Thermodynamics II

Solution Thermodynamics: Theory-
Part 2

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Content

- Fugacity
- Ideal solutions
- Excess properties

Definitions

The specific Gibbs function for a simple compressible substance is:

$$dg = v\,dP - s\,dT$$

As in a pure substance the specific Gibbs function equals the chemical potential, we can write for a isothermal process:

$$d\mu_T = v\,dP$$

and replacing by the ideal gas EOS we obtain:

$$d\mu_{T,ideal} = \frac{RT\,dP}{P} = RT\,d\ln P$$

For a real gas: $d\mu_{T,real} = RT\,d\ln f \quad = v\,dP$

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Definitions

$$d\ln f = \frac{v\,dP}{RT} \qquad \text{I}$$

$$RT\ln\frac{f}{f_0} = \int_{P_0}^{P} v\,dP$$

If the EOS is explicit in pressure, we can use the relation:

$$d(vP) = vdP + Pdv \qquad \text{II}$$

Replacing Eq. II in Eq. I and integrating we get:

$$RT\ln\frac{f}{f_0} = Pv - P_0v_0 - \int_{v_0}^{v} P\,dv$$

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Fugacity of Pure Species

- The chemical potential μ_i provides the fundamental criterion for phase as well as chemical reaction equilibria.

$$\mu_i^{\alpha} = \mu_i^{\beta} = \cdots = \mu_i^{\pi} \qquad (i = 1, 2, \cdots, N)$$

- The Gibbs energy, and hence μ_i , is defined in relation to the internal energy and entropy. Because absolute values of internal energy are unknown, the same is true for μ_i .
- For ideal gas $\overline{G}_i^{ig} = \mu_i^{ig} = \Gamma_i(T) + RT \ln(y_i P)$

$$G_i^{ig} = \Gamma_i(T) + RT \ln(P)$$

- The concept of fugacity is introduced when considering real fluid (gas or liquid)

$$G_i = \Gamma_i(T) + RT \ln f_i$$

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Fugacity of Pure Species

$f_i \equiv$ fugacity of pure species i (with unit of pressure)

i.e. f_i is a pseudopressure.

note : for a gas under an ideal gas condition, $f_i^{ig} = P$

and the fugacity of pure species i as an ideal gas is necessarily equal to its pressure

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Residual Gibbs energy &Fugacity of Pure Species

Eqn (11.31) – Eqn (11.28),

$$G_i - G_i^{ig} = RT\ln f_i - RT\ln P = RT\ln\frac{f_i}{P}$$

$$\Rightarrow \quad G_i^R = RT\ \ln\phi_i \qquad (11.33)$$

let's us defined ϕ_i as a fugacity coefficient for species i as follows,

$$\phi_i \equiv \frac{f_i}{P}$$, a dimensionless quantity

- These equations apply to pure species i in any phase at any condition
- **At low pressures (< 1 bar), the fugacity of real species approaches the pressure**
- **For ideal gas** $$\lim_{P\to 0}\phi_i = \lim_{P\to 0}\frac{f_i}{P} = 1 \quad \Rightarrow \quad G_i^R = 0.0$$

Residual Gibbs energy &Fugacity of Pure Species

Determination of fugacity coefficient

- Fugacity (or fugacity coefficient) is obtained from PVT data or equation of state
- Recall eq. (11.33) $$\frac{G_i^R}{RT} = \ln\phi_i$$

And combine with eq. (6.49) $$\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P} \qquad (\text{const } T)$$

$$\Rightarrow \quad \ln\phi_i = \int_0^P (Z_i - 1)\frac{dP}{P} \qquad (\text{const } T) \qquad (11.35)$$

where $Z = \dfrac{PV}{RT}$ $\quad P = Pc\,\text{Pr}$ $\quad \Rightarrow \quad \ln\phi = \displaystyle\int_0^{P_r}\left(\frac{Z-1}{P_r}\right)dP_r$

Correspondence principle

- Correspondence principles and generalized charts exist for fugacity and other thermodynamic properties.
- For fugacity, both two- and three-parameter generalized charts have been developed.
- Again, these are to be used only in the absence of reliable experimental data.

Correspondence principle

Reduced variables of a gas are defined as:

$$P_r = P/P_c \qquad T_r = T/T_c \qquad V_r = V/V_c$$

Principle of corresponding states - real gases in the same state of reduced volume and temperature exert approximately the same pressure. Another way to say this is, real gases in the same reduced state of temperature and pressure have the same reduced compressibility factor.

This fact can be used to calculate PVT properties of gases for which no EOS is available.

Correspondence principle

I. We can use this equation together with the generalized Z charts.

1) Look up P_c and T_c of gas
2) Calculate P_r and T_r values for desired T's and P's
3) Make a Table of Z from the generalized charts at various values of T_r and P_r. Of course, we must have P_r values from 0 to the pressure of interest at each temperature.
4) Graph $(Z-1)/P_r$ vs. P_r for each T_r.
5) Determine the area under the the graph from $P_r = 0$ to $P_r = P_r$ to get ln φ.

