Atomistic Solution Models

Consider a system with N interacting particles and a number of energy states numbered with the j index

Partition Function $$Z = \sum_j \exp\left(-\frac{U_j}{k_B T}\right)$$

$A = -k_B T \ln(Z)$ $G \approx -k_B T \ln Z$ Relative to T = 0K

Energy states will be degenerate, that is more than one state can have the same energy, then,

$$Z = \sum_i g_i \exp\left(-\frac{U_i}{k_B T}\right)$$

Ideal Solution Model

$$U = N_{\mathrm{A}} \langle u_{\mathrm{A}} \rangle + N_{\mathrm{B}} \langle u_{\mathrm{B}} \rangle = U_{\mathrm{A}} + U_{\mathrm{B}}$$

$$Z = g \exp\left(-\frac{U}{k_{\mathrm{B}} T} \right) = \left(\frac{N!}{N_A! N_B!} \right) \exp\left(-\frac{U_{\mathrm{A}} + U_{\mathrm{B}}}{k_{\mathrm{B}} T} \right)$$

$$G \approx A = -k_{\mathrm{B}} T \ln Z = -k_{\mathrm{B}} T \ln\left(\frac{N!}{N_{\mathrm{A}}! N_{\mathrm{B}}!} \right) + U_{\mathrm{A}} + U_{\mathrm{B}}$$

$$\Delta_{\mathrm{mix}} G = -k_{\mathrm{B}} T \ln\left(\frac{N!}{N_{\mathrm{A}}! N_{\mathrm{B}}!} \right)$$

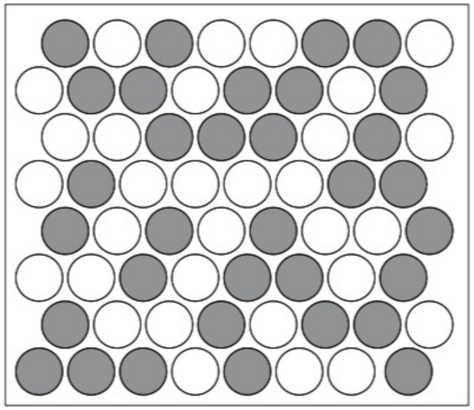


Figure 9.1 Two-dimensional lattice model for a solution of two different atoms of similar radius.

$$(\ln M! = M \ln M - M \text{ for } M \text{ large})$$ Sterling's Approximation

$$\Delta_{\mathrm{mix}} G = -k_{\mathrm{B}} T [(N_{\mathrm{A}} + N_{\mathrm{B}}) \ln N - N_{\mathrm{A}} \ln N_{\mathrm{A}} - N_{\mathrm{B}} \ln N_{\mathrm{B}}] + k_{\mathrm{B}} T (N - N_{\mathrm{A}} - N_{\mathrm{B}})$$

$$= k_{\mathrm{B}} T \left[N_{\mathrm{A}} \ln\left(\frac{N_{\mathrm{A}}}{N} \right) + N_{\mathrm{B}} \ln\left(\frac{N_{\mathrm{B}}}{N} \right) \right] = k_{\mathrm{B}} T [N_{\mathrm{A}} \ln x_{\mathrm{A}} + N_{\mathrm{B}} \ln x_{\mathrm{B}}]$$

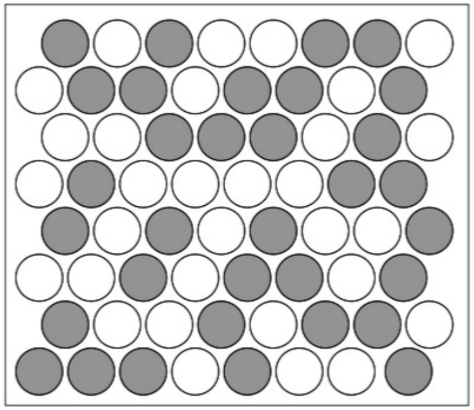
Ideal Solution Model

$$\Delta_{\text{mix}}G = k_B T[N_A \ln x_A + N_B \ln x_B]$$

$$\Delta_{\text{mix}}G_m = RT[x_A \ln x_A + x_B \ln x_B]$$

$$\Delta_{\text{mix}}S_m = -\left(\frac{\partial \Delta_{\text{mix}}G_m}{\partial T}\right)_p = -R[x_A \ln x_A + x_B \ln x_B]$$

$$\Delta_{\text{mix}}H_m = \Delta_{\text{mix}}G_m + T\Delta_{\text{mix}}S_m = 0$$



Two-dimensional lattice model for a solution of two different atoms of similar

Regular Solution Model

Coordination number ”z” z = 6 for Cartesian Coordinates

N_{AA} = number of A-A contacts with an energy of u_{AA}
Lattice has N sites
Total number of pairs is zN/2
Average energy of pure A is $U_A = zN_Au_{AA}/2$

For A atoms there are zN_A pairwise interactions made up of 2 interactions for each A and one for each AB

$$zN_{\mathrm{A}} = 2N_{\mathrm{AA}} + N_{\mathrm{AB}}$$

$$\tfrac{1}{2}z(N_{\mathrm{B}} + N_{\mathrm{A}}) = N_{\mathrm{AA}} + N_{\mathrm{BB}} + N_{\mathrm{AB}}$$

$$U = N_{\mathrm{AA}}u_{\mathrm{AA}} + N_{\mathrm{BB}}u_{\mathrm{BB}} + N_{\mathrm{AB}}u_{\mathrm{AB}}$$

$$\begin{aligned} U &= \tfrac{1}{2}(zN_{\mathrm{A}} - N_{\mathrm{AB}})u_{\mathrm{AA}} + \tfrac{1}{2}(zN_{\mathrm{B}} - N_{\mathrm{AB}})u_{\mathrm{BB}} + N_{\mathrm{AB}}u_{\mathrm{AB}} \\ &= \tfrac{1}{2}zN_{\mathrm{A}}u_{\mathrm{AA}} + \tfrac{1}{2}zN_{\mathrm{B}}u_{\mathrm{BB}} + N_{\mathrm{AB}}[u_{\mathrm{AB}} - \tfrac{1}{2}(u_{\mathrm{AA}} + u_{\mathrm{BB}})] \end{aligned}$$

Regular Solution Model

$$U = \frac{1}{2}(zN_A - N_{AB})u_{AA} + \frac{1}{2}(zN_B - N_{AB})u_{BB} + N_{AB}u_{AB}$$
$$= \frac{1}{2}zN_A u_{AA} + \frac{1}{2}zN_B u_{BB} + N_{AB}[u_{AB} - \frac{1}{2}(u_{AA} + u_{BB})]$$

$$\omega_{AB} = u_{AB} - \frac{1}{2}(u_{AA} + u_{BB})$$

$$U = U_A + U_B + N_{AB}\omega_{AB}$$

$$N_{AB} = \frac{1}{2}zN2x_A x_B = z\left(\frac{N_A N_B}{N}\right)$$

$$Z = g\exp\left(-\frac{U}{k_B T}\right) = \frac{N!}{N_A!N_B!}\exp\left[-\frac{[U_A + U_B + (zN_A N_B/N)\omega_{AB}]}{k_B T}\right]$$

$$G \approx A = -k_B T\ln\left[\frac{N!}{N_A!N_B!}\right] + U_A + U_B + \frac{zN_A N_B}{N}\omega_{AB}$$

Regular Solution Model

$$G \approx A = -k_B T \ln\left[\frac{N!}{N_A! N_B!}\right] + U_A + U_B + \frac{z N_A N_B}{N}\omega_{AB}$$

$$\Delta_{mix} G_m = RT[x_A \ln x_A + x_B \ln x_B] + \Omega_{AB} x_A x_B$$

$$\Omega_{AB} = zL\omega_{AB}$$

$$\Delta_{mix} H_m \approx \Delta_{mix} U_m = \Omega_{AB} x_A x_B$$

$\mu_A \sim dG/dx_A$

$$\mu_A - \mu_A^o = RT \ln a_A = RT \ln x_A + \Omega_{AB} x_B^2$$

$$RT \ln \gamma_A = \Omega_{AB} x_B^2$$

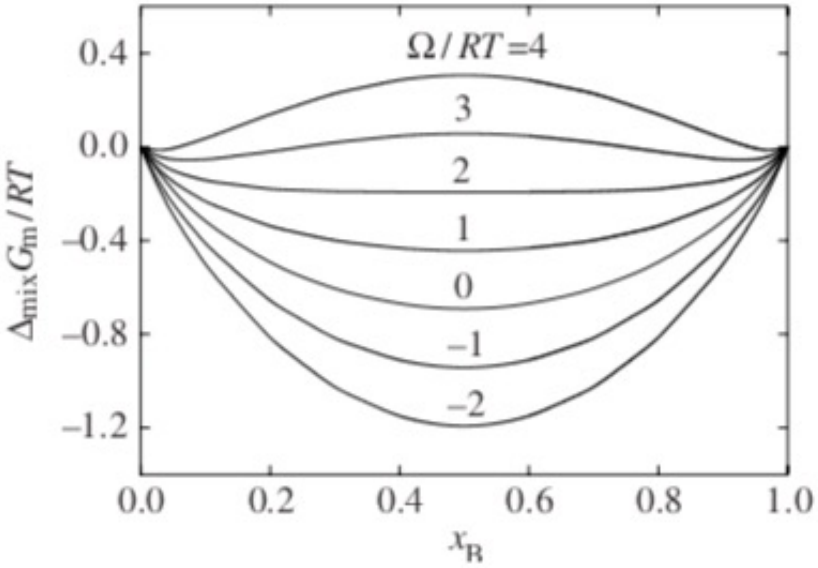
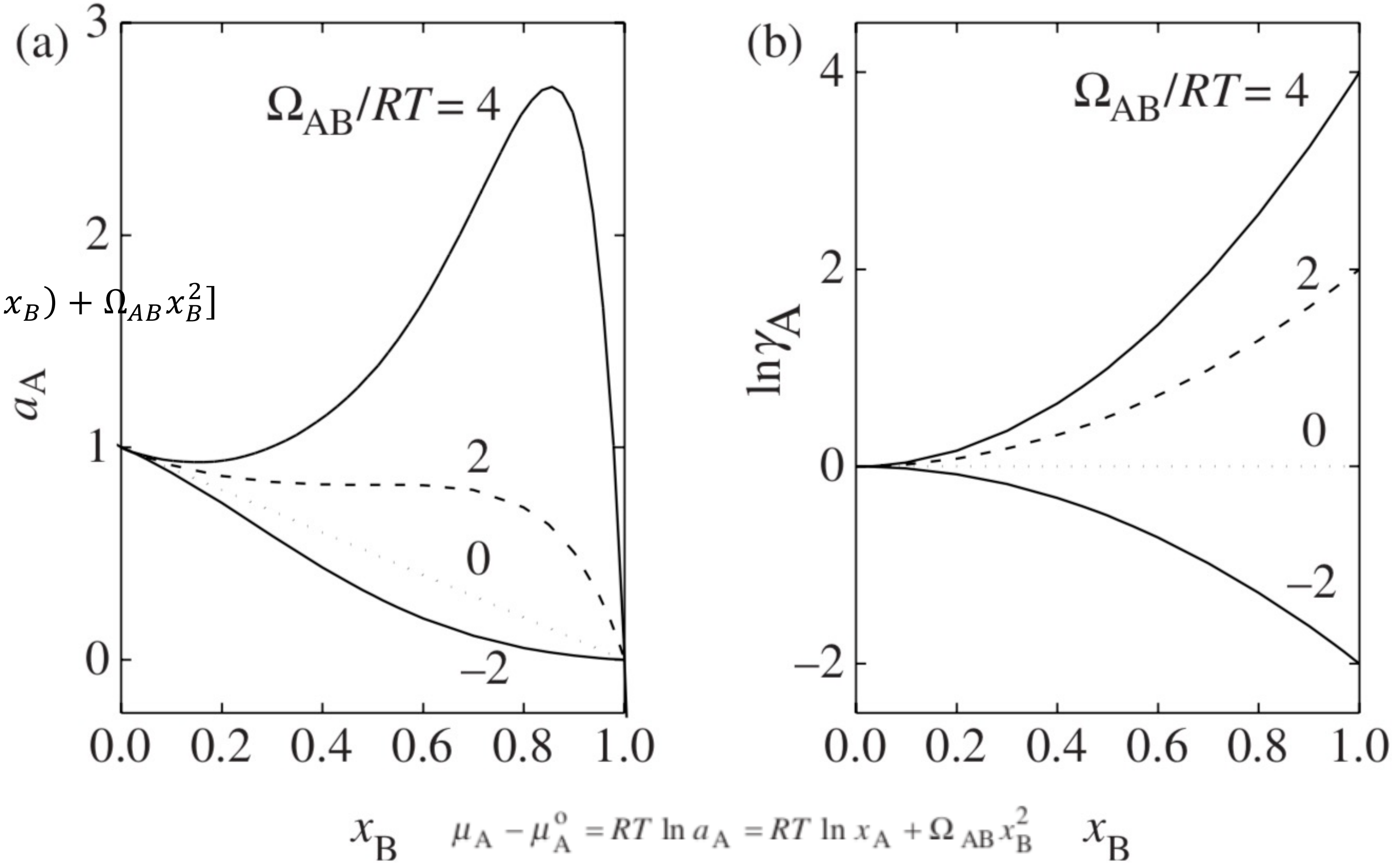


Figure 3.10 The molar Gibbs energy of mixing of a regular solution A–B for different values of Ω/RT.

$a_A = exp[ln(1 - x_B) + \Omega_{AB} x_B^2]$



$\gamma_A = exp\left[\frac{\Omega_{AB} x_B^2}{RT}\right]$

$\mu_A - \mu_A^o = RT \ln a_A = RT \ln x_A + \Omega_{AB} x_B^2$

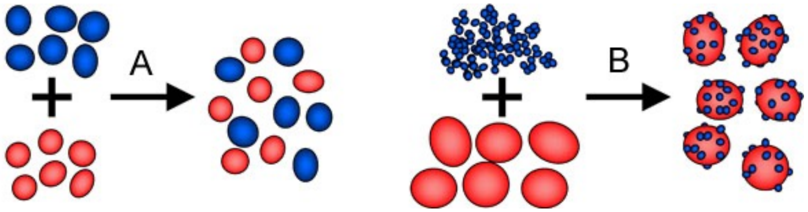
Figure 9.2 (a) a_A and (b) $\ln\gamma_A$ $RT \ln \gamma_A = \Omega_{AB} x_B^2$ on A–B as a function of composition for selected values of Ω_{AB}/RT.

