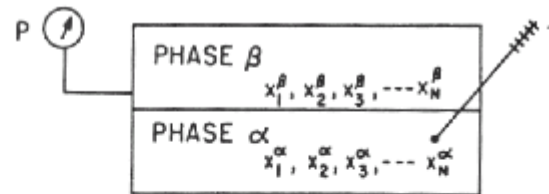


Chapter 1. The Phase-Equilibrium Problem



Given:

MOLE FRACTIONS $x_1^\alpha, x_2^\alpha, x_3^\alpha, \dots, x_N^\alpha$
and T (or P)

Find:

MOLE FRACTIONS $x_1^\beta, x_2^\beta, x_3^\beta, \dots, x_N^\beta$
and P (or T)

Figure 1-2 Statement of problem.

Homogeneous phase: a region where the intensive properties are everywhere the same.

Intensive property: a property that is independent of the size
temperature, pressure, and composition, density(?)

Gibbs phase rule (no reaction)

Number of independent intensive properties = Number of components – Number of phases + 2

e.g. for a two-component, two-phase system No. of intensive properties = 2

1.2 Application of Thermodynamics to Phase-Equilibrium Problem

Chemical potential : Gibbs (1875)

At equilibrium the chemical potential of each component must be the same in every phase.

$$\mu_i^\alpha = \mu_i^\beta$$

how μ_i^α is related to T, P , and $x_1^\alpha, x_2^\alpha, \dots$?

Fugacity, Activity: more convenient auxiliary functions

$$\phi_i y_i P = \gamma_i x_i f_i^0$$

fugacity coefficient activity coefficient fugacity at the standard state

For ideal gas mixture, $\phi_i = 1$

For ideal liquid mixture at low pressures, $\gamma_i = 1$, $f_i^0 = P_{sat}$

In the general case

$$\phi_i = \phi_i(T, P, y_1, y_2, \dots) \quad (1-3)$$

$$\gamma_i = \gamma_i(T, P, x_1, x_2, \dots) \quad (1-4)$$

Chapter 2. Classical Thermodynamics of Phase Equilibria

For simplicity, we exclude surface effect, acceleration, gravitational or electromagnetic field, and chemical and nuclear reactions.

2.1 Homogeneous Closed Systems

A closed system is one that does not exchange matter, but it may exchange energy.

$$dn_i = 0 \quad i = 1, 2, \dots, m \quad (2-1)$$

A combined statement of the first and second laws of thermodynamics

$$dU \leq T_B dS - P_E dV \quad (2-2)$$

U, S, V are state functions (whose value is independent of the previous history of the system).

T_B temperature of thermal bath, P_E external pressure

Equality holds for reversible process with $T_B = T, P_E = P$

$$dU = TdS - PdV$$

(2-3)

and $TdS = \delta Q_{rev}, PdV = \delta W_{rev}$

$U(S, V)$ is state function.

The group of U, S, V is a fundamental group.

Integrating over a reversible path,

$$\Delta U = U_2 - U_1 = \int_{S_1}^{S_2} T dS - \int_{V_1}^{V_2} P dV \quad (2-5)$$

ΔU is independent of the path of integration, and also independent of whether the system is maintained in a state of internal equilibrium or not during the actual process.

It requires only that the initial and final states be equilibrium states.

For irreversible process (spontaneous changes)

$$dU_{S,V} \leq 0 \quad \text{or} \quad dS_{U,V} \geq 0$$

If the entropy of a system is unchanged at constant volume, the energy of the system decreases as energy flows out as heat

In an isolated system at constant volume, entropy increases for spontaneous change

Enthalpy is defined by

$$H \equiv U - (-PV) = U + PV \quad (2-7)$$

Differentiation of (2-7) and substitution for dU gives

$$\boxed{dH = TdS + VdP} \quad (2-8)$$

For spontaneous changes

$$dH_{S,P} \leq 0 \quad (2-9)$$

Helmholtz energy is defined by

$$A \equiv U - TS \quad (2-10)$$

giving

$$\boxed{dA = -SdT - PdV} \quad (2-11)$$

The minimum of Helmholtz energy at const. T and V

$$dA_{T,V} \leq 0 \quad (2-12)$$

Gibbs energy is defined by

$$G \equiv U - TS - (-PV) = H - TS \quad (2-13)$$

giving

$$\boxed{dG = -SdT + VdP} \quad (2-14)$$

The minimum of Gibbs energy at const. T and P

$$dG_{T,P} \leq 0 \quad (2-15)$$

Table 2-1 Some important thermodynamic relations for a homogeneous closed system.

