Atomistic Solution Models

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

**Partition Function**

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

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

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

\[ U = N_A \langle u_A \rangle + N_B \langle u_B \rangle = U_A + U_B \]

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

\[ G \approx A = -k_B T \ln Z = -k_B T \ln \left( \frac{N!}{N_A! N_B!} \right) + U_A + U_B \]

\[ \Delta_{\text{mix}} G = -k_B T \ln \left( \frac{N!}{N_A! N_B!} \right) \]

\[ \ln M! = M \ln M - M \text{ for } M \text{ large} \]

\[ \Delta_{\text{mix}} G = -k_B T \left[ (N_A + N_B) \ln N - N_A \ln N_A - N_B \ln N_B \right] + k_B T (N - N_A - N_B) \]

\[ = k_B T \left[ N_A \ln \left( \frac{N_A}{N} \right) + N_B \ln \left( \frac{N_B}{N} \right) \right] = k_B T [N_A \ln x_A + N_B \ln x_B] \]
Ideal Solution Model

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

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

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

\[ \Delta_{\text{mix}} H_m = \Delta_{\text{mix}} G_m + T \Delta_{\text{mix}} S_m = 0 \]
Regular Solution 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 $U_A = zN_{AA}u_{AA}/2$

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

$zN_A = 2N_{AA} + N_{AB}$

$\frac{1}{2}z(N_B + N_A) = N_{AA} + N_{BB} + N_{AB}$

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

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

$\frac{1}{2}zN_Au_{AA} + \frac{1}{2}zN_Bu_{BB} + N_{AB}[u_{AB} - \frac{1}{2}(u_{AA} + u_{BB})]$
Regular Solution Solution Model

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

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

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

\[ U = U_A + U_B + N_{AB}\omega_{AB} \]

\[ N_{AB} = \frac{1}{2} zN2 x_A x_B = \frac{N_A N_B}{N} \]

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

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

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

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

\[ \Omega_{AB} = zL \omega_{AB} \]

\[ \Delta_{\text{mix}} H_m \approx \Delta_{\text{mix}} U_m = \Omega_{AB} x_A x_B \]

\[ \mu_A \sim \frac{dG}{dx_A} \]

\[ \mu_A - \mu_A^0 = RT \ln a_A = RT \ln x_A + \Omega_{AB} x_B^2 \]

\[ RT \ln \gamma_A = \Omega_{AB} x_B^2 \]
Figure 3.10 The molar Gibbs energy of mixing of a regular solution A–B for different values of $\Omega/RT$. 
\( a_A = \exp[\ln(1 - x_B) + \Omega_{AB} x_B^2] \)

\[
\frac{x_B}{\mu_A - \mu_A^0} = RT \ln a_A = RT \ln x_A + \Omega_{AB} x_B^2
\]

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 \( \Omega_{AR}/RT \).
Vibrational Contribution

With vibrational part

\[
Z = g \exp \left( -\frac{U}{k_B T} \right) = \left( \frac{N!}{N_A!N_B!} \right) \exp \left( -\frac{U_A + U_B}{k_B T} \right) \quad Z = g Z_A^{N_A} Z_B^{N_B} \exp \left( -\frac{U'}{k_B T} \right)
\]

\( Z_A \) 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

\[
\Delta_{\text{mix}}^\text{conf} S = L k_B \ln g = R \ln g
\]

\[
\Delta_{\text{mix}}^\text{non-conf} S_m = k_B L (\ln Z_A^{N_A} + \ln Z_B^{N_B}) \approx z L x_A x_B \eta_{AB}
\]
Excess molar Gibbs energy of mixing for quasi-regular solution

\[ \Delta_{\text{mix}}^{\text{exc}} G_m = zL x_A x_B (\omega_{AB} - T \eta_{AB}) \]

\[ \Delta_{\text{mix}}^{\text{exc}} G_m = x_A x_B \Omega_{AB} \left( 1 - \frac{T}{\tau} \right) \]

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

\( \tau \) is a characteristic temperature, when \( T = \tau \) ideal solution behavior is seen
For Positive $\Omega$

$T = \tau$ Ideal

$T > \tau$ Mix

$T < \tau$ Demix

For Negative $\Omega$

$T = \tau$ Ideal

$T > \tau$ Demix

$T < \tau$ Mix

For $\Omega = 0$

Ideal

**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 $\Omega_{AB}$. 
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

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 \( \Pi \)

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

\[ P/\rho = \text{energy} \sim \rho RT \ A_2 = \rho (RT \ b - a) \]

\[ \Delta_{\text{mix}}^{\text{exc}} G_m = x_A x_B \Omega_{AB} \left( 1 - \frac{T}{\tau} \right) \]
Virial Coefficient Approach for Weak Interactions

\[ P/\rho = \text{energy} \sim \rho RT A_2 = \rho (RT b - a) \]

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

\[ \Delta_{mix}^{exc} G_m = x_A x_B \Omega_{AB} \left( 1 - \frac{T}{\tau} \right) \]

Dilute: Ideal behavior, there are no interactions

Semi-dilute
\[ \Omega = 0 \text{ Ideal} \]
\[ \Omega < 0 \text{ Miscible} \]
\[ \Omega > 0 \text{ Immiscible} \]

T = \tau Ideal
T > \tau Miscible
T < \tau Immiscible
Strong Interactions

Ornstein and Zernike function

Correlation Function, $h(r)$

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

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, $\rho$ indicates the number density of particles/nanoaggregates.