Entropy of Mixing

$$\Delta_{\text{mix}} G_{\text{m}} = RT[x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}] + \Omega_{\text{AB}} x_{\text{A}} x_{\text{B}}$$

$$\Omega_{AB} = zN_A\omega_{AB}$$

A) Here we consider a combinatorial entropy of mixing and a binary enthalpy of mixing



B) A change in organization can also occur which leads to an additional entropic term

$$\Omega_{AB} = zN_A(\omega_{AB} - T\eta_{AB})$$
$$= zN_A\omega_{AB}\left(1 - \frac{T}{\tau}\right)$$

Where $\tau = \frac{\omega_{AB}}{\eta_{AB}}$, a critical temperature

$T_f = \Delta H_f/\Delta S_f$

Vibrational Contribution

With vibrational part $G_A = N_A \ln Z_A = \ln Z_A^{NA}$

$$Z = g\exp\left(-\frac{U}{k_B T}\right) = \left(\frac{N!}{N_A!N_B!}\right)\exp\left(-\frac{U_A + U_B}{k_B T}\right)$$

$$Z = gZ_A^{N_A} Z_B^{N_B} \exp\left(-\frac{U'}{k_B T}\right)$$

Z_A is vibrational partition function of A
U' is internal energy minus vibrational part

$$G \approx -k_B T \ln Z \approx U' - k_B T \ln g - k_B T \ln Z_A^{N_A} Z_B^{N_B}$$

G = H –TS so last term is the non-configurational (non-combinatorial) entropic terms

$$\Delta_{\text{mix}}^{\text{conf}} S = Lk_B \ln g = R \ln g$$

$$\Delta_{\text{mix}}^{\text{non-conf}} S_m = k_B L(\ln Z_A^{N_A} + \ln Z_B^{N_B}) \approx zLx_A x_B \eta_{AB}$$

Hildebrandt type parameter for vibrational contributions

Excess molar Gibbs energy of mixing for quasi-regular solution

$$\Delta_{\text{mix}}^{\text{exc}} G_{\text{m}} = zLx_{\text{A}}x_{\text{B}}(\omega_{\text{AB}} - T\eta_{\text{AB}})$$

G = H –TS so first term is enthalpic, second is entropic

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

τ is a characteristic temperature, when T = τ ideal solution behavior is seen

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

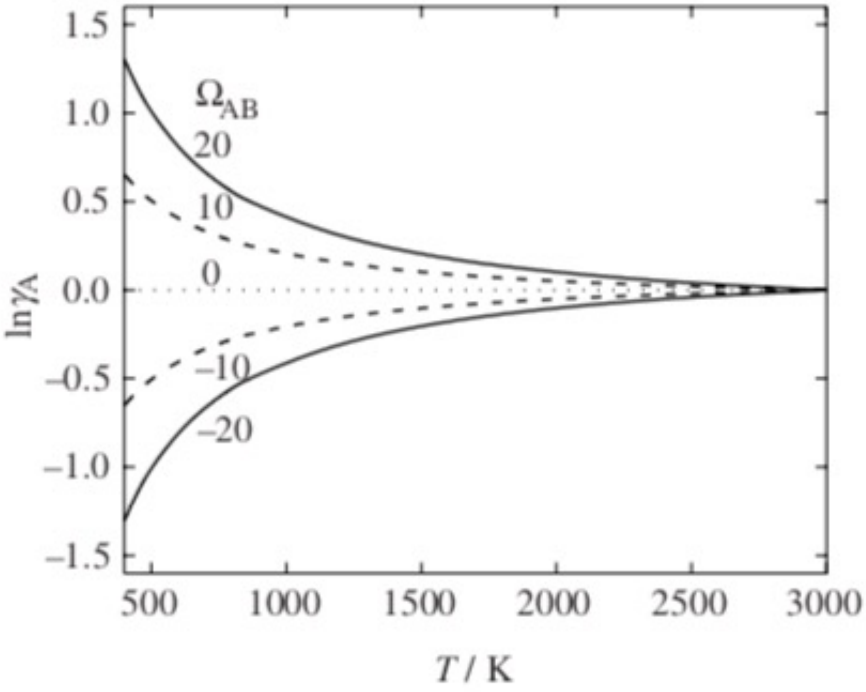


Figure 9.3 $\ln \gamma_A$ of a quasi-regular solution A–B for $x_A = x_B = 0.5$ as a function of temperature for selected values of Ω_{AB}.

For Positive Ω

$T = \tau$ Ideal
$T > \tau$ Mix
$T < \tau$ Demix

For Negative Ω

$T = \tau$ Ideal
$T > \tau$ Demix
$T < \tau$ Mix

For $\Omega = 0$
Ideal

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

$\chi \sim \Omega/kT$

$\chi \sim A + B/T$

A positive B positive Demix

A negative B negative Mix

A negative B positive UCST

A positive B negative LCST

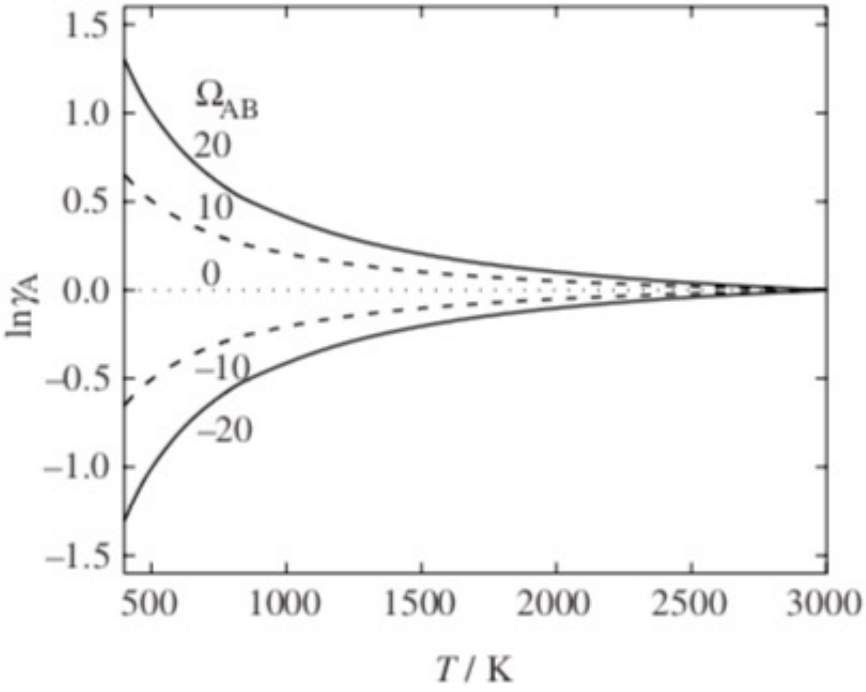


Figure 9.3 $\ln\gamma_A$ of a quasi-regular solution A–B for $x_A = x_B = 0.5$ as a function of temperature for selected values of Ω_{AB}.

For Positive Ω

$T = \tau$ Ideal

$T > \tau$ Mix

$T < \tau$ Demix

For Negative Ω

$T = \tau$ Ideal

$T > \tau$ Demix

$T < \tau$ Mix

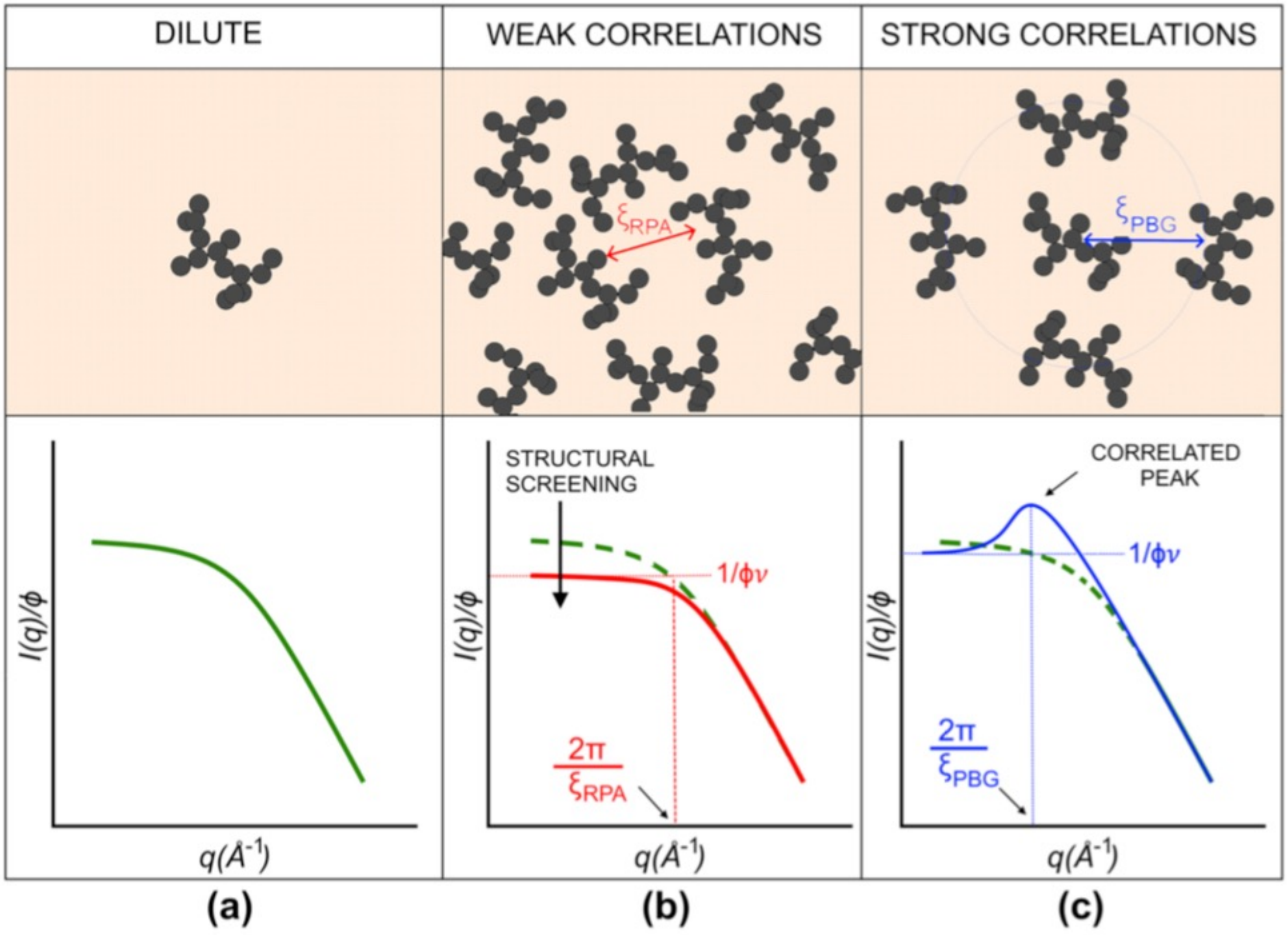
For $\Omega = 0$

Ideal

Mean Field (what we have considered) Interactions are random, there is no structuring

Specific Interactions Interactions are not random, there is identity between interacting pairs
Coulombic Interaction for instance

Correlations



Dilute: Ideal behavior, there are no interactions

Semi-dilute: weak or strong interactions are possible

With weak interactions the system can be treated with a "*mean field*". No correlation is observed, we can use the second virial coefficient and Hildebrand Model

With strong interactions we need to use detailed information about interactions, *correlation function* or other models

Virial Coefficient Approach for Weak Interactions (Mean Field)

Consider that two materials mix, A is matrix and B is diluent

B behaves like an ideal gas in A when B is dilute

$P = \rho RT$

The presence of B creates a pressure called an osmotic pressure Π

This pressure can be measured for particles in a solution such as proteins in water

At higher concentrations with a mean-field we can use a virial expansion to describe the pressure

$\Pi = \rho RT(1 + A_2 \rho + A_3 \rho^2 + A_4 \rho^3 + \ldots)$ Where A_2 is the second virial coefficient and reflects binary interactions in a mean field

By comparison with the Van der Waals equation of state where $v = 1/\rho$ $$P = \frac{RT}{(v-b)} - \frac{a}{v^2}$$

$A_2 = b - a/RT$ where "b" is the "excluded volume" and "a" is the attractive interaction potential for B's

$P/\rho = \text{energy} \sim \rho RT A_2 = \rho(RT b - a)$ $$\Delta_{\text{mix}}^{\text{exc}} G_{\text{m}} = x_{\text{A}} x_{\text{B}} \Omega_{\text{AB}} \left(1 - \frac{T}{\tau}\right)$$

Virial Coefficient Approach for Weak Interactions (Mean Field)

P/ρ = energy ~ $\rho RT A_2 = \rho(RT\, b - a)$

Dilute: Ideal behavior, there are no interactions

Semi-Dilute
$A_2 = 0$ Ideal/critical point
$A_2 > 0$ Miscible
$A_2 < 0$ Immiscible

$T = a/(bR)$ Ideal
$T < a/bT$ Miscible
$T > a/bT$ Immiscible

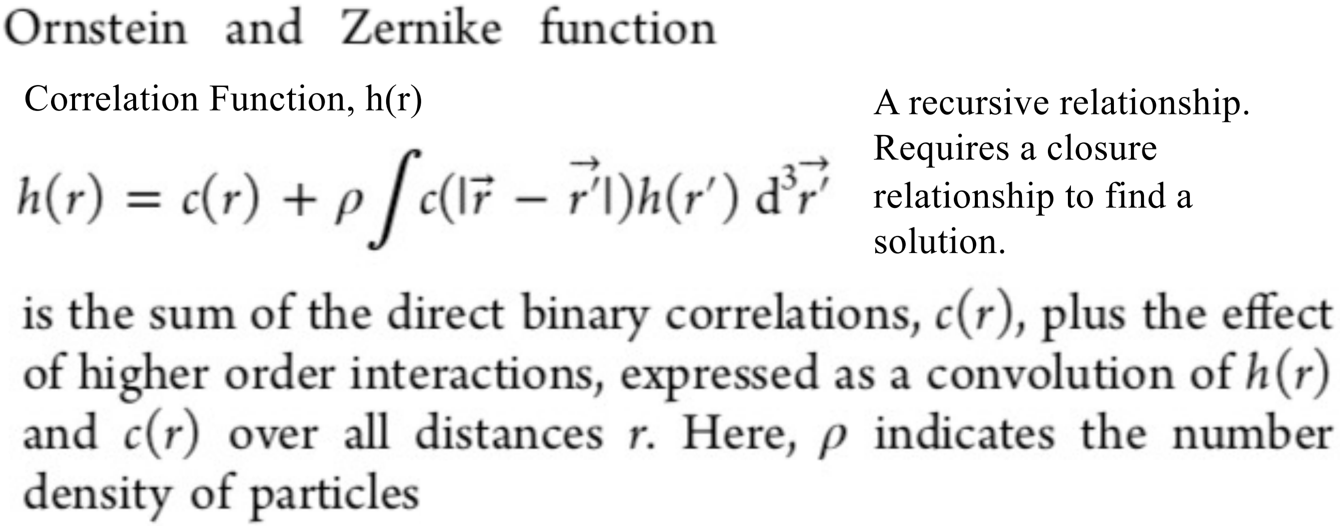
$$\Delta_{\text{mix}}^{\text{exc}} G_{\text{m}} = x_{\text{A}} x_{\text{B}} \Omega_{\text{AB}} \left(1 - \frac{T}{\tau}\right)$$

Dilute: Ideal behavior, there are no interactions

Semi-dilute
$\Omega = 0$ Ideal
$\Omega < 0$ Miscible
$\Omega > 0$ Immiscible

$T = \tau$ Ideal
$T > \tau$ Miscible
$T < \tau$ Immiscible

A. How to deal with more than (h(r) or g(r)) binary interactions c(r)



Ornstein and Zernike function

Correlation Function, h(r)

$$h(r) = c(r) + \rho \int c(|\vec{r} - \vec{r}'|)h(r')\, \mathrm{d}^3\vec{r}'$$

A recursive relationship. Requires a closure relationship to find a solution.

is the sum of the direct binary correlations, $c(r)$, plus the effect of higher order interactions, expressed as a convolution of $h(r)$ and $c(r)$ over all distances r. Here, ρ indicates the number density of particles

Closure relationships: Random Phase Approximation (RPA) ρ => 0
Percus-Yevick Approximation (complex)
Born-Green Approximation (simpler)

Strong Interactions (Specific Interactions)

Ornstein and Zernike function

Correlation Function, h(r)

$$h(r) = c(r) + \rho \int c(|\vec{r} - \vec{r}'|) h(r') \, d^3\vec{r}'$$

A recursive relationship.
Requires a closure relationship to find a solution.

Fourier transform of the OZ function; a convolution becomes a product.

