Lecture 3.1
Properties Relative to Ideal Gases

O'Connell & Haile

Chapter 4

Topics:

- **Ideal Gases: Pure & Mixed IG Properties**
- **Difference Deviations from IG: Residuals**
- **Fugacity**
- **Ratio Deviation from IG:**
  - **Compressibility Factor**
  - **Fugacity Coefficient**
- **Equations of State**
  - **Using for Values of Conceptuals**
  - **Some Models & Comparisons**

IDEAL GASES

Equation of state (EoS) $PV = NRT$

For pure components, do Chapter 3 operations

Get $U^{ig} = Nu^{ig}(T) \qquad H^{ig} = Nh^{ig}(T)$

$\Rightarrow C_p^{ig} = Nc_p^{ig}(T), c_v^{ig} = c_v^{ig}(T)$

but $c_p^{ig}(T) - c_v^{ig}(T) = R$ **!**

Integrate to get $u^{ig}(T_2, P_2) - u(T_1, P_1) = \int_{T_1}^{T_2} c_v^{ig}(T)dT$**, etc.**

Note: Change independent variable by writing

$v = v(T,P) \Rightarrow v^{ig} = RT/P$ **or** $P = P(T,v) \Rightarrow P^{ig} = RT/v$

Two identical physical descriptions

Macroscopic: *P* = 0 limit of "real stuff" (p.123)

Microscopic: "no intermolecular forces", but has molecular kinetic energy (gives *T*) & momentum change at walls (gives *P, V*)

IDEAL GAS MIXTURES

Similarities & differences with pures (4.1.15)

$$F^{ig}(T,V,\{N\}) = \sum_{i=1}^{C} F_{pure\,i}^{ig}(T,V,N_i) = \sum_{i=1}^{C} N_i f_{pure\,i}^{ig}(T,V/N_i)$$

Equation of state

$$P^{ig} = NRT/V = \sum_i N_i\left(\frac{RT}{V}\right) = \sum_i P_{pure\,i}^{ig}(T, v_{pure\,i}) \quad \textbf{(4.1.19)}$$

Note: *derived* from 4.1.15, not merely asserted

Partial molar properties very subtle

$$\overline{F}_i^{ig}(T,v,\{x\}) = f_{\text{pure i}}^{ig}(T, v_{\text{pure i}}) \Rightarrow$$

$$\overline{F}_i^{ig}(T,P,\{x\}) = f_{\text{pure i}}^{ig}\left(T, P_{\text{pure i}}^{ig} = \frac{N_i RT}{V}\right)$$

Properties from 1st Law(thermal/mechanical) different from those of 2nd Law(entropic)

$$\overline{V}_i^{ig}(T,P,\{x\}) = v_{\text{pure i}}(T,P); \; \overline{U}_i^{ig}(T,v,\{x\}) = u_{\text{pure i}}^{ig}(T)$$

$$\overline{S}_i^{ig}(T,v,\{x\}) = s_{\text{pure i}}^{ig}(T, v_i = Nv/N_i) \qquad (4.1.29)$$

$$\overline{S}_i^{ig}(T,P,\{x\}) = s_{\text{pure i}}^{ig}\left(T, P_{\text{pure i}} = \frac{N_i RT}{V} \neq P\right) \qquad (4.1.30)$$

$$= s_{\text{pure i}}^{ig}(T,P) - R\ln x_i \qquad (4.1.35)$$

$$\overline{G}_i(T,P,\{x\}) = g_{\text{pure i}}^{ig}(T,P) + RT\ln x_i \qquad (4.1.37)$$

Note: $R\ln x_i < 0 \Rightarrow \overline{S}_i^{ig}(T,P,\{x\}) > s_{pure\,i}^{ig}(T,P)$

$$RT\ln x_i < 0 \Rightarrow \overline{G}_i^{ig}(T,P,\{x\}) < g_{pure\,i}^{ig}(T,P)$$

Implications are *component i*'s entropy increases upon mixing at constant *T, P,* & chemical potential of *i* is less in mixture than if pure at same *T, P*.

