



Phase equilibrium Thermodynamics

Summary of Chapters 6 and 7



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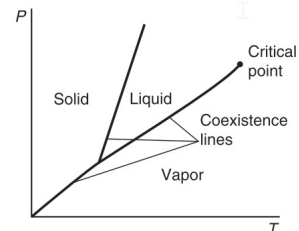
Clausius eq. and Clausius-Clapeyron eq. (Lecture 2)

phases α and β of pure i @ equilibrium at constant T, P :

$$g_i^\alpha = g_i^\beta \rightarrow dg_i^\alpha = dg_i^\beta$$

The **Clausius eq.** gives the variation of P with T for two phases at equilibrium:

$$\frac{dP}{dT} = \frac{h_i^\alpha - h_i^\beta}{T(v_i^\alpha - v_i^\beta)} \quad (6.8)$$



The **Clausius-Clapeyron eq.** is a useful approximation of the Clausius eq for VLE with some assumptions ($v_i^l \ll v_i^v$, $v_i^v = \frac{RT}{P}$, P is P_i^{sat} for VLE)

$$d \ln P_i^{\text{sat}} = -\frac{\Delta h_{\text{vap},i}}{R} d\left(\frac{1}{T}\right) \quad (6.9b) \rightarrow \ln \frac{P_{i,2}^{\text{sat}}}{P_{i,1}^{\text{sat}}} = -\frac{\Delta h_{\text{vap},i}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (6.10)$$

If $\Delta h_{\text{vap},i}$ independent of T

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Partial molar property \bar{K}_i , \bar{K}_i^∞ , ΔK_{mix} , Δk_{mix} (Lectures 3,4,5)

$$K = K(T, P, n_1, n_2, \dots, n_i, \dots, n_m) \quad (6.13)$$

$$\bar{K}_i \equiv \left(\frac{\partial K}{\partial n_i} \right)_{T, P, n_{j \neq i}} = \left(\frac{\partial (n_{total} k)}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

K : total property of a mixture

k : molar property of a mixture

\bar{K}_i : partial molar property of i in a mixture

k_i : molar property of pure i

Note in partial derivative
that $n_{total} = n_1 + n_2 + \dots$

$$\bar{K}_i^\infty = \bar{K}_i (@x_i \rightarrow 0)$$

$$K = \sum_{i=1}^m n_i \bar{K}_i \quad (6.17)$$

$$k = \sum_{i=1}^m x_i \bar{K}_i \quad (6.18)$$

$$\Delta K_{mix} = \sum_i n_i (\bar{K}_i - k_i) \quad (6.21)$$

$$\Delta k_{mix} = \sum_i x_i (\bar{K}_i - k_i) \quad (6.23)$$

$$\text{Gibbs-Duhem at constant } T, P: \quad \sum n_i d\bar{K}_i = 0 \quad (6.19)$$

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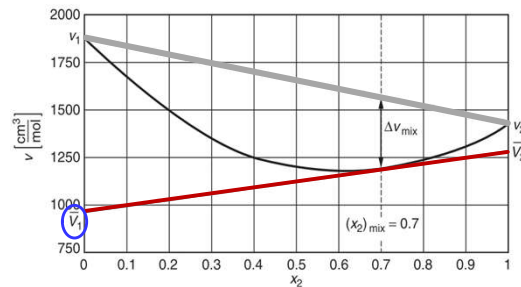
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Other formula relating \bar{K}_i and k (Lecture 4)

$$k = \bar{K}_1 + x_2 \frac{dk}{dx_2} \quad (6.29)$$

Or

$$\bar{K}_1 = k + (1 - x_1) \left(\frac{\partial k}{\partial x_1} \right)_{T, P, x_2}$$



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Condition for equilibrium (Lectures 5,6)

criterion for phase equilibrium at constant T and P : $\rightarrow dG = dG^\alpha + dG^\beta = 0$

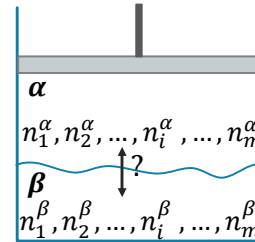
Therefore:

$$T^\alpha = T^\beta$$

$$P^\alpha = P^\beta$$

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

$$(6.39) \rightarrow \hat{f}_i^\alpha = \hat{f}_i^\beta \quad (7.6)$$



where $\mu_i \equiv \bar{G}_i \equiv \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}}$ (6.38)

