Solutions

Mole fraction of component A = x_A
Mass Fraction of component A = m_A (or weight fraction w_A)
Volume Fraction of component A = ϕ_A

Typically, we make a binary blend, A + B, with mass fraction, m_A, and want volume fraction, ϕ_A, or mole fraction , x_A.

$\phi_A = (m_A/\rho_A)/((m_A/\rho_A) + (m_B/\rho_B))$

$x_A = (m_A/MW_A)/((m_A/MW_A) + (m_B/MW_B))$

$m_A = (x_A MW_A)/((x_A MW_A) + (x_B MW_B))$

Solutions

-S U V
H A
-p G T

We need the free energy of mixing to determine equilibrium

$G = H - TS$ $A = U - ST$; $U = H - PV$
We can measure H and P and V and T but not S

Need the Entropy S

Three ways to get entropy and free energy of mixing

A) Isothermal free energy expression, pressure expression

B) Isothermal volume expansion approach, volume expression

C) From statistical thermodynamics

A. Pressure Expression: Mix two ideal gasses, A and B

-S U V
H A
-p G T

$p = p_A + p_B$ p_A is the partial pressure $p_A = x_A p$ (Raoult's Ideal Mixing Law)

For single component molar $G = \mu$
μ_0 is at $p_{0,A} = 1$ bar
At pressure p_A for a pure component isothermal ideal gas
$\boldsymbol{\mu_A = \mu_{0,A} + RT \ln(p/p_{0,A}) = \mu_{0,A} + RT \ln(p)}$

dG=-SdT+Vdp
Isothermal and Ideal Gas
$dG = RTdp/p$
$G = RT \ln(p/p_0)$

For a mixture of A and B with a total pressure $p_{tot} = p_{0,A} = 1$ bar and $p_A = x_A\, p_{tot}$

For component A in a binary mixture

$\boldsymbol{\mu_A(x_A) = \mu_{0.A} + RT \ln (x_A\, p_{tot}/p_{0,A}) = \mu_{0.A} + RT \ln (x_A)}$ Isothermal ideal gas (no enthalpy)

Notice that x_A must be less than or equal to 1, so $\ln x_A$ must be negative or 0
So, the chemical potential must drop in the solution for a solution to exist.
Ideal gasses only have entropy so entropy drives mixing in this case.

This can be written, $x_A = \exp((\mu_A(x_A) - \mu_{0.A})/RT)$
Which indicates that x_A is the Boltzmann probability of finding A

Mix two real gasses, A and B

$$\mu_A(x_A) = \mu_A^o + RT \ln\left(\frac{f_A}{p_A^o}\right) = \mu_A^o + RT \ln(f_A)$$ Gas

$$\mu_A = \mu_A^* + RT \ln a_A$$ Solution

$\mu_A^* = \mu_{0.A}$ if $p = 1$

Solutions

-S U V
H A
-p G T

G = H – TS A = U – ST U = H – PV
Need the Entropy S

Three ways to get entropy and free energy of mixing

A) Isothermal free energy expression, pressure expression

B) Isothermal volume expansion approach, volume expression

C) From statistical thermodynamics

B. Volume Expression: Ideal Gas Mixing

$-S\ U\ V$
$H\quad A$
$-p\ G\ T$

$dU=-pdV+TdS$
Isothermal and Ideal Gas
$dG = RTdp/p$

For isothermal $\Delta U = C_V\, dT = 0 = dQ + dW$
$dQ = -dW = pdV$
For ideal gas $dQ = -dW = nRT\ln(V_f/V_i)$

$dQ = T\Delta S$
$\Delta S = nR\ \ln(V_f/V_i)$
Consider a process of expansion of a gas from V_A to V_{tot}
The change in entropy is $\Delta S_A = n_A R\ln(V_{tot}/V_A) = -\ n_A R\ln(V_A/V_{tot})$

Consider an isochoric mixing process of ideal gasses A and B.
A is originally in V_A and B in V_B
V_{tot} is $V_A + V_B$
The change in entropy for mixing of A and B is

$\Delta S_{\text{mixing A and B}} = -\ n_A R\ln(V_A/V_{tot}) - n_B R\ln(V_B/V_{tot}) = -\ nR(x_A\ln x_A + x_B\ln x_B)$
For an isothermal, isochoric mixture of ideal gasses (also isobaric since P ~ T/V)

For ideal gasses $\Delta H_{mixing} = 0$ since there is no interaction
$\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing} = -\ T\Delta S_{mixing} = nRT(\ln x_A + \ln x_B)$
So, the molar Gibbs Free energy for mixing is $\boldsymbol{\Delta G_{mixing} = RT(x_A\ln x_A + x_B\ln x_B)}$

Solutions

-S U V
 H A
-p G T

G = H – TS   A = U – ST   U = H – PV
Need the Entropy S

Three ways to get entropy and free energy of mixing

A) Isothermal free energy expression, pressure expression

B) Isothermal volume expansion approach, volume expression

C) <u>From statistical thermodynamics</u>

C. Statistical Thermodynamics

Boltzmann's Law: $\Delta S = k_B \ln\Omega$

Ω Is the number of states

For mixing of n_A and n_B with n total molecules

$\Omega = n!/(n_A!\, n_B!)$

Sterling's approximation for large n, $\ln(n!) \sim n \ln(n) - n$

We assume that n is large then

$$\ln\Omega = n \ln(n) - (n_A \ln(n_A) + n_B \ln(n_B))$$

$$= (n_A + n_B) \ln(n) - (n_A \ln(n_A) + n_B \ln(n_B))$$

$$\ln\Omega = -(n_A \ln(n_A/n) + n_B \ln(n_B/n))$$

$$\Delta S = -k_B (n_A \ln(n_A/n) + n_B \ln(n_B/n)) = -nk_B (x_A \ln(x_A) + x_B \ln(x_B))$$

$$\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing} = - T\Delta S_{mixing} = nRT(x_A \ln x_A + x_B \ln x_B)$$

Some Types of Entropy

Thermodynamic entropy measured experimentally, Q/T

Configurational also called Combinatorial
Conformational
Translational and Rotational Entropy (Brownian motion)
Vibrational entropy
Conformational entropy computed in internal or Cartesian coordinates (which can even be different from each other)
Conformational entropy computed on a lattice
Entropy associated with organization on mixing (Hyrophobic effect and many other unexpected features on mixing)

-S U V
 H A
-p G T

An “Ideal Solution” means:

The change on mixing:

$\Delta S = -nk_B (x_A \ln(x_A) + x_B \ln(x_B))$

Since (ln x) is always negative or 0, ΔS is always positive for ideal solutions

$\Delta G = -T\, \Delta S$

Since (ln x) is always negative or 0, ΔG is always negative (or 0) and ideal solutions **always mix**

ΔH is 0, there is no interaction in ideal mixtures, there is no excluded volume, particles are ghosts to each other

$\Delta V = (d\Delta G/dp)_T = 0$, there is no loss or gain of volume compared to the summed volume

-S U V
H A
-p G T

Boltzmann Probability of a Thermally Reversible Event = $\exp(-\Delta G/\mathrm{k}T)$
ΔG is the change in free energy for the event
$\Delta G = \Delta H - T\Delta S$ (Const. T & P, e.g. an experimental measurement)
$\Delta A = \Delta U - T\Delta S$ (Const. T & V, e.g. a simulation on a grid)

Consider an ideal gas with no enthalpic interactions, $\Delta H = 0$
The probability of finding an atom A in a mixture of A and B is the molar concentration x_A
$\Delta S_A/\mathrm{k} = -\ln x_A$ from the Boltzmann probability
and
$\Delta S/\mathrm{k} = -\, x_A \ln x_A - x_B \ln x_B$ by a rule of random mixtures
$\Delta G_{\mathrm{ideal}}/\mathrm{k}T = x_A \ln x_A + x_B \ln x_B$ this is always negative since "ln" of a number less than 1 is negative, so mixing always reduces the free energy so *it always occurs for an ideal mixture*

Hildebrandt Real Solution model considers binary interactions.
The odds of a binary interaction of A and B is $x_A x_B$
This interaction has an average enthalpy (or internal energy) $\Delta H = x_A x_B\, \Omega_{AB}$ or $x_1 x_2\, A_{12}$
Where the first term is the Hildebrandt binary interaction parameter and the second is the Margules one-parameter interaction term. For polymers χ_{12} is used, the Flory –Huggins interaction parameter (with a few modifications).

$$\Delta G_{\mathrm{real\ solution}}/\mathrm{k}T = x_1 \ln x_1 + x_2 \ln x_2 + x_1 x_2\, A_{12} = x_1 \ln a_1 + x_2 \ln a_2 = x_1 \ln \gamma_1 x_1 + x_2 \ln \gamma_2 x_2$$

$$\Delta H/\mathrm{k}T = \Delta G_{\mathrm{excess}}/\mathrm{k}T = x_1 x_1\, A_{12} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

Activity Coefficients as Derivatives

$$\boxed{G^E = RT\sum_i x_i \ln(\gamma_i)}$$

Excess free energy per mole

$\underline{G}^E$ is the excess free energy value, so nG^E

The excess chemical potential of component “i” in phase L or V, μ_i^E is given by

$$\boxed{\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \overline{G}_i^E = \mu_i^E = RT\ln\gamma_i} \qquad 11.28$$

Activity coefficients are related to the partial molar excess Gibbs energy.