II. Used generalized fugacity charts.

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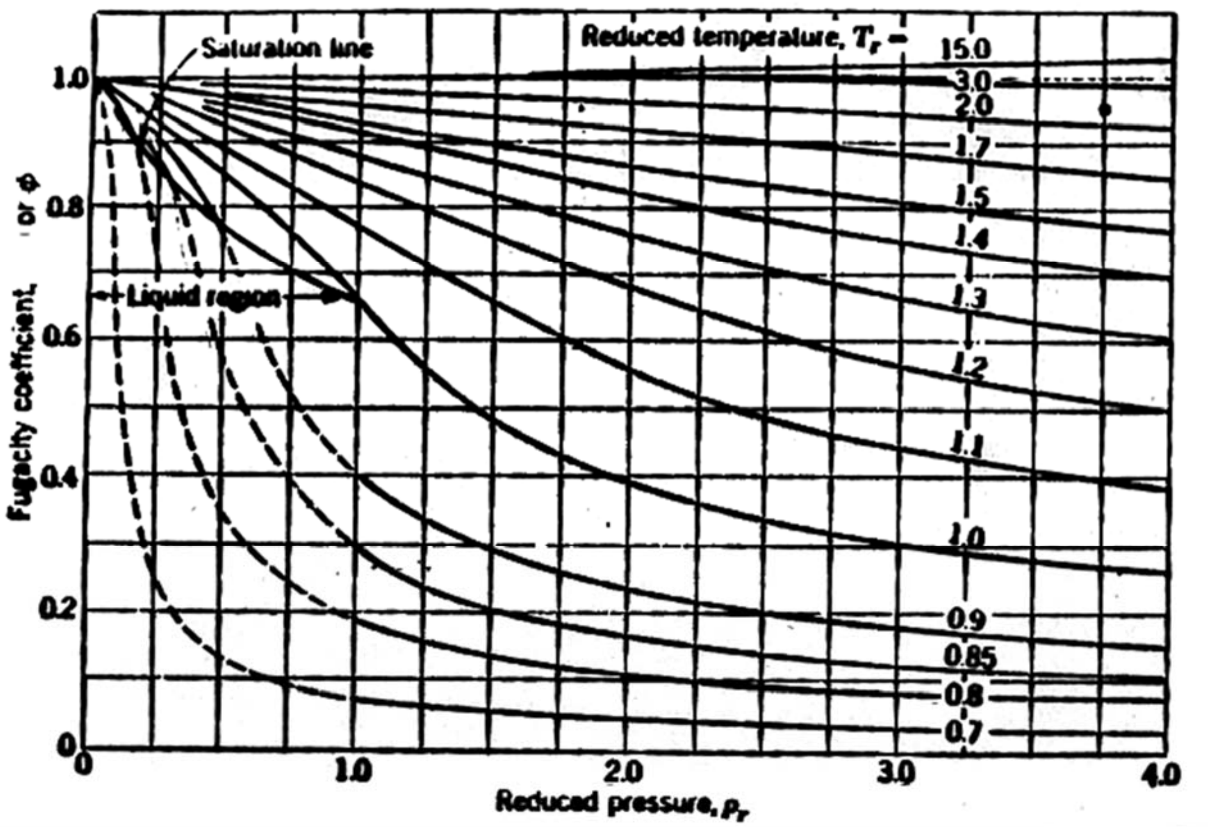
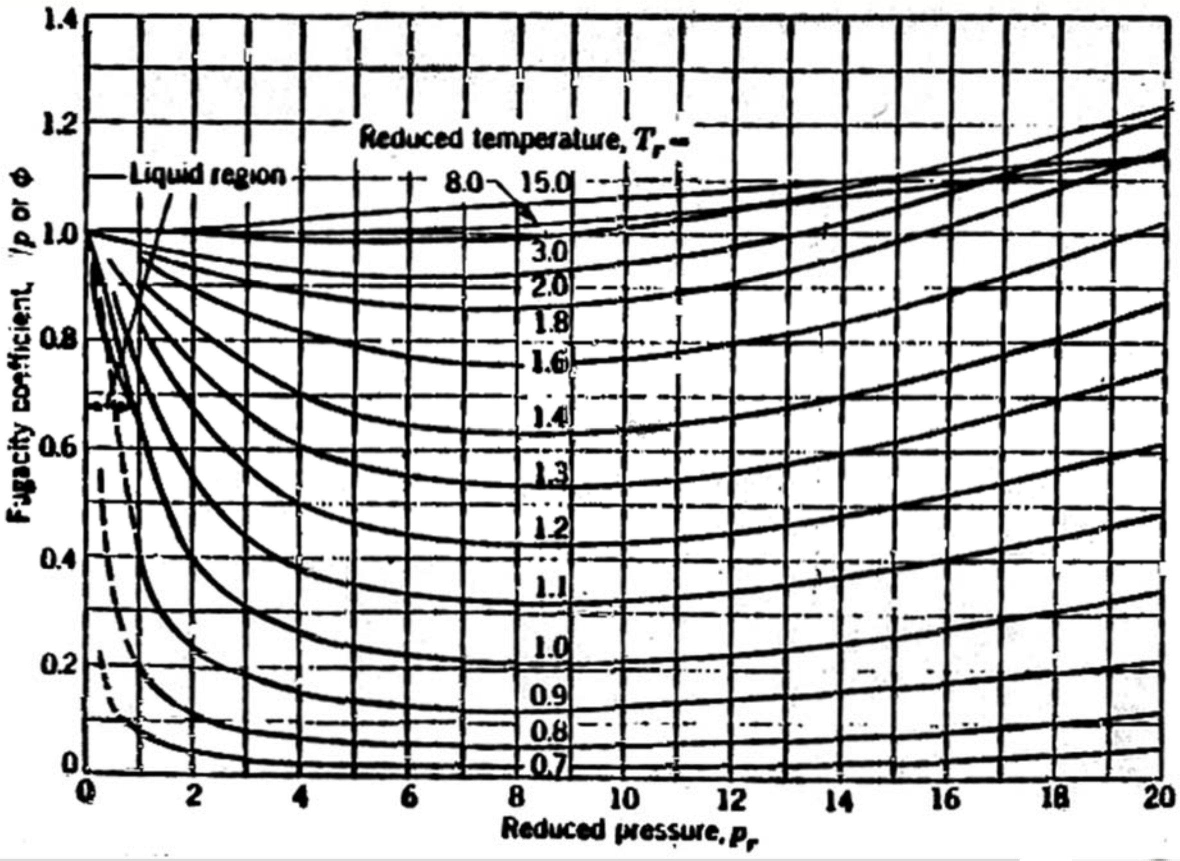
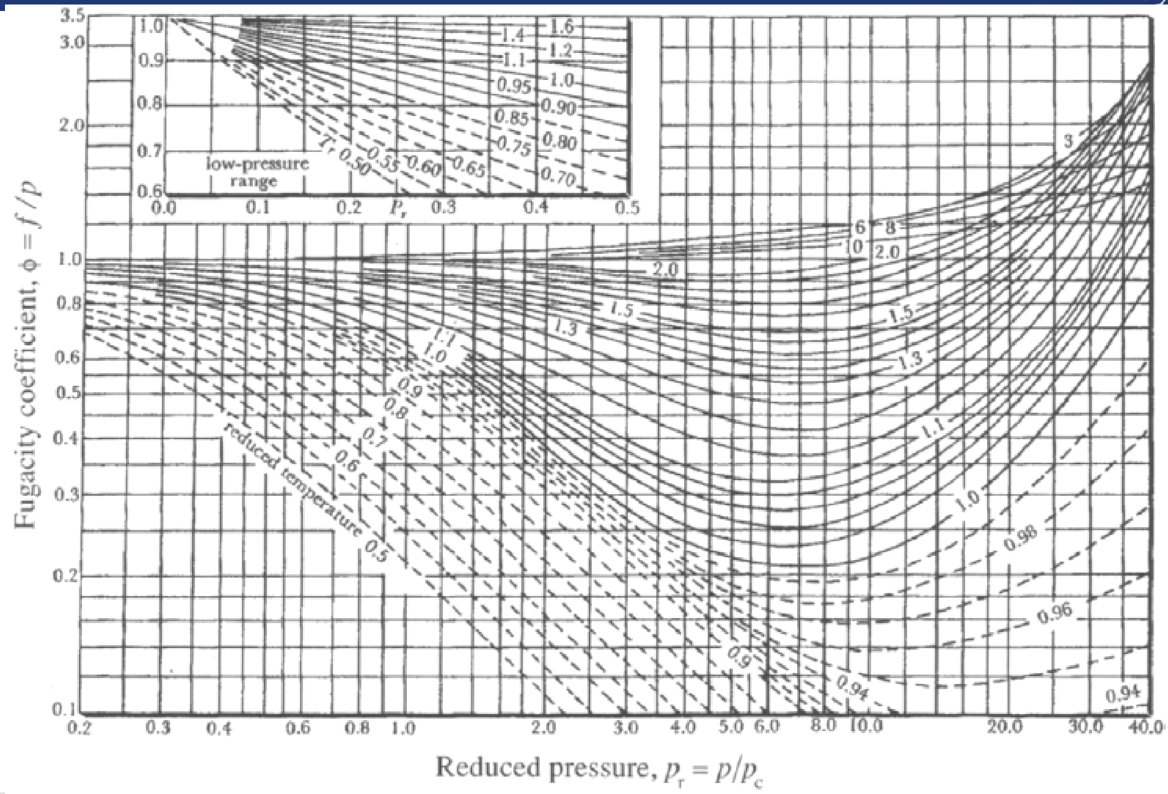