μ_i = Chemical potential (partial molar Gibbs energy) of component i , describes the contribution of species i to the Gibbs energy of the mixture

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T and P dependence of $\mu_i = \bar{G}_i$ (Lecture 5)

$$\left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T,n_i} = \bar{V}_i \quad (6.36) \rightarrow \left(\frac{\partial \mu_i}{\partial P} \right)_{T,n_i} = \bar{V}_i$$

$$\left(\frac{\partial \left(\frac{\bar{G}_i}{T} \right)}{\partial T} \right)_{P,n_i} = \frac{-\bar{H}_i}{T^2} \quad (6.35) \rightarrow \left(\frac{\partial \left(\frac{\mu_i}{T} \right)}{\partial T} \right)_{P,n_i} = \frac{-\bar{H}_i}{T^2}$$

Equilibrium at constant T, P : $\mu_i^\alpha = \mu_i^\beta \rightarrow \frac{\mu_i^\alpha}{T} = \frac{\mu_i^\beta}{T}$ (6.40)

$$-\frac{\bar{H}_i^\alpha}{T^2} dT + \frac{\bar{V}_i^\alpha}{T} dP + \frac{1}{T} \left[\frac{\partial \mu_i^\alpha}{\partial x_i^\alpha} \right]_{T,P} dx_i^\alpha = -\frac{\bar{H}_i^\beta}{T^2} dT + \frac{\bar{V}_i^\beta}{T} dP + \frac{1}{T} \left[\frac{\partial \mu_i^\beta}{\partial x_i^\beta} \right]_{T,P} dx_i^\beta \quad (6.41)$$

When α phase is ideal gas, and β phase is liquid:

$$-\frac{h_i^v}{T^2} dT + R \frac{dP}{P} + R \frac{dy_i}{y_i} = -\frac{\bar{H}_i^l}{T^2} dT + \frac{\bar{V}_i^l}{T} dP + \frac{1}{T} \left[\frac{\partial \mu_i^l}{\partial x_i} \right]_{T,P} dx_i \quad (6.46)$$

Example of application: boiling point elevation

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Fugacity \hat{f}_i and fugacity coefficient $\hat{\varphi}_i$ (Lecture 6)

Fugacity

$$\mu_i - \mu_i^0 \equiv RT \ln \left[\frac{\hat{f}_i}{\hat{f}_i^0} \right] \quad (7.3)$$

$$\lim_{P \rightarrow 0} \left(\frac{\hat{f}_i}{p_i} \right) \equiv 1 \quad (7.4) \text{ (ideal gas limit)}$$

Fugacity coefficient

$$\hat{\varphi}_i \equiv \frac{\hat{f}_i}{p_{i,sys}} = \frac{\hat{f}_i}{y_i P_{sys}} \quad (7.5)$$

$p_{i,sys}$: partial pressure that species i would have in the system as an ideal gas

Fugacity of pure

$$g_i - g_i^0 \equiv RT \ln \left[\frac{f_i}{f_i^0} \right] \quad (7.3p)$$

$$\lim_{P \rightarrow 0} \left(\frac{f_i}{P} \right) \equiv 1 \quad (7.4p)$$

Fugacity coefficient

$$\varphi_i \equiv \frac{f_i}{P_{sys}} \quad (7.5p)$$

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Fugacity of a pure gas (Lecture 7)

$$g_i - g_i^0 \equiv RT \ln \left[\frac{f_i^v}{P_{low}} \right] \quad (7.7) \quad \text{and} \quad \varphi_i^v \equiv \frac{f_i^v}{P_{sys}} \quad (7.5p)$$

Obvious choice of reference state: $f_i^0 \rightarrow P_{low}$ and $\varphi_i^0 \rightarrow 1$

3 possible sources of data for pure gases to calculate f_i^v :

1. Tables

@ T, P_{sys} : read h, s from the table $\rightarrow g_i = h_i - Ts_i$

@ T , find P_{low} that gas behave as an ideal gas, for the reference state

@ T, P_{low} : read h, s from the table $\rightarrow g_i^0 = h_i^0 - Ts_i^0$

Example 7.1

2. Equation of state (EOS): EOS is used to relate v_i to P at constant $T \rightarrow f_i^v$

$$g_i - g_i^0 = \int_{P_{low}}^P v_i dP = RT \ln \left[\frac{f_i^v}{P_{low}} \right] \quad (7.8)$$

