Lecture 4.1
Relations Between Ideal Gas & Ideal Solution Deviations

O'Connell & Haile Chapter 6

Topics:

Relating IG and IS Deviations
Some Models & Comparisons

Sections 6.2.2 & 6.2.4:
Symmetry in Routes to conceptuals

Tables 6.1-6.3 show symmetries of difference & ratio deviations

	Deviations from Ideality	
Ideality	**Differences**	**Ratios**
Ideal gas	Residual properties	Fugacity coefficient
	$f^{res} = f - f^{ig}$	$\varphi_i = f_i / f_i^{ig}$
Ideal solution	Excess properties	Activity coefficient
	$f^{E} = f - f^{is}$	$\gamma_i = f_i / f_i^{is}$

Residual & excess property forms are the same except superscripts changed

RELATING THE DIFFERENT APPROACHES

Sect. 6.1 - Note that approaches may have different variables:

EoS of $P(T, v, \{x\})$ or $a(T, v, \{x\})$
Excess property of $g^E(T, P, \{x\})$

Strategy

1. **Determine Nature's variables for system/process**
2. **Find model's natural variables**
3. **Match them**

Sect 6.2.1, 6.2.3: Generalized difference measures can be used, but normally are not

Table 6.2

Property	Pressure Effect		Temperature Effect	
Chemical potential	$\left[\frac{\partial}{\partial P}\left(\frac{\bar{G}_i}{RT}\right)\right]_{Tx} = \frac{\bar{V}_i}{RT}$	(3.4.15)	$\left[\frac{\partial}{\partial T}\left(\frac{\bar{G}_i}{RT}\right)\right]_{Px} = \frac{-\bar{H}_i}{RT^2}$	(3.4.17)
Fugacity	$\left(\frac{\partial \ln f_i}{\partial P}\right)_{Tx} = \frac{\bar{V}_i}{RT}$	(4.3.13)	$\left(\frac{\partial \ln f_i}{\partial T}\right)_{Px} = \frac{-\bar{H}_i^{res}}{RT^2}$	(4.3.14)
Fugacity coefficient	$\left(\frac{\partial \ln \varphi_i}{\partial P}\right)_{Tx} = \frac{\bar{V}_i^{res}}{RT}$	(4.3.23)	$\left(\frac{\partial \ln \varphi_i}{\partial T}\right)_{Px} = \frac{-\bar{H}_i^{res}}{RT^2}$	(4.3.24)
Activity	$\left(\frac{\partial \ln a_i}{\partial P}\right)_{Tx} = \frac{\bar{V}_i^{m}}{RT}$	(6.2.15)	$\left(\frac{\partial \ln a_i}{\partial T}\right)_{Px} = \frac{-\bar{H}_i^{m}}{RT^2}$	(6.2.16)
Activity coefficient	$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{Tx} = \frac{\bar{V}_i^{E}}{RT}$	(5.4.17)	$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{Px} = \frac{-\bar{H}_i^{E}}{RT^2}$	(5.4.18)

Table 6.3

Property	Identity of f in (3.4.10)	Form of Gibbs-Duhem Equation	
Chemical potential	g	$\sum_i x_i\, d\bar{G}_i = -s\,dT + v\,dP$	(3.4.19)
Fugacity	$\frac{g}{RT}$	$\sum_i x_i\, d\ln f_i = -\frac{h}{RT^2}dT + \frac{v}{RT}dP$	(4.3.15)
Fugacity coefficient	$\frac{g^{res}}{RT}$	$\sum_i x_i\, d\ln \varphi_i = -\frac{h^{res}}{RT^2}dT + \frac{v^{res}}{RT}dP$	(4.3.25)
Activity	$\frac{g^{m}}{RT}$	$\sum_i x_i\, d\ln a_i = -\frac{h^{m}}{RT^2}dT + \frac{v^{m}}{RT}dP$	(6.2.17)
Activity coefficient	$\frac{g^{E}}{RT}$	$\sum_i x_i\, d\ln \gamma_i = -\frac{h^{E}}{RT^2}dT + \frac{v^{E}}{RT}dP$	(5.4.19)

