{\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{\rho_1}}{\left(\frac{\partial P}{\partial \rho_1}\right)_T} \tag{202}$$

From equation (194), we may write

$$\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{\rho_1} = \frac{P}{T(Z_1 - Z_3)} \int_{\rho_1}^{\rho_3} \left[\frac{\partial(TZ)}{\partial T}\right]_{\rho} \frac{d\rho}{\rho} - \left(\frac{\partial P}{\partial T}\right)_{\rho_1} \qquad (203)$$

Substituting for $\left(\frac{\partial P}{\partial T}\right)_{\rho_1}$ from equation (25), we have

$$\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{\rho_1} = \frac{P}{T(Z_1 - Z_3)} \int_{\rho_1}^{\rho_3} \left[\frac{\partial(TZ)}{\partial T}\right]_{\rho} \frac{d\rho}{\rho} - \frac{P}{T}\left[1 + \frac{T}{Z_1}\left(\frac{\partial Z_1}{\partial T}\right)_{\rho_1}\right] \qquad (204)$$

We have from equation (28)

$$\left(\frac{\partial P}{\partial \rho_1}\right)_T = \frac{P}{\rho_1}\left[1 + \frac{\rho_1}{Z_1}\left(\frac{\partial Z_1}{\partial \rho_1}\right)_T\right] \qquad (205)$$

Substituting equations (204) and (205) into equation (202), we have

$$\rho_1' = \frac{\frac{\rho_1}{(Z_1 - Z_3)} \int_{\rho_1}^{\rho_3}\left[\frac{\partial(TZ)}{\partial T}\right]_{\rho} \frac{d\rho}{\rho} - \rho_1\left[1 + \frac{T}{Z_1}\left(\frac{\partial Z_1}{\partial T}\right)_{\rho_1}\right]}{T\left[1 + \frac{\rho_1}{Z_1}\left(\frac{\partial Z_1}{\partial \rho_1}\right)_T\right]} \qquad (206)$$

Similarly

$$\rho_3' = \frac{\frac{\rho_3}{(Z_1 - Z_3)} \int_{\rho_1}^{\rho_3}\left[\frac{\partial(TZ)}{\partial T}\right]_{\rho} \frac{d\rho}{\rho} - \rho_3\left[1 + \frac{T}{Z_3}\left(\frac{\partial Z_3}{\partial T}\right)_{\rho_3}\right]}{T\left[1 + \frac{\rho_3}{Z_3}\left(\frac{\partial Z_3}{\partial \rho_3}\right)_T\right]} \qquad (207)$$

In terms of reduced variables, we have

$$\alpha_1' = \frac{\dfrac{\alpha_1}{Z_1 - Z_3} \displaystyle\int_{\alpha_1}^{\alpha_3} \left(\frac{\partial \gamma Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha} - \alpha_1\left[1 + \frac{\gamma}{Z_1}\left(\frac{\partial Z_1}{\partial \gamma}\right)_{\alpha_1}\right]}{\gamma\left[1 + \dfrac{\alpha_1}{Z_1}\left(\dfrac{\partial Z_1}{\partial \alpha_1}\right)_\gamma\right]} \tag{208}$$

and

$$\alpha_3' = \frac{\dfrac{\alpha_3}{Z_1 - Z_3} \displaystyle\int_{\alpha_1}^{\alpha_3} \left[\frac{\partial (\gamma Z)}{\partial \gamma}\right]_\alpha \frac{d\alpha}{\alpha} - \alpha_3\left[1 + \frac{\gamma}{Z_3}\left(\frac{\partial Z_3}{\partial \gamma}\right)_{\alpha_3}\right]}{\gamma\left[1 + \dfrac{\alpha_3}{Z_3}\left(\dfrac{\partial Z_3}{\partial \alpha_3}\right)_\gamma\right]} \tag{209}$$