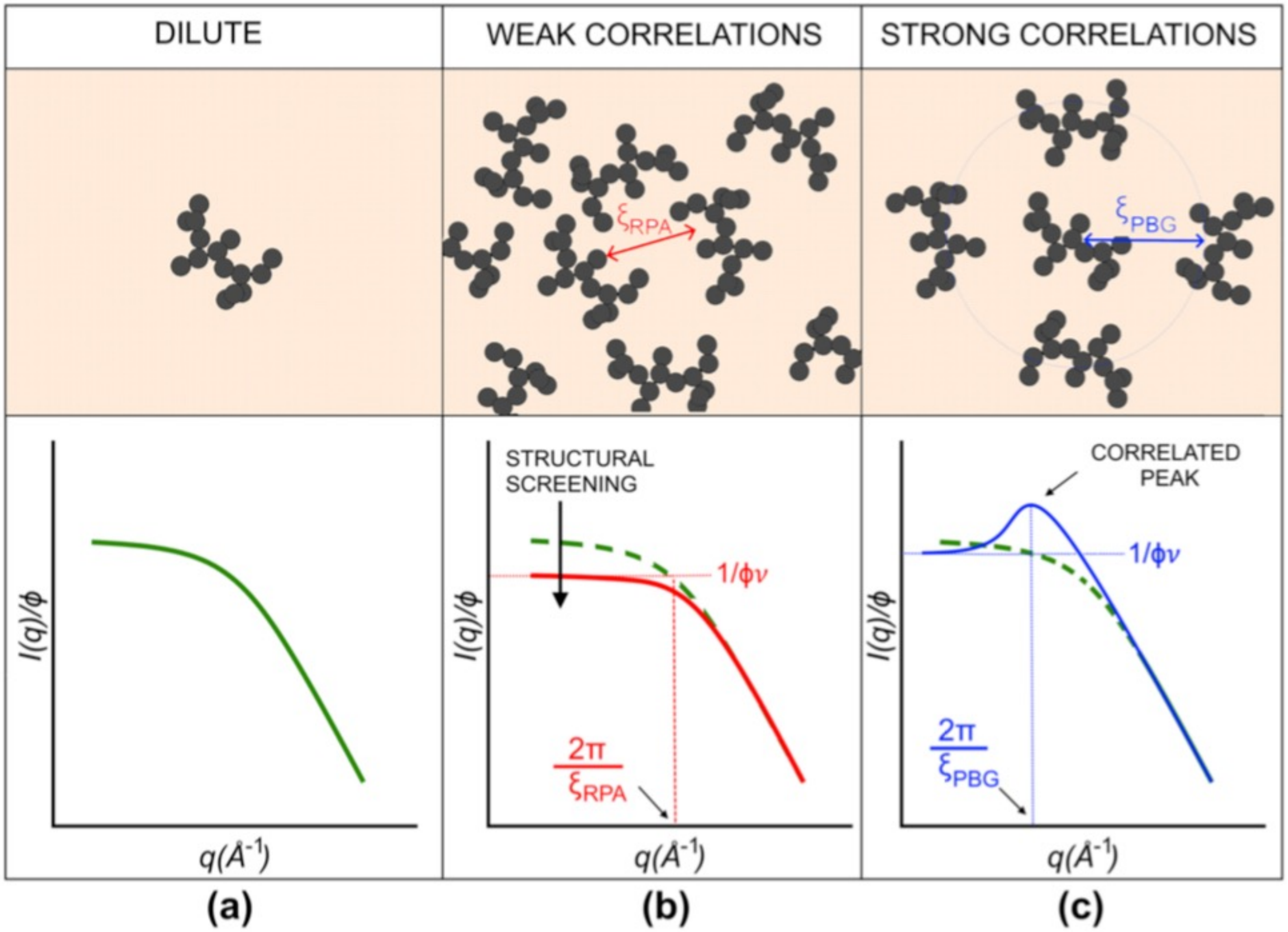
$$\hat{h}(\mathbf{k}) = \hat{c}(\mathbf{k}) + \rho \, \hat{h}(\mathbf{k}) \, \hat{c}(\mathbf{k})$$

$$\hat{c}(\mathbf{k}) = \frac{\hat{h}(\mathbf{k})}{1 + \rho \, \hat{h}(\mathbf{k})} \qquad \text{and} \qquad \hat{h}(\mathbf{k}) = \frac{\hat{c}(\mathbf{k})}{1 - \rho \, \hat{c}(\mathbf{k})}$$

Fourier Transform of a structural correlation function is the scattered intensity which is composed of a form factor $F^2(q)$ and a structure factor S(q). If we measure a dilute system with no correlations $I_0(q)$ and if
$I(q) = S(q) F^2(q) = S(q) I_0(q) (\phi/\phi_0)$

We can assume a model for c(k) and calculate $S(q) = I(q)/I_0(q) (\phi_0/\phi)$ Structure factor (the peak part of scattering)

Correlations



Dilute: Ideal behavior, there are no interactions

Semi-dilute: weak or strong interactions are possible

With weak interactions the system can be treated with a "*mean field*". No correlation is observed, we can use the second virial coefficient and Hildebrand Model

With strong interactions we need to use detailed information about interactions, *correlation function* or other models

Strong Interactions (Specific Interactions)

Ornstein and Zernike function

Correlation Function, h(r)

$$h(r) = c(r) + \rho \int c(|\vec{r} - \vec{r}'|)h(r')\, \mathrm{d}^3\vec{r}'$$

$$h(r_{12}) = c(r_{12}) + \rho \int d\mathbf{r}_3 c(r_{13})h(r_{23})$$

Percus-Yevick Approximation Closure.

$$c(r) = e^{-\beta w(r)} - e^{-\beta[w(r)-u(r)]}$$

Binary RDF = Total RDF - RDF with no binary interaction

g(r) or h(r)

Binary correlation $c(r) = g_{\text{total}}(r) - g_{\text{indirect}}(r)$

Correlation fun. without direct interactions $g_{\text{indirect}}(r) = \exp[-\beta(w(r) - u(r))]$

Use a function $y(r) = e^{\beta(u(r)-\omega(r))}$ then

$$c(r) = g(r) - y(r) = y(r)\left(e^{-\beta u(r)} - 1\right) = y(r)f(r)$$

g(r) = h(r)

Use this in the OZ equation yields the RDF with no binary interactions

$$y(r_{12}) = 1 + \rho \int f(r_{13})y(r_{13})h(r_{23})d\mathbf{r_3}$$

https://www.chemeurope.com/en/encyclopedia/Percus-Yevick_approximation.html

B. How to deal with more than binary interactions

BBGKY hierarchy (Bogoliubov-Born-Green-Kirkwood-Yvon)

$$f_N = f_N(\mathbf{q}_1 \dots \mathbf{q}_N, \mathbf{p}_1 \dots \mathbf{p}_N, t)$$

Probability density function in position, q_i, and momentum, p_i, per particle

$$\frac{\partial f_N}{\partial t} + \sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \frac{\partial f_N}{\partial \mathbf{q}_i} + \sum_{i=1}^{N} \mathbf{F}_i \frac{\partial f_N}{\partial \mathbf{p}_i} = 0$$

Liouville Equation

$$\mathbf{F}_i = -\sum_{j=1 \neq i}^{N} \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i} - \frac{\partial \Phi_i^{\text{ext}}}{\partial \mathbf{q}_i}$$

Force acting on particle ”i”

$\Phi_{ij}(\mathbf{q}_i, \mathbf{q}_j)$ is the pair potential

$\Phi^{\text{ext}}(\mathbf{q}_i)$ is the external-field potential

Integrate the Liouville Equation yields a chain of equations relating binary interactions with ternary interactions; ternary interactions with quaternary interactions etc. This cannot be solved unless a model is used for f_{s+1}.

Strong Interactions (Specific Interactions)

Ornstein and Zernike function

Correlation Function, h(r)

$$h(r) = c(r) + \rho \int c(|\vec{r} - \vec{r}'|)h(r')\, d^3\vec{r}'$$

A recursive relationship.
Requires a closure relationship to find a solution.

is the sum of the direct binary correlations, $c(r)$, plus the effect of higher order interactions, expressed as a convolution of $h(r)$ and $c(r)$ over all distances r. Here, ρ indicates the number density of particles/nanoaggregates.

Closure relationships: **Random Phase Approximation** (RPA) $\rho \Rightarrow 0$ $g(r) = h(r)$
Percus-Yevick Approximation; Born-Green Approximation

$$\frac{U}{N} = \frac{3}{2}k_B T + \frac{\rho}{2}\int d\mathbf{r}\, g(r)v(r).$$

$$P = \rho k_B T - \frac{\rho^2}{6}\int d\mathbf{r}\, g(r) r \frac{dv(r)}{dr}$$

$$P = \rho RT(1 + A_2 \rho + A_3 \rho^2 + A_4 \rho^3 + \ldots)$$

$$S(\mathbf{k}) = 1 + \rho \int d\mathbf{r}\,(g(\mathbf{r}) - 1)\exp(i\mathbf{k}.\mathbf{r}).$$

For a square well potential: $A_2 = 2\pi N_A \int_0^\infty \left(1 - \exp\left(-\frac{u}{kT}\right)\right) r^2 dr$

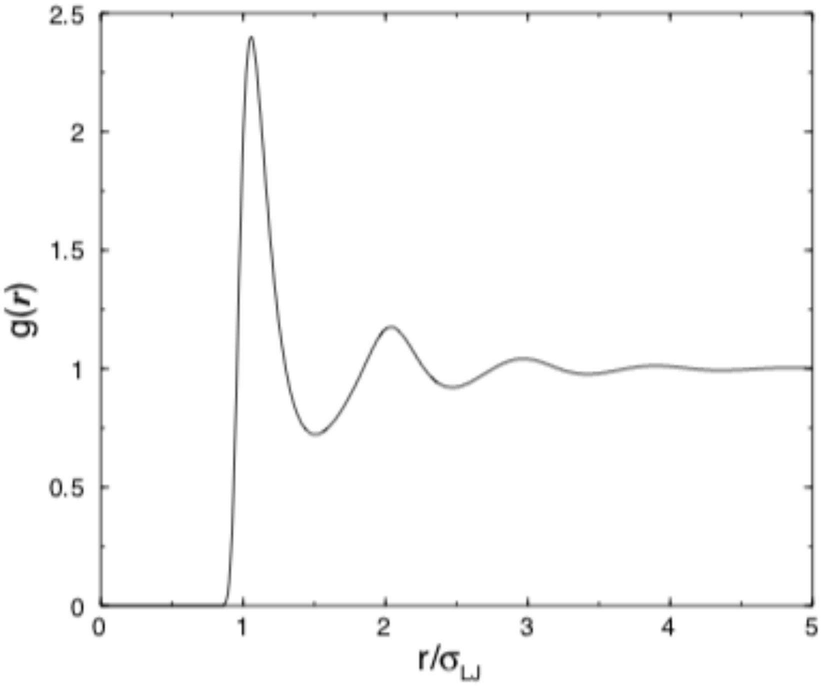


Figure 2.1: The radial distribution function for a Lennard-Jones fluid, at a reduced temperature $k_B T/\epsilon = 2.0$ and fluid density $\rho\sigma_{LJ}^3 = 0.8$, calculated using the Percus-Yevick closure to the Ornstein-Zernike equation.

$$S(\mathbf{k}) = 1 + \rho \int d\mathbf{r}\,(g(\mathbf{r}) - 1)\exp(i\mathbf{k}.\mathbf{r}).$$

$S(q) = \phi_0 I(q)/(\phi I_0(q))$
Structure factor

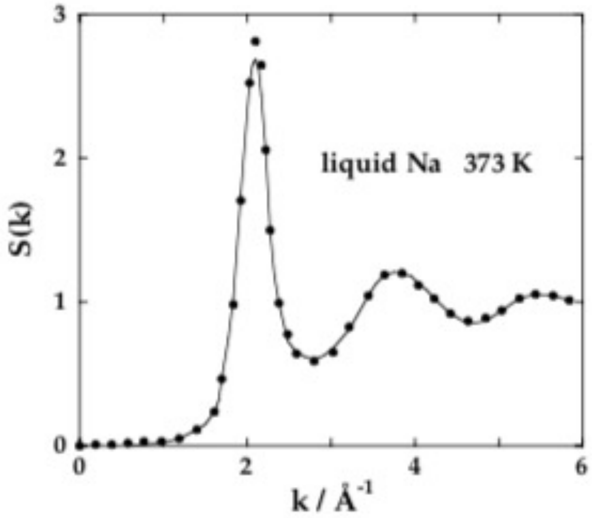
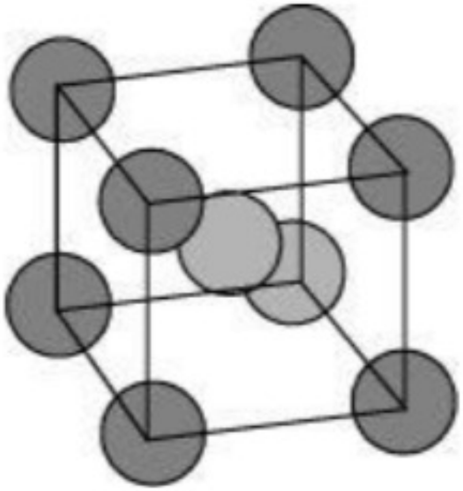
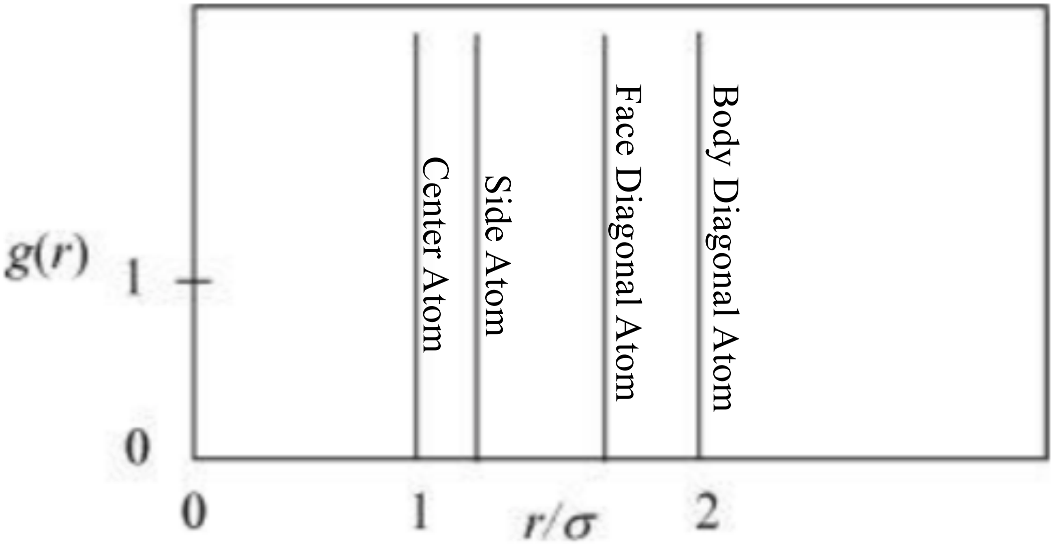


FIG. 3.2. Structure factor of liquid sodium near the normal melting temperature. The points are experimental x-ray scattering results[8] and the curve is obtained from a Monte Carlo calculation[9] for the r^{-4} potential under the same thermodynamic conditions.