Definition of H , A , and G	
$H = U + PV$	
$A = U - TS$	
$G = U + PV - TS = H - TS = A + PV$	
Fundamental Equations	
$dU = TdS - PdV$	$dA = -SdT - PdV$
$dH = TdS + VdP$	$dG = -SdT + VdP$
Extensive Functions as Thermodynamic Potentials	
$dU_{S,V} \leq 0$	$dA_{T,V} \leq 0$
$dH_{S,P} \leq 0$	$dG_{T,P} \leq 0$
Maxwell Relations Resulting from the Fundamental Equations	
$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$
Identities Resulting from the Fundamental Equations	
$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$	$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$
$\left(\frac{\partial U}{\partial S}\right)_V = T = \left(\frac{\partial H}{\partial S}\right)_P$	$\left(\frac{\partial H}{\partial P}\right)_S = V = \left(\frac{\partial G}{\partial P}\right)_T$
$\left(\frac{\partial U}{\partial V}\right)_S = -P = \left(\frac{\partial A}{\partial V}\right)_T$	$\left(\frac{\partial A}{\partial T}\right)_V = -S = \left(\frac{\partial G}{\partial T}\right)_P$
Heat Capacities	
$\left(\frac{\partial U}{\partial T}\right)_V = C_V$	$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$
$\left(\frac{\partial H}{\partial T}\right)_P = C_P$	$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$

2.2. Homogeneous Open Systems

An open system can exchange matter as well as energy with its surroundings.

$$U = U(S, V, n_1, n_2, \dots, n_m) \quad (2-17)$$

The total differentials is

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_i \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} dn_i \quad (2-18)$$

We define the chemical potential as

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} \quad (2-19)$$

Rewriting

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad (2-20)$$

which is the fundamental equation for an open system

Substituting the definition of H , A , and G

$$dH = TdS + Vdp + \sum_i \mu_i dn_i \quad (2-21)$$

$$dA = -SdT - PdV + \sum_i \mu_i dn_i \quad (2-22)$$

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (2-23)$$

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_j} = \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \quad (2-24)$$

Partial molar Gibbs energy



For pure substance

$$\mu = \frac{G}{n} \quad (\text{very simple!})$$

2.3 Equilibrium in a Heterogeneous Closed System

For a closed, heterogeneous system consisting of π phases and m component at equilibrium with respect to the processes of heat transfer, boundary displacement, and mass transfer

$$T^{(1)} = T^{(2)} = \dots = T^{(\pi)} \quad (2-25)$$

$$P^{(1)} = P^{(2)} = \dots = P^{(\pi)} \quad (2-26)$$

$$\begin{aligned} \mu_1^{(1)} &= \mu_1^{(2)} = \dots = \mu_1^{(\pi)} \\ \mu_2^{(1)} &= \mu_2^{(2)} = \dots = \mu_2^{(\pi)} \\ &\vdots \quad \quad \quad \vdots \\ \mu_m^{(1)} &= \mu_m^{(2)} = \dots = \mu_m^{(\pi)} \end{aligned} \quad (2-27)$$

2.4 The Gibbs-Duhem Equation

A total of $m+2$ variables for a phase in a heterogeneous system are not all independent.

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad (2-28)$$

Integrating from a state of zero mass to a state of finite mass constant T , P , and composition

(note: integrating variables are extensive properties, and on the integration, all coefficients are kept constant)

$$U = TS - PV + \sum_i \mu_i n_i \quad (2-29)$$

Differentiation of (2-29) gives

$$dU = TdS + SdT - PdV - VdP + \sum_i \mu_i dn_i + \sum_i n_i d\mu_i \quad (2-30)$$

Comparing the two equations

$$\boxed{SdT - VdP + \sum_i n_i d\mu_i = 0} \quad (2-31)$$

Gibbs-Duhem equation (an inherent constraint).