Reduced temperature, T_r =
Liquid region
Fugacity coefficient, f/p or φ
Reduced pressure, p_r


low-pressure range
reduced temperature
Fugacity coefficient, $\phi = f/p$
Reduced pressure, $p_r = p/p_c$

Example

Calculate the fugacity of CO_2 at 600°C (873 K) and 1200 atm.

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Fugacity coefficient of Pure Species

Virial equation of state

$$Z_i - 1 = \frac{B_{ii} P}{RT}$$

- Where the second virial coefficient B_{ii} is a function of temperature only for a pure species

$$\ln \phi_i = \int_0^P (Z_i - 1)\frac{dP}{P} \qquad (\text{const } T)$$

$$\Rightarrow \quad \ln \phi_i = \int_0^P \frac{B_{ii} P}{RT}\frac{dP}{P} \quad (const\ T)$$

$$\ln \phi_i = \frac{B_{ii} P}{RT}$$

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Fugacity coefficient of Pure Species

Alternatively for the 2-term Virial Equation for Z_i :

$$Z_i - 1 = \frac{B\,P}{RT} = \frac{BP_c}{RT_c}\frac{P_r}{T_r} = \hat{B}\frac{P_r}{T_r}\;\frac{P_r}{T_r} = (B^0 + \omega B^1)\frac{P_r}{T_r}$$

$$\ln\phi_i = \int_0^P (Z_i - 1)\frac{dP}{P} = \int_0^{P_r} (Z_i - 1)\frac{dP_r}{P_r}$$

$$\ln\phi_i = \int_0^{P_r} \frac{(B^0 + \omega B^1)}{T_r} dP_r = (B^0 + \omega B^1)\frac{P_r}{T_r}$$

$$\Rightarrow \quad \phi_i = \exp\left[\frac{P_r}{T_r}(B^0 + \omega B^1)\right]$$

for B^0 and B^1, see eqn 3.65 and 3.66

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad \text{and} \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

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Fugacity coefficient of Pure Species

Lee/Kesler correlation,

$$\ln\phi_i = \int_0^P (Z_i - 1)\frac{dP}{P}$$

for $P = P_c P_r \qquad dP = P_c dP_r$

$$\ln\phi_i = \int_0^{P_r} (Z - 1)\frac{P_c dP_r}{P_c P_r} = \int_0^{P_r} (Z - 1)\frac{dP_r}{P_r} = \int_0^{P_r} (Z^0 + \omega Z^1 - 1)\frac{dP_r}{P_r}$$

$$\ln\phi_i = \int_0^{P_r} (Z^0 - 1)\frac{dP_r}{P_r} + \omega\int_0^{P_r} Z^1\frac{dP_r}{P_r}$$

$$\ln\phi_i = \ln\phi_i^0 + \omega\ln\phi_i^1 \quad \Rightarrow \quad \phi_i = \phi_i^0(\phi_i^1)^\omega$$

Lee-Kesler correlation

Values for ϕ_i^0 and ϕ_i^1 are found from Table E13-E16

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Fugacity and Fugacity coefficient of Pure Species

$$d\mu_{T,real} = RT\, d\ln f = v\, dP$$

$$\Rightarrow \quad d\ln f = \frac{v\, dP}{RT}$$

But $\quad \phi \equiv \dfrac{f}{p} \quad \Rightarrow \quad d\ln\phi = d\ln f - d\ln p$

Hence $\quad d\ln\phi = \left(\dfrac{v}{RT} - \dfrac{1}{P}\right) dP$

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Fugacity and Fugacity coefficient of Pure Species

Integration of the equation at constant temperature from zero pressure (φ = 1) to a state pressure P gives

$$\ln\frac{f}{P} = \int_0^P \left(\frac{v}{RT} - \frac{1}{P}\right) dP$$

OR $\quad \ln\phi = \displaystyle\int_0^P \left(\frac{\overline{V}}{RT} - \frac{1}{P}\right) \partial P = \int_0^P \left(\frac{Z-1}{P}\right) dP$

OR $\quad \ln\phi_i = \displaystyle\int_0^P (Z_i - 1)\frac{dP}{P} \qquad (\text{const } T)$

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Fugacity and Fugacity coefficient of Pure Species

- If the EOS is explicit in pressure, we can use the relation

$$RT\ln\frac{f}{f_0} = Pv - P_0v_0 - \int_{v_0}^{v} P\,dv$$

Using the original Redlich-Kwong equation:

$$P = \frac{RT}{(\bar{V}-b)} - \frac{a}{T^{1/2}\bar{V}(\bar{V}+b)}$$

$$RT\ln\frac{f}{f_0} = Pv - P_0v_0 - RT\ln\frac{v-b}{v_0-b} - \frac{a}{b\sqrt{T}}\ln\frac{(v+b)v_0}{(v_0+b)v}$$

Taking $P_0 \to 0$ the gas behaves as ideal,

$$\ln f = \frac{Pv}{RT} - 1 + \ln\frac{RT}{v-b} - \frac{a}{bRT^{3/2}}\ln\frac{(v+b)}{v}$$