Strong Interactions





Strong Interactions

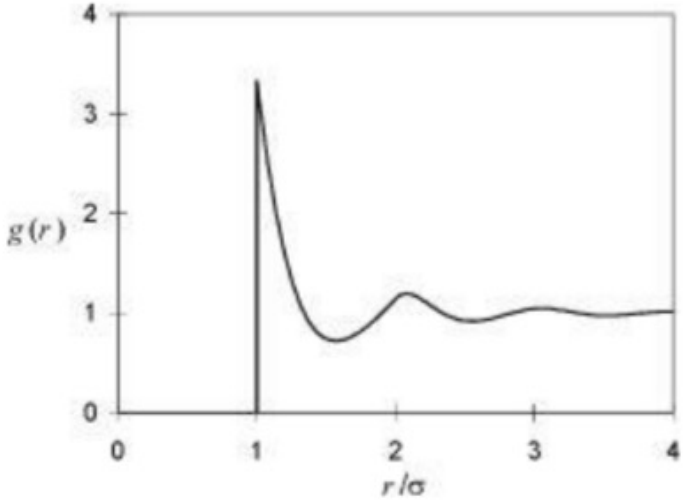
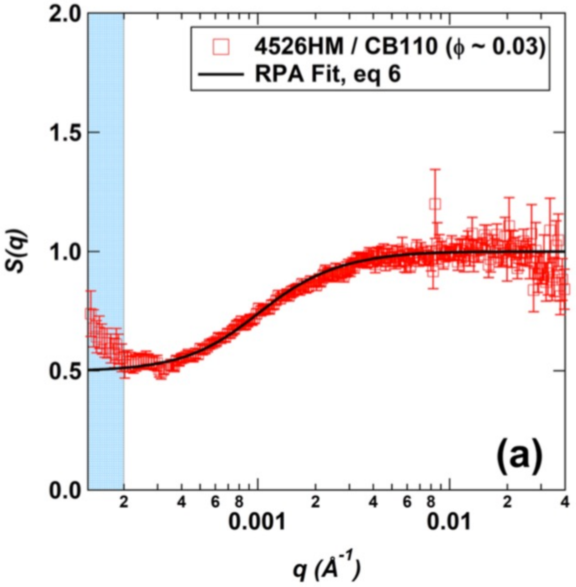
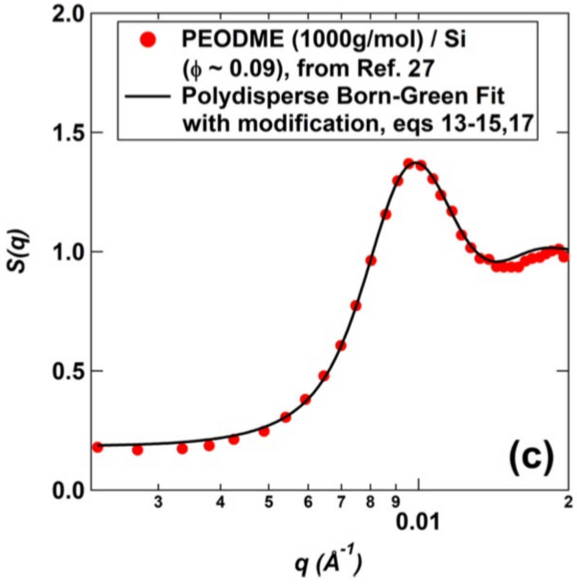


Figure 7.13. The radial distribution function for the hard-sphere fluid at a packing fraction of bρ = 0.4.

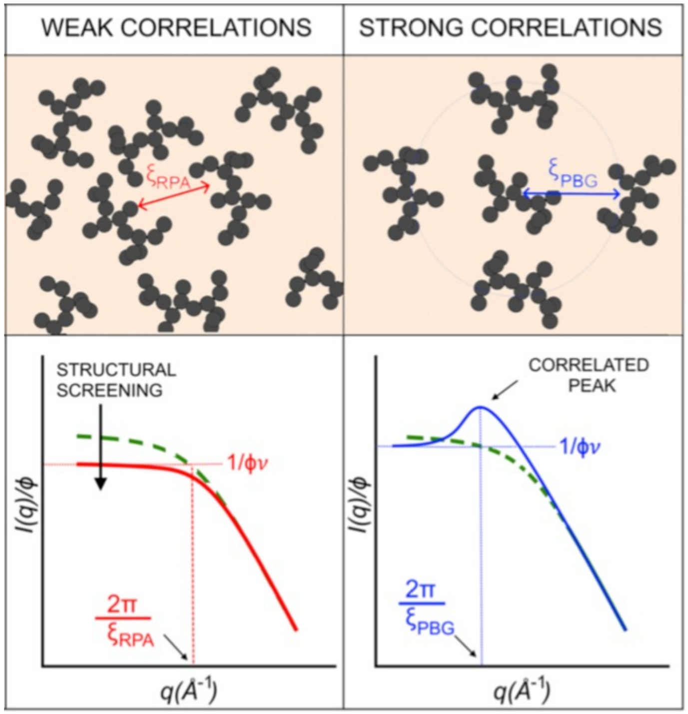
Weak Interactions



Strong Interactions



$$S(\mathbf{k}) = 1 + \rho \int \mathrm{d}\mathbf{r}\,(g(\mathbf{r}) - 1)\exp(i\mathbf{k}.\mathbf{r}).$$



$$\mathbf{I(q,\phi) = I(q,\phi_0)\,S(q,\phi)\,\phi/\phi_0}$$

$$\mathbf{A_2 \sim \nu}$$

Models for Interactions Based on a Mean Field Approach

There are many models, the book mentions the Quasi-Chemical Model which is used in Calphad and ThermoCalc
Elliot and Lira give a reasonable discussion of various models in Chapters 7, 11, 12
Chapter 7
<u>Van der Waals</u>: Includes excluded volume, ”b”, and attractive interaction “a”

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{\rho RT}{1-b\rho} - a\rho^2 \qquad a \equiv \frac{27}{64}\frac{R^2T_c^2}{P_c} \quad ; \quad b \equiv \frac{RT_c}{8P_c}$$

<u>Peng-Robinson</u>: Attractive interaction term is more complicated and includes the acentric factor ω. ”a” has a temperature dependence.

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

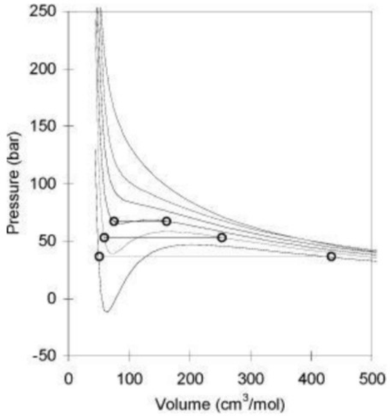
$$a \equiv a_c\alpha; \quad a_c \equiv 0.45723553\frac{R^2T_c^2}{P_c} \qquad b \equiv 0.07779607R\frac{T_c}{P_c}$$

$$\alpha \equiv [1+\kappa(1-\sqrt{T_r})]^2 \qquad \kappa \equiv 0.37464 + 1.54226\omega - 0.26992\omega^2$$

These equations have a cubic form:

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0$$

$$A \equiv aP/R^2T^2$$
$$B \equiv bP/RT$$



Hard core model for Van der Waals

$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{\rho RT}{1-b\rho} - a\rho^2$ Z = PV/RT = 1/(1-bρ) – (a/RT) ρ

Hard core no attractive interaction, $\eta_P = b\rho$

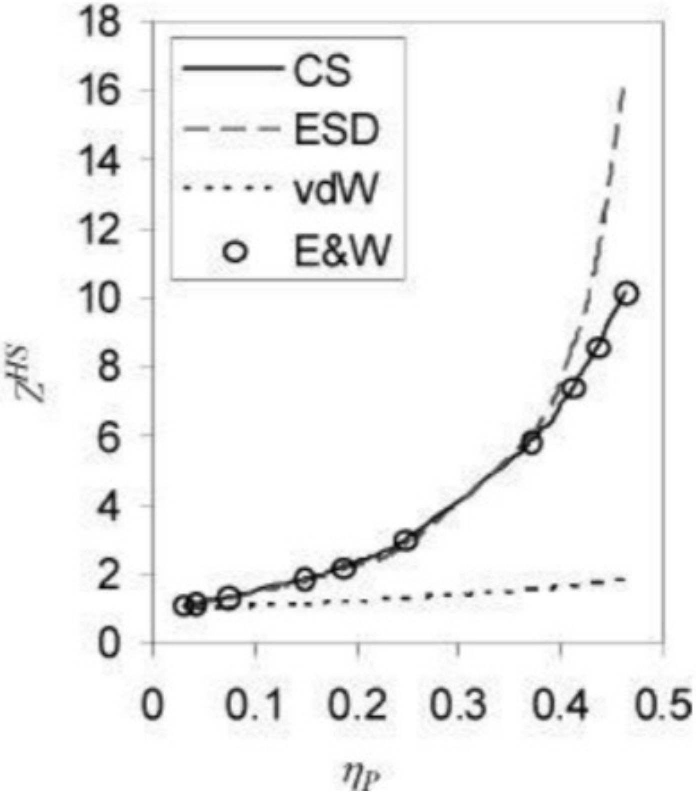
$Z^{HS} = 1/(1 - \eta_P)$; the van der Waals model

$Z^{HS} = (1 + 2\eta_P)/(1 - 2\eta_P)$; the Scott model

$Z^{HS} = 1 + 4\eta_P/(1 - 1.9\eta_P)$; the ESD model

$Z^{HS} = 1 + 4\eta_P(1 - \eta_P/2)/(1 - \eta_P)^3$; the Carnahan-Starling model

Compare with Molecular Dynamics (o) for Hard Spheres E&W



Chapter 11 Elliot and Lira

Margulis one-parameter Model

$$\frac{G^E}{RT} = A_{12}x_1x_2$$

$$\ln\gamma_i = A_{12}(1-x_i)^2$$

Hildebrand Model

$$\Delta_{\text{mix}}^{\text{exc}}G_{\text{m}} = x_{\text{A}}\,x_{\text{B}}\,\Omega_{\text{AB}}$$

Margulis acid-base Model

acidity parameter, α, and **basicity parameter,** β.

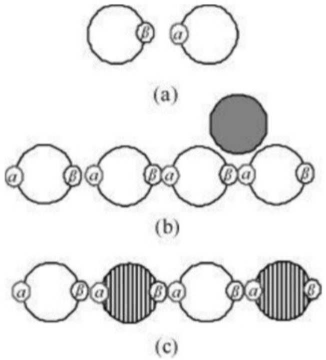


Figure 11.7. Observations about complexation. (a) A mixture of acid with base suggests favorable interactions, as in acetone + chloroform. (b) Hydrogen bonding leads to unfavorable interactions when one component associates strongly and the other is inert, as in isooctane + water. (c) Hydrogen bonding solutions can also be ideal solutions if both components have similar acidity and basicity, as in methanol + ethanol.

$$A_{12} = (\alpha_2 - \alpha_1)(\beta_2 - \beta_1)(V_1 + V_2)/(4RT)$$

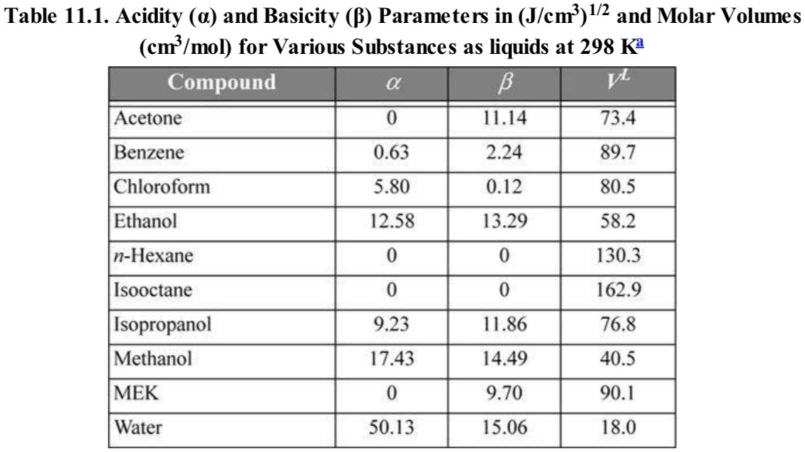


Table 11.1. Acidity (α) and Basicity (β) Parameters in $(\text{J/cm}^3)^{1/2}$ and Molar Volumes (cm^3/mol) for Various Substances as liquids at 298 K[a]

Compound	α	β	V^L
Acetone	0	11.14	73.4
Benzene	0.63	2.24	89.7
Chloroform	5.80	0.12	80.5
Ethanol	12.58	13.29	58.2
n-Hexane	0	0	130.3
Isooctane	0	0	162.9
Isopropanol	9.23	11.86	76.8
Methanol	17.43	14.49	40.5
MEK	0	9.70	90.1
Water	50.13	15.06	18.0

Redlich-Kister Model (asymmetric phase diagrams)

$$\frac{G^E}{RT} = x_1x_2(B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2 + \dots)$$

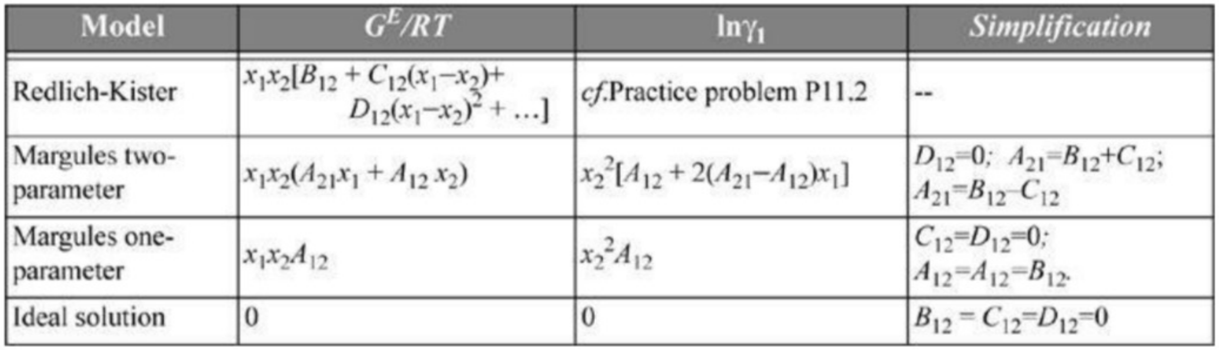
Two-parameter Margulis Model

$$\frac{G^E}{RT} = x_1x_2(A_{21}x_1 + A_{12}x_2)$$

$A_{21} = B_{12} + C_{12}, A_{21} = B_{12} - C_{12}$ $D_{12} = 0$

$$\ln\gamma_1 = x_2^2\ [A_{12} + 2(A_{21} - A_{12})x_1] \qquad \ln\gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2]$$

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



Model	G^E/RT	$\ln\gamma_1$	*Simplification*
Redlich-Kister	$x_1x_2[B_{12} + C_{12}(x_1-x_2) + D_{12}(x_1-x_2)^2 + \dots]$	*cf.*Practice problem P11.2	--
Margules two-parameter	$x_1x_2(A_{21}x_1 + A_{12}x_2)$	$x_2^2[A_{12} + 2(A_{21}-A_{12})x_1]$	$D_{12}=0;\ A_{21}=B_{12}+C_{12};$ $A_{21}=B_{12}-C_{12}$
Margules one-parameter	$x_1x_2A_{12}$	$x_2^2A_{12}$	$C_{12}=D_{12}=0;$ $A_{12}=A_{12}=B_{12}.$
Ideal solution	0	0	$B_{12} = C_{12}=D_{12}=0$

Van der Waals Models

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

$$b = \sum_i x_i b_i \qquad a = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22} = \sum\sum x_i x_j a_{ij}$$

$$a_{12} = (1 - k_{12})(a_{11} a_{22})^{1/2}$$

Consider 11, 22, and 12 interactions

Regular Solution Models

$$G^E = U^E + PV^E - TS^E,$$

Ignore PV which is small G ~ A

If V ~ S ~ 0 then G = U
This is a regular solution

-SUV
 H A
-pGT

G = H – ST
H = U + PV
So
G = U + PV – TS
(A = U – TS)