Properties of Ideal Gas Mixtures

$$f^{ig}(T,P,\{x\}) = \sum_{i=1}^{C} x_i \bar{F}_i{}^{ig}(T,) \qquad \textbf{(3.4.4)}$$

$$v^{ig}(T,P,\{x\}) = \sum_{i=1}^{C} x_i v^{ig}_{\text{pure i}}(T,P) \qquad \textbf{(4.1.38)}$$

$$h^{ig}(T,\{x\}) = \sum_{i=1}^{C} x_i h^{ig}_{\text{pure i}}(T) \qquad \textbf{(4.1.40)}$$

$$c_p^{ig}(T,\{x\}) = \sum_{i=1}^{C} x_i c^{ig}_{p\ \text{pure i}}(T) \qquad \textbf{(4.1.42)}$$

$$s^{ig}(T,P,\{x\}) = \sum_{i=1}^{C} x_i s^{ig}_{\text{pure i}}(T,P) - R\sum_{i=1}^{C} x_i \ln x_i \qquad \textbf{(4.1.43)}$$

$$g^{ig}(T,P,\{x\}) = \sum_{i=1}^{C} x_i g^{ig}_{\text{pure i}}(T,P) + RT\sum_{i=1}^{C} x_i \ln x_i \qquad \textbf{(4.1.44)}$$

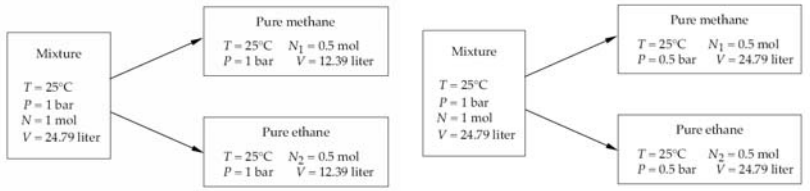
Separation: Less Work if *Fix T & P* or *T & V*?

$$W^{ig}_{sh,rev}(T,P,\{x\}) = -RT\sum_{i=1}^{C} N_i \ln x_i \qquad \textbf{(4.1.47)}$$

$$W^{ig}_{sh,rev}(T,V,\{x\}) = 0 \qquad \textbf{(4.1.50)}$$

Separation work negative of mixing work

Separate gases at *T* & *P* **Separate gases at *T* & *V***



Samples of same ideal gas: $\Delta S < 0$ $\Delta S = 0$

Different ideal gases: $\Delta S = 0$ $\Delta S > 0$

FLUID NONIDEALITY FROM EQUATIONS OF STATE (EoS)

All can be obtained from

$$f(P,V,T,\{N\}) = 0 = f(P,v,T,\{x\})$$

Difference Measures of Nonideality - Residuals

Depend on Use of *P* or *V*

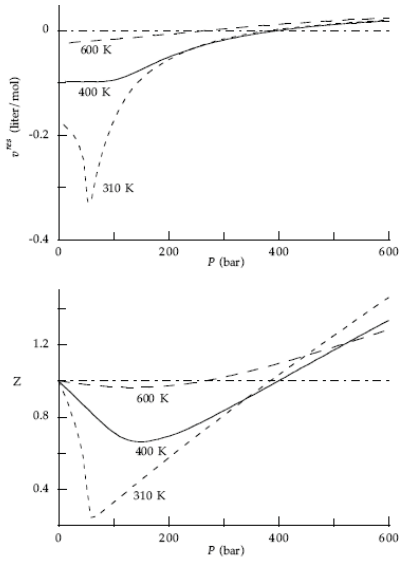
$$F^{res}(T,P,\{N\}) \equiv F(T,P,\{N\}) - F^{ig}(T,P,\{N\})$$

$$\mathcal{F}^{res}(T,V,\{N\}) \equiv F(T,V,\{N\}) - F^{ig}(T,V,\{N\})$$

Pick F^{res} or $\mathcal{F}^{res}$ depending on case's variables

***e.g.*, $H^{res}, S^{res}, G^{res}, V^{res}$ & $\mathcal{U}^{res}, \mathcal{S}^{res}, \mathcal{A}^{res}, \mathcal{P}^{res}$**