$$\frac{G^E}{RT} = A_{12}x_1x_2 \qquad \frac{\underline{G}^E}{RT} = n(A_{12}x_1x_2) = (A_{12}n_2)\left(\frac{n_1}{n}\right) \qquad 11.29$$

$$\frac{1}{RT}\left(\frac{\partial G^E}{\partial n_1}\right)_{T,P,n_2} = \ln\gamma_1 = An_2\left[\frac{1}{n} - \frac{n_1}{n^2}\right] = A\frac{n_2}{n}\left[1 - \frac{n_1}{n}\right] = Ax_2(1-x_1) \qquad 11.30$$

$$\ln\gamma_1 = Ax_2^2 \text{ ; similarly } \ln\gamma_2 = Ax_1^2 \qquad 11.31$$

This is how you can find the activity coefficients from the Margules one-parameter coefficient (or the Hildebrandt or Flory-Huggins interaction parameters)

Real Solutions

Molar excess functions or departure functions:

Difference between real value and ideal value

Excess $\Delta G_{mixing} = \Delta G_{mixing} - RT(x_A \ln x_A + x_A \ln x_B)$
Excess $\Delta S_{mixing} = \Delta S_{mixing} + R(x_A \ln x_A + x_A \ln x_B)$
Excess $\Delta H_{mixing} = \Delta H_{mixing}$
Excess $\Delta V_{mixing} = \Delta V_{mixing}$

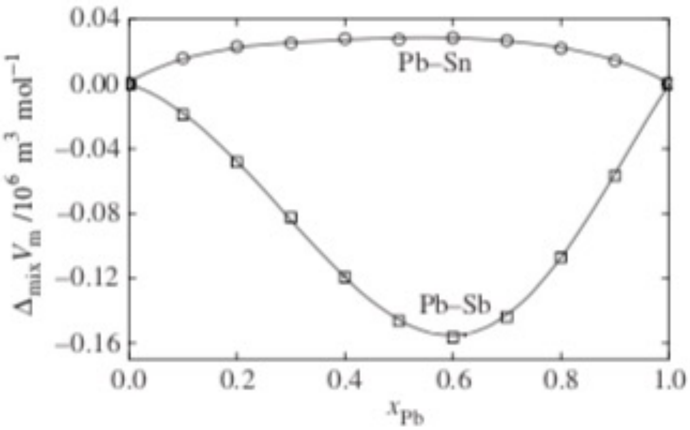


Figure 3.2 Molar volume of mixing of molten Pb–Sn at 1040 K [1] and Pb–Sb at 907 K [2] as a function of composition.

Real Solutions

x_A becomes a_A the activity so

$\Delta G_{mixing} = RT(x_A \ln a_A + x_A \ln a_B)$

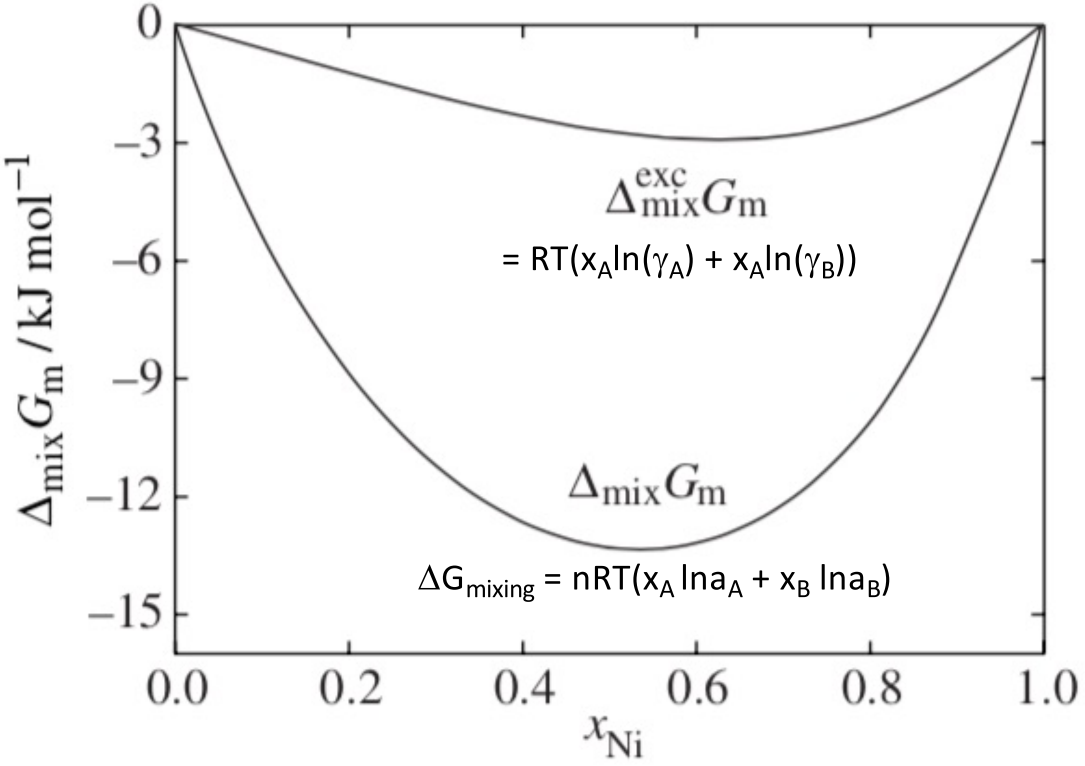
$\text{Excess } \Delta G_{mixing} = \Delta G_{mixing} - RT(x_A \ln x_A + x_B \ln x_B)$
$= RT(x_A \ln(a_A/x_A) + x_B \ln(a_B/x_B))$
$= RT(x_A \ln(\gamma_A) + x_B \ln(\gamma_B))$

γ Is the activity coefficient

$\text{Excess } \Delta S_{mixing} = -R(x_A \ln(\gamma_A) + x_B \ln(\gamma_B))$

Method to use departure functions for calculations (PREOS.xls)

1) Calculation of properties in the ideal state is simple
2) With an equation of state the departure function can be calculated
3) For any transition first calculate the departure function to the ideal state
4) Then carry out the desired change as an ideal mixture or gas
5) Then use the departure function to return to the real state



$= RT(x_A \ln(\gamma_A) + x_A \ln(\gamma_B))$

$\Delta G_{\text{mixing}} = nRT(x_A \ln a_A + x_B \ln a_B)$

Figure 3.5 The molar Gibbs energy of mixing and the molar excess Gibbs energy of mixing of molten Fe–Ni at 1850 K. Data are taken from reference [3].

$a = \gamma x$ so $da/dx = \gamma$

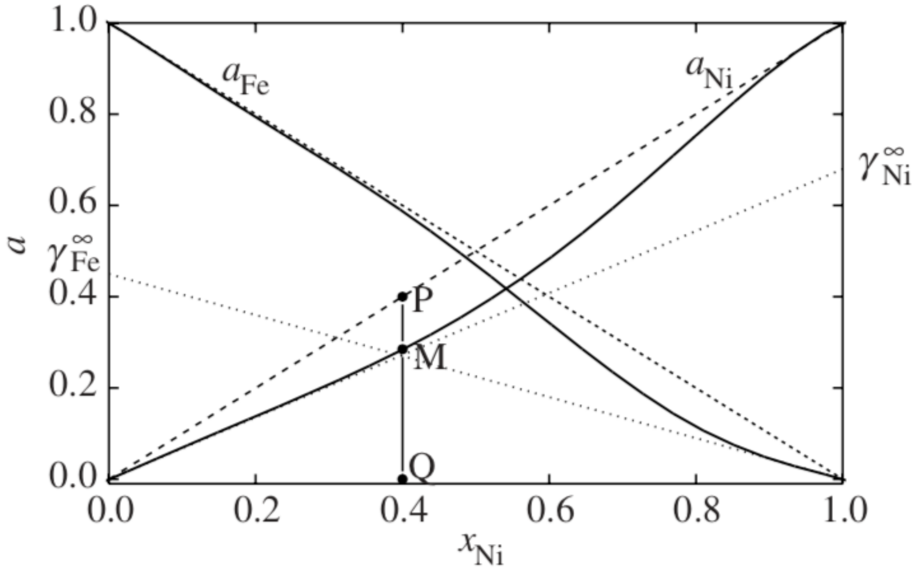


Figure 3.4 The activity of Fe and Ni of molten Fe–Ni at 1850 K [3]. At $x_{Ni} = 0.4$ the activity coefficient of Ni is given by MQ/PQ.

Get the activity coefficient at infinite dilution by extrapolating the slope for pure component to x = 0
This is used for Henry's Law and a few other places.

(Activity coefficient is a/x)

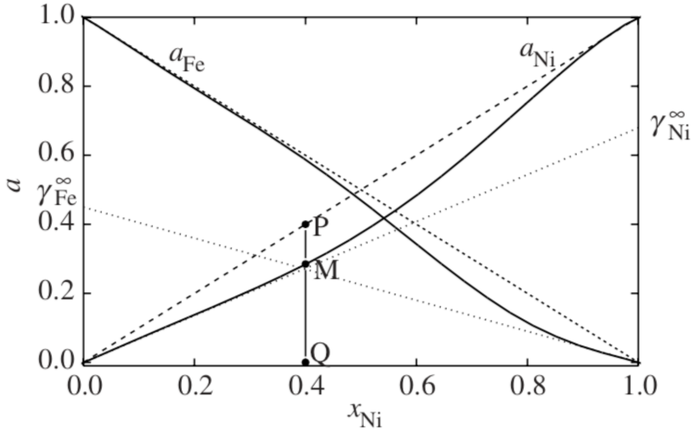


Figure 3.4 The activity of Fe and Ni of molten Fe–Ni at 1850 K [3]. At $x_{\mathrm{Ni}} = 0.4$ the activity coefficient of Ni is given by MQ/PQ.