Example 7.2

3. Generalized correlations $\log \varphi_i = \log \varphi^{(0)} + \omega \log \varphi^{(1)}$ (7.11)

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Fugacity in a gas mixture from EOS (Lecture 8)

Pure gas	$RT \ln \left[\frac{f_i^v}{P_{\text{low}}} \right] = g_i - g_i^0 = \int_{P_{\text{low}}}^P \mathbf{v}_i dP \quad (7.8) \quad @ \text{ const } T$
	EOS $\rightarrow P = \text{function}(T, \mathbf{v}_i, \text{EOS parameters})$ or $\mathbf{v}_i = \text{function}(T, P, \text{EOS parameters})$
Gas mixture	$RT \ln \left[\frac{\hat{f}_i^v}{y_i P_{\text{low}}} \right] = \mu_i - \mu_i^0 = \int_{P_{\text{low}}}^P \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_{j \neq i}} dP \quad (7.13) \quad @ \text{ const } T$
	$RT \ln \left[\frac{\hat{f}_i^v}{y_i P_{\text{low}}} \right] = - \int_{\frac{n_{\text{total}} RT}{P_{\text{low}}}}^V \left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} dV \quad (7.14) \quad @ \text{ const } T$
	EOS $\rightarrow P = \text{function}(T, V, \text{EOS parameters})$ Table 4.3 \rightarrow Table 7.1 Note in taking partial derivative that: $y_i = n_i/n_{\text{total}}$ and $n_{\text{total}} = n_1 + \dots + n_m$

EOS parameters

- T_c , P_c , and ω from Appendix A.1
- For pure i : EOS parameters a_i , b_i , ... from eqs such as (4.21) to (4.25), based on T_c and P_c
- For mixture: EOS parameters a_{mix} , b_{mix} , ... with the mixing rules, eqs (7.15) to (7.18)

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Mixing rules for cubic EOS parameters, review section 4.5 (Lecture 8)

for example van der Waals EOS:
$$P = \frac{RT}{v - b_{\text{mix}}} - \frac{a_{\text{mix}}}{v^2}$$

a : “force” parameter,

representing the strength of two-body attractions (ij interactions)

ij interactions are proportional to $y_i y_j$ since molecules of “ i ” must find “ j ”

$$a_{\text{mix}} = \sum_i \sum_j y_i y_j a_{ij} \quad (7.15)$$

$$a_{ij} = a_{ji} = \sqrt{a_{ii} a_{jj}} \quad (7.16) \quad \text{or} \quad a_{ij} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) \quad (7.17)$$

where k_{ij} is an empirical fitting parameter.

Note that a_{ii} is also shown by a_i

b : “size” parameter \rightarrow average molecule volumes

$$b_{\text{mix}} = \sum_i y_i b_i \quad (7.18)$$

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Fugacity in a gas mixture, 3 levels of approximation (Lecture 8)

General ($i - j$ interactions)	$\hat{f}_i^v = y_i \hat{\phi}_i^v P$ (7.19)	$\hat{\phi}_i^v$ requires mixing rules
Lewis fugacity rule (all the interactions in the mixture are identical)	$\hat{\phi}_i^v = \phi_i^v$ $\hat{f}_i^v = y_i \phi_i^v P$ (7.20) or $\hat{f}_i^v = y_i f_i^v$ (7.22)	No mixing rule is required for $\hat{\phi}_i^v = \phi_i^v$
Ideal gas behaviour (no intermolecular interactions)	$\hat{f}_i^v = y_i P$ (7.21)	

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Fugacity in a liquid mixture (Lecture 9) $\mu_i - \mu_i^0 \equiv RT \ln \left[\frac{\hat{f}_i}{\hat{f}_i^0} \right]$ (7.3)