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

Closure relationships: Random Phase Approximation (RPA); Percus-Yevick Approximation; Born-Green Approximation

$$g(r) = h(r)$$

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

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

For a square well potential: $A_2 = 2\pi N \int_0^1 (1 - \exp(-u/kT))r^2 \, dr$

$$P = \rho RT(1 + A_2 \rho + A_3 \rho^2 + A_4 \rho^3 + ...)$$
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.
\[ S(k) = 1 + \rho \int \text{d}r \left( g(r) - 1 \right) \exp(\imath k \cdot r). \]

Fig. 3.2. Structure factor of liquid sodium near the normal melting temperature. The points are experimental x-ray scattering results and the curve is obtained from a Monte Carlo calculation 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 $\beta \rho = 0.4$. 
**Weak Interactions**

**Strong Interactions**

\[ I(q, f) = I(q, f_0) S(q, f) / f_0 \]

\[ S(k) = 1 + \rho \int dr \left( g(r) - 1 \right) \exp(i k \cdot r) \]
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

Van der Waals: Includes excluded volume, “b”, and attractive interaction “a”

\[ p = \frac{RT}{V-b} - \frac{a}{v^2} = \rho RT \left( 1 - \frac{b}{V} - \frac{a}{v^2} \right) \]
\[ a = \frac{27RT^2}{64P_c} \]
\[ b = \frac{RT_c}{8P_c} \]

Peng-Robinson: Attractive interaction term is more complicated and includes the acentric factor \( \omega \). “a” has a temperature dependence.

\[ p = \frac{RTP}{(1-bp) - \frac{aP^2}{1 + 2bP - b^2P^2}} \]
\[ a = a_c \alpha_c \]
\[ a_c = 0.4572355 \frac{RT_c^2}{P_c} \]
\[ b = 0.0779607 \frac{RT_c}{P_c} \]
\[ \alpha = 1 + \kappa (1 - \sqrt{T_c})^2 \]
\[ \kappa = 0.37464 + 1.54226 \omega - 0.25992 \omega^2 \]

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

\[ p = \frac{RT}{V-b} = \frac{\rho RT}{1-b \rho} \]

\[ Z = \frac{PV}{RT} = \frac{1}{(1-b \rho)} - \frac{\rho}{RT} \rho \]

Compare with Molecular Dynamics (o) for Hard Spheres

\[ Z^{HS} = \frac{1}{(1-\eta_P)}; \text{ the van der Waals model} \]

\[ Z^{HS} = \frac{1+2\eta_P}{(1-2\eta_P)}; \text{ the Scott model} \]

\[ Z^{HS} = \frac{1+4\eta_P}{(1-1.9\eta_P)}; \text{ the ESD model} \]

\[ Z^{HS} = \frac{1+4\eta_P(1-\eta_P/2)}{(1-\eta_P)^3}; \text{ the Carnahan-Starling model} \]
Margulis one-parameter Model

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

\[ \ln \gamma = A_{12}(1-x) \]

Margulis acid-base Model

acidity parameter, \( \alpha \), and basicity parameter, \( \beta \).

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

Hildebrand Model

\[ \Delta_{mix}^E G_m = x_A x_B \Omega_{AB} \]

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.
Redlich-Kister Model (asymmetric phase diagrams)

\[
\frac{G^E}{RT} = x_1 x_2 (B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2 + \ldots)
\]

Two-parameter Margulis Model

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

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

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

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

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

<table>
<thead>
<tr>
<th>Model</th>
<th>(\frac{G^E}{RT})</th>
<th>(\ln \gamma_1)</th>
<th>Simplification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redlich-Kister</td>
<td>(x_1 x_2 (B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2 + \ldots))</td>
<td>cf. Practice problem P11.2</td>
<td>--</td>
</tr>
<tr>
<td>Margules two-parameter</td>
<td>(x_1 x_2 (A_{21} x_1 + A_{12} x_2))</td>
<td>(x_2^2 [A_{12} + 2(A_{21} - A_{12}) x_1])</td>
<td>(D_{12}=0; A_{21}=B_{12}+C_{12}; A_{21}=B_{12}-C_{12})</td>
</tr>
<tr>
<td>Margules one-parameter</td>
<td>(x_1 x_2 A_{12})</td>
<td>(x_2^2 A_{12})</td>
<td>(C_{12}=D_{12}=0; A_{12}=A_{12}=B_{12})</td>
</tr>
<tr>
<td>Ideal solution</td>
<td>0</td>
<td>0</td>
<td>(B_{12} = C_{12} = D_{12} = 0)</td>
</tr>
</tbody>
</table>
Van der Waals Models