Fig 4.3 shows $v^{res} = RT(Z\text{-}1)/P$ & Z



Component Chemical Potentials

$$\overline{G}_i^{res}(T,P,\{x\}) \equiv \overline{G}_i(T,P,\{x\}) - \overline{G}_i^{ig}(T,P,\{x\})$$
$$= \overline{G}_i(T,P,\{x\}) - g^{ig}_{\text{pure i}}(T,P) - RT\ln x_i$$

Issue: if $x_i \to 0$, ln $x_i \to -\infty$!

Consider an alternative:

Now $\frac{\overline{G}_i^{ig}(T,P,\{x\})}{RT} = \frac{g^{ig}_{pure\,i}(T,P)}{RT} + \ln x_i$ **(4.1.37)**

Variations at constant *T*

$$d\left.\frac{\overline{G}_i^{ig}}{RT}\right|_T = \left.\frac{\partial\left(g_i^{ig}/RT\right)}{\partial P}\right|_T dP + d\ln x_i \qquad \textbf{(4.3.6)}$$

$$= \tfrac{1}{P}dP + d\ln x_i = d\ln x_i P \qquad \textbf{(4.3.7)}$$

For nonideal gases, G.N. Lewis defined fugacity,

$$d\ln f_i\big|_T \equiv d\left.\frac{\overline{G}_i}{RT}\right|_T \qquad \textbf{(4.3.8)}$$

with boundary condition of

$$f_i^{ig}(T,P,\{x\}) = x_i P \qquad \textbf{(4.3.9)}$$

Integration from <u>any</u> convenient state gives

$$\overline{G}_i(T,P,\{x\}) = \overline{G}_i^{\circledR}(T,P_i^{\circledR},\{x^{\circledR}\}_i) + RT\ln\frac{f_i(T,P,\{x\})}{f_i^{\circledR}(T,P_i^{\circledR},\{x^{\circledR}\}_i)} \qquad \textbf{(4.3.12)}$$

Specific boundary conditions (*T,P,{x}*,phase)

1. $T, P_i^{\circledR} = 1\text{ bar}, \{x^{\circledR}\}_i \Rightarrow x_i = 1$**, ideal gas**

$$\overline{G}_i(T,P,\{x\}) = \overline{G}_{pure\,i}(T,1\text{ bar}) + RT\ln f_i(T,P,\{x\})$$

2. $T, P_i^{\circledR} = P\text{ bar}, \{x^{\circledR}\}_i = x_i$**, ideal gas**

$$\overline{G}_i(T,P,\{x\}) = \overline{G}_i^{ig}(T,P) + RT\ln\frac{f_i(T,P,\{x\})}{x_i P}$$

$$\overline{G}_{\text{pure i}}(T,P) = g^{ig}_{\text{pure i}}(T,P) + RT\ln\frac{f_i(T,P,\{x\})}{P}$$

3. $T, P_i^{\circledR} = P_i^{sat}(T)\text{ bar}, \{x^{\circledR}\}_i \Rightarrow x_i = 1$**, sat. liquid**

$$\overline{G}_i(T,P,\{x\}) = g^{sat}_{\text{pure i}}(T) + RT\ln\frac{f_i(T,P,\{x\})}{f_i^{sat}(T)}$$

NOTE: Fugacity is <u>not</u> "corrected pressure"
It is a substitute for $\overline{G}_i(T,P,\{x\})$

Fugacity is a conceptual intensive state property; varies with *T*, *P*, *{x}*, phase

Commonly modeled in ChE applications
Not commonly used in Chemistry, Biology, Materials Science