We want the infinite dilution activity coefficients to write a function to predict the activity and the activity coefficient.

This is one of the parameters for the functions.

With the function for activity we can predict the free energy and the miscibility.

Solute

Henry's law for dilute solutions

Vapor pressure of solute = $k_i\ x_i$
k_i is the **Henry's Law Constant**
x_i is the solute molar fraction (low ~0)

Solvent or ideal mixture

Raoult's Law for solvent or ideal mixtures
Vapor pressure = $p^*\ x_j$
x_j is the solvent molar fraction (high ~1)
p^* is the vapor pressure of the pure solvent

If a solution is ideal, then $x_A = a_A$ and $\gamma_A = 1$
As concentration goes to 1, a solvent is ideal (follows Raoult's law) so
$(da_A/dx_A)_{xA \Rightarrow 1} = 1 = (d\gamma_A x_A/dx_A)_{xA \Rightarrow 1} = \gamma_A + x_A(d\gamma_A/dx_A)_{xA \Rightarrow 1}$
But $\gamma_A = 1$ at $x_A = 1$, then **Raoult's law** is followed if
$(d\gamma_A/dx_A)_{xA \Rightarrow 1} \Rightarrow 0$ (**See next slide**)

A solute follows **Henry's Law** if
$(da_B/dx_B)_{xB \Rightarrow 0} = \gamma_B$ infinite dilution
$= (d\gamma_B x_B/dx_B)_{xB \Rightarrow 0} = (\gamma_B + x_B(d\gamma_B/dx_B))_{xB \Rightarrow 0}$
So
$(x_B(d\gamma_B/dx_B))_{xB \Rightarrow 0} = 0$
This isn't that useful

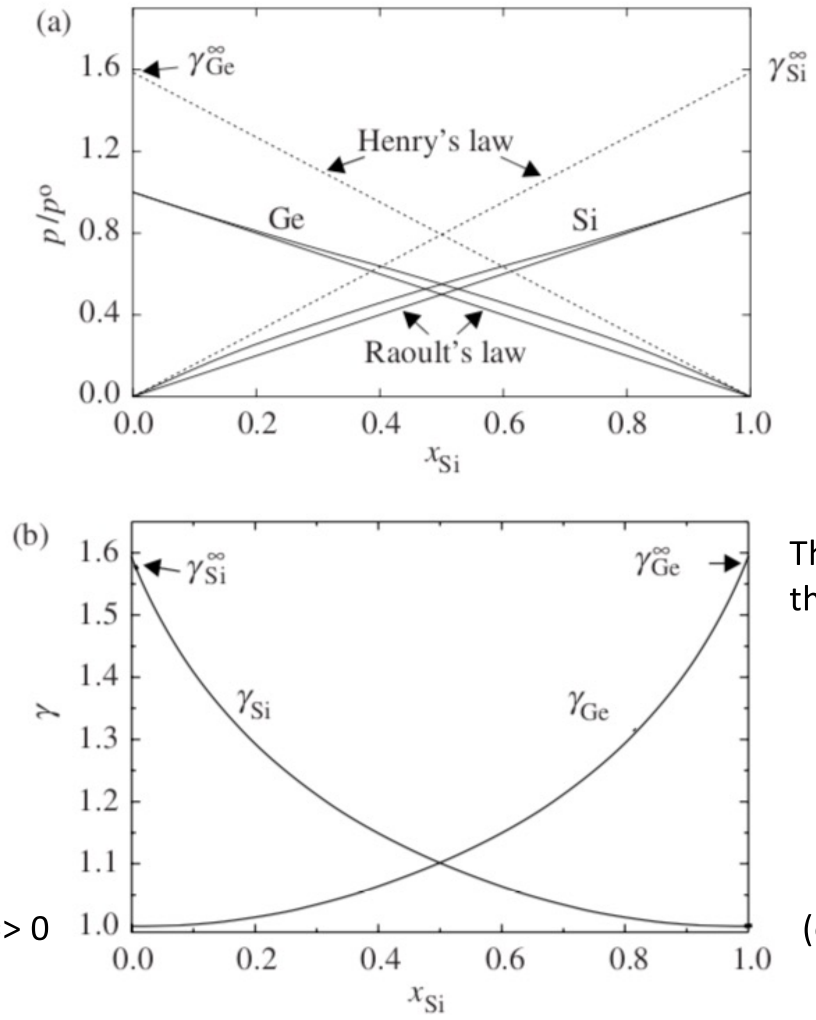


Figure 3.6 (a) The vapour pressure above molten Si–Ge at 1723 K [4]. (b) The corresponding activity coefficients of the two components.

Henry's law for dilute solutions
Vapor pressure of solute = $k_i\ x_i$

Raoult's Law for solvent or ideal mixtures
Vapor pressure = $p^*\ x_j$

The infinite dilution value comes from the activity plot extrapolation

The infinite dilution value comes from the activity plot extrapolation

$(d\gamma_B/dx_B)_{xB \Rightarrow 1} \Rightarrow 0$

$(d\gamma_A/dx_A)_{xA \Rightarrow 1} \Rightarrow 0$

Activity of a component in a solution must be defined relative to a standard state, either
Henrian (extrapolated) or
Raoultian (measured at x = 1 :: a = 1)

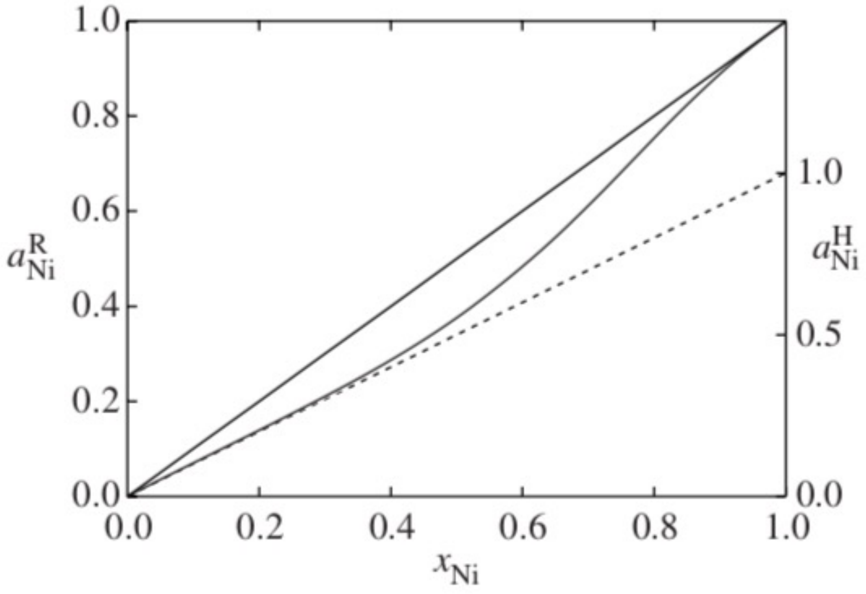


Figure 3.7 The activity of Ni of molten Fe–Ni at 1850 K using both a Raoultian and a Henrian standard state. Data are taken from reference [3].

You would use Henrian standard state if the solute had limited solubility like PCBs or oil in water and you wanted the infinite dilution of the water component

The activities on the two standard states are related since

$$\mu_i = \mu_i^{\mathrm{R}} + RT \ln a_i^{\mathrm{R}} = \mu_i^{\mathrm{H}} + RT \ln a_i^{\mathrm{H}}$$

which gives

$$\frac{a_i^{\mathrm{R}}}{a_i^{\mathrm{H}}} = \exp\left[-\frac{(\mu_i^{\mathrm{R}} - \mu_i^{\mathrm{H}})}{RT}\right]$$

Analytic Solution Models

Want to calculate the miscibility of components
Need to generate a phase diagram
Calculation of the vapor pressure

Simplest approach could be a polynomial. However, this generally doesn't inherently have any real meaning. The polynomial just reproduces existing data within experimental limits. Extrapolation is dangerous.

$$Y(x_B) = Q_0 + Q_1 x_B + Q_2 x_B^2 + \ldots + Q_n x_B^n = \sum_{i=0}^{n} Q_i x_B^i$$

Asymmetric feature: vapor pressure

or

$$Y(x_B) = x_A x_B \sum_{i=0}^{n} R_i (x_A - x_B)^i = x_B(1 - x_B) \sum_{i=0}^{n} R_i (1 - 2x_B)^i$$

Symmetric Feature: Phase behavior

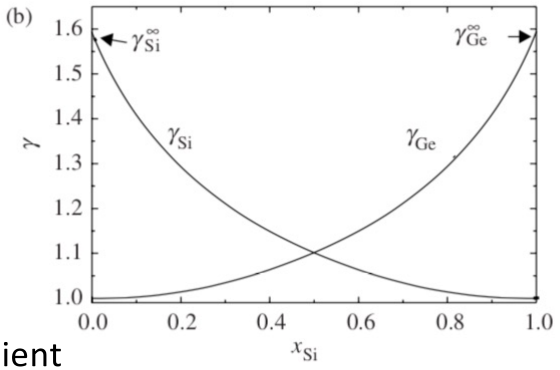
A Taylor Series Expansion For Example (starting with the infinite dilution value)

$$\ln \gamma_{\mathrm{B}} = \ln \gamma_{\mathrm{B}}^{\infty} + \left(\frac{\partial \ln \gamma_{\mathrm{B}}}{\partial x_{\mathrm{B}}} \right)_{x_{\mathrm{B}} \to 0} x_{\mathrm{B}} + \frac{1}{2} \left(\frac{\partial^2 \ln \gamma_{\mathrm{B}}}{\partial x_{\mathrm{B}}^2} \right)_{x_{\mathrm{B}} \to 0} x_{\mathrm{B}}^2 + \dots$$

$$+ \frac{1}{i!} \left(\frac{\partial^i \ln \gamma_{\mathrm{B}}}{\partial x_{\mathrm{B}}^i} \right)_{x_{\mathrm{B}} \to 0} x_{\mathrm{B}}^i$$