Looking for	Reference point	
For i in gas mixture \hat{f}_i^v	Ideal gas $\hat{f}_i^0 = y_i P_{low}$	$RT \ln \left[\frac{\hat{f}_i^v}{y_i P_{low}} \right] = - \int_{P_{low}}^V \frac{n_{total} RT}{P} \left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} dV$ (7.14) + EOS: $P = \text{function}(T, V, \text{EOS parameters})$
For i in liquid mixture \hat{f}_i^l	Ideal gas $\hat{f}_i^0 = y_i P_{low}$	$RT \ln \left[\frac{\hat{f}_i^l}{y_i P_{low}} \right] = - \int_{P_{low}}^V \frac{n_{total} RT}{P} \left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} dV$ (7.83) + EOS: $P = \text{function}(T, V, \text{EOS parameters})$ Challenging (accurate EOS and mixing rules for liquids)
For i in liquid mixture \hat{f}_i^l	Ideal solution $\hat{f}_i^0 = \hat{f}_i^{ideal}$	$\hat{f}_i^l = \gamma_i \hat{f}_i^{ideal}$ (7.32) γ_i : activity coefficient Different models were developed for γ_i

Next: What is ideal solution?

Models for **activity coefficient**, γ_i ?

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\hat{f}_i^l from activity coefficient method (Lecture 9)

The solution is ideal when the intermolecular interactions are the same between all components of the mixture. 2 choices:

- Lewis/Randall rule $x_i \rightarrow 1$
- Henry's law $x_i \rightarrow 0$

$$\hat{f}_i^l = \gamma_i x_i f_i = \gamma_i^{\text{Henry's}} x_i \mathcal{H}_i$$

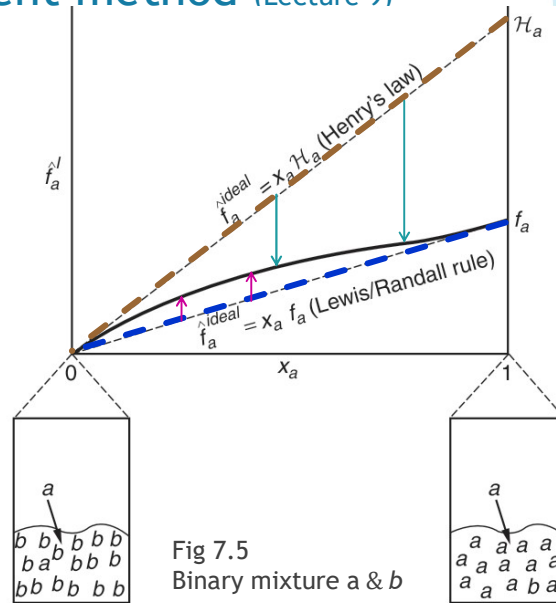


Fig 7.5 Binary mixture a & b

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Activity coefficient (Lecture 10)

Ideal solution reference state	Activity coefficient eq (7.32)	$x_a \rightarrow 0$	$x_a \rightarrow 1$
	$\gamma_i = \frac{\hat{f}_i^l}{\hat{f}_i^{\text{ideal}}} = \frac{\hat{f}_i^l}{x_i f_i^0}$		
Lewis/ Randall rule eq (7.30) (a - a interactions) $f_a^0 = f_a$	$\gamma_a = \frac{\hat{f}_a^l}{x_a f_a}$ γ_a : $\gamma_a^{\text{Lewis/Randall}}$	$\hat{f}_a^l \rightarrow x_a \mathcal{H}_a$ $\gamma_a^\infty = \frac{x_a \mathcal{H}_a}{x_a f_a} = \frac{\mathcal{H}_a}{f_a}$	$\hat{f}_a^l \rightarrow f_a$ $\gamma_a \rightarrow 1$
Henry's law eq (7.31) (a - b interactions) $f_a^0 = \mathcal{H}_a$	$\gamma_a^{\text{Henry's}} = \frac{\hat{f}_a^l}{x_a \mathcal{H}_a}$	$\lim_{x_a \rightarrow 0} \frac{\hat{f}_a^l}{x_a} \equiv \mathcal{H}_a$ $\gamma_a^{\text{Henry's}} \rightarrow 1$	$(\gamma_a^{\text{Henry's}})_{\text{pure a}} = \frac{f_a}{\mathcal{H}_a}$

$$\gamma_a^\infty = \frac{\mathcal{H}_a}{f_a} \text{ and } (\gamma_a^{\text{Henry's}})_{\text{pure a}} = \frac{f_a}{\mathcal{H}_a} \rightarrow$$

$$\hat{f}_a^l = x_a \gamma_a f_a = x_a \gamma_a^{\text{Henry's}} \mathcal{H}_a = x_a \gamma_a^{\text{Henry's}} \gamma_a^\infty f_a \rightarrow$$