THE HEAT OF VAPORIZATION

The heat of vaporization, ΔH_v, is given by

$$\Delta H_v = H_1 - H_3 = L_1 - L_3 \tag{210}$$

From equation (70), we have

$$L_1 = RT(Z_1 - 1) - RT^2 \int_0^{\rho_1} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} \tag{211}$$

and

$$L_3 = RT(Z_3 - 1) - RT^2 \int_0^{\rho_3} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} \tag{212}$$

So that

$$L_1 - L_3 = RT(Z_1 - Z_3) + RT^2 \int_{\rho_1}^{\rho_3} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} \tag{213}$$

Substituting for $(Z_1 - Z_3)$ from equation (186), we have

$$L_1 - L_3 = RT \int_{\rho_1}^{\rho_3} Z \frac{d\rho}{\rho} + RT^2 \int_{\rho_1}^{\rho_3} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} \tag{214}$$

which may be written

$$\Delta H_v = L_1 - L_3 = RT \int_{\rho_1}^{\rho_3} \left[\frac{\partial(TZ)}{\partial T}\right]_\rho \frac{d\rho}{\rho} \tag{215}$$

In terms of reduced variables, we have

$$\frac{\Delta H_v}{RT_c} = \gamma \int_{\alpha_1}^{\alpha_3} \left[\frac{\partial(\gamma Z)}{\partial \gamma}\right]_\alpha \frac{d\alpha}{\alpha} \tag{216}$$

THE ENTROPY OF VAPORIZATION

The entropy of vaporization, ΔS_v, is given by

$$\Delta S_v = \frac{\Delta H_v}{T} \tag{217}$$

So that

$$\Delta S_v = R \int_{\rho_1}^{\rho_3} \left[\frac{\partial(TZ)}{\partial T}\right]_\rho \frac{d\rho}{\rho} \tag{218}$$

In reduced variables, we have

$$\frac{\Delta S_v}{R} = \int_{\alpha_1}^{\alpha_3} \left[\frac{\partial (\gamma Z)}{\partial \gamma} \right]_\alpha \frac{d\alpha}{\alpha} \tag{219}$$

A FUNCTION RELATED TO THE HEAT OF VAPORIZATION, NAMELY THE HEAT OF VAPORIZATION PER MOLE OF GAS COLLECTED OUTSIDE OF THE CALORIMETER

When the heat of vaporization is determined by adding electrical energy to a calorimeter, all of the gas formed does not leave the calorimeter because the volume of the liquid evaporated is occupied by gas. The quantity measured directly is the heat of vaporization per mole of gas collected outside the calorimeter. This quantity must then be corrected to calculate the heat of vaporization.

Suppose an amount of heat, q, has been added to the calorimeter so that one mole of gas has been evaporated. Then

$$q = \Delta H_v \tag{220}$$

The number of moles of the evaporated liquid that does not leave the calorimeter is then just

$$\frac{V_1}{V_g} = \frac{\rho_g}{\rho_1} = \frac{\rho_1}{\rho_3} \tag{221}$$

where V_1 is the molal volume of the liquid and V_g is the molal volume of the gas.

The number of moles collected outside the calorimeter is then

$$1 - \frac{V_1}{V_g} = 1 - \frac{\rho_1}{\rho_3} \tag{222}$$

The heat of vaporization per mole of gas collected is then given by

$$\Delta H_E = \frac{q}{1 - \frac{V_1}{V_g}} = \frac{\Delta H_v \cdot V_g}{V_g - V_1} \tag{223}$$

where ΔH_E is the experimental heat of vaporization per mole of gas collected. Then

$$\Delta H_E = \frac{\Delta H_v \cdot V_g}{\Delta V_v} \tag{224}$$

From the Clapeyron equation, we have

$$\frac{\Delta H_v}{\Delta V_v} = T \frac{dP}{dT} \tag{225}$$

Substituting equation (225) into (224), we have

$$\Delta H_E = TV_g \frac{dP}{dT} = \frac{T}{\rho_1} \frac{dP}{dT} \tag{226}$$

Then

$$\Delta H_E \rho_1 = \frac{dP}{d \ln T} \tag{227}$$

or

$$\frac{d \ln T}{dP} = \frac{1}{\rho_1 \Delta H_E} \tag{228}$$

Equation (228) can be used to determine the absolute thermodynamic temperature scale. If ΔH_E has been experimentally determined as a function of the vapor pressure, and if ρ_1, the density of the saturated vapor, has also been determined, then