Excess ΔG_{mixing} = $RT(x_A \ln(\gamma_A) + x_A \ln(\gamma_B))$

Excess ΔS_{mixing} = $-R(x_A \ln(\gamma_A) + x_A \ln(\gamma_B))$



$$\ln \gamma_{\mathrm{B}} = \sum_{i=0}^{n} J_i^{\mathrm{B}} x_{\mathrm{B}}^i$$

$$J_i^{\mathrm{B}} = \frac{1}{i!} \left(\frac{\partial^i \ln \gamma_{\mathrm{B}}}{\partial x_{\mathrm{B}}^i} \right)_{x_{\mathrm{B}} \to 0}$$

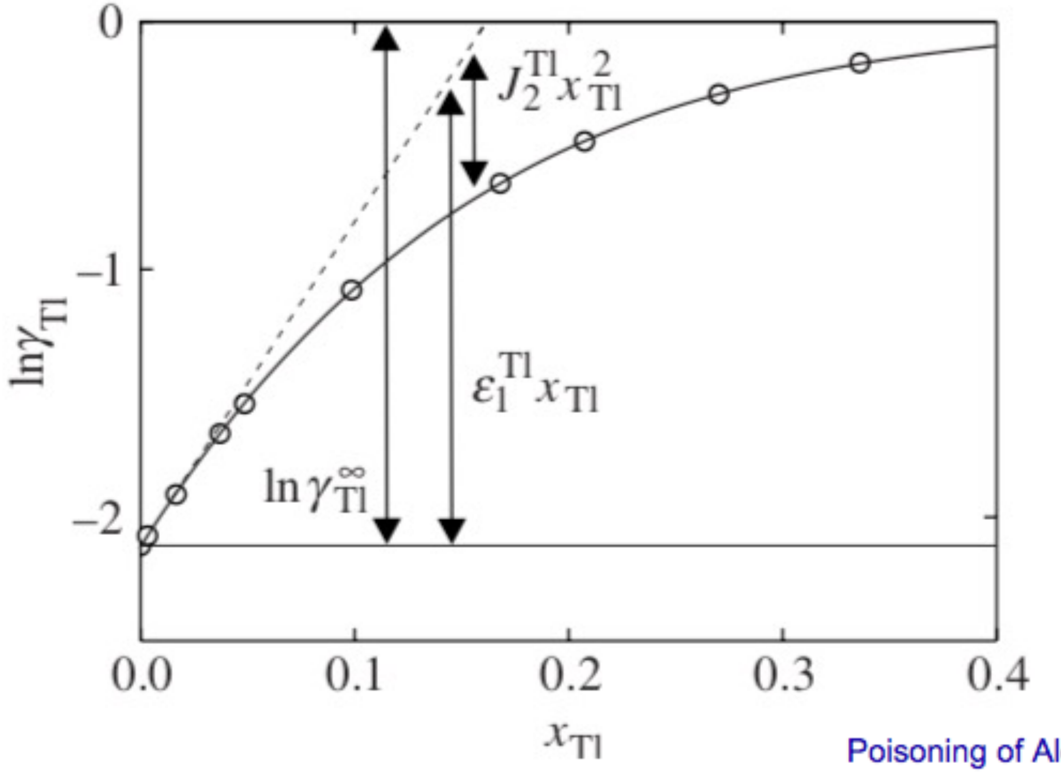
Interaction coefficients

Zeroth order infinite dilution (trivial)

First order ε_1^B self-interaction coefficient

$$\ln \gamma_{\mathrm{B}} = \ln \gamma_{\mathrm{B}}^{\infty} + \varepsilon_1^{\mathrm{B}} x_{\mathrm{B}} + J_2^{\mathrm{B}} x_{\mathrm{B}}^2$$

This is similar to a virial expansion



Thallium/Mercury

Lower freezing point of Mercury for thermometer and switches 8.5% -60°C versus -40°C

Also Rat poison

Poisoning of Alexander Litvinenko - Wikipedia

Figure 3.9 An illustration of low-order terms in the Taylor series expansion of $\ln\gamma_i$ for dilute solutions using $\ln\gamma_{\mathrm{Tl}}$ for the binary system Tl–Hg at 293 K as example. Here $\ln\gamma_{\mathrm{Tl}}^{\infty} = -2.069$, $\varepsilon_1^{\mathrm{Tl}} = 10.683$ and $J_2^{\mathrm{Tl}} = -14.4$. Data are taken from reference [8].

Hildebrand Regular Solution Model

The change on mixing:

$\Delta S = -nk_B (x_A \ln(x_A) + x_B \ln(x_B))$ Ideal Solution

Since (ln x) is always negative or 0, ΔS is always positive for ideal solutions

$\Delta G = \Delta H - T \Delta S$

Since (ln x) is always negative or 0, ΔG is positive or negative depending on ΔH :: can **mix or demix**

Depending on the sign of ΔH

$\Delta V = (d\Delta G/dp)_T = 0$, there is no loss or gain of volume compared to the summed volume

$\Delta H = n\, \Omega\, x_A x_B$

Ω is the interaction coefficient or regular solution constant

Molar Gibbs free energy of mixing

$\Delta G_m = RT(x_A \ln(x_A) + x_B \ln(x_B)) + \Omega\, x_A x_B$

$\Omega = zN_A[u_{AB} - (u_{AA}+u_{BB})/2]$

The equation is symmetric

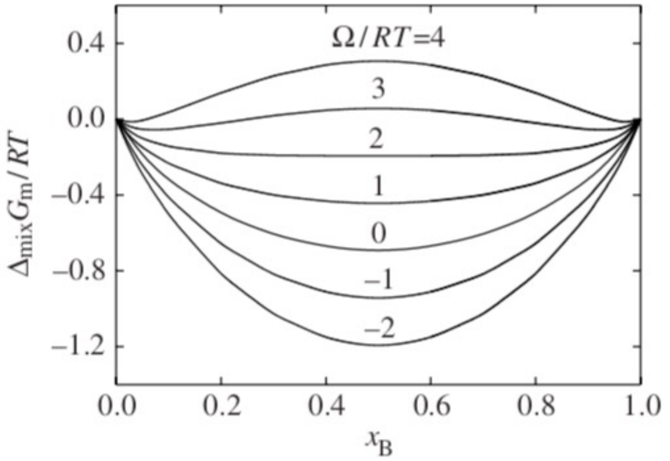
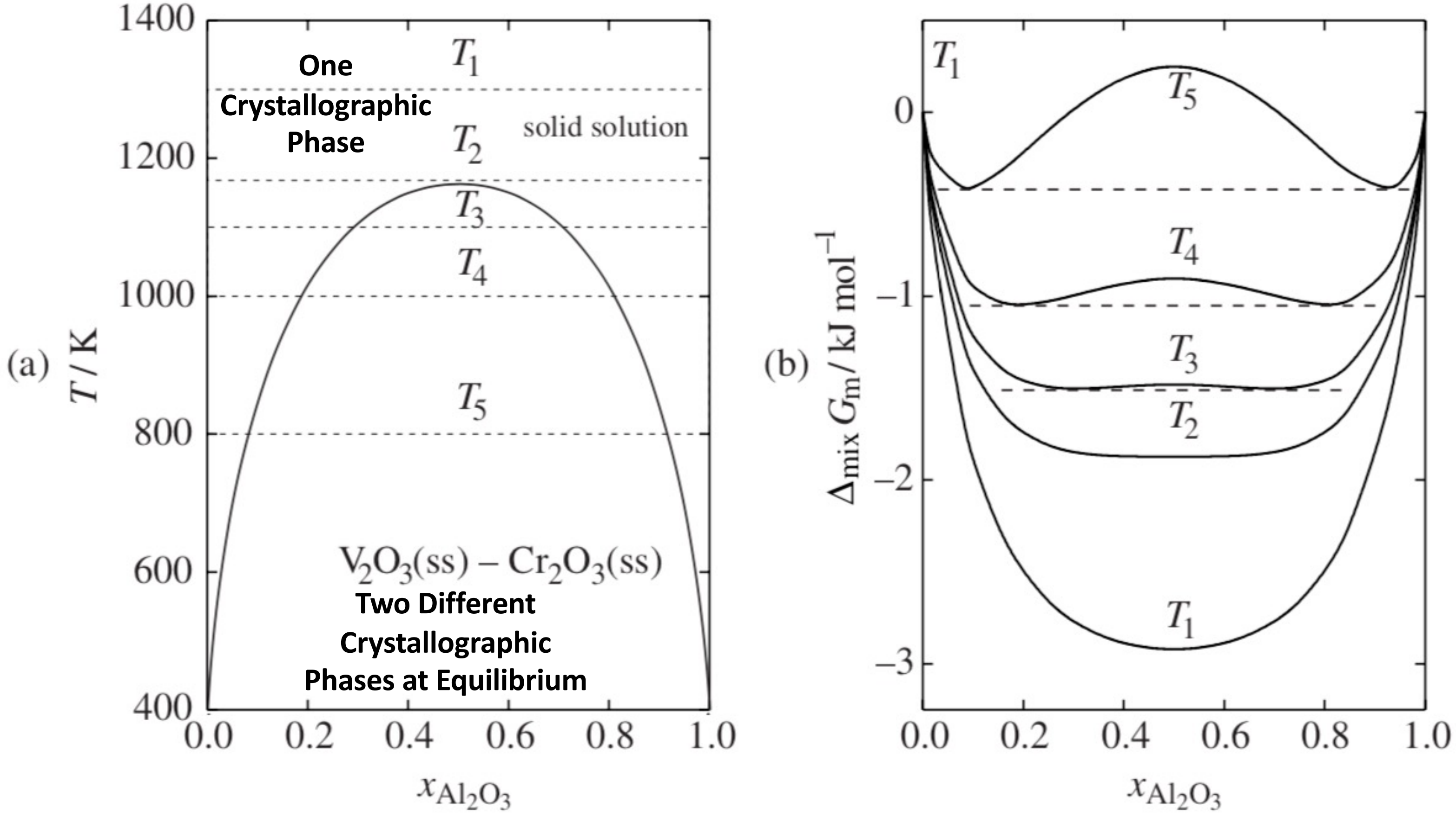


Figure 3.10 The molar Gibbs energy of mixing of a regular solution A–B for different values of Ω/RT.