Fugacity and Fugacity coefficient of Pure Species

and replacing by the definition of the pressure we get:

$$\ln f = \frac{b}{v-b} + \ln\frac{RT}{v-b} - \frac{a}{RT^{3/2}}\left[\frac{1}{v+b} + \frac{1}{b}\ln\frac{(v+b)}{v}\right]$$

Using the equation

$$\ln\phi = \int_0^P \left(\frac{\bar{V}}{RT} - \frac{1}{P}\right)\partial P$$

$$\ln\phi = \ln\left(\frac{\bar{V}}{\bar{V}-b}\right) + \frac{b}{\bar{V}-b} - \frac{2a}{RT^{3/2}b}\ln\left(\frac{\bar{V}+b}{\bar{V}}\right) + \frac{a}{RT^{3/2}b}\left(\ln\left(\frac{\bar{V}+b}{\bar{V}}\right) - \frac{b}{\bar{V}+b}\right) - \ln\frac{P\bar{V}}{RT}$$

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- For the equation $$\ln\phi = \int_0^P \left(\frac{\overline{V}}{RT} - \frac{1}{P}\right)\partial P$$

Change the integrating variable from P to v using the product rule

$$d(Pv) = P\,dv + v\,dP \Rightarrow dP = \frac{1}{v}d(Pv) - \frac{P}{v}dv$$

Using the definition of the compressibility factor, $Z = \frac{Pv}{RT}$

then $$d(Pv) = RT\,dZ \Rightarrow dP = \frac{RT}{v}dZ - \frac{P}{v}dv = \frac{P}{Z}dZ - \frac{P}{v}dv$$

Substituting dP from the above equation

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_{v=\infty}^{v}\left(v - \frac{RT}{P}\right)\left(\frac{P}{Z}dZ - \frac{P}{v}dv\right)$$

$$\Rightarrow \ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_{v=\infty}^{v}\left(\frac{RT}{v} - P\right)dv + \frac{1}{RT}\int_{Z=1}^{Z}\left(\frac{Pv}{Z} - \frac{RT}{Z}\right)dZ$$

$$\Rightarrow \ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_{v=\infty}^{v}\left(\frac{RT}{v} - P\right)dv - \ln Z + (Z-1)$$

Using the van der Waals equation:

$$P = \frac{RT}{(\bar{V} - b)} - \frac{a}{\bar{V}^2}$$

$$\ln f = \frac{b}{v-b} + \ln\frac{RT}{v-b} - \frac{2a}{RTv}$$

OR

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_{v=\infty}^{v}\left(\frac{RT}{v} - P\right)dv - \ln Z + (Z-1)$$

But $\frac{RT}{v} - P = \frac{RT}{v} - \frac{RT}{v-b} + \frac{a}{v^2}$

Fugacity and Fugacity coefficient of Pure Species

$$\ln\phi = \ln\left(\frac{\bar{V}}{\bar{V} - b}\right) + \frac{b}{\bar{V} - b} - \frac{2a}{\bar{V}RT} - \ln\frac{P\bar{V}}{RT}$$

Generic Cubic EOS

Combined eqn 11.33 with 6.66b (and apply for species *i*),

$$G_i^R = RT\ln\phi_i \qquad (11.33)$$

$$\frac{G_i^R}{RT} = Z_i - 1 - \ln(Z_i - \beta_i) - q_i I_i \qquad (6.66b)$$

We get,

$$\ln\phi_i = Z_i - 1 - \ln(Z_i - \beta_i) - q_i I_i \qquad (11.37)$$

Example

Determine the fugacity (MPa) for acetylene at: (a) 250K and 10 bar; (b) 250K and 20 bar. Use the virial equation and the shortcut vapor pressure equation.

for acetylene: $T_c = 308.3$ K, $P_c = 6.139$, $\omega = 0.187$, $Z_c = 0.271$. $\quad P^{sat} = 1.387$ MPa.

Example

Determine the fugacity, in bars, for R134a for a Redlich-Kwong gas at 90 °C and 10 bar. Compare against Van der Waals EOS.

$$p = \frac{RT}{v-b} - \frac{a}{\sqrt{T}\, v\,(v+b)}, \qquad a = 0.42748\frac{R^2 T_c^{2.5}}{P_c}, \qquad b = 0.08664\frac{RT_c}{P_c}$$

In R134, $(C_2F_4H_2)$, we have $T_c = 374.3\ K$, $P_c = 40.6\ bar$, $M = 102.3\ kg/kmol$.

$$a = 197.1 \frac{bar\, m^3 K^{2.5}}{kmol^2}, \qquad b = 0.06634\frac{m^3}{kmol}$$

the specific volume $\left(v = 2.724\ m^3/kg\right)$:

$$\ln f = \frac{b}{v-b} + \ln\frac{RT}{v-b} - \frac{a}{RT^{3/2}}\left[\frac{1}{v+b} + \frac{1}{b}\ln\frac{(v+b)}{v}\right] \Rightarrow f = 9.09\ bar$$

for a Van der Waals gas $f = 9.21\ bar$.

Vapor-Liquid Equilibrium for Pure Species

- For a saturated vapor and a saturated liquid at the same *T*, *P*

$$G_i^v = \Gamma_i(T) + RT\ln f_i^v \qquad G_i^l = \Gamma_i(T) + RT\ln f_i^l$$

They are in equilibrium

$$G_i^v = G_i^l \qquad \text{or} \qquad \mu_i^v = \mu_i^l$$

$$G_i^v - G_i^l = RT\ln\frac{f_i^v}{f_i^l} = 0$$

$$f_i^v = f_i^l = f_i^{sat} \qquad (11.39)$$

Coexisting vapor and liquid phases have the same fugacity

Vapor-Liquid Equilibrium for Pure Species

- Also,

$$\phi_i^{sat} = \frac{f_i^{sat}}{P_i^{sat}} \qquad (11.40)$$

$$\phi_i^v P^{sat} = \phi_i^l P^{sat}$$

- And hence

$$\phi_i^f = \phi_i^v = \phi_i^{sat} \qquad (11.41)$$

the same fugacity coefficient

Fugacity of a Pure (compressed) Liquid

- At constant temperature, as the pressure increases

superheated vapor $\rightarrow$ saturated vapor $\rightarrow$ saturated liquid $\rightarrow$ compressed liquid

f_i^v $\qquad f_i^v = f_i^l = f_i^{sat}$ $\qquad f_i^l$

For saturated vapor

$$\ln \phi_i^{sat} = \ln \frac{f_i^{sat}}{P_i^{sat}} = \int_0^{P_i^{sat}} \left(Z_i^v - 1\right)\frac{dP}{P} \qquad (const\ T)$$

- Calculation of the fugacity change resulting from changes the state from saturated liquid to compressed liquid