$$\ln \frac{T_2}{T_1} = \int_{P_1}^{P_2} \frac{dP}{\rho_1 \Delta H_E} \tag{229}$$

and equation (229) establishes the thermodynamic temperature scale. From equation (226), we can write

$$\Delta H_E = \frac{P}{\rho_1} \frac{d \ln P}{d \ln T} \tag{230}$$

$$\Delta H_E = RTZ_1 \frac{d \ln P}{d \ln T} \tag{231}$$

Substituting for $\frac{d \ln P}{d \ln T}$ from equation (197), we have

$$\Delta H_E = RTZ_1 \left[1 + \frac{T \int_{\rho_1}^{\rho_3} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho}}{\int_{\rho_1}^{\rho_3} Z \frac{d\rho}{\rho}} \right] \tag{232}$$

In reduced variables, we find

$$\frac{\Delta H_E}{RT_C} = \gamma Z_1 \left[1 + \frac{\gamma \int_{\alpha_1}^{\alpha_3} \left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha}}{\int_{\alpha_1}^{\alpha_3} Z \frac{d\alpha}{\alpha}} \right] \tag{233}$$

THE SECOND DERIVATIVE OF THE VAPOR PRESSURE CURVE WITH REGARD TO THE TEMPERATURE

Equation (190) may be written

$$\frac{dP}{dT} (V_3 - V_1) = \int_{V_1}^{V_3} \left(\frac{\partial P}{\partial T}\right)_V dV \tag{234}$$

Differentiating, totally with regard to the temperature, we have

$$\frac{d^2 P}{dT^2} (V_3 - V_1) + \frac{dP}{dT} (V_3' - V_1') = \int_{V_1}^{V_3} \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + \left(\frac{\partial P}{\partial T}\right)_{V_3} V_3' - \left(\frac{\partial P}{\partial T}\right)_{V_1} V_1' \tag{235}$$

Then

$$\frac{d^2 P}{dT^2} = \frac{1}{V_3 - V_1} \int_{V_1}^{V_3} \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + \frac{\left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{V_1}\right] V_1' - \left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{V_3}\right] V_3'}{V_3 - V_1} \tag{236}$$

We have

$$\frac{dP}{dT} = \left(\frac{\partial P}{\partial T}\right)_{V_1} + \left(\frac{\partial P}{\partial V_1}\right)_T V_1' \tag{237}$$

So that

$$V_1' = \frac{\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{V_1}}{\left(\frac{\partial P}{\partial V_1}\right)_T} \tag{238}$$

Similarly

$$V_3' = \frac{\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{V_3}}{\left(\frac{\partial P}{\partial V_3}\right)_T} \tag{239}$$

Substituting equations (238) and (239) into equation (236), we have

$$\frac{d^2P}{dT^2} = \frac{1}{V_3 - V_1} \int_{V_1}^{V_3} \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + \frac{\left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{V_1}\right]^2}{\left(V_3 - V_1\right)\left(\frac{\partial P}{\partial V_1}\right)_T} - \frac{\left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{V_3}\right]^2}{\left(V_3 - V_1\right)\left(\frac{\partial P}{\partial V_3}\right)_T} \tag{240}$$