Advantages of f_i to be described as we go along

Ratio Measures of Gas Nonideality

Fluid compressibility factor $Z \equiv PV/NRT = Pv/RT$

Fugacity Coefficient of a Component $\varphi_i \equiv f_i/x_i P$

Figure 4.4 shows pure component behavior

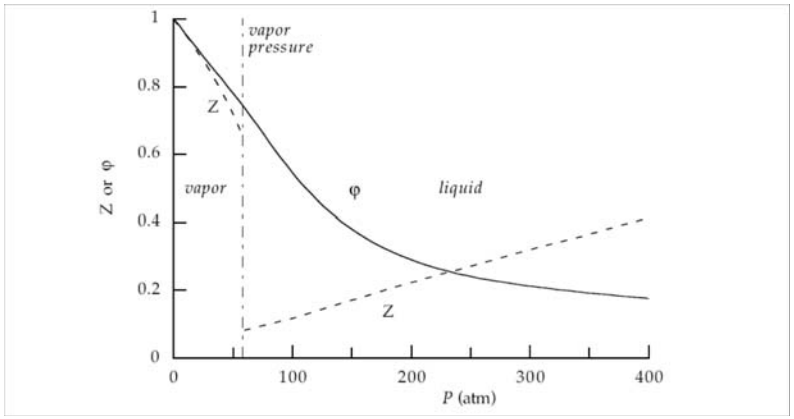
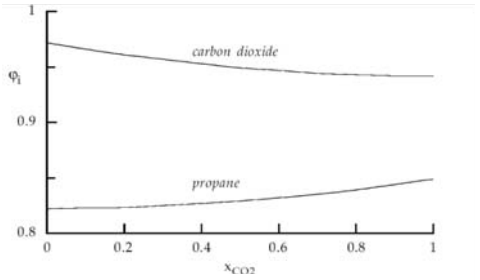
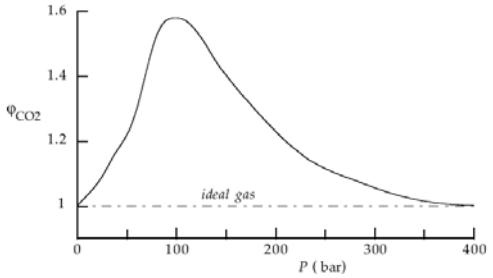


Fig. 4.5 & 4.6 for mixture components

CO_2 in C_3H_8 @ 100°F, 200psia





CO_2 in n-C_4H_{10}

$x_{n\text{-}C4H10}$ = 0.85 @ 171°C

Strategy for Getting Conceptual Properties from Measurable Variables

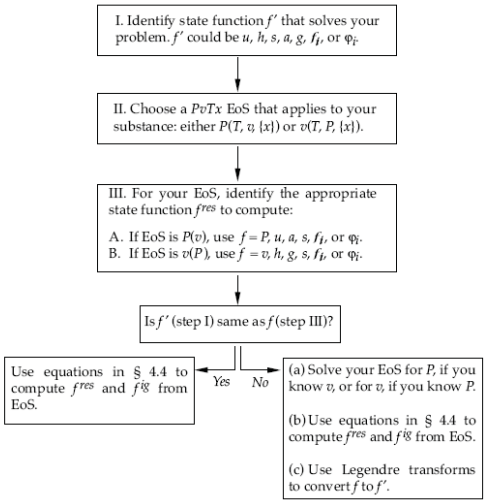


Fig. 4.7

SOME EXAMPLE FORMULAE

For independent variables $T, P, \{N\}$
with model for $V(T, P, \{N\})$

$$H^{res}(T,P,\{N\}) = \int_0^P V(1 - T\alpha)\big|_{T,\{x\}} d\pi \qquad \textbf{(4.4.4)}$$

$$S^{res}(T,P,\{N\}) = \int_0^P \left(\frac{NR}{\pi} - V\alpha\right)\Big|_{T,\{x\}} d\pi \qquad \textbf{(4.4.6)}$$

$$\overline{G}_i^{res}(T,P,\{x\}) = \int_0^P \overline{V}_i^{res}\Big|_{T,\{x\}} d\pi = \int_0^P \left[\overline{V}_i - \frac{RT}{\pi}\right]_{T,\{x\}} d\pi \qquad \textbf{(4.4.8)}$$

$$\ln \phi_i(T,P,\{x\}) = \int_0^P \left(\frac{\overline{V}_i}{RT} - \frac{1}{\pi}\right)\Big|_{T,\{x\}} d\pi \qquad \textbf{(4.4.10)}$$