$$(\gamma_a^{\text{Henry's}})_{\text{pure a}} = \frac{1}{\gamma_a^\infty}$$

$$\gamma_a^{\text{Henry's}} = \frac{\gamma_a}{\gamma_a^\infty}$$

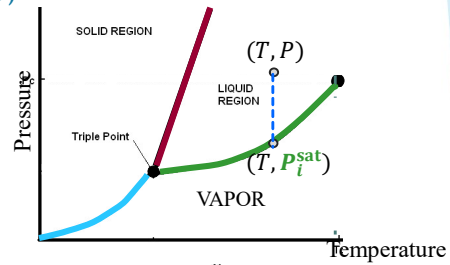
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Fugacity of pure liquid i (Lecture 9, 10)

Note: φ_i^{sat} is at T, P_i^{sat} , and f_i is at T and P

$$f_i^l = \varphi_i^{sat} P_i^{sat} \exp \left[\int_{P_i^{sat}}^P \frac{v_i^l}{RT} dP \right] \quad \text{at } T, P \quad (7.36)$$



φ_i^{sat} must be calculated at T and P_i^{sat} .

Note: $\varphi_i^{sat} = \frac{f_i^v}{P_i^{sat}}$

\mathcal{H}_i at T and P from \mathcal{H}_i at $T_{\text{experiment}}$ and $P_{\text{experiment}}$ (Lecture 10)

$$\left(\frac{\partial \ln \mathcal{H}_i}{\partial P} \right)_T = \frac{\bar{V}_i^\infty}{RT} \quad (7.39) \quad \rightarrow \quad \mathcal{H}_i^{\text{at } P} = \mathcal{H}_i^{\text{at } 1 \text{ bar}} \exp \left\{ \int_{1 \text{ bar}}^P \frac{\bar{V}_i^\infty}{RT} dP \right\} \quad (7.41)$$

$$\left(\frac{\partial \ln \mathcal{H}_i}{\partial T} \right)_P = \frac{h_i^v - \bar{H}_i^\infty}{RT^2} \quad (7.40)$$

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Gibbs-Duhem eq (Lecture 11)

Gibbs-Duhem relation at constant T and P :

$$\sum n_i d\bar{K}_i = 0 \quad (6.19)$$

$$\sum n_i d\mu_i = 0 \quad \text{recall } \mu_i = \bar{G}_i$$

$$\sum x_i d \ln \gamma_i = 0 \quad (7.42)$$

Of all the $\bar{K}_1, \bar{K}_2, \dots, \bar{K}_i, \dots, \bar{K}_m$,
only $m - 1$ partial molar properties are independent.
Gibbs-Duhem tells the relation between \bar{K}_i 's.

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γ_i and excess Gibbs energy (Lecture 11)

$$\mu_i - \mu_i^{\text{ideal}} = \bar{G}_i - \bar{G}_i^{\text{ideal}} = \bar{G}_i^E = RT \ln \left[\frac{\hat{f}_i}{\hat{f}_i^{\text{ideal}}} \right] = RT \ln \gamma_i$$

$$RT \ln \gamma_i = \bar{G}_i^E = \left(\frac{\partial G^E}{\partial n_i} \right)_{T,P,n_{j \neq i}} = \left(\frac{\partial (n_{\text{total}} g^E)}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad (7.48)$$

$$g^E = \sum x_i \bar{G}_i^E = RT \sum x_i \ln \gamma_i \quad (7.49)$$

Various g^E models such as Margules, van Laar, NRTL, UNIQUAC, UNIFAC

Note in partial derivative that $n_{\text{total}} = n_1 + n_2 + \dots$

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Excess Properties (Lecture 11)

$$k^E \equiv k(T, P, x_i) - k^{\text{ideal}}(T, P, x_i) \quad (7.44)$$

$$k^E \equiv \left(k - \sum x_i k_i \right) - \left(k^{\text{ideal}} - \sum x_i k_i \right) \quad (7.44) \quad \rightarrow \quad k^E = \Delta k_{\text{mix}} - \Delta k_{\text{mix}}^{\text{ideal}} \quad (7.46)$$

➤ for u, h, v , recall from P. 414: $\Delta k_{\text{mix}}^{\text{ideal}} = 0 \rightarrow k^E = \Delta k_{\text{mix}}$