In terms of the molal densities, equation (240) may be written

$$\frac{d^2P}{dT^2} = \frac{\rho_1 \rho_3}{\rho_3 - \rho_1} \int_{\rho_1}^{\rho_3} \left(\frac{\partial^2 P}{\partial T^2}\right)_\rho \frac{d\rho}{\rho^2} + \frac{\rho_3 \left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{\rho_1}\right]^2}{\rho_1 \left(\rho_3 - \rho_1\right)\left(\frac{\partial P}{\partial \rho_1}\right)_T} - \frac{\rho_1 \left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{\rho_3}\right]^2}{\rho_3 \left(\rho_3 - \rho_1\right)\left(\frac{\partial P}{\partial \rho_3}\right)_T} \tag{241}$$

In terms of reduced variables, we have

$$\frac{d^2\beta}{d\gamma^2} = \beta'' = \frac{\alpha_1 \alpha_3}{\alpha_3 - \alpha_1} \int_{\alpha_1}^{\alpha_3} \left(\frac{\partial^2 \beta}{\partial \gamma^2}\right)_\alpha \frac{d\alpha}{\alpha^2} + \frac{\alpha_3 \left[\beta' - \left(\frac{\partial \beta}{\partial \gamma}\right)_{\alpha_1}\right]^2}{\alpha_1 \left(\alpha_3 - \alpha_1\right)\left(\frac{\partial \beta}{\partial \alpha_1}\right)_\gamma} - \frac{\alpha_1 \left[\beta' - \left(\frac{\partial \beta}{\partial \gamma}\right)_{\alpha_3}\right]^2}{\alpha_3 \left(\alpha_3 - \alpha_1\right)\left(\frac{\partial \beta}{\partial \alpha_3}\right)_\gamma} \tag{242}$$

Equation (241) shows that the second derivative of the vapor pressure curve at the critical point is not necessarily continuous with the second derivative of the critical isometric.

THE HEAT CAPACITY OF THE SATURATED GAS

By the heat capacity of the saturated gas, we mean

$$C(\text{sat. gas}) = T \frac{dS_1}{dT} \tag{243}$$

where $\frac{dS_1}{dT}$ is the total derivative of the entropy of the saturated gas with regard to the temperature. We have

$$\frac{dS_1}{dT} = \left(\frac{\partial S_1}{\partial T}\right)_{V_1} + \left(\frac{\partial S_1}{\partial V_1}\right)_T \frac{dV_1}{dT} \tag{244}$$

Now

$$\left(\frac{\partial S_1}{\partial T}\right)_{V_1} = \frac{C_{V_1}}{T} \tag{245}$$

$$\left(\frac{\partial S_1}{\partial V_1}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{V_1} \tag{246}$$

$$\frac{dV_1}{dT} = -\frac{1}{\rho_1^2} \frac{d\rho_1}{dT} = -\frac{1}{\rho_1^2} \rho_1' \tag{247}$$

Substituting equations (244), (245), (246), and (247) into equation (243), we have

$$C(\text{sat. gas}) = C_{V_1} - \frac{T}{\rho_1^2} \left(\frac{\partial P}{\partial T}\right)_{\rho_1} \rho_1' \tag{248}$$

Substituting for C_{V_1} from equation (63), we have

$$C(\text{sat. gas}) - C_V^o = -2RT \int_0^{\rho_1} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - RT^2 \int_0^{\rho_1} \left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho \frac{d\rho}{\rho} - \frac{T}{\rho_1^2} \left(\frac{\partial P}{\partial T}\right)_{\rho_1} \rho_1' \quad (249)$$

In reduced variables, we have

$$\frac{C(\text{sat. gas}) - C_V^o}{R} = -2\gamma \int_0^{\alpha_1} \left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha} - \gamma^2 \int_0^{\alpha_1} \left(\frac{\partial^2 Z}{\partial \gamma^2}\right)_\alpha \frac{d\alpha}{\alpha} - \frac{Z_c \gamma}{\alpha_1^2} \left(\frac{\partial \beta}{\partial \gamma}\right)_{\alpha_1} \alpha_1' \quad (250)$$