$\gamma \Rightarrow \alpha + \beta$

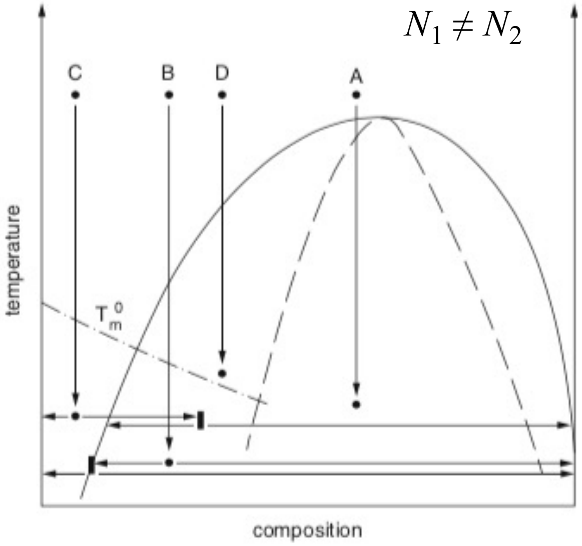


One Crystallographic Phase

Two Different Crystallographic Phases at Equilibrium

Figure 4.9 (a) Immiscibility gap of the binary solid solution V_2O_3–Cr_2O_3 as described by the regular solution model. (b) Gibbs energy of mixing curve of the solid solution at the temperatures marked in the phase diagram. Thermodynamic data are taken from reference [7].

Fig. 3.41 Phase diagram of a binary polymer blend with miscibility gap (UCST) and intersecting crystal/melt coexistence curve. The T_m° curve is extrapolated into the miscibility gap. Quenching routes *A* to *D* are explained in the text. For routes *B* and *C*, the quenching-induced phase separation and crystallization are indicated. —— binodal, ——— spinodal, and —. crystal/melt coexistence curve (Li et al. 1991)



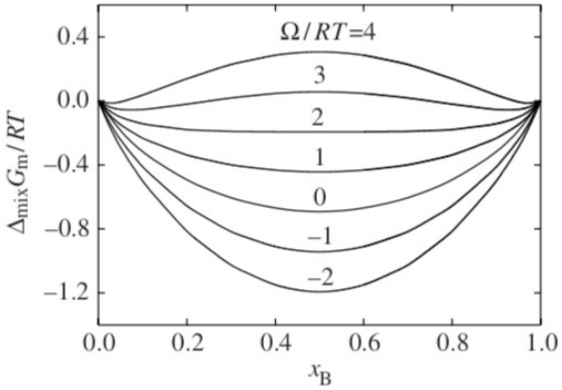
$N_1 \neq N_2$

A. Simultaneous spinodal decomposition and crystallization
   The blend is quenched into the unstable region of the miscibility gap and to a temperature below the crystallization/melt coexistence curve.
B. Simultaneous binodal decomposition and crystallization
   This type is similar to spinodal decomposition, but a composition is quenched into the metastable region of the miscibility gap.
C. Crystallization induced decomposition
   The blend is quenched outside the miscibility gap to a temperature below the crystallization/melt coexistence curve. The concentration of the noncrystallizable component increases with crystallization until the miscibility gap is reached inducing demixing.
D. Decomposition-induced crystallization
   The blend is quenched into the miscibility gap to a temperature that lies above the crystallization/melt coexistence curve for the actual composition but lies below the crystallization curve for the binodal composition. When the blend is quenched, demixing occurs resulting in two coexisting phases of which one is able to crystallize. The demixing can result in spinodally as well as in binodally decomposed material.

Only few experimental studies have been performed on polymer blends

Y. Li, M. Stein, B.-J. Jungnickel, Colloid Polym. Sci. 269, 772 (1991); and 'Mitteilungen aus dem Deutschen Kunststoff-Institut', Nr. 53, April, Darmstadt, 1991

$$\frac{\Delta_{\text{mix}} G}{k_B T V} = \frac{1}{\nu^*}\left(\frac{\varphi_1}{N_1}\ln\varphi_1 + \frac{\varphi_2}{N_2}\ln\varphi_2 + \varphi_1\varphi_2\chi\right)$$



$N_1 = N_2$

Figure 3.10 The molar Gibbs energy of mixing of a regular solution A–B for different values of Ω/RT.

Hildebrand solubility parameter, δ

$\Delta H = n\,\Omega\,x_A x_B$

Ω is the interaction coefficient or regular solution constant

Molar Gibbs free energy of mixing

$G_m = RT(x_A \ln(x_A) + x_B \ln(x_B)) + \Omega\, x_A x_B$

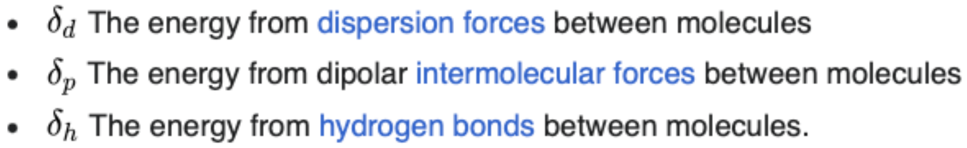
$\Omega = zN_A[u_{AB} - (u_{AA}+u_{BB})/2]$

Flory-Huggins chi parameter, $\sim\Omega/kT$

$$\Delta H_m = \frac{\chi \varphi_A \varphi_B kT}{V_0} \qquad \chi = \frac{V_0 V_M}{kT}(\delta_{T,A} - \delta_{T,B})^2 \qquad \delta_T = \sqrt{\mathrm{CED}} = \sqrt{\frac{E_{coh}}{V}}$$

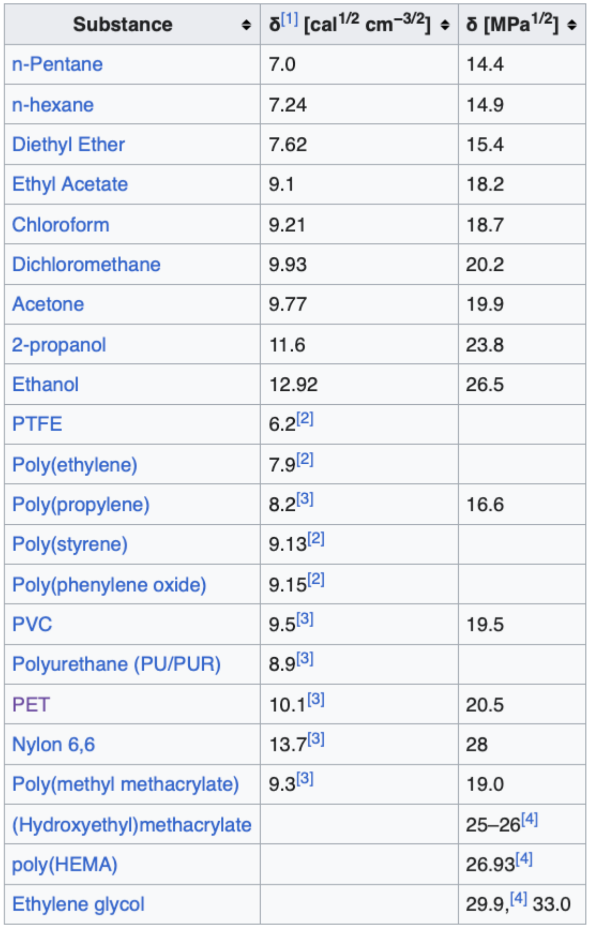
Hansen solubility parameters

$$\chi = \frac{V_0 V_M}{kT}[(\delta_{D,A} - \delta_{D,B})^2 + (\delta_{P,A} - \delta_{P,B})^2 + (\delta_{H,A} - \delta_{H,B})^2] \qquad \delta_D = \sqrt{\frac{E_{coh,D}}{V}},\ \ \delta_P = \sqrt{\frac{E_{coh,P}}{V}},\ \ \delta_H = \sqrt{\frac{E_{coh,H}}{V}}$$



- δ_d The energy from dispersion forces between molecules
- δ_p The energy from dipolar intermolecular forces between molecules
- δ_h The energy from hydrogen bonds between molecules.