Only $m+1$ intensive variables are independent

2.5 The Phase Rule

The number of independent variables = $\pi (m+1)$

The number of equilibrium relations = $(\pi-1) (m+2)$

The number of degree of freedom

$$\begin{aligned} F &= \pi(m+1) - (\pi-1)(m+2) \\ &= m+2 - \pi \end{aligned} \quad (2-32)$$

2.6 The Chemical Potential

It is difficult to calculate an absolute value of the chemical potential, so we must content ourselves with computing changes in the chemical potential. (in engineering calculation)

// Stat Mech can give rigorous expressions for absolute value of the chemical potential for ideal gases //

$$\mu(T, P) = \mu_0(T) + kT \ln P, \quad \mu_0(T) = -kT \ln \left[\left(\frac{2\pi m k T}{h^2} \right)^{3/2} kT \right] - kT \ln q_e q_n$$

For a pure substance i,

$$d\mu_i = -s_i dT + v_i dP \quad (2-33)$$

In integrating from some reference state to the state of interest

$$\mu_i(T, P) = \mu_i(T^r, P^r) - \int_{T^r}^T s_i dT + \int_{P^r}^P v_i dP \quad (2-34)$$

The standard state = the reference state

Successful application of thermodynamics to real systems frequently is based on a judicious choice of standard states.

2.7 Fugacity and Activity

From (2-33) $d\mu_i = -s_i dT + v_i dP$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = v_i \quad (2-35)$$

Consider ideal gas

$$v_i = \frac{RT}{P} \quad (2-36)$$

Integrating at constant temperature

$$\mu_i - \mu_i^0 = RT \ln \frac{P}{P^0} \quad (2-37)$$

chemical potential of an ideal gas

The abstract quantity μ is a simple logarithmic function of the physically real quantity, P .

Lewis defined fugacity as

$$\mu_i - \mu_i^0 = RT \ln \frac{f_i}{f_i^0} \quad (2-38)$$

isothermal change at const. T

the ratio f / f^0 the *activity*,

Ideal gas, $f = P$

Ideal gas mixture, $f_i = y_i P$ (fugacity = partial pressure)

All real systems approach ideal-gas behavior at very low pressures (e.g. $P < 1$ bar).

$$\frac{f_i}{y_i P} \rightarrow 1 \quad \text{as } P \rightarrow 0 \quad (2-39)$$

The temperature of the standard state must be the same as that of the state of interest, but compositions and pressures need not be the same.

Fugacity is a “corrected pressure”, and these corrections are due to nonidealities resulting from intermolecular forces

For phases α and β

$$\mu_i^\alpha - \mu_i^{0\alpha} = RT \ln \frac{f_i^\alpha}{f_i^{0\alpha}} \quad (2-40)$$

$$\mu_i^\beta - \mu_i^{0\beta} = RT \ln \frac{f_i^\beta}{f_i^{0\beta}} \quad (2-41)$$

Equating the chemical potentials

$$\mu_i^{0\alpha} + RT \ln \frac{f_i^\alpha}{f_i^{0\alpha}} = \mu_i^{0\beta} + RT \ln \frac{f_i^\beta}{f_i^{0\beta}} \quad (2-42)$$

Case I, the standard states for the two phases are the same

$$\mu_i^{0\alpha} = \mu_i^{0\beta} \quad (2-43)$$

Then

$$f_i^{0\alpha} = f_i^{0\beta} \quad (2-44)$$

(2-42) becomes

$$\boxed{f_i^\alpha = f_i^\beta} \quad (2-45)$$

Case II, the standard states are at the same T, but not at the same P, y.

Following the definition of fugacity

$$\mu_i^{0\alpha} - \mu_i^{0\beta} = RT \ln \frac{f_i^{0\alpha}}{f_i^{0\beta}} \quad (2-46)$$

we again have

$$f_i^\alpha = f_i^\beta$$

In either case, the fugacities must be the same in all phases.

The fundamental equations of phase equilibrium

$$T^{(1)} = T^{(2)} = \dots = T^{(\pi)} \quad (2-25)$$

$$P^{(1)} = P^{(2)} = \dots = P^{(\pi)} \quad (2-26)$$

$$f_i^\alpha = f_i^\beta \quad (2-45)$$

2.8 A Simple Application: Raoult's law

Consider a binary system containing a liquid and vapor phase

$$f_1^V = f_1^L \quad (2-47)$$

Assuming ideal solution behavior

Assumption 1. The fugacity f_1^V , at constant temperature and pressure, is proportional to the mole fraction y_1 . That is, we assume

$$f_1^V = y_1 f_{\text{pure } 1}^V \quad (2-48)$$

where $f_{\text{pure } 1}^V$ is the fugacity of pure component 1 as a vapor at the temperature and pressure of the mixture.