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

- \[ b = \sum_i x_i b_i \]
- \[ a = x_1^2 a_{11} + 2 x_1 x_2 a_{12} + x_2^2 a_{22} = \sum \sum x_i x_j a_{ij} \]
- \[ a_{12} = (1-k_{12})(a_{11}a_{22})^{1/2} \]

Regular Solution Models

- SUV
  \[ G = H - ST \]
- H A
  \[ H = U + PV \]
- pGT
  \[ So \]
  \[ G = U + PV - TS \]
  \[ (A = U - TS) \]

Ignore PV which is small \( G \sim A \)

If \( V \sim S \sim 0 \) then \( G = U \)

This is a regular solution

Van Laar Model

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

\[ U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} Q \]

where \( Q = \left( \frac{a_{11}}{V_1^2} + \frac{a_{22}}{V_2^2} - 2 \frac{a_{12}}{V_1 V_2} \right) \)
Van Laar Model

\[ U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} Q \]

where \( Q = \left( \frac{a_{11}}{V_1^2} + \frac{a_{22}}{V_2^2} - 2 \frac{a_{12}}{V_1 V_2} \right) \)

\[ A_{12} = \frac{Q V_1}{RT}; \quad A_{21} = \frac{Q V_2}{RT}; \quad A_{12} = \frac{V_1}{A_{21}} \]

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

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

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

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

\[ A_{21} = (\ln \gamma_2) \left[ 1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right]^2 \]
Scatchard-Hildebrand Theory
Theory based on **Volume Fraction** rather than Mole Fraction

\[ k_{12} = 0 \quad a_{12} = \sqrt{a_{11} a_{22}} \]

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

\[ \delta = \text{Solubility Parameter} \]

\[ \Phi_i \equiv \frac{x_i V_i}{\sum x_i V_i} \quad \delta_i \equiv \frac{\sqrt{a_{ii}}}{V_i} \]

\[ \delta_i = \sqrt{\frac{\Delta H_{i}^{\text{vap}} - RT}{V_i}} \]

Volume Fraction

Cohesive Energy Density
Table 12.1. Solubility Parameters in (J/cm³)¹/² and Molar Volumes (cm³/mol) for Various
Substances as liquids at 298 K

<table>
<thead>
<tr>
<th>1-Olefins</th>
<th>δ</th>
<th>V_L</th>
<th>Napthenics</th>
<th>δ</th>
<th>V_L</th>
<th>Aromatics</th>
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<td>74</td>
<td>furan</td>
<td>19.23</td>
<td>72</td>
</tr>
<tr>
<td>n-nonane</td>
<td>15.95</td>
<td>177</td>
<td>n-butanol</td>
<td>27.82</td>
<td>91</td>
<td>THF</td>
<td>18.61</td>
<td>81</td>
</tr>
<tr>
<td>n-decane</td>
<td>16.16</td>
<td>194</td>
<td>n-hexanol</td>
<td>21.89</td>
<td>124</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>n-dodecanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Scatchard-Hildebrand Theory

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

\[ RT \ln \gamma_1 = V_1 \Phi_2^2 (\delta_1 - \delta_2)^2 \]

\[ RT \ln \gamma_2 = V_2 \Phi_1^2 (\delta_1 - \delta_2)^2 \]
Scatchard-Hildebrand with Adjustable

\[ a_{12} = (1 - k_{12})(a_{11}a_{22})^{\frac{1}{2}} \]

\[ a_{12} = \sqrt{a_{11}a_{22}} (1 - k_{12}) \]

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

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

\[ \Delta S_{\text{mix}} = S - \sum_i x_i S_i = \sum_i x_i (\bar{S}_i - S_i) = -R \sum_i x_i \ln \Phi_i \]

\( \Phi \) accounts for the available volume

\[ G^E = H^E - T S^E = RT \left( x_1 \ln \left( \Phi_1 / x_1 \right) + x_2 \ln \left( \Phi_2 / x_2 \right) \right) \]

\[ G^E = H^E - T S^E = RT \left( x_1 \ln \left( \Phi_1 / x_1 \right) + x_2 \ln \left( \Phi_2 / x_2 \right) + \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 \right) (x_1 V_1 + x_2 V_2) \]

\[ \ln \gamma_1 = \ln \left( \Phi_1 / x_1 \right) + \left(1 - \Phi_1 / x_1 \right) \frac{V_1}{RT} \Phi_2^2 (\delta_1 - \delta_2)^2 \]