For independent variables $T, v, \{x\}$
with model for $P(T, v, \{x\})$

$$u^{res}(T, v, \{N\}) = N \int_{v}^{\infty} (P - T\gamma_v)|_{T,\{x\}} dv \qquad \textbf{(4.4.13)}$$

$$s^{res}(T, v, \{N\}) = \int_{v}^{\infty} \left(\frac{NR}{\psi} - \gamma_v\right)\Big|_{T,\{x\}} d\psi \qquad \textbf{(4.4.16)}$$

$$\overline{G}_i^{res}(T, v, \{x\}) = \int_{V}^{\infty} \left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}} - \frac{RT}{\Psi}\Big|_{T,\{x\}} d\Psi \qquad \textbf{(4.4.21)}$$

$$\ln \phi_i(T, P, \{x\}) = \int_{V}^{\infty} \left[\frac{1}{RT}\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}} - \frac{1}{\Psi}\Big]\Big|_{T,\{x\}} d\Psi - \ln Z \qquad \textbf{(4.4.23)}$$

Model Equations of State

Hard Spheres - $Z = Z(\eta)$ **where** $\eta \equiv b\rho = \frac{\pi\sigma^3}{6V}$**N**

Model - Carnahan-Starling form

$$Z = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} = 1 + 2\eta\,\frac{2-\eta}{(1-\eta)^3} \geq 1 \qquad \textbf{(4.5.4)}$$

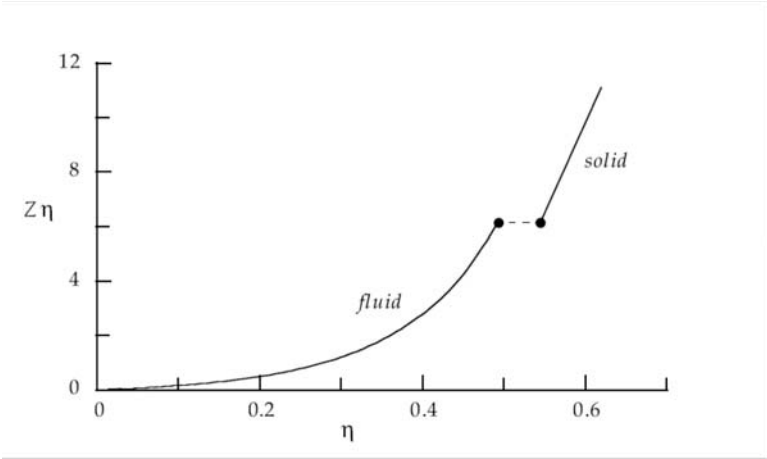
Residuals

$$v^{res}(T, P) = \frac{RT}{P} 2\eta\,\frac{2-\eta}{(1-\eta)^3} \geq 0 \qquad \textbf{(4.5.5)}$$

$$h^{res}(T, P) = 0 \qquad \textbf{(4.5.6)}$$

$$s^{res}(T, P) = RT \ln Z + R\frac{\eta(3\eta-4)}{(1-\eta)^2} \qquad \textbf{(4.5.7)}$$

Figure 4.8 shows EoS & Simulations

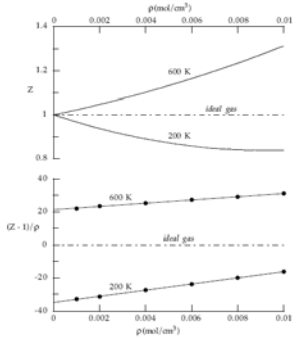


VIRIAL EQUATIONS

2nd Virial = 1st-Order Truncation of Series
Get Pure Component from mixture via

$$\lim_{C=1,\, x_i=1} \left\{ \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j B_{ij}(T) \right\} = \boldsymbol{B_{pure\ i}(T)}$$