For Symmetric Mean-Field Models there are two main problems, organizational entropy change on mixing and changes in volume on mixing

$$U^E = x_1 \frac{a_{11}}{V_1} + x_2 \frac{a_{22}}{V_2} - \left(\frac{x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}}{x_1 V_1 + x_2 V_2} \right)$$

Van Laar Model

Consider Lattice sites do not have the same volume, V_1, V_2

$$U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} Q \quad \text{where} \quad Q \equiv \left(\frac{a_{11}}{V_1^2} + \frac{a_{22}}{V_2^2} - 2\frac{a_{12}}{V_1 V_2} \right)$$

Van Laar Model

$$U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} Q \quad \text{where} \quad Q \equiv \left(\frac{a_{11}}{V_1^2} + \frac{a_{22}}{V_2^2} - 2\frac{a_{12}}{V_1 V_2} \right)$$

Include asymmetry

$$A_{12} = \frac{QV_1}{RT}; \quad A_{21} = \frac{QV_2}{RT}; \quad \frac{A_{12}}{A_{21}} = \frac{V_1}{V_2}$$

$$\frac{G^E}{RT} = \frac{U^E}{RT} = \frac{A_{12} A_{21} x_1 x_2}{(x_1 A_{12} + x_2 A_{21})}$$

$$\ln \gamma_1 = \frac{A_{12}}{\left[1 + \frac{A_{12} x_1}{A_{21} x_2}\right]^2} \qquad \ln \gamma_2 = \frac{A_{21}}{\left[1 + \frac{A_{21} x_2}{A_{12} x_1}\right]^2}$$

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

Scatchard-Hildebrand Theory

$a_{12} = (1 - k_{12})(a_{11}a_{22})^{1/2}$

Theory based on <u>Volume Fraction</u> rather than Mole Fraction

$k_{12} = 0 \qquad a_{12} = \sqrt{a_{11}a_{22}}$

$$U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2}\left(\frac{a_{11}}{V_1^2} + \frac{a_{22}}{V_2^2} - 2\sqrt{\frac{a_{11}}{V_1^2}\frac{a_{22}}{V_2^2}}\right) = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2}\left(\frac{\sqrt{a_{11}}}{V_1} - \frac{\sqrt{a_{22}}}{V_2}\right)^2$$

$$U^E = \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 (x_1 V_1 + x_2 V_2)$$

δ = **Solubility Parameter**

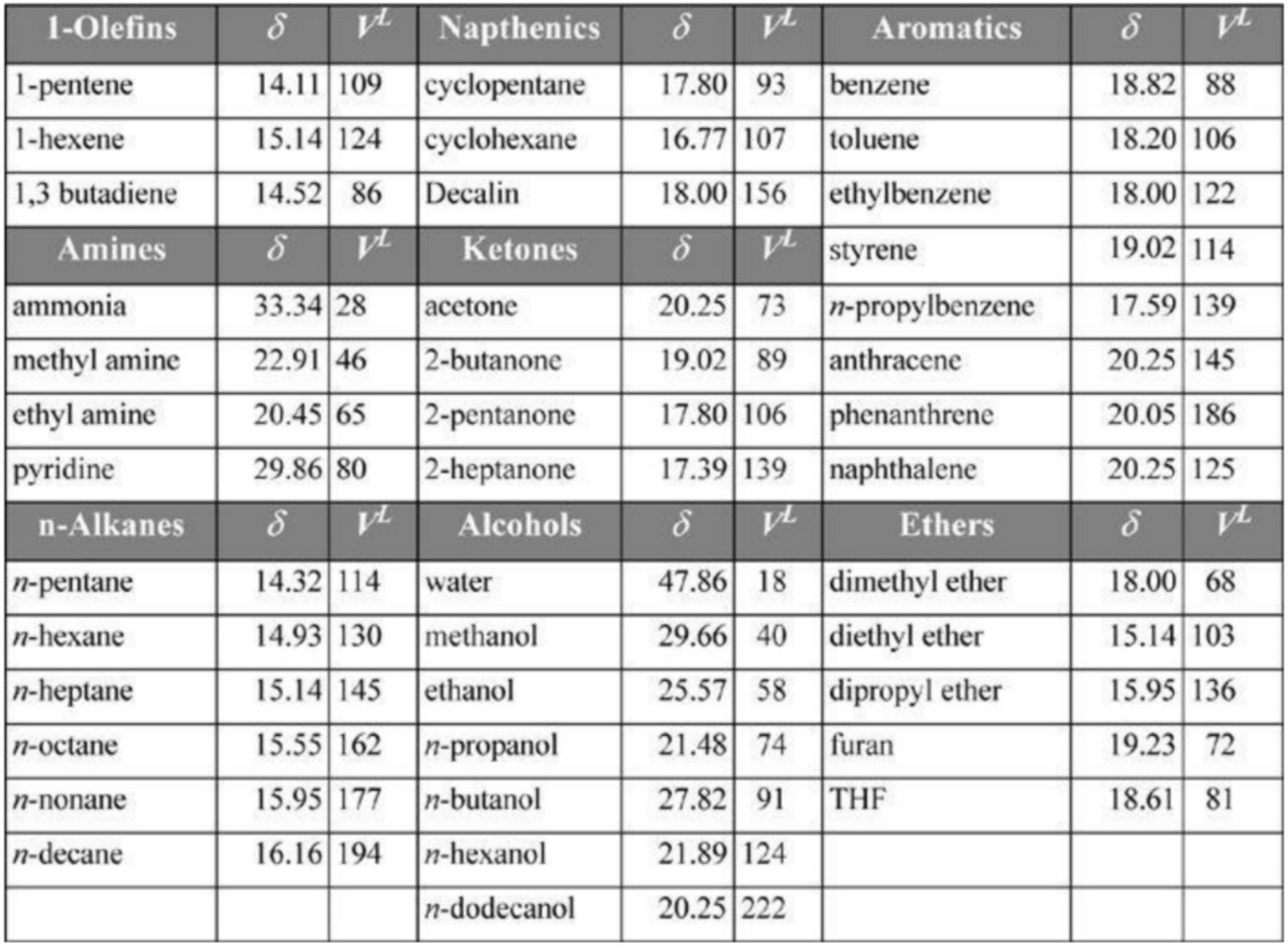
$\Phi_i \equiv x_i V_i / \sum x_i V_i$ **Volume Fraction**

U = H – PV

$\delta_i \equiv \sqrt{a_{ii}} / V_i \qquad \delta_i \equiv \sqrt{\frac{\Delta U_i^{vap}}{V_i}} = \sqrt{\frac{\Delta H_i^{vap} - RT}{V_i}}$

Cohesive Energy Density

Table 12.1. Solubility Parameters in $(J/cm^3)^{1/2}$ and Molar Volumes (cm^3/mol) for Various Substances as liquids at 298 K



1-Olefins	δ	V^L	**Napthenics**	δ	V^L	**Aromatics**	δ	V^L
1-pentene	14.11	109	cyclopentane	17.80	93	benzene	18.82	88
1-hexene	15.14	124	cyclohexane	16.77	107	toluene	18.20	106
1,3 butadiene	14.52	86	Decalin	18.00	156	ethylbenzene	18.00	122
Amines	δ	V^L	**Ketones**	δ	V^L	styrene	19.02	114
ammonia	33.34	28	acetone	20.25	73	*n*-propylbenzene	17.59	139
methyl amine	22.91	46	2-butanone	19.02	89	anthracene	20.25	145
ethyl amine	20.45	65	2-pentanone	17.80	106	phenanthrene	20.05	186
pyridine	29.86	80	2-heptanone	17.39	139	naphthalene	20.25	125
n-Alkanes	δ	V^L	**Alcohols**	δ	V^L	**Ethers**	δ	V^L
n-pentane	14.32	114	water	47.86	18	dimethyl ether	18.00	68
n-hexane	14.93	130	methanol	29.66	40	diethyl ether	15.14	103
n-heptane	15.14	145	ethanol	25.57	58	dipropyl ether	15.95	136
n-octane	15.55	162	*n*-propanol	21.48	74	furan	19.23	72
n-nonane	15.95	177	*n*-butanol	27.82	91	THF	18.61	81
n-decane	16.16	194	*n*-hexanol	21.89	124			
			n-dodecanol	20.25	222			

Scatchard-Hildebrand Theory

$$G^E = U^E = \Phi_1\Phi_2(\delta_1 - \delta_2)^2(x_1V_1 + x_2V_2)$$

$$RT\ln\gamma_1 = V_1\Phi_2^2\,(\delta_1 - \delta_2)^2$$

$$RT\ln\gamma_2 = V_2\Phi_1^2\,(\delta_1 - \delta_2)^2$$

Scatchard-Hildebrand with Adjustable Parameter $a_{12} = (1 - k_{12})(a_{11}a_{22})^{1/2}$

$$a_{12} = \sqrt{a_{11}a_{22}}\,(1-k_{12})$$

$$RT\ln\gamma_1 = V_1\Phi_2^2\,[(\delta_1 - \delta_2)^2 + 2k_{12}\delta_1\delta_2]$$

$$RT\ln\gamma_2 = V_2\Phi_1^2\,[(\delta_1 - \delta_2)^2 + 2k_{12}\delta_1\delta_2]$$

Flory-Huggins Model for Polymers

Point Masses have no volume
Real molecules have excluded volume
Only the available volume can be used to mix so the entropy of mixing should be modified

$$\bar{S}_i - S_i = R\ln\frac{V_{f,\,mixture}}{V_{f,\,i}} = R\ln\frac{(n_1V_1 + n_2V_2)\varpi}{(n_iV_i)\varpi} = -R\ln\Phi_i$$

$$\Delta S_{mix} = S - \sum_i x_iS_i = \sum_i x_i(\bar{S}_i - S_i) = -R\sum_i x_i\ln\Phi_i$$

ω accounts for the available volume

$$G^E = H^E - TS^E = RT(x_1\ln(\Phi_1/x_1) + x_2\ln(\Phi_2/x_2))$$

$$G^E = H^E - TS^E = RT(x_1\ln(\Phi_1/x_1) + x_2\ln(\Phi_2/x_2)) + \Phi_1\Phi_2(\delta_1 - \delta_2)^2(x_1V_1 + x_2V_2)$$

$$\ln\gamma_1 = \ln(\Phi_1/x_1) + (1 - \Phi_1/x_1) + \frac{V_1}{RT}\Phi_2^2\,(\delta_1 - \delta_2)^2$$

$$\ln\gamma_2 = \ln(\Phi_2/x_2) + (1 - \Phi_2/x_2) + \frac{V_2}{RT}\Phi_1^2(\delta_1 - \delta_2)^2$$

Flory-Huggins Model for Polymers

$$G^E = H^E - TS^E = RT(x_1 \ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2)) + \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 (x_1 V_1 + x_2 V_2)$$

$$G^E = RT(x_1 \ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2)) + \Phi_1 \Phi_2 (x_1 + x_2 r)\chi RT$$

$$\chi \equiv V_1(\delta_1 - \delta_1)^2/RT.$$

$r = V_2/V_1$ 2 is polymer

Account for Hydrogen Bonding

MOSCED Model (MOdified Separation of Cohesive Energy Density)

$$\ln\gamma_2^{\infty} = \frac{V_2}{RT}\left[(\lambda_2-\lambda_1)^2 + q_1^2 q_2^2\frac{(\tau_2^T-\tau_1^T)^2}{\psi_1} + \frac{(\alpha_2^T-\alpha_1^T)(\beta_2^T-\beta_1^T)}{\xi_1}\right] + d_{12}$$

$$d_{12} = 1-\left(\frac{V_2}{V_1}\right)^{aa} + aa\ln\left(\frac{V_2}{V_1}\right)$$

Calculates the infinite dilution activity coefficient

This is used in another model to fit parameters at infinite dilution to the MOSCED model

Such as Redlich-Kister, van Laar, or below

λ_i dispersion factor

τ_i is the polarity

q_i is .9 to 1

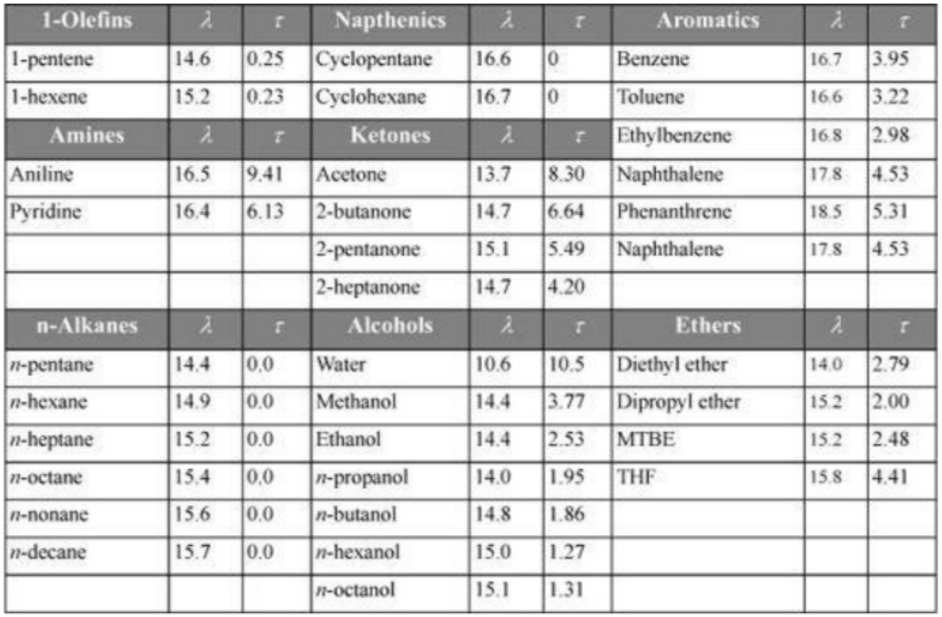
$$aa = 0.953 - 0.002314((\tau_2^T)^2 + \alpha_2^T\beta_2^T)$$

$$\alpha_i^T = \alpha_i\left(\frac{293}{T(K)}\right)^{0.8};\beta_i^T = \beta_i\left(\frac{293}{T(K)}\right)^{0.8};\tau_i^T = \tau_i\left(\frac{293}{T(K)}\right)^{0.4}$$

$$\psi_1 = POL + 0.002629\alpha_1^T\beta_1^T$$

$$\xi_1 = 0.68(POL-1) + [3.24 - 2.4\exp(-0.002687(\alpha_1\beta_1)^{1.5})]^{(293/T)^2}$$

$$POL = 1 + 1.15q_1^4[1-\exp(-0.002337(\tau_1^T)^3)]$$



1-Olefins	λ	τ	Napthenics	λ	τ	Aromatics	λ	τ
1-pentene	14.6	0.25	Cyclopentane	16.6	0	Benzene	16.7	3.95
1-hexene	15.2	0.23	Cyclohexane	16.7	0	Toluene	16.6	3.22
Amines	λ	τ	**Ketones**	λ	τ	Ethylbenzene	16.8	2.98
Aniline	16.5	9.41	Acetone	13.7	8.30	Naphthalene	17.8	4.53
Pyridine	16.4	6.13	2-butanone	14.7	6.64	Phenanthrene	18.5	5.31
			2-pentanone	15.1	5.49	Naphthalene	17.8	4.53
			2-heptanone	14.7	4.20			
n-Alkanes	λ	τ	**Alcohols**	λ	τ	**Ethers**	λ	τ
n-pentane	14.4	0.0	Water	10.6	10.5	Diethyl ether	14.0	2.79
n-hexane	14.9	0.0	Methanol	14.4	3.77	Dipropyl ether	15.2	2.00
n-heptane	15.2	0.0	Ethanol	14.4	2.53	MTBE	15.2	2.48
n-octane	15.4	0.0	*n*-propanol	14.0	1.95	THF	15.8	4.41
n-nonane	15.6	0.0	*n*-butanol	14.8	1.86			
n-decane	15.7	0.0	*n*-hexanol	15.0	1.27			
			n-octanol	15.1	1.31			