THE HEAT CAPACITY OF THE SATURATED LIQUID

By the heat capacity of the saturated liquid, we mean

$$C(\text{sat. liq.}) = T \frac{dS_3}{dT} \quad (251)$$

The derivation is similar to the last section and we obtain

$$C(\text{sat. liq.}) - C_V^o = -2RT \int_0^{\rho_3} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - RT^2 \int_0^{\rho_3} \left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho \frac{d\rho}{\rho} - \frac{T}{\rho_3^2} \left(\frac{\partial P}{\partial T}\right)_{\rho_3} \rho_3' \quad (252)$$

In reduced variables, we have

$$\frac{C(\text{sat. liq.}) - C_V^o}{R} = -2\gamma \int_0^{\alpha_3} \left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha} - \gamma^2 \int_0^{\alpha_3} \left(\frac{\partial^2 Z}{\partial \gamma^2}\right)_\alpha \frac{d\alpha}{\alpha} - \frac{Z_c \gamma}{\alpha_3^2} \left(\frac{\partial \beta}{\partial \gamma}\right)_{\alpha_3} \alpha_3' \quad (253)$$

THE SECOND DERIVATIVE OF THE CHEMICAL POTENTIAL OR
GIBBS FREE ENERGY WITH REGARD TO THE TEMPERATURE

We have for the saturated gas

$$\frac{dG_1}{dT} = -S_1 + V_1 \frac{dP}{dT} \tag{254}$$

Differentiating equation (254), we have

$$\frac{d^2 G_1}{dT^2} = -\frac{dS_1}{dT} - \frac{1}{\rho_1^2} \frac{dP}{dT} \rho_1' + \frac{1}{\rho_1} \frac{d^2 P}{dT^2} \tag{255}$$

$$-T \frac{d^2 G_1}{dT^2} = T \frac{dS_1}{dT} + \frac{T}{\rho_1^2} \frac{dP}{dT} \rho_1' - \frac{T}{\rho_1} \frac{d^2 P}{dT^2} \tag{256}$$

Substituting from equation (243), we have

$$-T \frac{d^2 G_1}{dT^2} = C(\text{sat. gas}) + \frac{T}{\rho_1^2} \frac{dP}{dT} \rho_1' - \frac{T}{\rho_1} \frac{d^2 P}{dT^2} \tag{257}$$

Substituting for C(sat. gas) from equation (248), we have

$$-T \frac{d^2 G_1}{dT^2} = C_{V_1} + \frac{T}{\rho_1^2} \left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T} \right)_{\rho_1} \right] \rho_1' - \frac{T}{\rho_1} \frac{d^2 P}{dT^2} \tag{258}$$

Substituting for C_{V_1} from equation (63), we have

$$-T \frac{d^2 G}{dT^2} - C_V^o = -2RT \int_0^{\rho_1} \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} - RT^2 \int_0^{\rho_1} \left(\frac{\partial^2 Z}{\partial T^2} \right)_\rho \frac{d\rho}{\rho} + \frac{T}{\rho_1^2} \left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T} \right)_{\rho_1} \right] \rho_1' - \frac{T}{\rho_1} \frac{d^2 P}{dT^2} \tag{259}$$

As $G_1 = G_3$, we have dropped the subscript and set $G_1 = G$.

In reduced variables, we have

$$\frac{-T\frac{d^2G}{dT^2} - C_V^o}{R} = -2\gamma \int_0^{\alpha_1} \left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha} \alpha \, d\alpha - \gamma^2 \int_0^{\alpha_1} \left(\frac{\partial^2 Z}{\partial \gamma^2}\right)_{\alpha} \alpha \, d\alpha + \frac{Z_c \gamma}{\alpha_1^2}\left[\beta' - \left(\frac{\partial \beta}{\partial \gamma}\right)_{\alpha_1}\right]\alpha_1' - \frac{Z_c \gamma}{\alpha_1}\beta'' \quad (260)$$

THE HEAT CAPACITY AT CONSTANT VOLUME WITH
TWO PHASES PRESENT IN THE CALORIMETER

With two phases present in the calorimeter, we define the

heat capacity at constant volume as

$$C_V\left(2 \text{ phases}\right) = \frac{T}{n}\left(\frac{dS_{Total}}{dT}\right)_{V_{Total}} \quad (261)$$

where S_{Total} is the total entropy of the contents of the calori-

meter, V_{Total} is the total volume of the calorimeter, and n is the

total number of moles in the calorimeter.