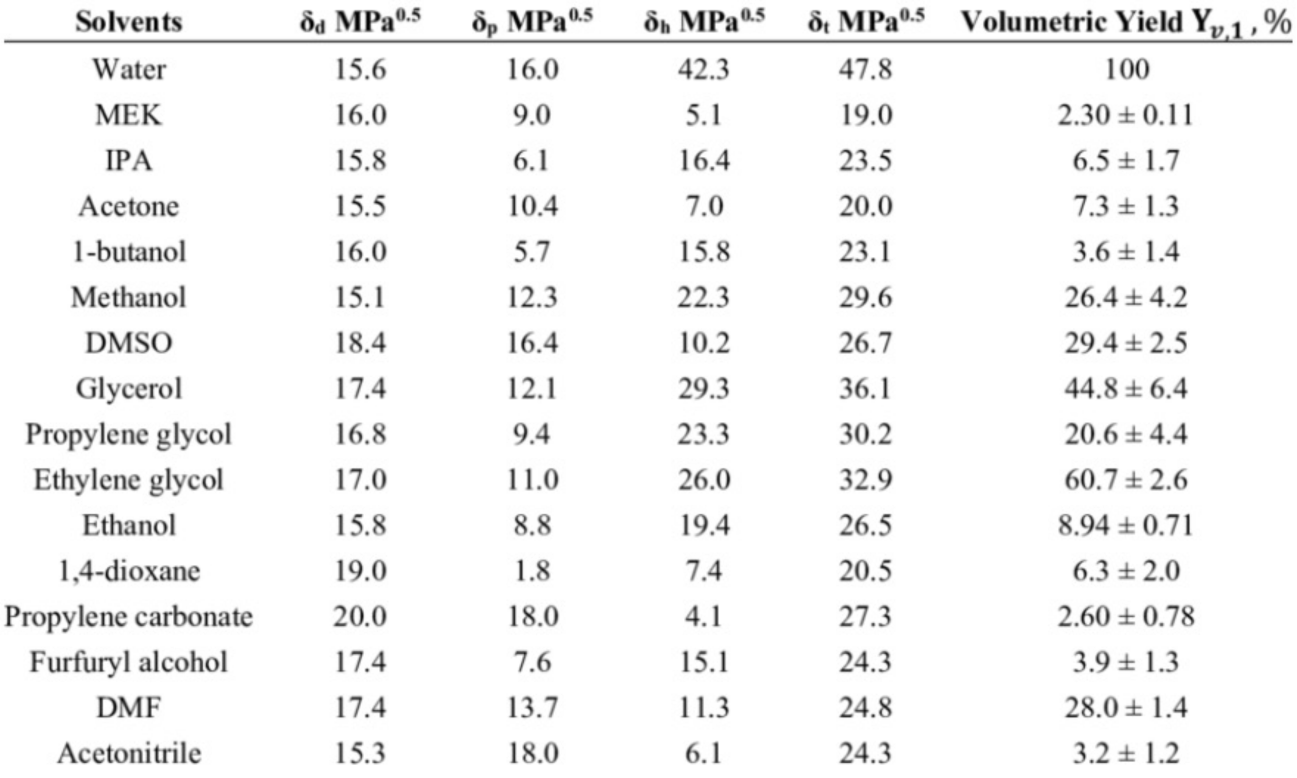
Hildebrand solubility parameter, δ



Substance	δ[1] [cal$^{1/2}$ cm$^{-3/2}$]	δ [MPa$^{1/2}$]
n-Pentane	7.0	14.4
n-hexane	7.24	14.9
Diethyl Ether	7.62	15.4
Ethyl Acetate	9.1	18.2
Chloroform	9.21	18.7
Dichloromethane	9.93	20.2
Acetone	9.77	19.9
2-propanol	11.6	23.8
Ethanol	12.92	26.5
PTFE	6.2[2]	
Poly(ethylene)	7.9[2]	
Poly(propylene)	8.2[3]	16.6
Poly(styrene)	9.13[2]	
Poly(phenylene oxide)	9.15[2]	
PVC	9.5[3]	19.5
Polyurethane (PU/PUR)	8.9[3]	
PET	10.1[3]	20.5
Nylon 6,6	13.7[3]	28
Poly(methyl methacrylate)	9.3[3]	19.0
(Hydroxyethyl)methacrylate		25–26[4]
poly(HEMA)		26.93[4]
Ethylene glycol		29.9,[4] 33.0

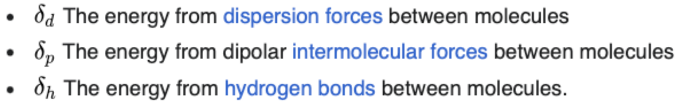
$$\delta = \sqrt{\frac{\Delta H_v - RT}{V_m}}.$$

Hansen solubility parameter, δ



Solvents	δ_d MPa$^{0.5}$	δ_p MPa$^{0.5}$	δ_h MPa$^{0.5}$	δ_t MPa$^{0.5}$	Volumetric Yield $Y_{v,1}$, %
Water	15.6	16.0	42.3	47.8	100
MEK	16.0	9.0	5.1	19.0	2.30 ± 0.11
IPA	15.8	6.1	16.4	23.5	6.5 ± 1.7
Acetone	15.5	10.4	7.0	20.0	7.3 ± 1.3
1-butanol	16.0	5.7	15.8	23.1	3.6 ± 1.4
Methanol	15.1	12.3	22.3	29.6	26.4 ± 4.2
DMSO	18.4	16.4	10.2	26.7	29.4 ± 2.5
Glycerol	17.4	12.1	29.3	36.1	44.8 ± 6.4
Propylene glycol	16.8	9.4	23.3	30.2	20.6 ± 4.4
Ethylene glycol	17.0	11.0	26.0	32.9	60.7 ± 2.6
Ethanol	15.8	8.8	19.4	26.5	8.94 ± 0.71
1,4-dioxane	19.0	1.8	7.4	20.5	6.3 ± 2.0
Propylene carbonate	20.0	18.0	4.1	27.3	2.60 ± 0.78
Furfuryl alcohol	17.4	7.6	15.1	24.3	3.9 ± 1.3
DMF	17.4	13.7	11.3	24.8	28.0 ± 1.4
Acetonitrile	15.3	18.0	6.1	24.3	3.2 ± 1.2

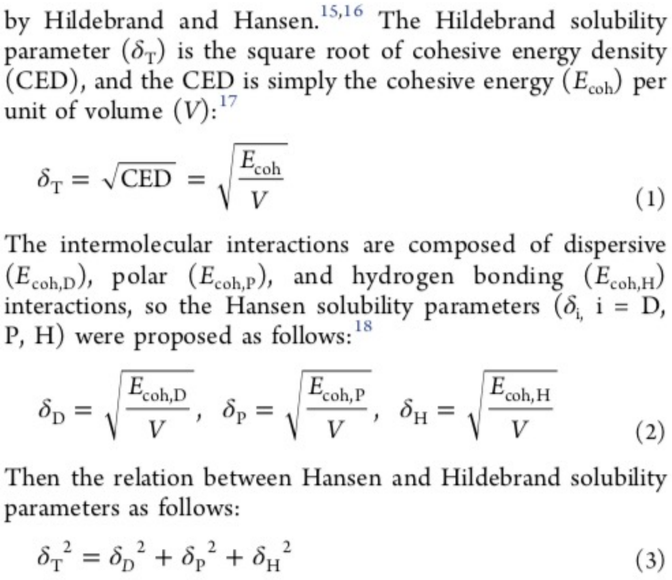
The Hansen solubility parameters of solvents and experimentally measured volumetric yields after one step solvent exchange.



- δ_d The energy from dispersion forces between molecules
- δ_p The energy from dipolar intermolecular forces between molecules
- δ_h The energy from hydrogen bonds between molecules.

Hildebrand Solubility Parameter, δ

Two materials with similar δ are miscible



by Hildebrand and Hansen.[15,16] The Hildebrand solubility parameter (δ_T) is the square root of cohesive energy density (CED), and the CED is simply the cohesive energy (E_{coh}) per unit of volume (V):[17]

$$\delta_T = \sqrt{CED} = \sqrt{\frac{E_{coh}}{V}} \qquad (1)$$

The intermolecular interactions are composed of dispersive ($E_{coh,D}$), polar ($E_{coh,P}$), and hydrogen bonding ($E_{coh,H}$) interactions, so the Hansen solubility parameters ($\delta_{i,}$ i = D, P, H) were proposed as follows:[18]

$$\delta_D = \sqrt{\frac{E_{coh,D}}{V}}, \quad \delta_P = \sqrt{\frac{E_{coh,P}}{V}}, \quad \delta_H = \sqrt{\frac{E_{coh,H}}{V}} \qquad (2)$$

Then the relation between Hansen and Hildebrand solubility parameters as follows:

$$\delta_T^{\,2} = \delta_D^{\,2} + \delta_P^{\,2} + \delta_H^{\,2} \qquad (3)$$

London dispersion forces (attractive)

Luo Y, Chen X, Wu S, Ca S Luo Z, Shi Y, *Molecular Dynamics Simulation Study on Two-Component Solubility Parameters of Carbon Nanotubes and Precisely Tailoring the Thermodynamic Compatibility between Carbon Nanotubes and Polymers*, Langmuir **36** 9291-9305 (2020).