Knowing that $\qquad dG = V\,dP - S\,dT$

For compressed liquid at constant T $\qquad G_i - G_i^{sat} = \int_{P_i^{sat}}^{P} V_i\,dP$

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Fugacity of a Pure (compressed) Liquid

Also $\qquad G_i - G_i^{sat} = RT \ln \frac{f_i}{f_i^{sat}}$

Then, $\qquad G_i - G_i^{sat} = RT\ \ln \frac{f_i}{f_i^{sat}} = \int_{P_i^{sat}}^{P} V_i^l\ dP$

$$f_i = f_i^{sat} \exp\left[\frac{1}{RT}\int_{P_i^{sat}}^{P} V_i^l dP\right] = \phi_i^{sat} P_i^{sat} \exp\left[\frac{1}{RT}\int_{P_i^{sat}}^{P} V_i^l dP\right]$$

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Fugacity of a Pure (compressed) Liquid

- The molar volume of liquid phase is a weak function of pressure if $T << T_c$. When V_i^l is assumed constant, the value of saturated liquid, then

fugacity of pure liquid *i*

$$f_i = f_i^{sat} \exp\left[\frac{V_i^l\left(P - P_i^{sat}\right)}{RT}\right] = \phi_i^{sat} P_i^{sat} \exp\left[\frac{V_i^l\left(P - P_i^{sat}\right)}{RT}\right] \qquad (11.44)$$

The exponential is known as a Poynting factor

≅ 1 usually small for moderate pressure

OR

$$\ln \frac{f}{f_{sat}}\bigg|_{liq} = \frac{1}{RT}\int_{P_{sat}}^{P} v\, dP \;\Rightarrow\; \ln f_2 - \ln f_1 = \frac{\overline{V}}{RT}(P_2 - P_1)$$

Example

What is the fugacity of liquid Cl_2 at 25°C and 100 atm? The vapor pressure of Cl_2 at 25°C is 7.63 atm.

Example

Fugacity of liquid rises very slowly with increasing pressure

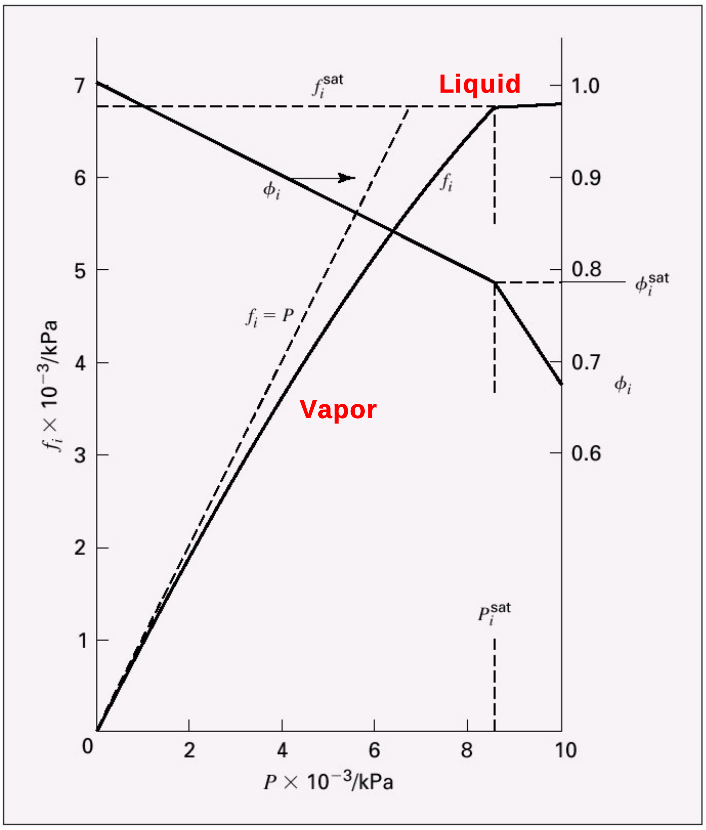

Figure 11.3: Fugacity and fugacity coefficient of steam at 300°C.

Fugacity and fugacity coefficient: Species in solution

- For an ideal gas mixture, the chemical potential is

$$\mu_i^{ig} = \Gamma_i(T) + RT\ln(y_i P)$$

- For real fluid (gas or liquid)

$$G_i = \Gamma_i(T) + RT\ln f_i$$

- For species I in a mixture of real gases or in a solution of liquids, the equilibrium analogous to Eq. (11.20), the ideal-gas expression, is:

$$\mu_i \equiv \Gamma_i(T) + RT\ln \hat{f}_i$$

f_i **fugacity of species pure species**

$\hat{f}_i$ **fugacity of species in solution (mixture)**

Fugacity and fugacity coefficient: Species in solution

at VLE

$$\mu_i^l = \mu_i^v$$

$$\Gamma_i(T) + RT\ln \hat{f}_i^{\,l} \equiv \Gamma_i(T) + RT\ln \hat{f}_i^{\,v}$$

$$\Rightarrow \quad \hat{f}_i^{\,v} = \hat{f}_i^{\,l}$$

Criteria for multicomponent vapor/liquid equilibrium

- For multiple phases and the same T and P in equilibrium

$$\mu_i^\alpha = \mu_i^\beta = \cdots = \mu_i^\pi \qquad (i = 1, 2, \cdots, N)$$

$$\Rightarrow \quad \hat{f}_i^{\,\alpha} = \hat{f}_i^{\,\beta} = \cdots = \hat{f}_i^{\,\pi} \qquad (i = 1, 2, \cdots, N)$$

- The fugacity of each species is the same in all phases
- The equality of the fugacity can be used for the criteria of phase equilibrium instead of the equ ality of chemical potential.

Fugacity and fugacity coefficient: Species in solution

- The definition of a residual property is given in Sec. 6.2:

$$M^R \equiv M - M^{ig} \qquad (6.41)$$

- Where M is the molar (or unit mass) value of a thermodynamic property and M^{ig} is the value that the property would have for an ideal gas of the same composition at same T and P. The defining equation for a partial residual property

- The residual Gibbs energy is $\quad nG^R \equiv nG - nG^{ig}$

$$\left[\frac{\partial(nG^R)}{\partial n_i}\right]_{P,T,n_j} = \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} - \left[\frac{\partial(nG^{ig})}{\partial n_i}\right]_{P,T,n_j}$$

the partial residual Gibbs energy is $\quad \bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig}$