Assumption 2. The fugacity f_1^L , at constant temperature and pressure, is proportional to the mole fraction x_1 . That is, we assume

$$f_1^L = x_1 f_{\text{pure } 1}^L \quad (2-49)$$

where $f_{\text{pure } 1}^L$ is the fugacity of pure component 1 as a liquid at the temperature and pressure of the mixture.

Substituting into (2-47)

$$y_1 f_{\text{pure } 1}^V = x_1 f_{\text{pure } 1}^L \quad (2-50)$$

Assuming ideal gas for the vapor, and incompressible liquid

Assumption 3. Pure component 1 vapor at temperature T and pressure P is an ideal gas. It follows that

$$f_{\text{pure } 1}^V = P \quad (2-51)$$

Assumption 4. The effect of pressure on the fugacity of a condensed phase is negligible at moderate pressures. Further, we assume that the vapor in equilibrium with pure liquid 1 at temperature T is an ideal gas. It follows that

$$f_{\text{pure } 1}^L = P_1^s \quad (2-52)$$

where P_1^s is the saturation (vapor) pressure of pure liquid 1 at temperature T .

We obtain Raoult's law

$$\boxed{y_1 P = x_1 P_1^s} \quad (2-53)$$

CH.3 Thermodynamic Properties from Volumetric Data

Most thermodynamic properties of interest in phase equilibria can be calculated from thermal and volumetric measurements.

Thermal measurement (heat capacity)

How thermodynamic properties vary with temperature

Volumetric measurement (PVT data)

How properties vary with pressure or density at constant temperature

3.1 Thermodynamic Properties with Independent Variable P and T

Thermodynamic Properties as functions of T, P

We use Maxwell's relations

$$dH = \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P, n_T} \right] dP \quad (3-1)$$

$$dS = - \left(\frac{\partial V}{\partial T} \right)_{P, n_T} dP \quad (3-2)$$

First, obtain H , S and then U , A , G , μ_i , f_i , from definitions

$$U = H - PV \quad (3-3)$$

$$A = H - PV - TS \quad (3-4)$$

$$G = H - TS \quad (3-5)$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} \quad (3-6)$$

$$RT \ln \frac{f_i}{f_i^0} = \mu_i - \mu_i^0 \quad (3-7)$$

Extensive properties for n_T moles by capital letters (V , U , H , S , A , G)

Properties on a molar basis by lowercase letters (v , u , h , s , a , g)

h_i^0 = molar enthalpy of pure i as an ideal gas at temperature T ;

s_i^0 = molar entropy of pure i as an ideal gas at temperature T and 1 bar;

$\mu_i^0 = h_i^0 - Ts_i^0$ and $f_i^0 = 1$ bar;

n_i = number of moles of i ;

n_T = total number of moles;

$y_i = n_i / n_T$ = mole fraction of i .

$$U = \int_0^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P, n_T} \right] dP - PV + \sum_i n_i h_i^0 \quad (3-8)$$

$$H = \int_0^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P, n_T} \right] dP + \sum_i n_i h_i^0 \quad (3-9)$$

$$S = \int_0^P \left[\frac{n_T R}{P} - \left(\frac{\partial V}{\partial T} \right)_{P, n_T} \right] dP - R \sum_i n_i \ln y_i P + \sum_i n_i s_i^0 \quad (3-10)$$

$$A = \int_0^P \left(V - \frac{n_T R T}{P} \right) dP + R T \sum_i n_i \ln y_i P - P V + \sum_i n_i (h_i^0 - T s_i^0) \quad (3-11)$$

$$G = \int_0^P \left(V - \frac{n_T R T}{P} \right) dP + R T \sum_i n_i \ln y_i P + \sum_i n_i (h_i^0 - T s_i^0) \quad (3-12)$$

$$\mu_i = \int_0^P \left(\bar{v}_i - \frac{R T}{P} \right) dP + R T \ln y_i P + h_i^0 - T s_i^0 \quad (3-13)$$

$$\boxed{R T \ln \phi_i = R T \ln \frac{f_i}{y_i P} = \int_0^P \left(\bar{v}_i - \frac{R T}{P} \right) dP} \quad (3-14)$$

Pressure P is in bars.