➤ for s, g, a , recall from P. 414: $\Delta k_{\text{mix}}^{\text{ideal}} \neq 0 \rightarrow k^E = \Delta k_{\text{mix}} - \Delta k_{\text{mix}}^{\text{ideal}}$

$$\text{Recall } \Delta g_{\text{mix}}^{\text{ideal}} = \Delta h_{\text{mix}}^{\text{ideal}} - T \Delta s_{\text{mix}}^{\text{ideal}} = RT \sum_{i=1}^m y_i \ln y_i \quad (7.24)$$

$$\text{in (7.46)} \rightarrow g^E = \Delta g_{\text{mix}} - RT \sum x_i \ln x_i \rightarrow g^E = g - \sum x_i g_i - RT \sum x_i \ln x_i \quad (7.47)$$

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Note: For ideal solution

refer to Smith Van Ness ed 8, section 10.8
or refer to Koretsky pages 355-357 and 412-414

Partial molar properties	$\Delta k_{\text{mix}}^{\text{ideal}} = k^{\text{ideal}} - \sum x_i k_i$	$k^{\text{ideal}} = \sum x_i \bar{k}_i^{\text{ideal}}$
\bar{K}_i^{ideal}		
$\bar{V}_i^{\text{ideal}} = v_i$	$\Delta v_{\text{mix}}^{\text{ideal}} = 0$	$v^{\text{ideal}} = \sum x_i v_i$
$\bar{H}_i^{\text{ideal}} = h_i$	$\Delta h_{\text{mix}}^{\text{ideal}} = 0$	$h^{\text{ideal}} = \sum x_i h_i$
$\bar{U}_i^{\text{ideal}} = u_i$	$\Delta u_{\text{mix}}^{\text{ideal}} = 0$	$u^{\text{ideal}} = \sum x_i u_i$
$\bar{S}_i^{\text{ideal}} = s_i - R \ln x_i$	$\Delta s_{\text{mix}}^{\text{ideal}} = -R \sum x_i \ln x_i$	$s^{\text{ideal}} = \sum x_i s_i - R \sum x_i \ln x_i$
$\bar{G}_i^{\text{ideal}} = g_i + RT \ln x_i$	$\Delta g_{\text{mix}}^{\text{ideal}} = RT \sum x_i \ln x_i$	$g^{\text{ideal}} = \sum x_i g_i + RT \sum x_i \ln x_i$
$\bar{A}_i^{\text{ideal}} = a_i + RT \ln x_i$	$\Delta a_{\text{mix}}^{\text{ideal}} = RT \sum x_i \ln x_i$	$a^{\text{ideal}} = \sum x_i a_i + RT \sum x_i \ln x_i$

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Temperature and pressure dependence of g^E (Lecture 14)

Fundamental relation: (6.33) $\rightarrow dG^E = -S^E dT + V^E dP + \sum \bar{G}_i^E dn_i$ (7.73) \rightarrow

$$\left(\frac{\partial g^E}{\partial P} \right)_{T, n_i} = v^E = \Delta v_{\text{mix}} \quad (7.74)$$

$$\left(\frac{\partial \left(\frac{g^E}{T} \right)}{\partial T} \right)_{P, n_i} = \frac{-h^E}{T^2} = \frac{-\Delta h_{\text{mix}}}{T^2} \quad (7.75)$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P} \right)_{T, x_i} = \frac{1}{RT} \left[\left(\frac{\partial \mu_i}{\partial P} \right)_{T, x_i} - \left(\frac{\partial g_i}{\partial P} \right)_T \right] = \frac{\bar{V}_i - v_i}{RT} \quad (7.80)$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P, x_i} = -\frac{\bar{H}_i - h_i}{RT^2} \quad (7.81)$$

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Fugacity in the solid phase (Lecture 14)

□ Pure solid

pure solid → all the intermolecular forces are the same → ideal

$$\Gamma_i^{\text{pure solid}} = 1 \quad \text{and} \quad \hat{f}_i^S = f_i^S$$

□ Solid solution

$$\hat{f}_i^S = X_i \Gamma_i f_i^S \quad (7.84)$$

to calculate \hat{f}_i^S → the same approach as for liquid solution

- defining a reference state
- g^E models to find Γ_i