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$\Delta H_m = \frac{\chi \varphi_A \varphi_B kT}{V_0}$$

Flory-Huggins Equation

χ ~ 1/T

$$\Delta H_m = \varphi_A \varphi_B (\delta_{T,A} - \delta_{T,B})^2 V_M$$

Hildebrand and Scratchard

$$\chi = \frac{V_0 V_M}{kT}(\delta_{T,A} - \delta_{T,B})^2$$

$$\chi = \frac{V_0 V_M}{kT}[(\delta_{D,A} - \delta_{D,B})^2 + (\delta_{P,A} - \delta_{P,B})^2 + (\delta_{H,A} - \delta_{H,B})^2]$$

Asymmetric equations for asymmetric phase diagram

Sub-regular solution model

$$\Delta_{\mathrm{mix}}^{\mathrm{exc}} G_{\mathrm{m}} = x_{\mathrm{A}}\, x_{\mathrm{B}} (A_{21} x_{\mathrm{A}} + A_{12}\, x_{\mathrm{B}})$$

$$\boxed{\ln \gamma_1 = x_2^2 \, [A_{12} + 2(A_{21} - A_{12}) x_1]} \text{ ; similarly } \boxed{\ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21}) x_2]}$$

$$\boxed{A_{12} = \left(2 - \frac{1}{x_2}\right) \frac{\ln \gamma_1}{x_2} + \frac{2 \ln \gamma_2}{x_1} \qquad A_{21} = \left(2 - \frac{1}{x_1}\right) \frac{\ln \gamma_2}{x_1} + \frac{2 \ln \gamma_1}{x_2}}$$

$$\Delta_{\mathrm{mix}}^{\mathrm{exc}} G_{\mathrm{m}} = \sum_{i=1}^{m} \sum_{j=1}^{n} x_{\mathrm{A}}^{i}\, x_{\mathrm{B}}^{j} A_{ij}$$

Redlich-Kister Expression

$$\Delta_{\mathrm{mix}}^{\mathrm{exc}} G_{\mathrm{m}} = x_{\mathrm{A}}\, x_{\mathrm{B}} [\Omega + A_1 (x_{\mathrm{A}} - x_{\mathrm{B}}) + A_2 (x_{\mathrm{A}} - x_{\mathrm{B}})^2 + A_3 (x_{\mathrm{A}} - x_{\mathrm{B}})^3 + \ldots]$$

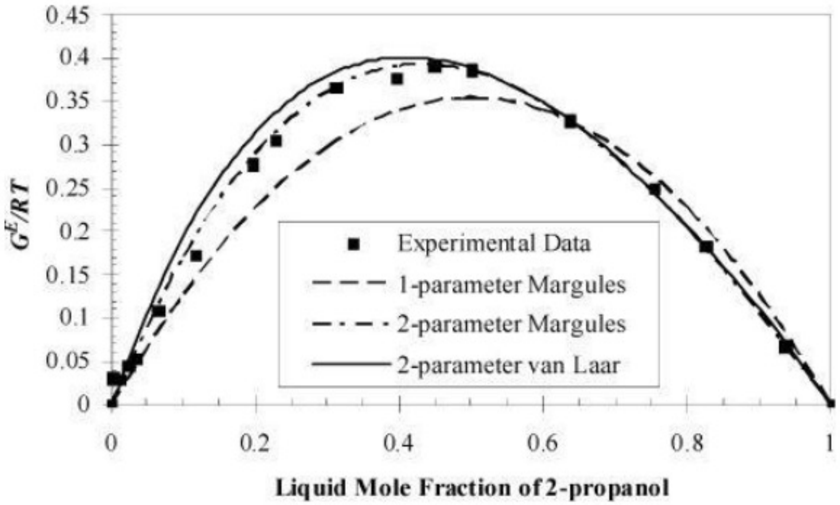
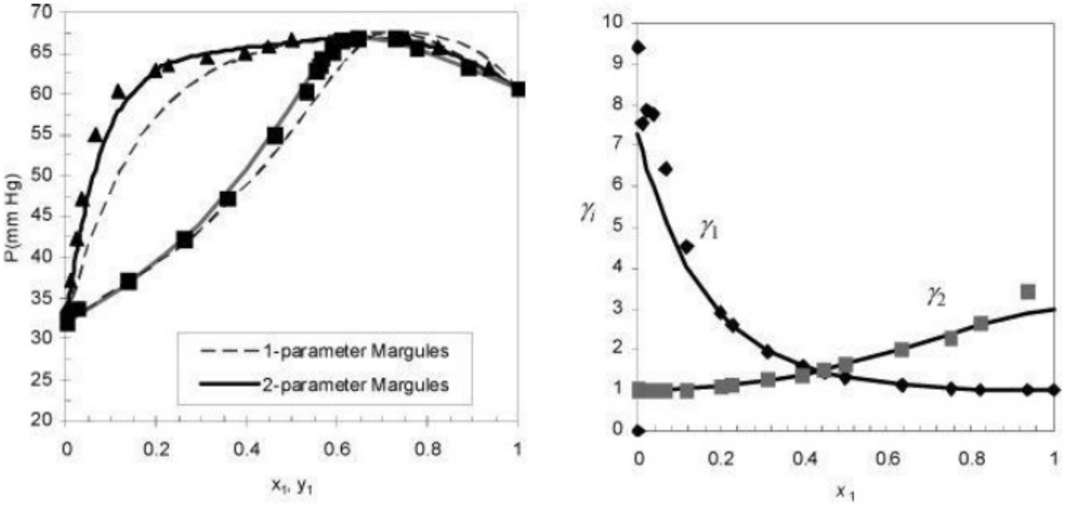


Figure 11.3. Illustration of calculation of G^E from experiment and fitting of Margules models to a single point as discussed in Examples 11.1 and 11.5, for 2-propanol + water, with the experimental data points from Fig. 10.8 on page 395. Data are tabulated in Example 11.8. The van Laar model fit to a single point is explained in Section 12.2.



(*a*) (*b*)

Figure 11.5. (a) One-parameter and two-parameter Margules equation fitted to a single measurement in Examples 11.2 and 11.5 compared with the experimental data points from Fig. 10.8 on page 395. Data are tabulated in Example 11.8. (b) Activity coefficients predicted from the parameters fitted in Example 11.5 compared with points calculated from the data.

Non-ideal entropy of mixing
Quasi-regular solution model

$$\Delta G_{\text{real solution}}/\mathrm{k}T = x_1 \ln x_1 + x_2 \ln x_2 + x_1 x_2 A_{12}$$

$A_{12} = \Omega_{12} = A/\mathrm{kT}$

The Margules interaction parameter should have a 1/T dependence, but it often displays a "non-combinatorial entropy term"

$A_{12} = A/\mathrm{kT} + B$

This can be interpreted that there is some kind of "ordering" that occurs on mixing

"Hydrophobic effect" is an example. When water and oil are mixed water organizes around oil/water interface reducing the entropy. Entropy depends on number not mass so a large number of water molecules at the interface leads to a large, dominating entropic reduction that causes immiscibility. The enthalpic interaction favors mixing (negative A).
$A_{12} = 0$ at the "athermal temperature" , T^*
$B = -A/(\mathrm{k}T^*)$

$A_{12} = (A/\mathrm{k}T)(1 - T/T^*) = \Omega_{12}(1 - T/T^*)$ T^* is a critical temperature

From “Single Component Systems” Slide 34. Landau Theory for Curie transition

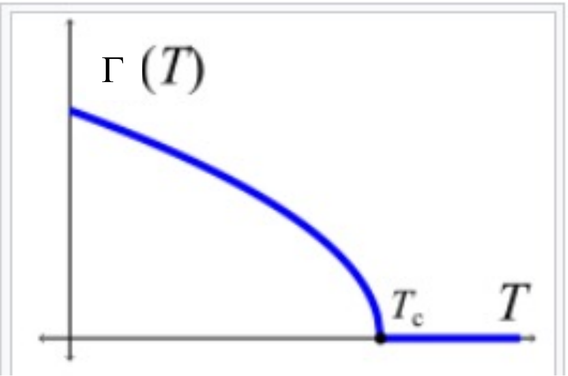
At the Curie transition (second order transition)

$$\frac{\partial \Delta_{\text{trs}} G}{\partial \Gamma} = 0 \quad \text{and} \quad \frac{\partial^2 \Delta_{\text{trs}} G}{\partial \Gamma^2} > 0$$

$$\Delta_{\text{trs}} G = \frac{1}{2} b\Gamma^2 + \frac{1}{3} c\Gamma^3 + \frac{1}{4} d\Gamma^4 + \ldots$$

$$\frac{\partial \Delta_{\text{trs}} G}{\partial \Gamma} = B(T - T_{\text{trs}})\Gamma + d\Gamma^3 = 0$$

$$\Gamma^2 = -\frac{B}{d}(T - T_{\text{trs}}) \quad \text{for} \quad T < T_{\text{trs}}$$



Order parameter is 1 at 0 K so $\frac{B}{d} = \frac{1}{T_{\text{trs}}}$ and $\Gamma = \left[\frac{T_{\text{trs}} - T}{T_{\text{trs}}}\right]^{1/2}$

Non-ideal entropy of mixing
Quasi-regular solution model

$$\Delta_{\text{mix}}^{\text{exc}} G_{\text{m}} = x_{\text{A}} x_{\text{B}} \Omega \left(1 - \frac{T}{\tau} \right)$$

$$\Delta_{\text{mix}}^{\text{exc}} S_{\text{m}} = -\frac{\partial(\Delta_{\text{mix}}^{\text{exc}} G_{\text{m}})}{\partial T} = x_{\text{A}} x_{\text{B}} \left(\frac{\Omega}{\tau} \right)$$

This is a non-combinatorial entropy

This would occur if there were ordering on mixing, say when you add oil to water. The enthalpy of mixing favors mixing!!! Water organizes at the surface of oil to a great extent; this reduces entropy and makes oil and water demix. Water actually “likes” oil. This is called the “***hydrophobic effect***” and is an important concept for protein folding.