Strategies to Compute Conceptual Property Differences

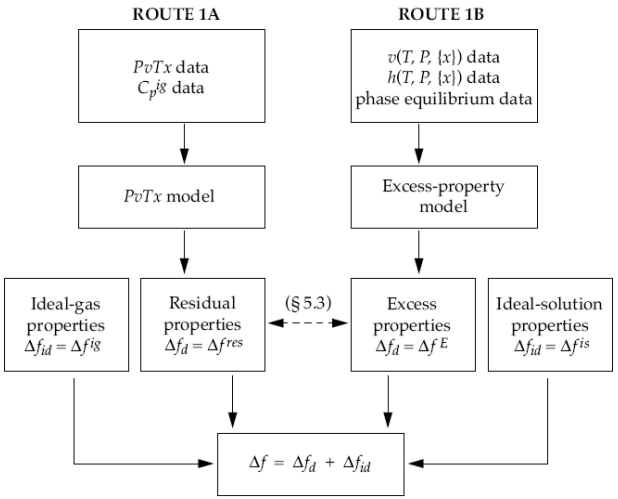


Fig. 6.1

Strategies to Compute Fugacities

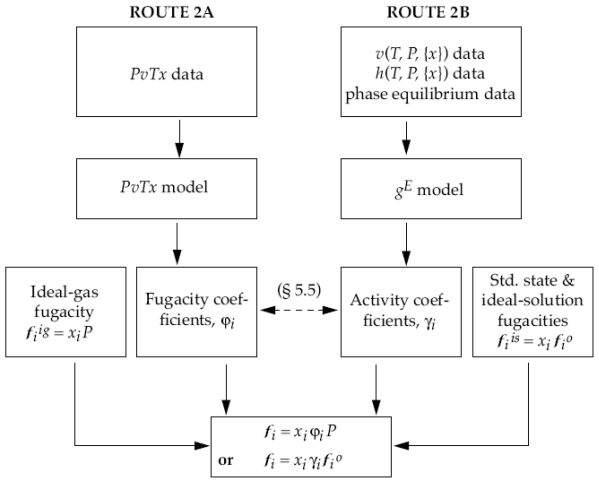


Fig. 6.2

Connecting Changes in Conceptuals to Physical Processes

Sect.6.3: Reversible work/heat effects of processes on mixtures

Book selects process & develops relations for work & heat in terms of conceptuals

Results

6.3.1 Add a component to a real mixture

$$w_{sh,rev} = RT\ln\left[f_i/f^{o}_{pure\ i}\right] \qquad q_{rev} = T\left[\bar{S}_i - s_{pure\ i}\right]$$

6.3.2 Change an ideal gas to a real fluid

$$w_{sh,rev} = g^{res} = RT\sum_i x_i \ln\phi_i \qquad q_{rev} = Ts^{res}$$

6.3.3 Change ideal solution to real mixture

$$w_{sh,rev} = g^{E} = RT\sum_i x_i \ln\gamma_i \qquad q_{rev} = Ts^{E}$$

Fugacity Formulae #1 & #2

5 ways to relate $f_i(T,P,x)$ to state;
"a fugacity is a fugacity, regardless of how you calculate it"

#1 from ideal gas; uses fugacity coefficient

$$f_i(T,P,\{x\}) = x_i\phi_i(T,P,\{x\})P \qquad \textbf{(6.4.1)}$$

Need EoS for phase; if liquid, Eq.(4.4.10) & (4.4.11) integrations from *P* = 0 difficult

#2 from ideal solution with activity coefficient

$$f_i(T,P,\{x\}) = x_i\gamma_i(T,P,\{x\};f_i^o(T,P))f_i^o(T,P) \qquad \textbf{(6.4.4)}$$

Need $g^E(T,P,\{x\})$, $f_i^o(T,P)$ for all states

Fugacity Formula #3

#3 from ideal solution with *P* independent standard state fugacity, standard-state Poynting Correction

$$f_i(T,P,\{x\}) = x_i\gamma_i(T,P,\{x\};f_i^o(T))f_i^o(T)\exp\left[\int_{P_i^o}^{P}\left|\frac{\overline{V}_i^o(T,\pi)}{RT}\right|_T d\pi\right] \qquad \textbf{(6.4.7)}$$