Fugacity and fugacity coefficient: Species in solution

$$\bar{G}_i^R = \mu_i - \mu_i^{ig} = RT\ln\frac{\hat{f}_i}{y_i P}$$

- **The fugacity coefficient of species *i*** $\hat{\phi}_i$ **in mixture is defined as**

$$\bar{G}_i^R = RT\ln\hat{\phi}_i \qquad \hat{\phi}_i \equiv \frac{\hat{f}_i}{y_i P}$$

$$\hat{f}_i = \hat{\phi}_i y_i P$$

- In an ideal gas mixture, the fugacity of species *i* is equal to its partial pressure

$$\hat{f}_i^{ig} = y_i P \qquad \hat{\phi}_i^{ig} = 1$$

- In an ideal gas of pure species, the fugacity is equal to (total) pressure

The Fundamental Residual-Property Relation

Determination of fugacity coefficient in solution

$$d\left(\frac{\mathbf{G}}{RT}\right) = \frac{1}{RT}d\mathbf{G} - \frac{\mathbf{G}}{RT^2}dT$$

$$d\mathbf{G} = \mathbf{V}\,dP - \mathbf{S}\,dT + \sum_i \bar{G}_i\,dn_i \qquad \mathbf{G} = \mathbf{H} - T\mathbf{S}$$

Substituting

$$d\left(\frac{\mathbf{G}}{RT}\right) = \frac{\mathbf{V}}{RT}dP - \frac{\mathbf{H}}{RT^2}dT + \sum_i \frac{\bar{G}_i}{RT}dn_i$$

- For an ideal gas

$$d\left(\frac{\mathbf{G}^{ig}}{RT}\right) = \frac{\mathbf{V}^{ig}}{RT}dP - \frac{\mathbf{H}^{ig}}{RT^2}dT + \sum_i \frac{\bar{G}_i^{ig}}{RT}dn_i$$

Subtraction gives

$$d\left(\frac{\mathbf{G}^R}{RT}\right) = \frac{\mathbf{V}^R}{RT}dP - \frac{\mathbf{H}^R}{RT^2}dT + \sum_i \frac{\bar{G}_i^R}{RT}dn_i$$

Determination of fugacity coefficient in solution

$$d\left(\frac{nG^R}{RT}\right)=\frac{nV^R}{RT}dP-\frac{nH^R}{RT^2}dT+\sum_i\frac{\bar{G}_i^R}{RT}dn_i$$

$$d\left(\frac{nG^R}{RT}\right)=\frac{nV^R}{RT}dP-\frac{nH^R}{RT^2}dT+\sum_i\ln\hat{\phi}_i\,dn_i \qquad (11.52)$$

$$\frac{nV^R}{RT}=\left(\frac{\partial(G^R/RT)}{\partial P}\right)_{T,x} \qquad (11.53)$$

$$\frac{H^R}{RT}=-T\left(\frac{\partial(G^R/RT)}{\partial T}\right)_{P,x} \qquad (11.54)$$

$$\ln\hat{\phi}_i=\left(\frac{\partial(nG^R/RT)}{\partial n_i}\right)_{P,T,x} \qquad (11.55)$$

$$\left(\frac{\partial\ln\hat{\phi}_i}{\partial P}\right)_{T,x}=\frac{\bar{V}_i^R}{RT} \qquad \left(\frac{\partial\ln\hat{\phi}_i}{\partial T}\right)_{P,x}=-\frac{\bar{H}_i^R}{RT^2}$$

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Determination of fugacity coefficient in solution

$\ln\hat{\phi}_i$ is a partial property of G^R/RT

$$\ln\hat{\phi}_i=\left(\frac{\partial(nG^R/RT)}{\partial n_i}\right)_{P,T,x}$$

And combine with eq. (6.49) $\quad \frac{G^R}{RT}=\int_0^P(Z-1)\frac{dP}{P} \qquad$ (const T)

$$\ln\hat{\phi}_i=\int_0^P\left[\frac{\partial(nZ-n)}{\partial n_i}\right]_{P,T,n_j}\frac{dP}{P}=\int_0^P\left[\frac{\partial nZ}{\partial n_i}-\frac{\partial n}{\partial n_i}\right]_{P,T,n_j}\frac{dP}{P}$$

$$=\int_0^P\left(\left[\frac{\partial nZ}{\partial n_i}\right]_{P,T,n_j}-\left[\frac{\partial n}{\partial n_i}\right]_{P,T,n_j}\right)\frac{dP}{P} \qquad \left[\frac{\partial n}{\partial n_i}\right]_{P,T,n_j}=1$$

$$\ln\hat{\phi}_i=\int_0^P\left(\bar{Z}_i-1\right)\frac{dP}{P} \qquad (11.60)$$

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Using Two-term Virial EOS

$$Z = 1 + \frac{BP}{RT} \qquad nZ = n + \frac{nBP}{RT}$$

$$\bar{Z}_1 = \left[\frac{\partial(nZ)}{\partial n_1}\right]_{P,T,n_2} = 1 + \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2}$$

Substitute into eqn 11.60

$$\ln\hat{\phi}_1 = \int_0^P \left(1 + \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} - 1\right)\frac{dP}{P} = \frac{1}{RT}\int_0^P \left(\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2}\right) dP$$

$$\ln\hat{\phi}_1 = \frac{1}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} P = \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2}$$

How to evaluate?

Determination of fugacity coefficient in solution

- Volume-explicit virial equation of state

$$Z = 1 + \frac{BP}{RT} + \cdots$$

- **The mixture second virial coefficient B is a function of T and composition.**

For mixture

$$B = \sum_i \sum_j y_i y_j B_{ij} \qquad (11.57) \qquad \text{[volume/mol]}$$

e.g. binary mixture

$$B = y_1 y_1 B_{11} + y_1 y_2 B_{12} + y_2 y_1 B_{21} + y_2 y_2 B_{22}$$

$$B = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22} \qquad (11.58)$$

$$B = y_1(1 - y_2)B_{11} + 2 y_1 y_2 B_{12} + y_2(1 - y_1)B_{22}$$

Determination of fugacity coefficient in solution

with $B_{ij} = B_{ji}$

B_{11}, B_{22} pure species virial coefficients

B_{12} cross virial coefficient (mixture property)

B_{ij} is a function only of temperature

Re-arrange

$$\begin{aligned} B &= y_1B_{11} - y_1y_2B_{11} + 2y_1y_2B_{12} + y_2B_{22} - y_1y_2B_{22} \\ &= y_1B_{11} + y_2B_{22} + 2y_1y_2B_{12} - y_1y_2B_{11} - y_1y_2B_{22} \\ &= y_1B_{11} + y_2B_{22} + y_1y_2(2B_{12} - B_{11} - B_{22}) \\ &= y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12} \end{aligned}$$

where $\delta_{12} = 2B_{12} - B_{11} - B_{22}$

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Determination of fugacity coefficient in solution