$\bar{v}_i \equiv (\partial V / \partial n_i)_{T, P, n_j}$ is the *partial molar volume* of i .

Fugacity coefficient

$f_i / y_i P = \phi_i$ is called the *fugacity coefficient*.

For a mixture of ideal gases, $\phi_i = 1$,

We can compute all the thermodynamic properties relative to the ideal-gas state at 1 bar and at the same temperature and composition, provided that we have volumetric information

$$V = F(T, P, n_1, n_2, \dots) \quad (3-15)$$

Volume explicit equation of state

For a pure component, $\bar{v}_i = v_i$

(3-14) simplifies to

$$RT \ln \left(\frac{f}{P} \right)_{\text{pure } i} = \int_0^P \left(v_i - \frac{RT}{P} \right) dP \quad (3-16)$$

Equivalently

$$\boxed{\ln \left(\frac{f}{P} \right)_{\text{pure } i} = \int_0^P \frac{z-1}{P} dP} \quad (3-17)$$

where the compressibility factor z is defined by

$$z \equiv \frac{Pv}{RT} \quad (3-18)$$

Ideal gas mixture

The equation of state for an ideal gas mixture is

$$V = \frac{(n_1 + n_2 + \dots)RT}{P} \quad (3-19)$$

The partial molar volume is

$$\bar{v}_i \equiv \left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_j} = \frac{RT}{P} \quad (3-20)$$

substituting into (3-14)

$$f_i = y_i P \quad (3-21)$$

equal to its partial pressure

Lewis fugacity rule

Assume that the gas mixture follows Amagat's law (additivity of volume) which is

$$V = \sum_i n_i v_i \quad (3-22)$$

There is no volume change in mixing at const. T and P ,

and the partial molar volume is equal to that in the pure state

$$\bar{v}_i \equiv \left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_j} = v_i \quad (3-23)$$

substituting into (3-14)

$$RT \ln \frac{f_i}{y_i P} = \int_0^P \left(v_i - \frac{RT}{P} \right) dP \quad (3-24)$$

comparing with (3-16)

$$RT \ln \left(\frac{f}{P} \right)_{\text{pure } i} = \int_0^P \left(v_i - \frac{RT}{P} \right) dP$$

$$f_i = y_i f_{\text{pure } i}$$

(3-25)

Lewis fugacity rule assumes the additivity of volume for the entire pressure range 0 to P .

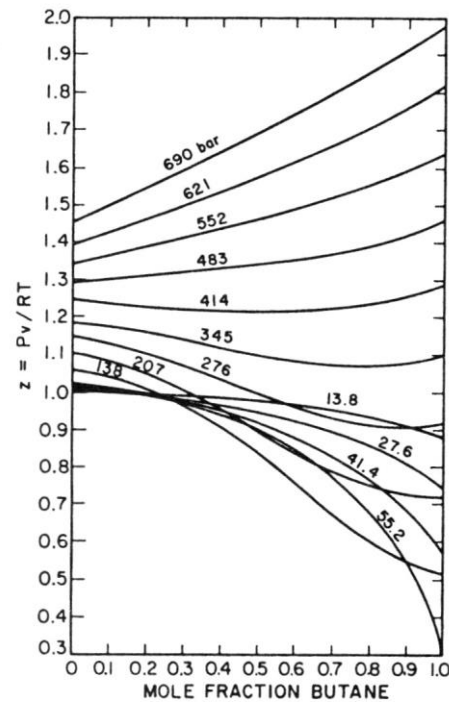


Figure 3-1 Compressibility factors for nitrogen/butane mixtures at 171°C (Evans and Watson, 1956).

At const P , T , the molar volume is linear to the composition only at high pressures, not over the entire pressure range. Thus, Lewis fugacity rule should not be valid.