\[ \ln \gamma_2 = \ln \left( \Phi_2 / x_2 \right) + \left(1 - \Phi_2 / x_2 \right) \frac{V_2}{RT} \Phi_1^2 (\delta_1 - \delta_2)^2 \]
Flory-Huggins Model for Polymers

\[ G^E = H^E - T S^E = RT \left( x_1 \ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2) \right) + \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 (x_1 V_1 + x_2 V_2) \]

\[ G^E = RT \left( x_1 \ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2) \right) + \Phi_1 \Phi_2 (x_1 + x_2 r) \chi RT \]

\[ \chi \equiv V_I (\delta_1 - \delta_1)^2 / RT. \]

\[ r = V_2 / V_1 \quad \text{2 is polymer} \]
Account for Hydrogen Bonding

MOSCED Model (MOdified Separation of Cohesive Energy Density)

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

\[ \ln \gamma^\infty = \frac{V_2}{RT} \left[ (\lambda_2 - \lambda_1)^2 + q_1 q_2 \left( \frac{\tau_2^2 - \tau_1^2}{\psi_1} \right)^2 \right] + d_{12} \]

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

\( \lambda_i \) dispersion factor

\( \tau_i \) is the polarity

\( q_i \) is .9 to 1
Account for Hydrogen Bonding

SSCED Model (Simplified Separation of Cohesive Energy Density)

\[ G^E = V \Phi_1 \Phi_2 [(\delta'_2 - \delta'_1)^2 + 2k_{12} \delta'_2 \delta'_1] \]

\[ RT \ln \gamma_k = V_k (1 - \Phi_k)^2 [(\delta'_2 - \delta'_1)^2 + 2k_{12} \delta'_2 \delta'_1] \]

\[ (\delta'_i)^2 = \delta_i^2 - 2\alpha_i \beta_i \]

\[ k_{12} = \frac{(\alpha_2 - \alpha_1)(\beta_2 - \beta_1)}{4\delta'_2 \delta'_1} \]
### Table 13.1. Nomenclature for Local Composition Variables

<table>
<thead>
<tr>
<th>Composition around a “1” Molecule</th>
<th>Composition around a “2” Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{21}$ – mole fraction of “2’s” around “1”</td>
<td>$x_{12}$ – mole fraction of “1’s” around “2”</td>
</tr>
<tr>
<td>$x_{11}$ – mole fraction of “1’s” around “1”</td>
<td>$x_{22}$ – mole fraction of “2’s” around “2”</td>
</tr>
<tr>
<td>local mole balance, $x_{11} + x_{21} = 1$</td>
<td>local mole balance, $x_{22} + x_{12} = 1$</td>
</tr>
</tbody>
</table>

\[
\frac{x_{21}}{x_{11}} = \frac{x_{2}}{x_{1}} \Omega_{21} \\
\frac{x_{12}}{x_{22}} = \frac{x_{1}}{x_{2}} \Omega_{12}
\]

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

\[
x_{11} = \frac{x_{1}}{x_{1} + x_{2} \Omega_{21}} \\
x_{21} = \frac{x_{2} \Omega_{21}}{x_{1} + x_{2} \Omega_{21}} \\
x_{12} = \frac{x_{1} \Omega_{12}}{x_{1} \Omega_{12} + x_{2}} \\
x_{22} = \frac{x_{2}}{x_{1} \Omega_{12} + x_{2}}
\]
\[(M - M^{ig}) = x_1(M - M^{ig})^{(1)} + x_2(M - M^{ig})^{(2)}\]

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

\[N_{c,j} \text{ is the coordination number}\]

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

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

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

\[ \int_{\infty}^{T} \frac{d(A^E)}{RT} = \left. \frac{A^E}{RT} \right|_{\infty} - \int_{\infty}^{T} \frac{U^E}{RT^2} dT \]

Need an expression for Ω as a function of temperature
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 $A$,

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

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

\[
\Omega_{ij} = \Lambda_{ji} = \frac{V_i}{V_j} \exp\left(\frac{-N AN_{c,j}(\varepsilon_{ij} - \varepsilon_{jj})}{2RT}\right) = \frac{V_i}{V_j} \exp\left(\frac{-A_{ji}}{RT}\right)
\]

Temperature dependence of \( \Omega \)

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

Two activation energies 1 around 2 and 2 around 1

Assume \( G \sim A \) (PV is insignificant)

Break \( G \) into a residual (energetic) contribution that vanishes at \( T \to \infty \) and a combinatorial (size and shape) contribution
Two activation energies 1 around 2 and 2 around 1

Assume $G \sim A$ (PV is insignificant)

Break $G$ into a residual (energetic) contribution that vanishes at $T \to \infty$
and a combinatorial (size and shape) contribution

\[
\frac{A^E}{RT} = -x_1 \ln(\Phi_1 + \Phi_2 \exp(-A_{12}/RT)) - x_2 \ln(\Phi_1 \exp(-A_{21}/RT) + \Phi_2) + \frac{A^E}{RT}\bigg|_{\infty}
\]