We may write

$$\frac{dG_{Total}}{dT} = -S_{Total} + V_{Total}\frac{dP}{dT} \quad (262)$$

But $G_{Total} = nG$, where G is the molal Gibbs free energy and since

$G_1 = G_3 = G$. Then

$$n\frac{dG}{dT} = -S_{Total} + V_{Total}\frac{dP}{dT} \quad (263)$$

$$n\left(\frac{d^2G}{dT^2}\right)_{V_{Total}} = -\left(\frac{dS_{Total}}{dT}\right)_{V_{Total}} + V_{Total}\left(\frac{d^2P}{dT^2}\right)_{V_{Total}} \qquad (264)$$

and since, as long as two phases are present, $\frac{d^2G}{dT^2}$ and $\frac{d^2P}{dT^2}$ are independent of the volume, we may write

$$n\frac{d^2G}{dT^2} = -\left(\frac{dS_{Total}}{dT}\right)_{V_{Total}} + V_{Total}\frac{d^2P}{dT^2} \qquad (265)$$

Substituting equation (265) into equation (261), we have

$$C_V(2 \text{ phases}) = -T\frac{d^2G}{dT^2} + \frac{V_{Total}}{n} T\frac{d^2P}{dT^2} \qquad (266)$$

A heat capacity determination, with two phases present in the calorimeter, has usually been thought of as the way to experimentally determine the heat capacity of the saturated liquid. However, equation (266) shows that if two heat capacity determinations are made, one with very little liquid in the calorimeter and the other with the calorimeter almost filled with liquid, then it is possible to calculate from the thermal measurements alone $-T\frac{d^2G}{dT^2}$ and $T\frac{d^2P}{dT^2}$. This was first pointed out by Yang and Yang (2).

Substituting equation (258) into equation (266), we have

$$C_V(2 \text{ phases}) = C_{V_1} + \frac{T}{\rho_1^2}\left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{\rho_1}\right]\rho_1' + \left[\frac{V_{Total}}{n} - \frac{1}{\rho_1}\right]T\frac{d^2P}{dT^2} \qquad (267)$$

Equation (267) shows that when the calorimeter is filled to the critical density, the heat capacity at constant volume is not

necessarily continuous through the critical point.

Substituting for C_{V_1} from equation (63) into equation (267), we have

$$C_V(2 \text{ phases}) - C_V^o = \left[\begin{array}{c} -2RT \int_0^{\rho_1} \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - RT^2 \int_0^{\rho_1} \left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho \frac{d\rho}{\rho} \\ \\ + \frac{T}{\rho_1^2} \left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{\rho_1}\right]\rho_1' + T\left[\frac{V_{Total}}{n} - \frac{1}{\rho_1}\right] \frac{d^2P}{dT^2} \end{array} \right] \quad (268)$$

In reduced variables, we find

$$\frac{C_V(2 \text{ phases}) - C_V^o}{R} = \left[\begin{array}{c} -2\gamma \int_0^{\alpha_1} \left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha} - \gamma^2 \int_0^{\alpha_1} \left(\frac{\partial^2 Z}{\partial \gamma^2}\right)_\alpha \frac{d\alpha}{\alpha} \\ \\ + \frac{Z_c \gamma}{\alpha_1'^2} \left[\beta' - \left(\frac{\partial \beta}{\partial \gamma}\right)_{\alpha_1}\right]\alpha_1' + Z_c\gamma\left[\frac{V_{Total}}{n}\rho_c - \frac{1}{\alpha_1}\right]\beta'' \end{array} \right] \quad (269)$$

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