Graphical Method to Estimate Chemical Potential

Does $dG/dx_i = dG/dn_i = \mu_i$?

No

$dG/dn_i = dG/dx_i \; dx_i/dn_i$

$dx_i/dn_i = d(n_i/(n_i+n_j))/dn_i = 1/(n_i+n_j) - n_i/(n_i+n_j)^2$

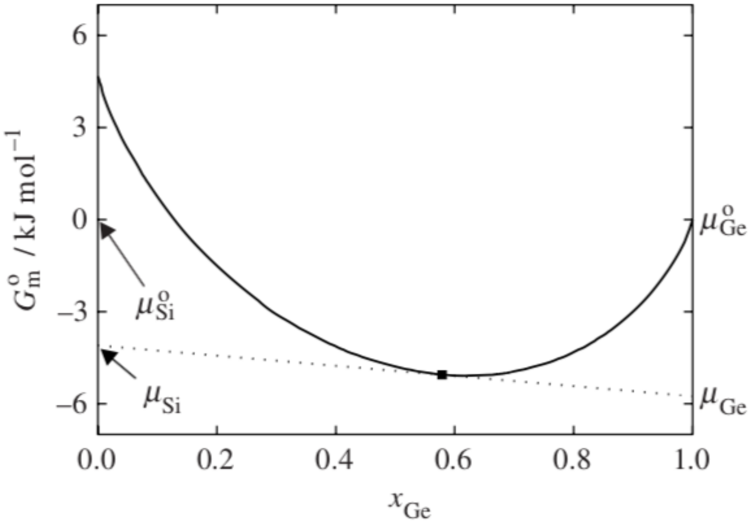


Figure 3.12 The integral molar Gibbs energy of liquid Ge–Si at 1500 K with pure liquid Ge and solid Si as standard states. Data are taken from reference [4].

Solving the Regular Solution Model

We know that the excess Gibbs free energy for mixing is given by:

$G^E/RT = x_A \ln \gamma_A + x_B \ln \gamma_B$ **Generic expression using activity coefficient**
And we have defined for the regular solution model that
$G^E/RT = \Omega\, x_A\, x_B$ **Hildebrand Regular Solution expression**

If we propose the answer $RT \ln \gamma_A = \Omega\, x_B^2$
We find by substitution generic expression that it equals the regular solution expression since $x_B + x_A = 1$
(Solving this directly **see next slide**.)

$$\frac{\Delta_{\text{mix}}^{\text{exc}} \overline{G}_{\text{A}}}{RT} = \ln \gamma_{\text{A}} = \frac{\Omega}{RT} x_{\text{B}}^2$$

$$\frac{\Delta_{\text{mix}}^{\text{exc}} \overline{G}_{\text{B}}}{RT} = \ln \gamma_{\text{B}} = \frac{\Omega}{RT} x_{\text{A}}^2$$

$$\boxed{G^E = RT\sum_i x_i \ln(\gamma_i)}$$

Activity Coefficients as Derivatives

$$\boxed{\left(\frac{\partial \underline{G}^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \bar{G}_i^E = \mu_i^E = RT\ln\gamma_i} \qquad 11.28$$

Activity coefficients are related to the partial molar excess Gibbs energy.

$$\frac{G^E}{RT} = A_{12}x_1x_2 \qquad \frac{\underline{G}^E}{RT} = n(A_{12}x_1x_2) = (A_{12}n_2)\left(\frac{n_1}{n}\right) \qquad 11.29$$

$$\frac{1}{RT}\left(\frac{\partial \underline{G}^E}{\partial n_1}\right)_{T,P,n_2} = \ln\gamma_1 = An_2\left[\frac{1}{n}-\frac{n_1}{n^2}\right] = A\frac{n_2}{n}\left[1-\frac{n_1}{n}\right] = Ax_2(1-x_1) \qquad 11.30$$

$$\ln\gamma_1 = Ax_2^2 \text{ ; similarly } \ln\gamma_2 = Ax_1^2 \qquad 11.31$$

Use of the Gibbs-Duhem Equation to determine the activity of a component

$$n_{\mathrm{A}}\mathrm{d}\mu_{\mathrm{A}} + n_{\mathrm{B}}\mathrm{d}\mu_{\mathrm{B}} = 0$$

Constant p, T

$$x_{\mathrm{A}}\mathrm{d}\ln a_{\mathrm{A}} + x_{\mathrm{B}}\mathrm{d}\ln a_{\mathrm{B}} = 0$$

$$x_{\mathrm{A}}\mathrm{d}\ln x_{\mathrm{A}} + x_{\mathrm{A}}\mathrm{d}\ln \gamma_{\mathrm{A}} + x_{\mathrm{B}}\mathrm{d}\ln x_{\mathrm{B}} + x_{\mathrm{B}}\mathrm{d}\ln \gamma_{\mathrm{B}} = 0$$

$$x_{\mathrm{A}}\mathrm{d}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\mathrm{d}\ln x_{\mathrm{B}} = x_{\mathrm{A}}\frac{\mathrm{d}x_{\mathrm{A}}}{x_{\mathrm{A}}} + x_{\mathrm{B}}\frac{\mathrm{d}x_{\mathrm{B}}}{x_{\mathrm{B}}} = \mathrm{d}x_{\mathrm{A}} + \mathrm{d}x_{\mathrm{B}} = 0$$

$$x_{\mathrm{A}}\mathrm{d}\ln \gamma_{\mathrm{A}} + x_{\mathrm{B}}\mathrm{d}\ln \gamma_{\mathrm{B}} = 0$$

Restatement of Gibbs-Duhem for Solutions

If you know γ_A you can obtain γ_B by integration

$$\ln \gamma_{\mathrm{B}} - \ln \gamma_{\mathrm{B}}(x_{\mathrm{B}} = 1) = -\int_{x_{\mathrm{B}}=1}^{x_{\mathrm{B}}} \frac{x_{\mathrm{A}}}{x_{\mathrm{B}}}\mathrm{d}\ln \gamma_{\mathrm{A}}$$

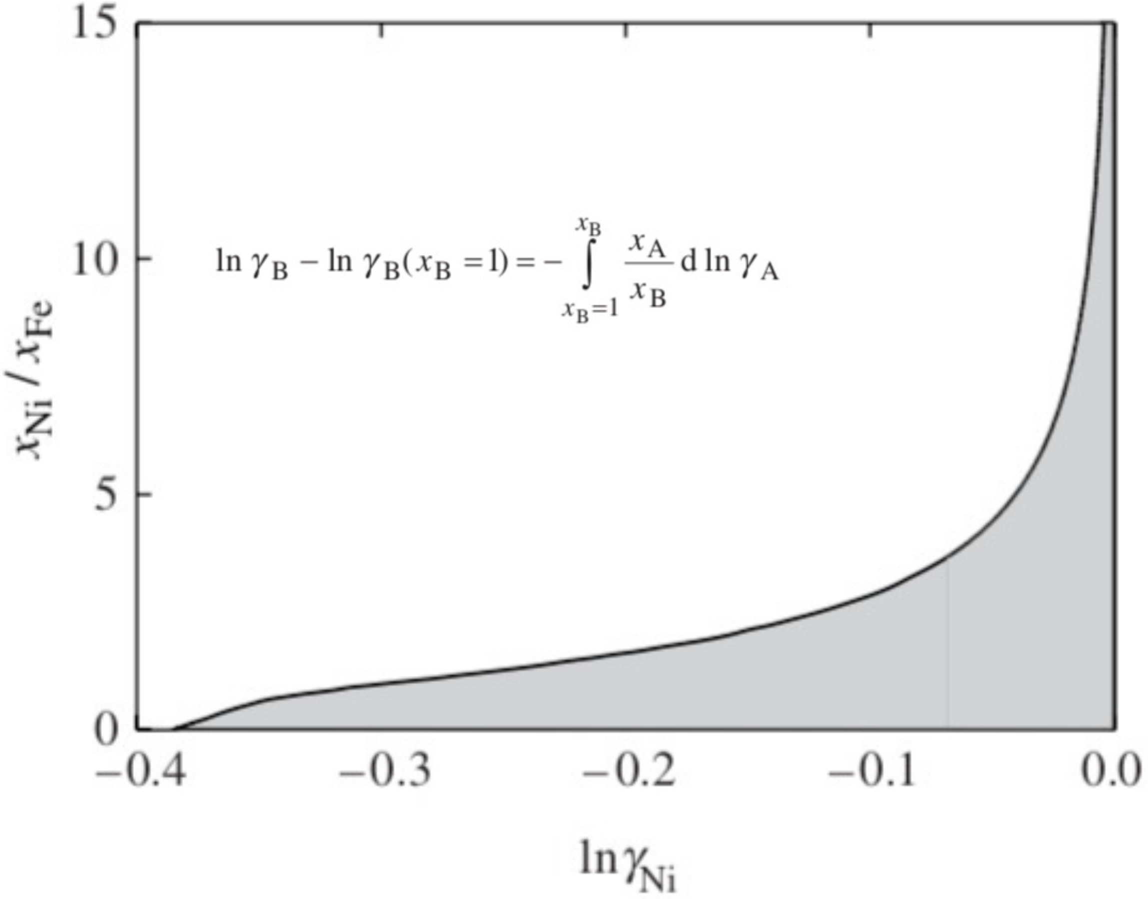


Figure 3.13 x_{Ni}/x_{Fe} versus $\ln \gamma_{Ni}$ of molten Fe–Ni at 1850 K. Data are taken from reference [3].