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

\[
\left.\frac{G^E}{RT}\right|_{\infty} = \left.\frac{G^E}{RT}\right|^{COMB} = x_1 \ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2)
\]

Use Flory’s expression for the combinatorial contribution
\[
\frac{G^E}{RT} = -x_1 \ln \left( \Phi_1 + \Phi_2 \exp \left( \frac{-A_{12}}{RT} \right) \right) - x_2 \ln \left( \Phi_1 \exp \left( \frac{-A_{21}}{RT} \right) + \Phi_2 \right) + x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2}
\]

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

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

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

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

\[
\Lambda_{12} = \frac{V_2}{V_1} \exp \left( \frac{-A_{12}}{RT} \right)
\]

\[
\Lambda_{21} = \frac{V_1}{V_2} \exp \left( \frac{-A_{21}}{RT} \right)
\]
Non-Random Two Liquid Model (NRTL)

\[ G = U + PV - ST \] if you ignore PV and ST and say \( G \sim U \) then an integration isn’t needed

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

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

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

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

\[ G_{ij} = \exp(-\alpha_{ij} \tau_{ij}); \quad \tau_{ij} = \frac{\Delta g_{ij}}{RT} \]

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

\[
\ln \gamma_2 = x_1^2 \left[ \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} + \tau_{12} \left( \frac{G_{12}}{x_1 G_{12} + x_2} \right)^2 \right]
\]
Universal Quasi-Chemical Model (UNIQUAC)

Temperature dependence of $\Omega$ depends on surface area rather than volume.
Interactions occur at surfaces $\Omega_{ij} \sim \text{surface area of component } "i"$

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

$$
\frac{A^E}{(RT)} = -x_1 q_1 \ln(\theta_1 + \theta_2 \tau_{21}) - x_2 q_2 \ln(\theta_1 \tau_{12} + \theta_2) + A^E/(RT)_{\infty}
$$

$$
\tau_{ij} = \exp(-a_{ij}/T) \quad \theta_i = x_i q_i / (x_1 q_1 + x_2 q_2)
$$

Surface Area Fraction

$$
(G^E/(RT))^{RES} = -x_1 q_1 \ln(\theta_1 + \theta_2 \tau_{21}) - x_2 q_2 \ln(\theta_1 \tau_{12} + \theta_2)
$$

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

$$
(G^E/(RT))^{COMB} = \left( x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} \right) - 5 \left[ q_1 x_1 \ln \left( \frac{\Phi_1}{\theta_1} \right) + q_2 x_2 \ln \left( \frac{\Phi_2}{\theta_2} \right) \right]
$$

Last term accounts for non-spherical surface area effects on mixing (branched chains).
Guggenheim Modification to Universal Quasi-Chemical Model (UNIQUAC)

\[
\Phi_j = \frac{x_j r_j}{\sum_i x_i r_i}
\]

\[
\theta_j = \frac{x_j q_j}{\sum_i x_i q_i}
\]