Graphical depiction of series in Figure 4.9



Variations of B, C

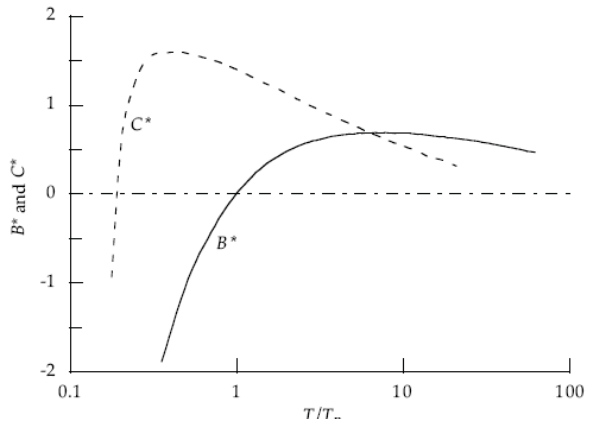
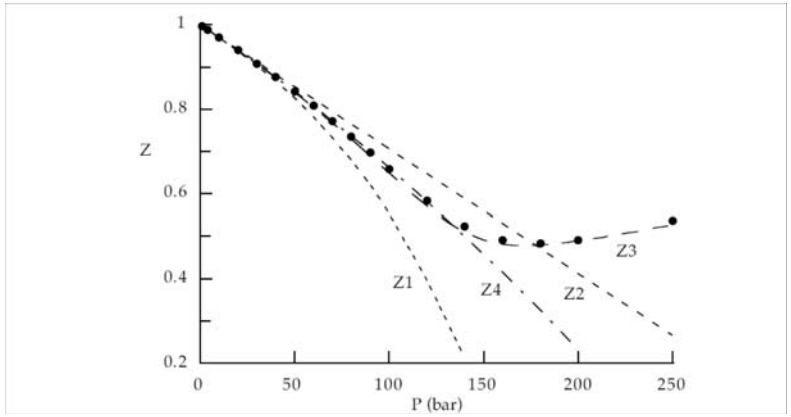


Figure 4.10

$B^* = B/v_B$, $C^* = C/(v_B)^2$

v_B from "Boyle Point" at B (T_B) = 0
Density/Volume Series≠Pressure Series
Figure 4.11



Virial Equation Residual Properties in Ex. 4.5.5

Z1 = 1 +

Z4 = 1 +

van der Waals Equations of State

From $Z = Z_{hs} + \beta \lim_{\beta \to 0} \frac{\partial Z}{\partial \beta}\Big)_{v,N}$ **where** $\beta \equiv \frac{1}{RT}$

Use different expressions for Z_{hs} & $\lim_{\beta \to 0} \frac{\partial Z}{\partial \beta}\Big)_{v,N}$

Get models:

Original van der Waals, Redlich-Kwong,

$$Z = 1 + \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT}$$

$$Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT^{3/2}(1+b\rho)}$$

Modified R-K

$$Z = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \frac{4a\eta}{bRT^{3/2}(1+4\eta)}.$$

Comparisons of EoS Models I.

TABLE 4.4 Expressions for Parameters a and b in Terms of Critical Properties for Three Semitheoretical Equations of State.

	vdW (4.5.54)	RK (4.5.66)	mRK (4.5.67)
Z_c	3/8	0.333	0.316
		in terms of T_c *and* v_c	
b/v_c	1/3	0.2599	0.3326
$a/(v_c RT_c)$	9/8	1.2824 $\sqrt{T_c}$	1.4630 $\sqrt{T_c}$
		in terms of T_c *and* P_c	
bP_c/RT_c	1/8	0.08664	0.1050
$aP_c/(RT_c)^2$	27/64	0.4275 $\sqrt{T_c}$	0.4619 $\sqrt{T_c}$

Comparison of EoS Models II.

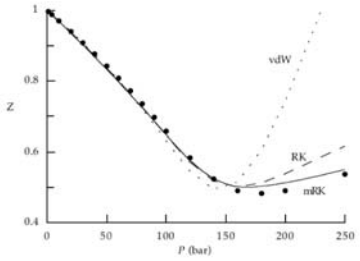


Fig. 4.14

Fig. 4.15