Must choose P_i^o, $f_i^o(T;P_i^o)$ & $g^E(T,P,\{x\})$ of mixture referred to all $f_i^o(T,P)$ & $\overline{V}_i^o(T,P)$

Fugacity Formula #4

#4 from ideal solution with *P* independent standard state fugacity, no Poynting Factor

$$f_i(T,P,\{x\}) = x_i\gamma_i(T,P,\{x\};f_i^o(T,P_i^o))f_i^o(T,P_i^o) \qquad \textbf{(6.4.10)}$$

Must choose P_i^o, $f_i^o(T;P_i^o)$ & have $g^E(T,P,\{x\})$ for mixture states referred to all $f_i^o(T;P_i^o)$

Fugacity Formula #5

#5 from ideal solution via 2 routes: see Fig. 6.3
Has *P* independent $f_i^o(T;P_i^o)$, solution-state Poynting Correction

$$f_i(T,P,\{x\}) = x_i\gamma_i(T,\{x\};f_i^o(T,P_i^o))f_i^o(T,P_i^o)\exp\left[\int_{P_i^o}^{P}\left|\frac{\overline{V}_i(T,\pi,\{x\})}{RT}\right|_{T,\{x\}} d\pi\right] \qquad \textbf{(6.4.11)}$$

Must choose P_i^o, $f_i^o(T;P_i^o)$, have $g^E(T,\{x\})$ of all states referred to all $f_i^o(T)$ & $\overline{V}_i(T,P,\{x\})$ from P_i^o to P

All Formulae Give Same Result

Table 6.4 shows results from all formulae

In common practice

1. **If *P* effect small ("low *P*" liquids), #2-5 all same**
2. **If *P* affects, don't use #2 & use #4 only for special cases**
3. **May ignore *P* effect on γ_i in #3 - same as ignoring {*x*} effect on $\overline{V}_i$ in #5**

Instead, match g^E_{EoS} of Ch. 4 to g^E_{Model} of Ch. 5

$$\frac{g^E_{Model}}{RT} = \frac{g^E_{EoS}}{RT} = Z - \ln Z + \int_{v(T,P,\{x\})}^{\infty} \left(\frac{Z-1}{v}\right) dv - \sum_i x_i \left[Z_i - \ln Z_i + \int_{v_i(T,P)}^{\infty} \left(\frac{Z-1}{v_i}\right) dv_i \right] \quad \textbf{(6.5.3)}$$

Must choose *v*'s via fitting or arbitrarily since g^E models do not contain density/volume

Note: Need accurate g^E model

Option for cubic EoS, choose mixing rule for b_m,

then get a_m from $a_m = b_m \left[\sum_i x_i \frac{a_i}{b_i} - C g^E_{Model} \right]$

where *C* value from EoS

Many choices taken in literature

***e.g.,* Huron-Vidal, Wong-Sandler, Twu, Gmehling, etc.); none perfect**

Activity Coefficients From EoS I.

Sect. 6.5 - EoS Mixing Rules from g^E Models

Though could use (6.5.1) to relate models

$$\phi_i(T,P,\{x\}) = \gamma_i(T,P,\{x\}; f_i^0(T,P))\phi_i^0(T,P)$$

involves complex integration & must do analysis on all components at mixture & standard states

$$\begin{aligned}\overline{G}_i^E(T,P,\{x\}) &= \int_{V}^{\infty} \left[\left.\frac{\partial P}{\partial N_i}\right|_{T,\mathbf{V},N_{j\neq i}} - \frac{RT}{\Psi} \right]_{T,\{N\}} d\Psi \\ &\quad - \int_{V^o}^{\infty} \left[\left.\frac{\partial P}{\partial N_i}\right|^{o}_{T,\mathbf{V},N_{j\neq i}} - \frac{RT}{\Psi} \right]_{T,\{N\}} d\Psi - RT\ln\frac{Z}{Z^o} \\ &= RT\ln\gamma_i(T,P,\{x\})\end{aligned}$$