\(r\) is volume ratio, \(q\) is surface area ratio
Both obtained from group contribution method
<table>
<thead>
<tr>
<th>Main Group</th>
<th>Sub-group</th>
<th>$R$(rel.vol.)</th>
<th>$Q$(rel.area)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH2</td>
<td>CH3</td>
<td>0.9011</td>
<td>0.8480</td>
<td></td>
</tr>
<tr>
<td>CH2</td>
<td>CH2</td>
<td>0.6744</td>
<td>0.5400</td>
<td>n-hexane: 4 CH2 + 2 CH3</td>
</tr>
<tr>
<td>CH</td>
<td></td>
<td>0.4469</td>
<td>0.2280</td>
<td>Isobutane: 1CH + 3 CH3</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>0.2195</td>
<td>0</td>
<td>Neopentane: 1C + 4 CH3</td>
</tr>
<tr>
<td>C=C</td>
<td>CH2=CH</td>
<td>1.3454</td>
<td>1.1760</td>
<td>1-hexene: 1 CH2=CH + 3 CH2 + 1 CH3</td>
</tr>
<tr>
<td>C=C</td>
<td>CH=CH</td>
<td>1.1167</td>
<td>0.8670</td>
<td>2-hexene: 1 CH=CH + 2 CH2 + 2 CH3</td>
</tr>
<tr>
<td>C=C</td>
<td>CH2=C</td>
<td>1.1173</td>
<td>0.9880</td>
<td></td>
</tr>
<tr>
<td>C=C</td>
<td>CH=C</td>
<td>0.8886</td>
<td>0.6760</td>
<td></td>
</tr>
<tr>
<td>ACH</td>
<td>ACH</td>
<td>0.3313</td>
<td>0.4000</td>
<td>Benzene: 6 ACH</td>
</tr>
<tr>
<td>ACH</td>
<td>AC</td>
<td>0.3652</td>
<td>0.1200</td>
<td>Benzoic acid: 5 ACH + 1 AC + 1 COOH</td>
</tr>
<tr>
<td>ACCH2</td>
<td>ACCH3</td>
<td>1.2263</td>
<td>0.9680</td>
<td>Toluene: 5 ACH + 1 ACCH3</td>
</tr>
<tr>
<td>ACCH2</td>
<td>ACCH2</td>
<td>1.0396</td>
<td>0.6600</td>
<td>Ethylbenzene: 5 ACH + 1 ACCH2 + 1 CH2</td>
</tr>
<tr>
<td>ACCH2</td>
<td>ACCH</td>
<td>0.8121</td>
<td>0.3480</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>OH</td>
<td>1.0000</td>
<td>1.2000</td>
<td>$n$-propanol: 1 OH + 1 CH3 + 2 CH2</td>
</tr>
<tr>
<td>CH3OH</td>
<td>CH3OH</td>
<td>1.4311</td>
<td>1.4320</td>
<td>Methanol is an independent group</td>
</tr>
<tr>
<td>water</td>
<td>H2O</td>
<td>0.9200</td>
<td>1.4000</td>
<td>Water is an independent group</td>
</tr>
<tr>
<td>furfural</td>
<td>furfural</td>
<td>3.1680</td>
<td>2.484</td>
<td>Furfural is an independent group</td>
</tr>
<tr>
<td>DOH</td>
<td>(CH2OH)2</td>
<td>2.4088</td>
<td>2.2480</td>
<td>Ethylene glycol is an independent group</td>
</tr>
<tr>
<td>ACOH</td>
<td>ACOH</td>
<td>0.8952</td>
<td>0.6800</td>
<td>Phenol: 1 ACOH + 5 ACH</td>
</tr>
<tr>
<td>CH2CO</td>
<td>CH3CO</td>
<td>1.6724</td>
<td>1.4880</td>
<td>Dimethylketone: 1 CH3CO + 1 CH3</td>
</tr>
<tr>
<td>CH2CO</td>
<td>CH2CO</td>
<td>1.4457</td>
<td>1.1800</td>
<td>Diethylketone: 1 CH2CO + 2 CH3 + 1 CH2</td>
</tr>
<tr>
<td>CHO</td>
<td>CHO</td>
<td>0.9980</td>
<td>0.9480</td>
<td>Acetaldehyde: 1 CHO + 1 CH3</td>
</tr>
<tr>
<td>CCOO</td>
<td>CH3COO</td>
<td>1.9031</td>
<td>1.7280</td>
<td>Methyl acetate: 1 CH3COO + 1 CH3</td>
</tr>
<tr>
<td>CCOO</td>
<td>CH2COO</td>
<td>1.6764</td>
<td>1.4200</td>
<td>Methyl propanate: 1 CH2COO + 2 CH3</td>
</tr>
<tr>
<td>COOH</td>
<td>COOH</td>
<td>1.3013</td>
<td>1.2240</td>
<td>Benzoic acid: 5 ACH + 1 AC + 1 COOH</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Main Group, ( i )</th>
<th>CH2, ( j = 1 )</th>
<th>ACH, ( j = 3 )</th>
<th>ACCH2, ( j = 4 )</th>
<th>OH, ( j = 5 )</th>
<th>CH3OH, ( j = 6 )</th>
<th>water, ( j = 7 )</th>
<th>ACOH, ( j = 8 )</th>
<th>CH2CO, ( j = 9 )</th>
<th>CHO, ( j = 10 )</th>
<th>COOH, ( j = 20 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, CH2</td>
<td>---</td>
<td>61.13</td>
<td>76.5</td>
<td>986.5</td>
<td>697.2</td>
<td>1318</td>
<td>1333</td>
<td>476.4</td>
<td>677</td>
<td>663.5</td>
</tr>
<tr>
<td>3, ACH</td>
<td>-11.12</td>
<td>---</td>
<td>167</td>
<td>636.1</td>
<td>637.3</td>
<td>903.8</td>
<td>1329</td>
<td>25.77</td>
<td>347.3</td>
<td>537.4</td>
</tr>
<tr>
<td>4, ACCH2</td>
<td>-69.7</td>
<td>-146.8</td>
<td>---</td>
<td>803.2</td>
<td>603.3</td>
<td>5695</td>
<td>884.9</td>
<td>-52.1</td>
<td>586.8</td>
<td>872.3</td>
</tr>
<tr>
<td>5, OH</td>
<td>156.4</td>
<td>89.6</td>
<td>25.82</td>
<td>---</td>
<td>-137.1</td>
<td>353.5</td>
<td>-259.7</td>
<td>84</td>
<td>-203.6</td>
<td>199</td>
</tr>
<tr>
<td>6, CH3OH</td>
<td>16.51</td>
<td>-50</td>
<td>-44.5</td>
<td>249.1</td>
<td>---</td>
<td>-181</td>
<td>-101.7</td>
<td>23.39</td>
<td>306.4</td>
<td>-202.0</td>
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<td>7, water</td>
<td>300</td>
<td>362.3</td>
<td>377.6</td>
<td>-229.1</td>
<td>289.6</td>
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<td>324.5</td>
<td>-193.4</td>
<td>-116.0</td>
<td>-14.09</td>
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<td>8, ACOH</td>
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<td>25.34</td>
<td>244.2</td>
<td>-451.6</td>
<td>-265.2</td>
<td>-601.8</td>
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<td>-356.1</td>
<td>-271.1</td>
<td>408.9</td>
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<tr>
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<td>26.76</td>
<td>140.1</td>
<td>365.8</td>
<td>164.5</td>
<td>108.7</td>
<td>472.5</td>
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<td>37.36</td>
<td>669.4</td>
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<td>23.39</td>
<td>106.0</td>
<td>529</td>
<td>-340.2</td>
<td>480.8</td>
<td>-155.6</td>
<td>128</td>
<td>---</td>
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<tr>
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<td>62.32</td>
<td>89.86</td>
<td>-151</td>
<td>339.8</td>
<td>-66.17</td>
<td>-11.00</td>
<td>-297.8</td>
<td>-165.5</td>
<td>---</td>
</tr>
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</table>
Solutions with multiple sub-lattices