Multiply by n (note: $y_i = n_i / n$), $nB = n_1B_{11} + n_2B_{22} + n_1\frac{n_2}{n}\delta_{12}$

$$nB = n_1B_{11} + n_2B_{22} + n_1\frac{n_2}{n}\delta_{12}$$

$$\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} = B_{11} + 0 + n_2\delta_{12}\left(\frac{\partial \frac{n_1}{n}}{\partial n_1}\right) \qquad \text{note: } \partial\frac{u}{v} = \frac{v\partial u - u\partial v}{v^2}$$

$$= B_{11} + n_2\left(\frac{\frac{n\partial n_1 - n_1 dn}{n^2}}{\partial n_1}\right)\delta_{12} = B_{11} + n_2\left(\frac{1}{n} - \frac{n_1\partial n}{n^2\partial n_1}\right)\delta_{12}$$

$$= B_{11} + \left(\frac{n_2}{n} - \frac{n_2n_1\partial n}{n^2\partial n_1}\right)\delta_{12} = B_{11} + \left(y_2 - y_2y_1\frac{\partial n}{\partial n_1}\right)\delta_{12}$$

$$\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} = B_{11} + (1 - y_1)y_2\delta_{12} = B_{11} + y_2^2\delta_{12}$$

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Determination of fugacity coefficient in solution

note,

$$B_{11} = B_1 \quad B_{22} = B_2$$

$$B_{12} = \frac{RT_{c12}}{P_{c12}}\left(B^0 + \omega_{12}B^1\right)$$

Interaction parameter (=0 if no data provided)

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \qquad T_{c12} = (T_{c1}T_{c2})^{1/2}(1 - k_{12})$$

$$P_{c12} = \frac{Z_{c12}RT_{c12}}{V_{c12}} \qquad V_{c12} = \left(\frac{V_{c1}^{1/3} + V_{c2}^{1/3}}{2}\right)^3 \qquad Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2}$$

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Determination of fugacity coefficient in solution

$$\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} = B_{11} + (1 - y_1)y_2\delta_{12} = B_{11} + y_2^2\delta_{12}$$

$$\Rightarrow \quad \ln\hat{\phi}_1 = \frac{P}{RT}\left(B_{11} + y_2^2\delta_{12}\right) \qquad (11.59)$$

$$\ln\hat{\phi}_2 = \frac{P}{RT}\left(B_{22} + y_1^2\delta_{12}\right) \qquad (11.60)$$

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Determination of fugacity coefficient in solution

In general, for multicomponent gas mixture,

$$\ln \hat{\phi}_k = \frac{P}{RT}\left(B_{kk} + \tfrac{1}{2}\sum_i \sum_l y_i y_l (2\delta_{ik} - \delta_{il})\right)$$

where,

$$\delta_{ik} = 2B_{ik} - B_{ii} - B_{kk} \quad \text{and} \quad \delta_{il} = 2B_{il} - B_{ii} - B_{ll}$$

$$\delta_{ii} = \delta_{ll} = 0 \quad \text{and} \quad \delta_{ik} = \delta_{ki}$$

$$B_{ij} = \frac{RT_{cij}}{P_{cij}}\left(B^0 + \omega_{ij} B^1\right) \qquad \omega_{ij} = \frac{\omega_i + \omega_j}{2} \qquad T_{cij} = (T_{ci}T_{cj})^{1/2}(1 - k_{ij})$$

$$P_{cij} = \frac{Z_{cij} RT_{cij}}{V_{cij}} \qquad V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right)^3 \qquad Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2}$$

Determination of fugacity coefficient in solution

Using Generic Cubic EOS

$$\ln \hat{\phi}_i = \frac{b_i}{b}(Z - 1) - \ln(Z - \beta) - \bar{q}_i I$$

Refer to chapter 14 if you interested in the details.

Example

N_2 / CH_4 $y_1 = 0.4$, $T = 200$K, $P = 30$ bar

$B_{11} = -35.2$ $\quad B_{22} = -105.0$ $\quad B_{12} = -59.8$ cm^3/mol

$\delta_{12} = 20.6$ cm^3/mol

The Ideal Solution

We know for an ideal-gas mixture, $\mu_i^{ig} = \overline{G}_i^{ig} = G_i^{ig}(T,P) + RT\ln y_i$

No intermolecular forces/interaction
and negligible particle volume (compare to molar volume).
Only for an ideal gas mixture.

For an ideal solution, we define $\mu_i^{id} = \overline{G}_i^{id} = G_i(T,P) + RT\ln x_i$

There exist intermolecular interaction but the various molecules have similar size, structure and intermolecular forces.
Applicable for real gas mixture and liquid solution.
However, application is most often to liquid solution.

So for an ideal solution, $G^{id} = \sum x_i \overline{G}_i^{id} = \sum x_i G_i + RT\sum x_i \ln x_i$

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Partial properties of an ideal solution

Entropy

Substitute $\mu_i = \overline{G}_i$ into Eqn 11.3,

$$dG = VdP - SdT + \sum_i \overline{G}_i dx_i$$

Apply criterion of exactness,

$$\overline{S}_i = \left[\frac{\partial(nS)}{\partial x_i}\right]_{P,T,x} = -\left(\frac{\partial \overline{G}_i}{\partial T}\right)_{P,x}$$

For ideal solution,

$$\overline{S}_i^{id} = -\left(\frac{\partial \overline{G}_i^{id}}{\partial T}\right)_{P,x} = -\left(\frac{\partial(G_i(T,P) + RT\ln x_i)}{\partial T}\right)_{P,x}$$

$$\overline{S}_i^{id} = -\left(\frac{\partial(G_i(T,P)}{\partial T}\right)_{P,x} - \left(\frac{R\ln x_i \partial T}{\partial T}\right)_{P,x} = S_i - R\ln x_i$$

$$S^{id} = \sum x_i(S_i - R\ln x_i) = \sum x_i S_i - R\sum x_i \ln x_i$$

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Partial properties of an ideal solution

Enthalpy

$$\bar{H}_i^{id} = \bar{G}_i^{id} + T\bar{S}_i^{id}$$

$$\begin{aligned}\bar{H}_i^{id} &= G_i + RT\ln x_i + T(S_i - R\ln x_i) \\ &= G_i + TS_i \\ &= H_i\end{aligned}$$

So for ideal solution,

$$H = \sum x_i H_i$$

Molar Volume

$$dG = VdP - SdT + \sum_i \bar{G}_i dx_i$$

Apply criterion of exactness,

$$\left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,x} = \left[\frac{\partial V}{\partial x_i}\right]_{P,T,x} = \bar{V}_i$$