3.2 Fugacity of a Component in a Mixture at Moderate Pressures

Consider a truncated form of the van der Waals equation of state

$$Pv = RT + \left(b - \frac{a}{RT}\right)P + \dots \text{ terms in } P^2, P^3, \text{ etc.} \quad (3-26)$$

Rewriting on a total basis using $V = n_T v$

$$V = \frac{n_T RT}{P} + n_T b - \frac{n_T a}{RT} \quad (3-27)$$

Partial molar volume is obtained as

$$\bar{v}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{T, P, n_2} = \frac{RT}{P} + \frac{\partial(n_T b)}{\partial n_1} - \frac{1}{RT} \frac{\partial(n_T a)}{\partial n_1} \quad (3-28)$$

Mixing rule (relation of a, b for the mixture on the composition)

$$a = y_1^2 a_1 + 2y_1 y_2 \sqrt{a_1 a_2} + y_2^2 a_2 \quad (3-29)$$

$$b = y_1 b_1 + y_2 b_2 \quad (3-30)$$

by van der Waals

Rewriting

$$n_T a = \frac{n_1^2 a_1 + 2n_1 n_2 \sqrt{a_1 a_2} + n_2^2 a_2}{n_T} \quad (3-31)$$

$$n_T b = n_1 b_1 + n_2 b_2 \quad (3-32)$$

The partial molar volume for component 1 is

$$\bar{v}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{T, P, n_2} = \frac{RT}{P} + b_1 - \frac{1}{RT} \frac{n_T (2n_1 a_1 + 2n_2 \sqrt{a_1 a_2}) - n_T^2 a}{n_T^2} \quad (3-33)$$

with n_2 held constant, not with n_T

Substitution into (3-14) gives

$$\phi_1 = \frac{f_1}{y_1 P} = \exp \left[\left(b_1 - \frac{a_1}{RT} \right) \frac{P}{RT} \right] \exp \left[\frac{(a_1^{1/2} - a_2^{1/2})^2 y_2^2 P}{(RT)^2} \right] \quad (3-34)$$

Consider the boundary condition

$$\text{as } y_2 \rightarrow 0, \quad f_1 \rightarrow f_{\text{pure } 1} = P \exp \left[\left(b_1 - \frac{a_1}{RT} \right) \frac{P}{RT} \right] \quad (3-35)$$

Thus

$$f_1 = y_1 f_{\text{pure } 1} \exp \left[\frac{(a_1^{1/2} - a_2^{1/2})^2 y_2^2 P}{(RT)^2} \right] \quad (3-36)$$

correction to the Lewis fugacity rule

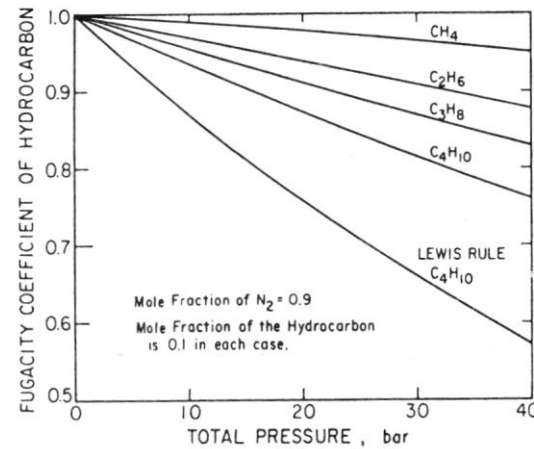
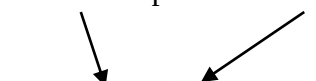


Figure 3-2 Fugacity coefficients of light hydrocarbons in binary mixtures with nitrogen at 343 K. Calculations based on simplified form of van der Waals' equation.

Lewis is poor for butane as the difference in intermolecular forces between butane and nitrogen is large.

3.3 Fugacity of a Pure Liquid and Solid

condensed phase saturated vapor



$$RT \ln \frac{f_i^c}{P} = \underbrace{\int_0^{P_i^s} \left(v_i - \frac{RT}{P} \right) dP}_{\text{fugacity of the saturated vapor}} + \int_{P_i^s}^P \left(v_i^c - \frac{RT}{P} \right) dP \quad (3-37)$$

$$RT \ln \frac{f_i^c}{P} = RT \ln \frac{f_i^s}{P_i^s} + \int_{P_i^s}^P v_i^c dP - RT \ln \frac{P}{P_i^s} \quad (3-38)$$

Rearrangement gives

$$\boxed{f_i^c = P_i^s \phi_i^s \underbrace{\exp \left(\int_{P_i^s}^P \frac{v_i^c dP}{RT} \right)}_{\text{Poynting correction}}} \quad (3-39)$$

where $\phi_i^s = f_i^s / P_i^s$.