NaCl-KBr or Spinel $\text{AB}_2\text{O}_4$

Cation sublattice
Anion sublattice

Disorder in the placement of $\text{Na}^+$ and $\text{K}^+$ and $\text{Cl}^-$ and $\text{Br}^-$ 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

\[ N_{A^+} + N_{B^+} = N_{C^-} = N \]

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

\[ X_{B^+} = 1 - X_{A^+} = \frac{N_{A^+}}{N_{A^+} + N_{B^+}} \]

\[ \Delta_{mix} S_m = -R \left[ X_{A^+} \ln X_{A^+} + X_{B^+} \ln X_{B^+} \right] \]
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

\[
U = N_A^+ A^- u_A^+ A^- + N_B^+ B^- u_B^+ B^- + N_A^+ B^- u_A^+ B^- + N_C^- C^- u_C^- C^- \\
+ N_A^+ C^- u_A^+ C^- + N_B^+ C^- u_B^+ C^-
\]

\[
U = \frac{1}{2} z[N_A^+ A^- u_A^+ A^- + N_B^+ B^- u_B^+ B^- + N_C^- C^- u_C^- C^- + N_A^+ A^- u_A^+ A^- + N_B^+ B^- u_B^+ B^- ] \\
+ N_A^+ B^- [u_A^+ B^- - \frac{1}{2}(u_A^+ A^- + u_B^+ B^- )]
\]

Same as for regular solution

\[
U_{AC} = \frac{1}{2} z N_A [u_A^+ A^- + u_C^- C^- + u_A^+ C^- ] \\
U_{BC} = \frac{1}{2} z N_B [u_B^+ B^- + u_C^- C^- + u_B^+ C^- ]
\]

\[
\omega_{A^+ B^-} = u_A^+ B^- - \frac{1}{2}(u_A^+ A^- + u_B^+ B^- ) \\
U = U_{AC} + U_{BC} + N_A^+ B^- \omega_{A^+ B^-}
\]
Solutions with multiple sub-lattices

\[ N_{AB} = \frac{1}{2} zN2X_A^+ X_{B^+} = z \left( \frac{N_A^+ N_{B^+}}{N} \right) \]

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

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

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

\[ \Omega_{A^+B^+} \approx zL\omega_{A^+B^+} \]

\[ \Delta_{mix} H_m \approx \Delta_{mix} U_m = \Omega_{A^+B^+} X_A^+ X_{B^+} \]

\[ \mu_{AC} - \mu_{AC}^0 = RT \ln X_A^+ + \Omega_{A^+B^+} X_{B^+}^2 \]

\[ = RT \ln x_{AC} + \Omega_{A^+B^+} x_{BC}^2 \]
Order-disorder systems

\( \sigma = \text{Order parameter a number that goes from 0 for disordered to 1 for ordered} \)

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 \( \frac{1}{2} (1 + \sigma) \)

\( N_A + N_B = 2N \) \( zN \) interactions

Disordered State \( U = N_{AA}u_{AA} + N_{BB}u_{BB} + N_{AB}u_{AB} \)

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

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

\( \Delta_{\text{dis}}H = H(\sigma) - H(\sigma = 1) = H(\sigma) - zN\sigma_{AB} \)