For ideal solution,

$$\bar{V}_i^{id} = \left(\frac{\partial \bar{G}_i^{id}}{\partial P}\right)_{T,x} = -\left(\frac{\partial (G_i(T,P) + RT\ln x_i)}{\partial P}\right)_{T,x}$$

$$\bar{V}_i^{id} = \left[\frac{\partial G_i(T,P)}{\partial P}\right]_{T,x} = V_i$$

$$V^{id} = \sum x_i V_i$$

The Lewis-Randall rule

$G_i \equiv \Gamma_i(T) + RT\ln f_i$ for pure species

$\mu_i \equiv \Gamma_i(T) + RT\ln \hat{f}_i$ for mixture

Subtraction gives $\mu_i = G_i + RT\ln(\hat{f}_i / f_i)$ generic relation for real mixtures

For an ideal solution $\mu_i^{id} = G_i + RT\ln(\hat{f}_i^{id} / f_i)$

Comparison with the definition of an ideal solution

$$\mu_i^{id} = G_i + RT\ln x_i$$

gives the Lewis-Randall rule $\hat{f}_i^{id} = x_i f_i$ Comment $\hat{f}_i^{id} \neq f_i$

The Lewis-Randall rule

- The fugacity of species *i* in an ideal solution is proportional to its mole fraction
- In terms of the fugacity coefficient

$$\frac{\hat{f}_i^{id}}{x_i P} = \frac{x_i f_i}{x_i P} = \frac{f_i}{P}$$

$$\hat{\phi}_i^{id} = \phi_i$$

- The fugacity coefficient of species *i* in an ideal solution is equal to the fugacity coefficient of pure species

Rault's law

- If we further assume further $f_i \approx P_i^{sat}$ (vapor phase is an ideal gas), we obtain

For vapor $\quad f_i \approx P_i^{sat}$

For liquid $\quad \hat{f}_i^{id} = x_i P_i^{sat}$

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Excess Properties

- Excess properties are measures of deviations from ideal solution behavior

$$M^E \equiv M - M^{id}$$

Excess = Real solution – Ideal solution

$$G^E \equiv G - G^{id} \qquad S^E \equiv S - S^{id} \qquad H^E \equiv H - H^{id}$$

They are related by

$$G^E = H^E - T S^E$$

The fundamental excess-property relation

$$d\left(\frac{\mathbf{G}^E}{RT}\right) = \frac{\mathbf{V}^E}{RT} dP - \frac{\mathbf{H}^E}{RT^2} dT + \sum_i \frac{\bar{G}_i^E}{RT} dn_i$$

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT} dP - \frac{nH^E}{RT^2} dT + \sum_i \frac{\bar{G}_i^E}{RT} dn_i$$

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The Excess Gibbs Energy and the Activity Coefficient

$$\bar{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i \qquad = \text{chemical potential}$$

- For an ideal solution

$$\bar{G}_i^{id} = \Gamma_i(T) + RT \ln x_i f_i$$

- Difference is the excess partial molar Gibbs energy

$$\bar{G}_i^E = \bar{G}_i - \bar{G}_i^{id} = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

- Define activity coefficient as $\gamma_i \equiv \dfrac{\hat{f}_i}{x_i f_i}$

$$\Rightarrow \quad \bar{G}_i^E = RT \ln \gamma_i$$

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The Excess Gibbs Energy and the Activity Coefficient

- The activity is defined as $a_i \equiv \dfrac{\hat{f}_i}{f_i}$ $\qquad a_i = \gamma_i x_i$

- For an ideal solution

$$\bar{G}_i^E = 0 \quad \Rightarrow \quad RT(\ln \frac{\hat{f}_i^{id}}{x_i f_i}) = RT(\ln \gamma_i) = 0$$

$$\Rightarrow \quad \gamma_i = \frac{\hat{f}_i^{id}}{x_i f_i} = 1$$

$$\hat{f}_i^{id} = x_i f_i \qquad \text{Lewis/Randall rule} \qquad a_i = x_i$$

divide by Px_i

$$\frac{\hat{f}_i^{id}}{Px_i} = \frac{x_i f}{Px_i}$$

$$\hat{\phi}_i^{id} = \phi_i$$

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$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}dP - \frac{nH^E}{RT^2}dT + \sum_i \ln\gamma_i \, dn_i$$

$$\frac{V^E}{RT} = \left[\frac{\partial\left(G^E/RT\right)}{\partial P}\right]_{T,x} \qquad \frac{H^E}{RT} = -T\left[\frac{\partial\left(G^E/RT\right)}{\partial T}\right]_{P,x}$$

$$\ln\gamma_i = \left[\frac{\partial\left(nG^E/RT\right)}{\partial n_i}\right]_{P,T,n_j}$$

- The effect of pressure and temperature on the activity coefficient

$$\left(\frac{\partial\ln\gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{V}_i^E}{RT} \qquad \left(\frac{\partial\ln\gamma_i}{\partial T}\right)_{P,x} = -\frac{\bar{H}_i^E}{RT^2}$$

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$\ln\gamma_i$ **is a partial property with respect to** G^E/RT

$$\frac{G^E}{RT} = \sum_i x_i \ln\gamma_i$$

- The Gibbs-Duhem equation is given by

$$\sum_i x_i \, d\ln\gamma_i = 0 \qquad \text{at constant } T, P$$

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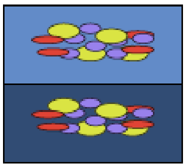
Consider a multicomponent system in VLE, the fugacity of species *i* for each phase,

For vapor mixture $\hat{f}_i^v = \hat{\phi}_i y_i P$

For liquid solution $\hat{f}_i^l = \gamma_i x_i f_i$

VLE criteria,

$$\hat{f}_i^v = \hat{f}_i^l$$



so

$$\hat{\phi}_i y_i P = \gamma_i x_i f_i$$

This is the VLE relation that relates the composition of vapor phase and that of liquid phase. See Chapter 10 for application of this relation. Chapter 12 for correlation for γ_i

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Example

Equimolar mixture of benzene and cyclohexane at 25°C and 1 bar

$$\left[\frac{\partial (G^E/RT)}{\partial P}\right]_{T,x} = \frac{V^E}{RT} = 2.62\times10^{-5} \quad \text{bar}^{-1}$$

$$\left[\frac{\partial (G^E/RT)}{\partial T}\right]_{P,x} = -\frac{H^E}{RT^2} = -1.08\times10^{-3} \ \text{K}^{-1}$$

- A pressure change of about 40 bar has nearly the same effect on the excess Gibbs energy as a temperature change of 1 K
- For this reason, the effect of pressure on the excess Gibbs energy is usually neglected for liquids with moderate pressure changes

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