At conditions remote from critical, a condensed phase (liquid or solid) is nearly incompressible, and the correction term becomes

$$\exp \left[\frac{v_i^c (P - P_i^s)}{RT} \right]$$

Fugacity coefficient of saturated liquids (without Poyning correction)

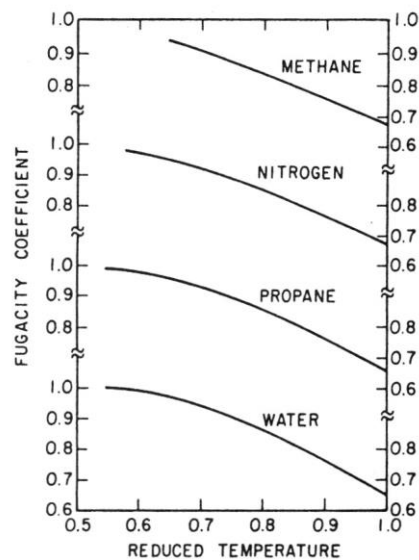


Figure 3-3 Fugacity coefficients from vapor-phase volumetric data for four saturated liquids.

ϕ_i^s differs from unity as the critical temperature is approached.

The Poynting correction may become large at high pressures

Table 3-1 The Poynting correction: effect of pressure on fugacity of a pure, condensed and incompressible substance whose molar volume is $100 \text{ cm}^3 \text{ mol}^{-1}$ ($T = 300 \text{ K}$).

Pressure in excess of saturation pressure (bar)	Poynting correction
1	1.00405
10	1.0405
100	1.499
1000	57.0

Fugacity of compressed liquid water

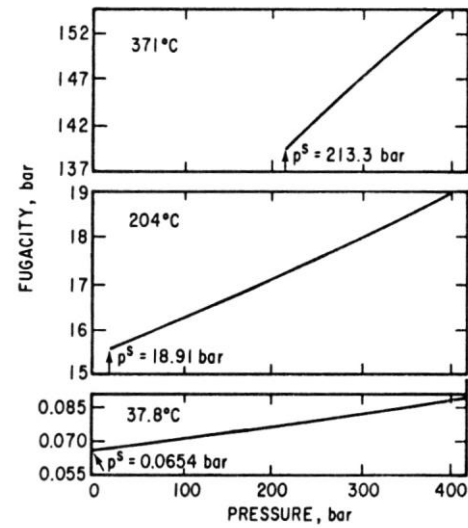


Figure 3-4 Fugacity of liquid water at three temperatures from saturation pressure to 414 bar. The critical temperature of water is 374°C.

$$f^c \sim P^s \quad f^c \neq P$$

The fugacity of condensed phase is close to the saturation pressure rather than the total pressure.

3.4 Thermodynamic Properties with Independent Variable V and T

Maxwell's relations

$$dU = \left[T \left(\frac{\partial P}{\partial T} \right)_{V, n_T} - P \right] dV \quad (3-40)$$

$$dS = \left(\frac{\partial P}{\partial T} \right)_{V, n_T} dV \quad (3-41)$$

Other properties are given by

$$H = U + PV \quad (3-42)$$

$$A = U - TS \quad (3-43)$$

$$G = U + PV - TS \quad (3-44)$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j} \quad (3-45)$$

$$RT \ln \frac{f_i}{f_i^0} = \mu_i - \mu_i^0 \quad (3-46)$$

Integrating

$$U = \int_V^\infty \left[P - T \left(\frac{\partial P}{\partial T} \right)_{V, n_T} \right] dV + \sum_i n_i u_i^0 \quad (3-47)$$

$$H = \int_V^\infty \left[P - T \left(\frac{\partial P}{\partial T} \right)_{V, n_T} \right] dV + PV + \sum_i n_i u_i^0 \quad (3-48)$$

$$S = \int_V^\infty \left[\frac{n_T R}{V} - \left(\frac{\partial P}{\partial T} \right)_{V, n_T} \right] dV + R \sum_i n_i \ln \frac{V}{n_i RT} + \sum_i n_i s_i^0 \quad (3-49)$$

$$A = \int_V^\infty \left(P - \frac{n_T RT}{V} \right) dV - RT \sum_i n_i \ln \frac{V}{n_i RT} + \sum_i n_i (u_i^0 - Ts_i^0) \quad (3-50)$$

$$G = \int_V^\infty \left(P - \frac{n_T RT}{V} \right) dV - RT \sum_i n_i \ln \frac{V}{n_i RT} + PV + \sum_i n_i (u_i^0 - Ts_i^0) \quad (3-51)$$

$$\mu_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln \frac{V}{n_i RT} + RT + u_i^0 - Ts_i^0 \quad (3-52)$$

$$\boxed{RT \ln \phi_i = RT \ln \frac{f_i}{y_i P} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln z} \quad (3-53)$$

$u_i^0 = h_i^0 - RT$ = molar energy of pure i as an ideal gas at temperature T .

the units of $V/n_i RT$ are bar^{-1}

No addition term for the change of phase (e.g., enthalpy of vaporization) need be added.