Account for Hydrogen Bonding

SSCED Model (Simplified Separation of Cohesive Energy Density)

$$G^E = V\Phi_1\Phi_2[(\delta_2' - \delta_1')^2 + 2k_{12}\delta_2'\delta_1']$$

$$RT\ln\gamma_k = V_k(1-\Phi_k)^2[(\delta_2' - \delta_1')^2 + 2k_{12}\delta_2'\delta_1']$$

$$(\delta_i')^2 = \delta_i^2 - 2\alpha_i\beta_i$$

$$k_{12} = \frac{(\alpha_2-\alpha_1)(\beta_2-\beta_1)}{4\delta_2'\delta_1'}$$

Local Clustering Models

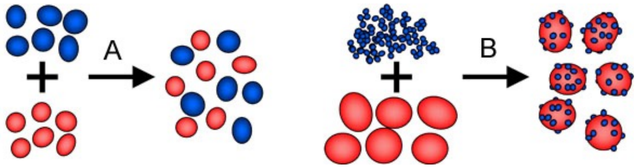


Table 13.1. Nomenclature for Local Composition Variables

Composition around a "1" Molecule	Composition around a "2" Molecule
x_{21} – mole fraction of "2's" around "1"	x_{12} – mole fraction of "1's" around "2"
x_{11} – mole fraction of "1's" around "1"	x_{22} – mole fraction of "2's" around "2"
local mole balance, $x_{11} + x_{21} = 1$	local mole balance, $x_{22} + x_{12} = 1$

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1}\Omega_{21}$$

$$\frac{x_{12}}{x_{22}} = \frac{x_1}{x_2}\Omega_{12}$$

if $\Omega_{12} = \Omega_{21} = 1$, the solution is random

$$x_{11} = \frac{x_1}{x_1 + x_2\Omega_{21}} \qquad x_{21} = \frac{x_2\Omega_{21}}{x_1 + x_2\Omega_{21}}$$

$$x_{22} = \frac{x_2}{x_1\Omega_{12} + x_2} \qquad x_{12} = \frac{x_1\Omega_{12}}{x_1\Omega_{12} + x_2}$$

Local Clustering Models

$$(M-M^{ig}) = x_1(M-M^{ig})^{(1)} + x_2(M-M^{ig})^{(2)}$$

$$U-U^{ig} = \frac{N_A}{2}[x_1 N_{c,1}(x_{11}\varepsilon_{11} + x_{21}\varepsilon_{21}) + x_2 N_{c,2}(x_{12}\varepsilon_{12} + x_{22}\varepsilon_{22})]$$

$N_{c,j}$ is the coordination number

$$(U-U^{ig})^{(1)} = \frac{N_A}{2}N_{c,1}(x_{11}\varepsilon_{11} + x_{21}\varepsilon_{21}) \text{ and } (U-U^{ig})^{(2)} = \frac{N_A}{2}N_{c,2}(x_{12}\varepsilon_{12} + x_{22}\varepsilon_{22})$$

For Pure components

$$(U-U^{ig})^{is} = x_1(U-U^{ig})_{pure1} + x_2(U-U^{ig})_{pure2} = \frac{N_A}{2}[x_1 N_{c,1}\varepsilon_{11} + x_2 N_{c,2}\varepsilon_{22}]$$

$$U^E = U-U^{is} = \frac{N_A}{2}[x_1 N_{c,1}((x_{11}\varepsilon_{11} + x_{21}\varepsilon_{21}) - \varepsilon_{11}) + x_2 N_{c,2}((x_{12}\varepsilon_{12} + x_{22}\varepsilon_{22}) - \varepsilon_{22})]$$

Local Clustering Models

$$U^E = U - U^{is} = \frac{N_A}{2}[x_1 N_{c,1}((x_{11}\varepsilon_{11} + x_{21}\varepsilon_{21}) - \varepsilon_{11}) + x_2 N_{c,2}((x_{12}\varepsilon_{12} + x_{22}\varepsilon_{22}) - \varepsilon_{22})]$$

$$(x_{11} - 1)\varepsilon_{11} = -x_{21}\varepsilon_{11}$$

$$U^E = \frac{N_A}{2}[x_1 x_{21} N_{c,1}(\varepsilon_{21} - \varepsilon_{11}) + x_2 x_{12} N_{c,2}(\varepsilon_{12} - \varepsilon_{22})]$$

$$x_{21} = \frac{x_2\Omega_{21}}{x_1 + x_2\Omega_{21}}$$

$$U^E = \frac{N_A}{2}\left[\frac{x_1 x_2 \Omega_{21} N_{c,1}(\varepsilon_{21} - \varepsilon_{11})}{x_1 + x_2\Omega_{21}} + \frac{x_2 x_1 \Omega_{12} N_{c,2}(\varepsilon_{12} - \varepsilon_{22})}{x_1\Omega_{12} + x_2}\right]$$

To obtain Helmholz Free energy use $\int_{\infty}^{T} d\left(\frac{A^E}{RT}\right) = \frac{A^E}{RT} - \frac{A^E}{RT}\bigg|_{\infty} = -\int_{\infty}^{T} \frac{U^E}{RT^2} dT$

Need an expression for Ω as a function of temperature

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1}\Omega_{21}$$

$$\frac{x_{12}}{x_{22}} = \frac{x_1}{x_2}\Omega_{12}$$

Example 6.7. The relation between Helmholtz energy and internal energy

Express the following in terms of U, H, S, G, and their derivatives: $(\partial(A/RT)/\partial T)_V$.

Solution

Applying the product rule,

$$\left(\frac{\partial(A/RT)}{\partial T}\right)_V = \frac{1}{RT}\left(\frac{\partial A}{\partial T}\right)_V - \frac{A}{RT^2}$$

Applying Eqn. 6.6 and the definition of A,

$$\left(\frac{\partial(A/RT)}{\partial T}\right)_V = \frac{-S}{RT} - \frac{(U-TS)}{RT^2} = \frac{-U}{RT^2}$$

Rearranging, and introducing a common definition $\beta \equiv 1/kT$,

$$\frac{U}{RT} = \left(-\frac{T\partial(A/RT)}{\partial T}\right)_V = \left(\frac{\beta\partial(A/RT)}{\partial\beta}\right)_V$$

Wilson’s Equation

Temperature dependence of Ω

$$\Omega_{ij} = \Lambda_{ji} = \frac{V_i}{V_j}\exp\left(\frac{-N_A N_{c,j}(\varepsilon_{ij} - \varepsilon_{jj})}{2RT}\right) = \frac{V_i}{V_j}\exp\left(\frac{-A_{ji}}{RT}\right)$$

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1}\Omega_{21}$$

$$\frac{x_{12}}{x_{22}} = \frac{x_1}{x_2}\Omega_{12}$$

Temperature dependence of Ω

$$\frac{A^E}{RT} = -x_1 \ln(\Phi_1 + \Phi_2 \exp(-A_{12}/RT)) - x_2 \ln(\Phi_1 \exp(-A_{21}/RT) + \Phi_2) + \left.\frac{A^E}{RT}\right|_{\infty}$$

Two activation energies 1 around 2 and 2 around 1

Assume G ~ A (PV is insignificant)

Break G into a residual (energetic) contribution that vanishes at T => ∞ and a combinatorial (size and shape) contribution

Wilson's Equation Temperature dependence of Ω

$$\frac{A^E}{RT} = -x_1 \ln(\Phi_1 + \Phi_2 \exp(-A_{12}/RT)) - x_2 \ln(\Phi_1 \exp(-A_{21}/RT) + \Phi_2) + \left.\frac{A^E}{RT}\right|_\infty$$

Two activation energies 1 around 2 and 2 around 1

Assume G ~ A (PV is insignificant)

Break G into a residual (energetic) contribution that vanishes at T => ∞
and a combinatorial (size and shape) contribution

$$(G^E/RT)^{RES} = -x_1\ln(\Phi_1 + \Phi_2\exp(-A_{12}/RT)) - x_2\ln(\Phi_1\exp(-A_{21}/RT) + \Phi_2)$$

$$G^E/(RT)\Big|_\infty = (G^E/RT)^{COMB} = x_1\ln(\Phi_1/x_1) + x_2\ln(\Phi_2/x_2)$$

Use Flory's expression for the combinatorial contribution

Wilson’s Equation

Temperature dependence of Ω

$$\frac{G^E}{RT} = -x_1 \ln\left(\Phi_1 + \Phi_2 \exp\left(\frac{-A_{12}}{RT}\right)\right) - x_2 \ln\left(\Phi_1 \exp\left(\frac{-A_{21}}{RT}\right) + \Phi_2\right) + x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2}$$

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + x_2\Lambda_{12}) - x_2 \ln(x_1\Lambda_{21} + x_2)$$

$$\Omega_{ij} = \Lambda_{ji} = \frac{V_i}{V_j}\exp\left(\frac{-A_{ji}}{RT}\right)$$

$$\ln\gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right)$$

$$\ln\gamma_2 = -\ln(x_1\Lambda_{21} + x_2) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right)$$

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left(\frac{-A_{12}}{RT}\right) \qquad \Lambda_{21} = \frac{V_1}{V_2}\exp\left(\frac{-A_{21}}{RT}\right)$$

Non-Random Two Liquid Model (NRTL)

G = U + PV –ST if you ignore PV and ST and say G ~ U then an integration isn't needed

$$G^E = U^E = \frac{N_A}{2}\left[\frac{x_1 x_2 \Omega_{21} N_{c,1}(\varepsilon_{21}-\varepsilon_{11})}{x_1 + x_2\Omega_{21}} + \frac{x_2 x_1 \Omega_{12} N_{c,2}(\varepsilon_{12}-\varepsilon_{22})}{x_1\Omega_{12} + x_2}\right]$$

$$N_{c,1} = N_{c,2} = 2;\ \tau_{ij} = \frac{N_A N_{c,j}(\varepsilon_{ij}-\varepsilon_{jj})}{2RT} = \frac{(g_{ij}-g_{jj})}{RT} = \frac{\Delta g_{ij}}{RT}$$

$$\Omega_{ij} = G_{ij} = \exp\left(\frac{-\alpha_{ij} N_A N_{c,j}(\varepsilon_{ij}-\varepsilon_{jj})}{2RT}\right) = \exp(-\alpha_{ij}\tau_{ij});\ \tau_{ii} = 0;\ G_{ii} = 1;\ g_{ij} = g_{ji}$$

$$\frac{G^E}{RT} = x_1 x_2\left[\frac{\tau_{12}G_{12}}{x_1 G_{12} + x_2} + \frac{\tau_{21}G_{21}}{x_1 + x_2 G_{21}}\right]$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad \tau_{ij} = \frac{\Delta g_{ij}}{RT}$$

$$\ln\gamma_1 = x_2^2\left[\frac{\tau_{12}G_{12}}{(x_1 G_{12} + x_2)^2} + \tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2\right] \qquad \ln\gamma_2 = x_1^2\left[\frac{\tau_{21}G_{21}}{(x_1 + x_2 G_{21})^2} + \tau_{12}\left(\frac{G_{21}}{x_1 G_{12} + x_2}\right)^2\right]$$

Universal Quasi-Chemical Model (UNIQUAC)

Temperature dependence of Ω depends on **surface area** rather than volume
Interactions occur at surfaces q_i ~ surface area of component ”i”

$$\Omega_{ij} = \frac{q_i}{q_j}\exp\left(\frac{-N_A z(\varepsilon_{ij}-\varepsilon_{jj})}{2RT}\right) = \frac{q_i}{q_j}\exp\left(\frac{-a_{ij}}{T}\right) = \frac{q_i}{q_j}\tau_{ij} = \frac{q_i}{q_j}\exp\left(\frac{-a_{ij}}{T}\right)$$

$$A^E/(RT) = -x_1q_1\ln(\theta_1+\theta_2\tau_{21}) - x_2q_2\ln(\theta_1\tau_{12}+\theta_2) + A^E/(RT)\Big|_\infty$$

$$\tau_{ij} = \exp(-a_{ij}/T) \qquad \theta_i = x_iq_i/(x_1q_1+x_2q_2)$$ **Surface Area Fraction**

$$(G^E/(RT))^{RES} = -x_1q_1\ln(\theta_1+\theta_2\tau_{21}) - x_2q_2\ln(\theta_1\tau_{12}+\theta_2)$$

$$G^E/(RT)\Big|_\infty = (G^E/RT)^{COMB} = x_1\ln(\Phi_1/x_1) + x_2\ln(\Phi_2/x_2)$$

$$\left(\frac{G^E}{RT}\right)^{COMB} = \left(x_1\ln\frac{\Phi_1}{x_1} + x_2\ln\frac{\Phi_2}{x_2}\right) - 5\left[q_1x_1\ln\left(\frac{\Phi_1}{\theta_1}\right) + q_2x_2\ln\left(\frac{\Phi_2}{\theta_2}\right)\right]$$

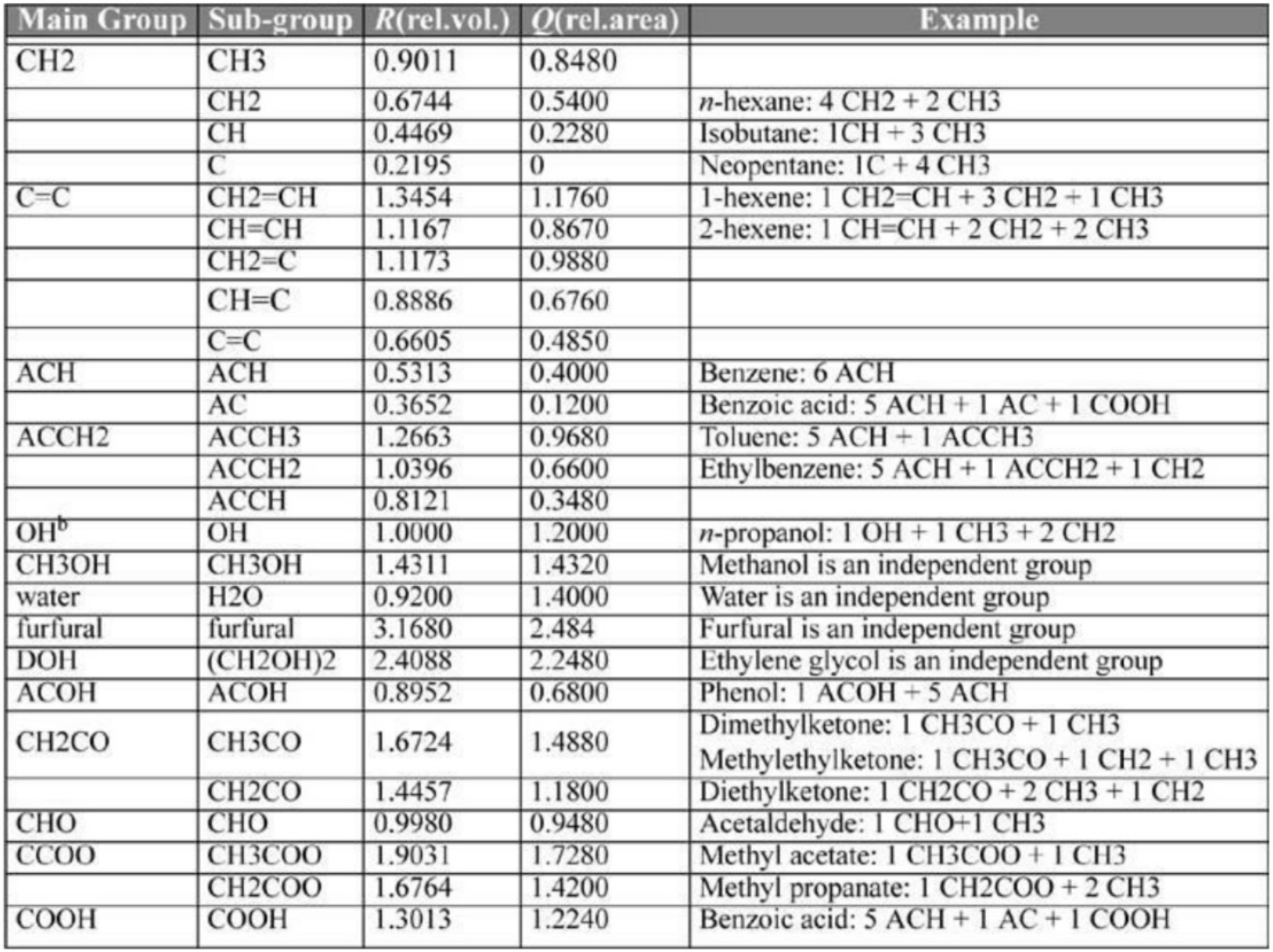
Last term accounts for non-spherical surface area effects on mixing (branched chains)