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

Disordered State

\[ U = N_{AA}u_{AA} + N_{BB}u_{BB} + N_{AB}u_{AB} \]

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

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

\[ \Delta_{\text{dis}}H = H(\sigma) - H(\sigma = 1) = H(\sigma) - zNu_{AB} \]

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

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

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

\[ + (1+\sigma)\ln(1+\sigma) - 2 \ln 2] \]

\[ d(\Delta_{\text{mix}}G)/d\sigma = 0 \text{ which yields} \]

\[ \ln \frac{1+\sigma}{1-\sigma} = \frac{\sigma z\omega_{AB}}{k_BT} = \frac{2\sigma T_{\text{trs}}}{T} \]
Figure 9.10 Order parameter $\sigma$ for the Bragg–Williams model as a function of reduced temperature.

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

Second Order Transition
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.

- **Normal Spinel**: $x = 0$
- **Inverse Spinel**: $x = 1$
- **Random Spinel**: $x = 2/3$

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

$S = 0$ for $x = 0$  Regular Spinel
Ordered and Regular Spinels disorder at high temperature to increase entropy

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

Figure 9.11 (a) Configurational entropy of a spinel \( \text{AB}_2\text{O}_4 \) as a function of the composition parameter, \( x \). (b) Degree of disorder, \( x \), as a function of temperature for selected values of \( \Delta_{\text{dis}} H \).
For a Normal Spinel the disordering process is:

\[
(A)_\text{tet} + (B)_\text{oct} = (A)_\text{oct} + (B)_\text{tet}
\]

\[
\Delta_{\text{dis}} G = \Delta_{\text{dis}} H - T \Delta_{\text{dis}} S = -RT \ln K
\]

\[
K = \frac{x^2}{(1-x)(2-x)}
\]
Non-stoichiometric Compounds

Mass action law treatment of defect equilibria

Perovskite type oxide

Three sublattices
A 12 coordination
B 6 coordination number
O

Oxygen vacancies on the O lattice randomly arranged

B atoms are reduced by oxygen vacancies

\[
\begin{align*}
2O_O^x + 4B_B^x &= 2V_O^- + 4B'_B + O_2 (g) \\
O_O^x \text{ and } V_O^- \text{ are an oxygen ion and an oxygen vacancy} \\
B_B^x \text{ and } B'_B \text{ are trivalent and divalent B-ions}
\end{align*}
\]

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

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

Solid Solution Approach

\[ Z = \sum_c \sum_s \exp \left( -\frac{H_{c,s}}{k_BT} \right) = \sum_c \exp \left( -\frac{G_c}{k_BT} \right) \]

\[ \Delta_f G = -k_BT \ln Z = -k_BT \ln \sum_c g_c \exp \left( -\frac{\Delta_f G_c}{k_BT} \right) \]

**Proposition:** A perovskite \( \text{ABO}_3-\delta \) is made up of \( \text{ABO}_3 \) and \( \text{ABO}_{2.5} \) in an ideal solution (no defect defect interactions)

\[ \Delta_f G_c (\text{ABO}_3-\delta) = (1-2\delta)\Delta_f G_m^o (\text{ABO}_3) + 2\delta \Delta_f G_m^o (\text{ABO}_{2.5}) \]

\[ g_c = \frac{(3N)!}{N!} \cdot \frac{N!}{N_{V_O}!(3N-N_{V_O})! \cdot N_{B^{2+}}!(N-N_{B^{2+}})!} \]

- \( N \) is the number of B atoms
- \( N_{V_O} \) is the number of oxygen vacancies
- \( N_{B^{2+}} \) is the number of \( B^{2+} \) in \( \text{ABO}_3-\delta \)

\[ \Delta_f G_m (\text{ABO}_3-\delta) = (1-2\delta)\Delta_f G_m^o (\text{ABO}_3) + 2\delta \Delta_f G_m^o (\text{ABO}_{2.5}) + RT \left[ (1-2\delta) \ln(1-2\delta) + 2\delta \ln(2\delta) + \delta \ln \left( \frac{\delta}{3} \right) + (3-\delta) \ln \left( 1-\frac{\delta}{3} \right) \right] \]
\[
\log pO_2 = \left( \frac{1}{RT \ln 10} \right) \left[ 4\Delta_f G_m^o (ABO_3) - 4\Delta_f G_m^o (ABO_{2.5}) \right] \\
+ 4[\log(1 - 2\delta) - \log(2\delta)] - 2 \log \left( \frac{\delta}{3 - \delta} \right)
\]

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

\[
\log K = \left( \frac{1}{RT \ln 10} \right) \left[ 4\Delta_f G_m^o (ABO_3) - 4\Delta_f G_m^o (ABO_{2.5}) \right]
\]
Figure 9.12 (a) Enthalpy of oxidation of $\text{La}_{1-x}\text{A}_x\text{BO}_3-\delta$ as a function of $x$. Open symbols represent 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.