For a pure component

$$RT \ln \left(\frac{f}{P} \right)_{\text{pure } i} = \int_V^{\infty} \left(\frac{P}{n_i} - \frac{RT}{V} \right) dV - RT \ln z + RT(z - 1) \quad (3-54)$$

We can compute all the thermodynamic properties relative to the ideal-gas state at 1 bar and at the same temperature and composition, provided that we have volumetric information

$$P = F(T, V, n_1, n_2, \dots) \quad (3-55)$$

Pressure explicit equation of state

For example, EOS in the form of the compressibility factor

$$z = \frac{P(\rho, T, x_i)}{\rho RT} \quad (3-56)$$

then, molar residual Helmholtz energy is

$$\tilde{A} = \int_0^{\rho} \frac{z(\rho, T, x_i) - 1}{\rho} d\rho \quad (3-57)$$

where $A^r = A_{(\text{real})} - A_{(\text{ideal mixture})}$, $\tilde{A} \equiv A^r / n_T RT$,

$$\ln \phi_i = \left[\frac{\partial(n_T \tilde{A})}{\partial n_i} \right]_{\rho, T, n_{j \neq i}} + (z - 1) - \ln z \quad (3-58)$$

The fugacity is obtained by differentiation rather than by integration of equation of state. More convenient when we have model for A .

3.5 Fugacity of a Component in a Mixture According to van der Waals' Equation

van der Waals equation of state

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (3-60)$$

On a total basis

$$P = \frac{n_T RT}{V - n_T b} - \frac{n_T^2 a}{V^2} \quad (3-61)$$

Differentiating with respect to n_i

$$\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} = \frac{RT}{V - n_T b} + \frac{n_T RT \left(\frac{\partial(n_T b)}{\partial n_i} \right)}{(V - n_T b)^2} - \frac{1}{V^2} \frac{\partial(n_T^2 a)}{\partial n_i} \quad (3-62)$$

$$RT \ln \phi_i = RT \ln \frac{f_i}{y_i P} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln z$$

Substituting in (3-53)

$$RT \ln \frac{f_i}{y_i P} = RT \ln \frac{V}{V - n_T b} + n_T RT \left[\frac{\partial(n_T b)}{\partial n_i} \right] \frac{1}{(V - n_T b)} - \left[\frac{\partial(n_T^2 a)}{\partial n_i} \right] \frac{1}{V} - RT \ln z \quad (3-65)$$

Mixing rules for a and b

$$b = \sum_{i=1}^m y_i b_i \quad (3-67)$$

(volume of molecule)

$$a = \sum_{i=1}^m \sum_{j=1}^m y_i y_j a_{ij} \quad (3-68)$$

(strength of attraction)

$$a_{ij} = (a_i a_j)^{1/2} \quad (3-69)$$

geometric-mean assumption
(some theoretical justification by London)

Adopting these mixing rules, the fugacity is given by

$$\ln \frac{f_i}{y_i P} = \ln \frac{v}{v-b} + \frac{b_i}{v-b} - \frac{2\sqrt{a_i} \sum_{j=1}^m y_j \sqrt{a_j}}{vRT} - \ln z \quad (3-70)$$

3.6 Phase Equilibria from Volumetric Properties

Equality of temperatures: $T^\alpha = T^\beta$

Equality of pressures: $P^\alpha = P^\beta$

For each component i ,

equality of fugacities: $f_i^\alpha = f_i^\beta$

$$RT \ln \phi_i = RT \ln \frac{f_i}{y_i P} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln z$$

We often do not have a satisfactory equation of state applicable to mixtures over a density range from zero density to liquid densities.

Phase-equilibrium calculations based on volumetric data alone are often doubtful.

It is practical for vapor mixtures, but may not be practical for condensed mixtures.

Promising equations of state based on statistical mechanical derivations are now available.