Guggenheim Modification to Universal Quasi-Chemical Model (UNIQUAC)

$$\Phi_j \equiv \frac{x_j r_j}{\sum_i x_i r_i} \qquad \theta_j \equiv \frac{x_j q_j}{\sum_i x_i q_i}$$

r is volume ratio, q is surface area ratio
Both obtained from group contribution method

$$r_j = \sum_k \nu_k^{(j)} R_k \ ; \qquad q_j = \sum_k \nu_k^{(j)} Q_k$$



Main Group	Sub-group	*R*(rel.vol.)	*Q*(rel.area)	Example
CH2	CH3	0.9011	0.8480	
	CH2	0.6744	0.5400	*n*-hexane: 4 CH2 + 2 CH3
	CH	0.4469	0.2280	Isobutane: 1CH + 3 CH3
	C	0.2195	0	Neopentane: 1C + 4 CH3
C=C	CH2=CH	1.3454	1.1760	1-hexene: 1 CH2=CH + 3 CH2 + 1 CH3
	CH=CH	1.1167	0.8670	2-hexene: 1 CH=CH + 2 CH2 + 2 CH3
	CH2=C	1.1173	0.9880	
	CH=C	0.8886	0.6760	
	C=C	0.6605	0.4850	
ACH	ACH	0.5313	0.4000	Benzene: 6 ACH
	AC	0.3652	0.1200	Benzoic acid: 5 ACH + 1 AC + 1 COOH
ACCH2	ACCH3	1.2663	0.9680	Toluene: 5 ACH + 1 ACCH3
	ACCH2	1.0396	0.6600	Ethylbenzene: 5 ACH + 1 ACCH2 + 1 CH2
	ACCH	0.8121	0.3480	
OH[b]	OH	1.0000	1.2000	*n*-propanol: 1 OH + 1 CH3 + 2 CH2
CH3OH	CH3OH	1.4311	1.4320	Methanol is an independent group
water	H2O	0.9200	1.4000	Water is an independent group
furfural	furfural	3.1680	2.484	Furfural is an independent group
DOH	(CH2OH)2	2.4088	2.2480	Ethylene glycol is an independent group
ACOH	ACOH	0.8952	0.6800	Phenol: 1 ACOH + 5 ACH
CH2CO	CH3CO	1.6724	1.4880	Dimethylketone: 1 CH3CO + 1 CH3 Methylethylketone: 1 CH3CO + 1 CH2 + 1 CH3
	CH2CO	1.4457	1.1800	Diethylketone: 1 CH2CO + 2 CH3 + 1 CH2
CHO	CHO	0.9980	0.9480	Acetaldehyde: 1 CHO+1 CH3
CCOO	CH3COO	1.9031	1.7280	Methyl acetate: 1 CH3COO + 1 CH3
	CH2COO	1.6764	1.4200	Methyl propanate: 1 CH2COO + 2 CH3
COOH	COOH	1.3013	1.2240	Benzoic acid: 5 ACH + 1 AC + 1 COOH

Universal Functional Activity Coefficient Model (UNIFAC)

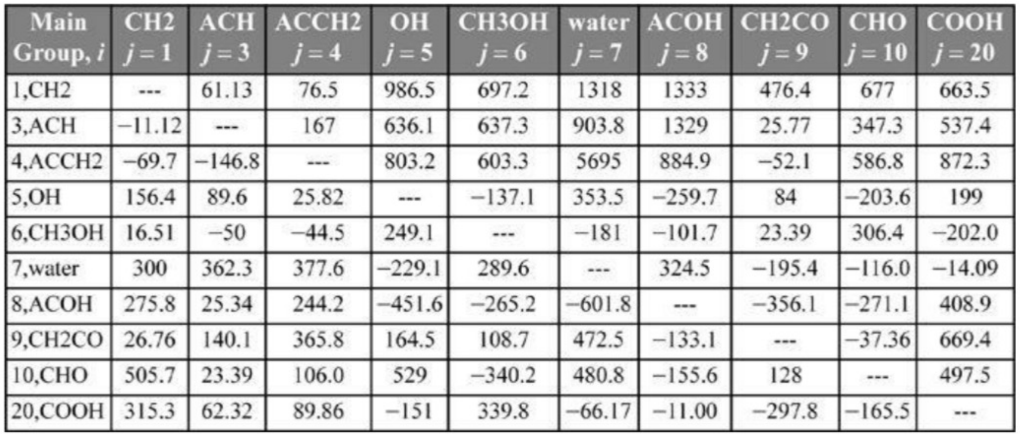
$$\ln \gamma_k = \ln \gamma_k^{COMB} + \ln \gamma_k^{RES}$$

Combinatorial term same as UNIQUAC (surface area based)

$$\ln \gamma_k^{COMB} = \ln(\Phi_k / x_k) + [1 - \Phi_k / x_k] - 5q_k [\ln(\Phi_k / \theta_k) + (1 - \Phi_k / \theta_k)]$$

Residual term involves group contribution rather than whole molecule

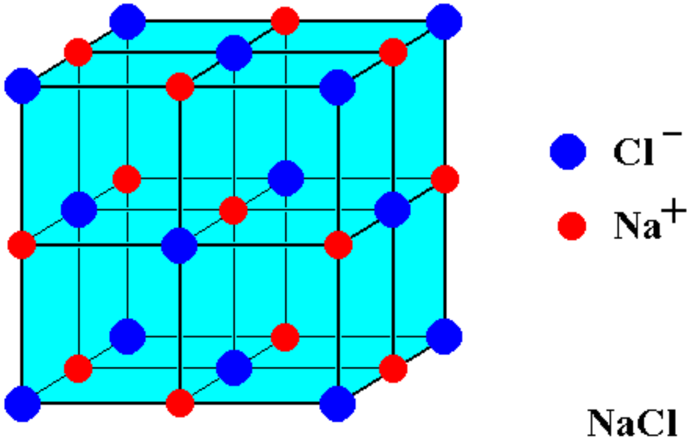
Table 13.3. Selected VLE Interaction Energies a_{ij} for the UNIFAC Equation in Units of Kelvin

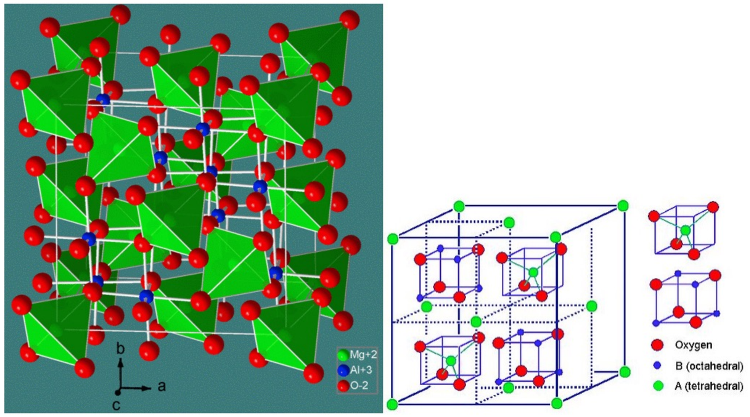


Main Group, *i*	CH2 $j = 1$	ACH $j = 3$	ACCH2 $j = 4$	OH $j = 5$	CH3OH $j = 6$	water $j = 7$	ACOH $j = 8$	CH2CO $j = 9$	CHO $j = 10$	COOH $j = 20$
1,CH2	---	61.13	76.5	986.5	697.2	1318	1333	476.4	677	663.5
3,ACH	−11.12	---	167	636.1	637.3	903.8	1329	25.77	347.3	537.4
4,ACCH2	−69.7	−146.8	---	803.2	603.3	5695	884.9	−52.1	586.8	872.3
5,OH	156.4	89.6	25.82	---	−137.1	353.5	−259.7	84	−203.6	199
6,CH3OH	16.51	−50	−44.5	249.1	---	−181	−101.7	23.39	306.4	−202.0
7,water	300	362.3	377.6	−229.1	289.6	---	324.5	−195.4	−116.0	−14.09
8,ACOH	275.8	25.34	244.2	−451.6	−265.2	−601.8	---	−356.1	−271.1	408.9
9,CH2CO	26.76	140.1	365.8	164.5	108.7	472.5	−133.1	---	−37.36	669.4
10,CHO	505.7	23.39	106.0	529	−340.2	480.8	−155.6	128	---	497.5
20,COOH	315.3	62.32	89.86	−151	339.8	−66.17	−11.00	−297.8	−165.5	---

Solutions with multiple sub-lattices

NaCl-KBr or Spinels AB_2O_4





The **spinel structure** is formulated MM'_2X_4, where M and M' are tetrahedrally and octahedrally coordinated cations, respectively, and X is an anion (typically O or F). The structure is named after the mineral $MgAl_2O_4$, and oxide spinels have the general formula AB_2O_4.

Cation sublattice
Anion sublattice

Disorder in the placement of Na+ and K+
And Cl- and Br- leads to entropy

Octahedral sublattice
Tetrahedral sublattice

Solutions with multiple sub-lattices

Ideal Solution Model (Temkin Model)
Cations surrounded by anions in crystal and in the melt
Quasi-lattice approach
Random mixing of cations and anions on their respective sub-lattices
Consider a system AC and BC

$$N_{\mathrm{A}^+} + N_{\mathrm{B}^+} = N_{\mathrm{C}^-} = N$$

$$\Delta_{\mathrm{mix}} G_{\mathrm{m}} = -RT \ln\left(\frac{N!}{N_{A^+}!N_{B^+}!}\right) = RT\,[X_{\mathrm{A}^+} \ln X_{\mathrm{A}^+} + X_{\mathrm{B}^+} \ln X_{\mathrm{B}^+}]$$

$$X_{\mathrm{B}^+} = 1 - X_{\mathrm{A}^+} = \frac{N_{\mathrm{A}^+}}{N_{\mathrm{A}^+} + N_{\mathrm{B}^+}}$$

$$\Delta_{\mathrm{mix}} S_{\mathrm{m}} = -R[X_{\mathrm{A}^+} \ln X_{\mathrm{A}^+} + X_{\mathrm{B}^+} \ln X_{\mathrm{B}^+}]$$

Solutions with multiple sub-lattices

Regular Solution Model (Temkin Model)

Need to account for next nearest neighbor interactions since nearest neighbor interactions do not change, that is Na+ Cl- interactions, you need Na+ K+ interactions

There are ½ zN nearest neighbor as well as next nearest neighbor interactions

$$U = N_{A^+A^+}u_{A^+A^+} + N_{B^+B^+}u_{B^+B^+} + N_{A^+B^+}u_{A^+B^+} + N_{C^-C^-}u_{C^-C^-} + N_{A^+C^-}u_{A^+C^-} + N_{B^+C^-}u_{B^+C^-}$$

$$U = \tfrac{1}{2}z[N_{A^+}u_{A^+A^+} + N_{B^+}u_{B^+B^+} + Nu_{C^-C^-} + N_{A^+}u_{A^+C^-} + N_{B^+}u_{B^+C^-}] + N_{A^+B^+}[u_{A^+B^+} - \tfrac{1}{2}(u_{A^+A^+} + u_{B^+B^+})]$$

Same as for regular solution

$$U_{AC} = \tfrac{1}{2}zN_A[u_{A^+A^+} + u_{C^-C^-} + u_{A^+C^-}]$$

$$\omega_{A^+B^+} = u_{A^+B^+} - \tfrac{1}{2}(u_{A^+A^+} + u_{B^+B^+})$$

$$U_{BC} = \tfrac{1}{2}zN_B[u_{B^+B^+} + u_{C^-C^-} + u_{B^+C^-}]$$

$$U = U_{AC} + U_{BC} + N_{A^+B^+}\omega_{A^+B^+}$$

Solutions with multiple sub-lattices

$$N_{AB} = \frac{1}{2} z N 2 X_{A^+} X_{B^+} = z\left(\frac{N_{A^+} N_{B^+}}{N}\right)$$

Same as for regular solution

$$Z = \frac{N!}{N_{A^+}! N_{B^+}!} \exp\left[-\frac{[U_{AC} + U_{BC} + (zN_{A^+} N_{B^+}/N)\omega_{A^+B^+}]}{k_B T}\right]$$

$$G \approx A = -k_B T \ln\left[\frac{N!}{N_{A^+}! N_{B^+}!}\right] + U_{AC} + U_{BC} + \frac{zN_{A^+} N_{B^+}}{N}\omega_{A^+B^+}$$

$$\Delta_{mix} G_m = RT[X_{A^+} \ln X_{A^+} + X_{B^+} \ln X_{B^+}] + \Omega_{A^+B^+} X_{A^+} X_{B^+}$$

$$\Omega_{A^+B^+} = zL\omega_{A^+B^+}$$

$$\Delta_{mix} H_m \approx \Delta_{mix} U_m = \Omega_{A^+B^+} X_{A^+} X_{B^+}$$

$$\begin{aligned} \mu_{AC} - \mu^{o}_{AC} &= RT \ln X_{A^+} + \Omega_{A^+B^+} X^2_{B^+} \\ &= RT \ln x_{AC} + \Omega_{A^+B^+} x^2_{BC} \end{aligned}$$

Bragg and Williams

Order-disorder systems

σ = Order parameter a number that goes from 0 for disordered to 1 for ordered

Convergent ordering occurs when two lattice sites are equivalent in the disordered state and crystallographically distinct in the ordered state

This occurs in solid solutions

Bragg and Williams

Solution of A and B with lattice sites a and b

AB forms at low temperatures A at a sites is ½ (1 + σ)

$N_A + N_B = 2N$ zN interactions

Disordered State $U = N_{AA}u_{AA} + N_{BB}u_{BB} + N_{AB}u_{AB}$ Regular Solution

$$N_{AA} = zN\left[\frac{1}{2}(1-\sigma)\frac{1}{2}(1+\sigma)\right] = zN\left[\frac{1}{4}(1-\sigma^2)\right]$$

σ = Order parameter

$$H(\sigma) \approx U(\sigma) = zN\left[\frac{1}{4}(1-\sigma^2)u_{AA} + \frac{1}{4}(1-\sigma^2)u_{BB} + \frac{1}{2}(1+\sigma^2)u_{AB}\right]$$

$$\Delta_{dis}H = H(\sigma) - H(\sigma=1) = H(\sigma) - zNu_{AB}$$

$$= \frac{1}{4}zN[(1-\sigma^2)(u_{AA} + u_{BB} - 2u_{AB})] = \frac{1}{2}zN\omega_{AB}(1-\sigma^2)$$

Bragg and Williams

Order-disorder systems

Disordered State $U = N_{AA}u_{AA} + N_{BB}u_{BB} + N_{AB}u_{AB}$ Regular Solution

$$N_{AA} = zN\left[\frac{1}{2}(1-\sigma)\frac{1}{2}(1+\sigma)\right] = zN\left[\frac{1}{4}(1-\sigma^2)\right]$$

H = U + PV

$$H(\sigma) \approx U(\sigma) = zN\left[\frac{1}{4}(1-\sigma^2)u_{AA} + \frac{1}{4}(1-\sigma^2)u_{BB} + \frac{1}{2}(1+\sigma^2)u_{AB}\right]$$

$$\Delta_{dis}H = H(\sigma) - H(\sigma=1) = H(\sigma) - zNu_{AB}$$

$$= \frac{1}{4}zN[(1-\sigma^2)(u_{AA}+u_{BB}-2u_{AB})] = \frac{1}{2}zN\omega_{AB}(1-\sigma^2)$$

$$\Delta_{mix}S_a = -k_BN\left(\frac{1}{2}(1+\sigma)\ln\left[\frac{1}{2}(1+\sigma)\right] + \frac{1}{2}(1-\sigma)\ln\left[\frac{1}{2}(1-\sigma)\right]\right)$$

Ideal Solution

$$\Delta_{dis}G = \Delta_{dis}H - T\Delta_{dis}S = \tfrac{1}{2}zN\omega_{AB}(1-\sigma^2) + k_BTN[(1-\sigma)\ln(1-\sigma) + (1+\sigma)\ln(1+\sigma) - 2\ln 2]$$

$d(\Delta_{mix}G)/d\sigma = 0$ which yields

$$\ln\frac{1+\sigma}{1-\sigma} = -\frac{\sigma z\omega_{AB}}{k_BT} = \frac{2\sigma T_{trs}}{T}$$

Bragg and Williams

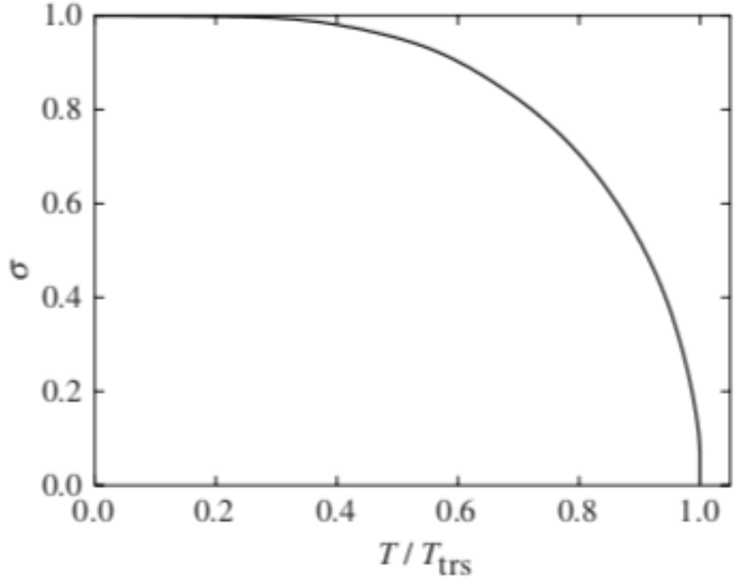


Figure 9.10 Order parameter σ for the Bragg–Williams model as a function of reduced temperature.

$$\ln\frac{1+\sigma}{1-\sigma} = -\frac{\sigma z\omega_{AB}}{k_B T} = \frac{2\sigma T_{trs}}{T}$$

Second Order Transition

Bragg and Williams

Order-disorder systems

Non-Convergent ordering occurs when two lattice sites are *distinct* in the disordered state *and* distinct in the ordered state

Spinels: One tetrahedral and two octahedral cations AB_2O_4

A can be in tetrahedral or octahedral sites $A_{1-x}B_x[A_xB_{2-x}]O_4$

Normal Spinel $(A)^{tetr}(B_2)^{octa}O_4$ x = 0

Inverse Spinel $(B)^{tetr}(A,B)^{octa}O_4$ x = 1

Random Spinel $A_{1-x}B_x[A_xB_{2-x}]O_4$ x = 2/3

$$\Delta_{\mathrm{config}}S_{\mathrm{m}} = -R\left[x\ln x + (1-x)\ln(1-x) + x\ln\left(\frac{x}{2}\right) + (2-x)\ln\left(1-\frac{x}{2}\right)\right]$$

S = 0 for x = 0 Regular Spinel

$$\Delta_{\text{config}} S_{\text{m}} = -R\left[x \ln x + (1-x)\ln(1-x) + x \ln\left(\frac{x}{2}\right) + (2-x)\ln\left(1-\frac{x}{2}\right)\right]$$

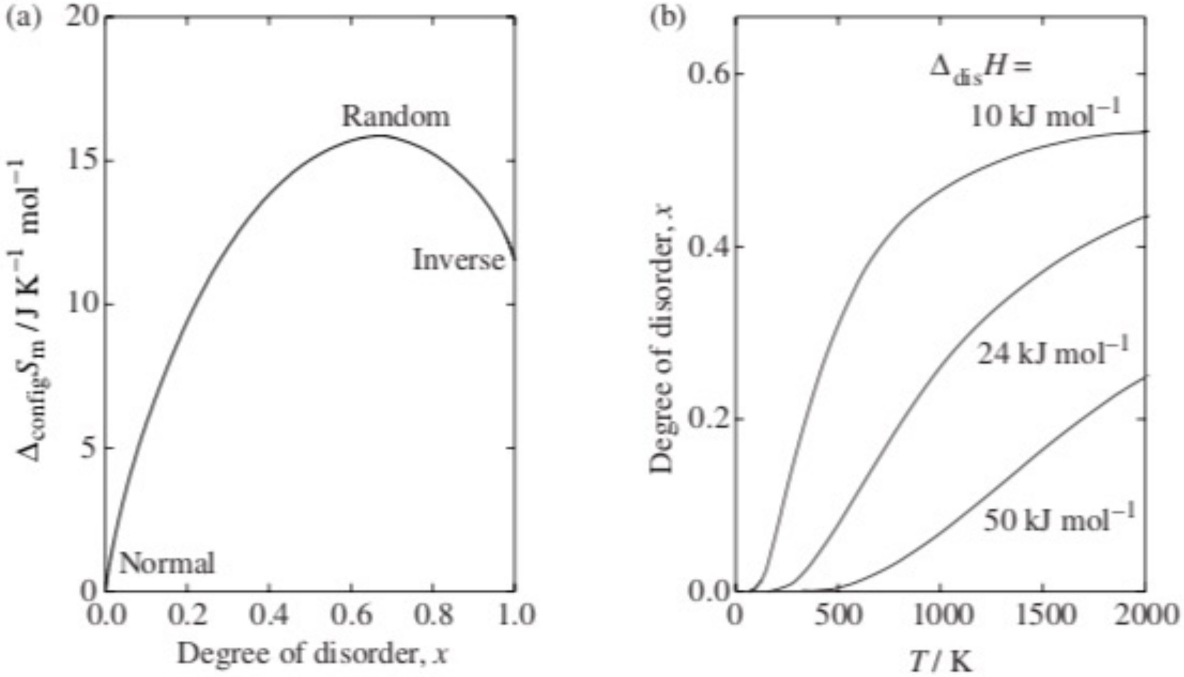


Figure 9.11 (a) Configurational entropy of a spinel AB_2O_4 as a function of the composition parameter, x. (b) Degree of disorder, x, as a function of temperature for selected values of $\Delta_{\text{dis}}H$.

Ordered and Regular Spinels disorder at high temperature to increase entropy

For a Normal Spinel the disordering process is:

$$(\mathrm{A})^{\mathrm{tetr}} + (\mathrm{B})^{\mathrm{octa}} = (\mathrm{A})^{\mathrm{octa}} + (\mathrm{B})^{\mathrm{tetr}}$$

$$\Delta_{\mathrm{dis}} G = \Delta_{\mathrm{dis}} H - T\Delta_{\mathrm{dis}} S = -RT \ln K$$

$$K = \frac{x^2}{(1-x)(2-x)}$$

Non-stoichiometric Compounds

Mass-action law treatment of defect equilibria

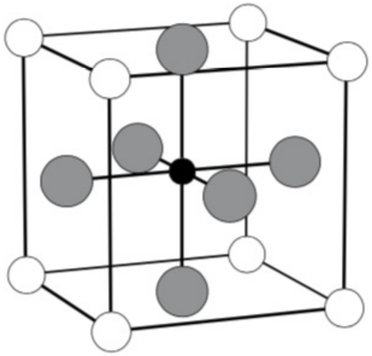


Figure 7.16 The perovskite-type structure. Small black circles represent the B atom, large grey circles represent O atoms and open circles represent the A atom.

A open circles 12
Black B 6
Grey O

$ABO_{3-\delta}$ Perovskite type oxide

Three sublattices
A 12 coordination
B 6 coordination number
O

O and vacancies on the O lattice randomly arranged

B atoms are reduced by oxygen vacancies

$$2O_O^x + 4B_B^x = 2V_O^{\cdot\cdot} + 4B'_B + O_2(g)$$

O_O^x and $V_O^{\cdot\cdot}$ are an oxygen ion and an oxygen vacancy

$$K = \frac{[V_O^{\cdot\cdot}]^2 [B'_B]^4}{[O_O^x]^2 [B_B^x]^4} \cdot pO_2(g)$$

B_B^x and B'_B are trivalent and divalent B-ions

$$\Delta G^o = \Delta H^o - T\Delta S^o = -RT \ln K$$

$$\log pO_2(g) = \log K + 4[\log(1-2\delta) - \log(2\delta)] - 2\log\left(\frac{\delta}{3-\delta}\right)$$

Non-stoichiometric Compounds

Solid Solution Approach

$$Z = \sum_{\mathrm{c}} \sum_{\mathrm{s}} \exp\left(-\frac{H_{\mathrm{c,s}}}{k_{\mathrm{B}}T}\right) = \sum_{\mathrm{c}} \exp\left(-\frac{G_{\mathrm{c}}}{k_{\mathrm{B}}T}\right)$$

Sum over all vibrational states “s”
Over all configurations “c”

$$\Delta_{\mathrm{f}} G = -k_{\mathrm{B}}T \ln Z = -k_{\mathrm{B}}T \ln \sum_{\mathrm{c}} g_{\mathrm{c}} \exp\left(-\frac{\Delta_{\mathrm{f}} G_{\mathrm{c}}}{k_{\mathrm{B}}T}\right)$$

Configurations with degeneracy g_c and
Gibbs energy of formation $\Delta_f G_c$

Proposition: A perovskite $ABO_{3-\delta}$ is made up of ABO_3 and $ABO_{2.5}$ in an ideal solution (no defect defect interactions)

$$\Delta_{\mathrm{f}} G_{\mathrm{c}}(\mathrm{ABO}_{3-\delta}) = (1-2\delta)\Delta_{\mathrm{f}} G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{ABO}_3) + 2\delta\Delta_{\mathrm{f}} G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{ABO}_{2.5})$$

$$g_{\mathrm{c}} = \frac{(3N)!}{N_{\mathrm{V_O}}!(3N - N_{\mathrm{V_O}})!} \cdot \frac{N!}{N_{\mathrm{B}^{2+}}!(N - N_{\mathrm{B}^{2+}})!}$$

N is the number of B atoms
$N_{\mathrm{V_O}}$ is the number of oxygen vacancies
$N_{\mathrm{B}^{2+}}$ is the number of B^{2+} in $\mathrm{ABO}_{3-\delta}$.

$$\Delta_{\mathrm{f}} G_{\mathrm{m}}(\mathrm{ABO}_{3-\delta}) = (1-2\delta)\Delta_{\mathrm{f}} G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{ABO}_3) + 2\delta\Delta_{\mathrm{f}} G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{ABO}_{2,5})$$
$$+ RT\left[(1-2\delta)\ln(1-2\delta) + 2\delta\ln(2\delta) + \delta\ln\left(\frac{\delta}{3}\right) + (3-\delta)\ln\left(1-\frac{\delta}{3}\right)\right]$$

$$\log pO_2 = \left(\frac{1}{RT \ln 10}\right)[4\Delta_f G_m^o(\mathrm{ABO_3}) - 4\Delta_f G_m^o(\mathrm{ABO_{2.5}})] + 4[\log(1-2\delta) - \log(2\delta)] - 2\log\left(\frac{\delta}{3-\delta}\right)$$

$$\log pO_2\,(\mathrm{g}) = \log K + 4[\log(1-2\delta) - \log(2\delta)] - 2\log\left(\frac{\delta}{3-\delta}\right)$$

$$\log K = \left(\frac{1}{RT \ln 10}\right)[4\Delta_f G_m^o(\mathrm{ABO_3}) - 4\Delta_f G_m^o(\mathrm{ABO_{2.5}})]$$

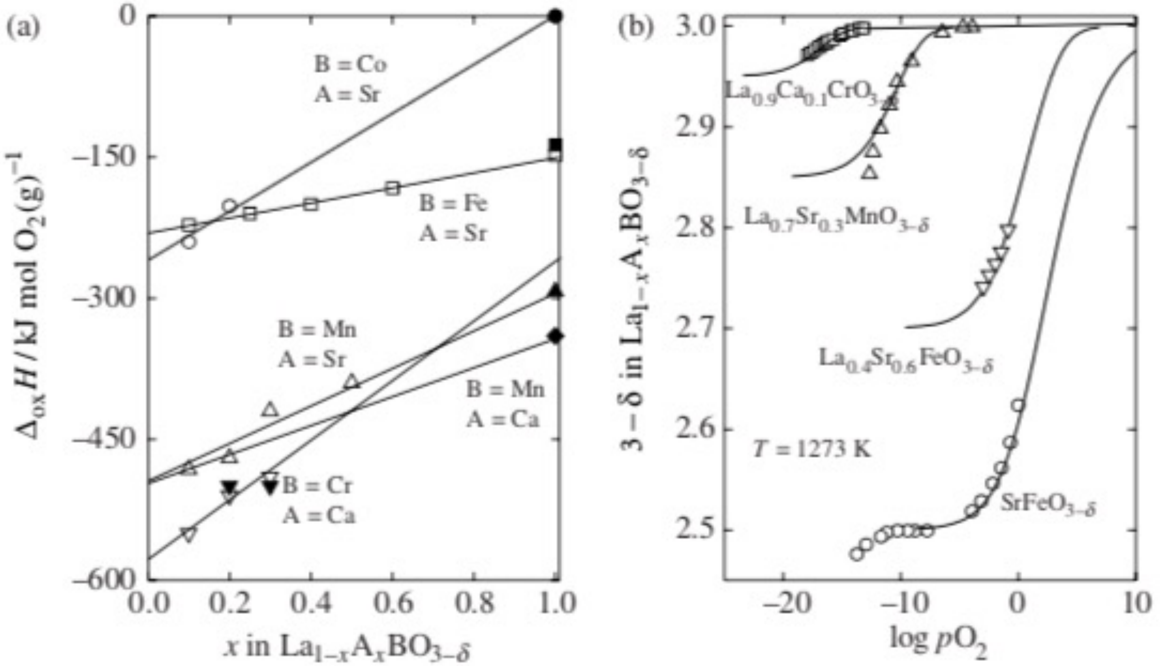


Figure 9.12 (a) Enthalpy of oxidation of $La_{1-x}A_xBO_{3-\delta}$ as a function of x. Open symbols represents values deduced from non-stoichiometry versus partial pressure isotherms. Closed symbols represent calorimetric values. (b) Comparison of experimental and calculated non-stoichiometry versus partial pressure isotherms [23]. Reproduced by permission of the Royal Society of Chemistry.