Solutions
Chapter 9
Ideal and Non-ideal

A solution is a homogeneous mixture of two or more substances. A solution can exist in any phase.

The major component in a solution is termed solvent (A) and all other constituents are solute(s) (B, C…).

For solutes to be soluble in a solvent their intermolecular forces (IMF) holding the solvent molecules (A-A) to form the condensed state must be broken to accommodate the solute particles. Also the forces holding the solute together (B-B) must be broken as well. These steps demand energy. The solute and solvent molecules then should then interact to make the ‘accommodation’ possible. That requires a release of energy that would compensate or exceed the total energy demand.

Vapor: gas phase molecule evaporated from solvent.
Gas: gas phase molecule of a different type than from the solvent.

The driving forces for dissolution are;

a. Entropy gain due to dissolution.
b. Heat release (net attractive or near zero repulsion) due to various inter-particle interactions such as H-bonding, dipole-dipole, ion-induced dipole.

London (also known as van der Walls forces…ever present).

Similar intermolecular forces in the solvent and solute (A-B ≈ A-A ≈ B-B) produces ideal solutions.

Deviations from the intermolecular forces mentioned above produces non-ideal solutions.

The liquid A is in equilibrium with its (saturated) vapor phase with partial pressure of A (saturated vapor pressure of pure A at the temperature = P*A).

If another liquid B (that is soluble in A) is added, the partial pressure of A is reduced. The vapor phase now contains both A and B; vapor pressure of A (P*A = x*A*P*A) and vapor pressure of B (P*B = x*B*P*B) at the temperature of the liquid.

\[ P = x*A*P*A + x*B*P*B \]

Raoult’s Law (followed by ideal solutions)

Very dilute solutions are ideal solutions.
Chemical Potential $\mu_i$ of a Component $i$ in the Gas and Solution Phases:

Because each $i$ in two phases are in equilibrium, for each component $i$,

For each $i$,

$$\mu_i^{vap} = \mu_i^{soln}$$

For each $i$ in solution,

$$\mu_i^{vap} = \mu_i^{soln} = \mu_i^\circ + RT \ln \left( \frac{P_i}{P^*} \right); \mu_i^\circ = \text{chemical potential (g) pure vap}$$

$$\mu_i^{soln} = \mu_i^\circ + RT \ln \left( \frac{P_i}{P^*} \right) \quad \text{Eq. 1}$$

For pure solvent, vapor.

$$\mu_i^{vap} = \mu_i^{soln} = \mu_i^\circ \quad \mu_i^\circ = \mu_i^0$$

$$\mu_i^{soln} = \mu_i^0 + RT \ln \left( \frac{P_i}{P^*} \right) \quad \text{Eq. 2}$$

For $i$ (solvent/solute);

$$\mu_i^{vap} = \mu_i^{soln} = \mu_i^\circ \quad \mu_i^\circ = \mu_i^0 + RT \ln \left( \frac{P_i}{P^*} \right)$$

Ideal solution

$$\mu_i^{vap} = \mu_i^{soln} = \mu_i^\circ \quad \mu_i^\circ = \mu_i^0 + RT \ln \left( \frac{P_i}{P^*} \right)$$

Relationship between the chemical potential of any component $i$, in an ideal solution to the chemical potential of the pure liquid form of component and the mole fraction of that component in the solution.

$$\mu_i^{vap} = \mu_i^{soln} = \mu_i^\circ + RT \ln \left( \frac{P_i}{P^*} \right) = \mu_i^0 + RT \ln \left( \frac{P_i}{P^*} \right)$$

Valid equation where all components are volatile and miscible in all proportions.

Thermodynamics of mixing (ideal solutions; $\Delta V_{mix} = 0$, $\Rightarrow \Delta H_{mix} = 0$)

Similar to gaseous mixtures; $\Delta G_{mix} = nRT \sum x_i \ln x_i$ and $\Delta S_{mix} = \left( \frac{\Delta G_{mix}}{T} \right)_{p, n, v, i} = -nRT \sum x_i \ln x_i$

Also $\Delta V_{mix} = \left( \frac{\Delta G_{mix}}{p} \right)_{n, v, i} = 0$ by definition

Therefore $\Delta H_{mix} = \Delta G_{mix} + T \Delta S_{mix}$

$$\Delta H_{mix} = nRT \sum x_i \ln x_i + T(-nRT \sum x_i \ln x_i) = 0$$

Summary:

$$\Delta G_{mix} < 0$$ \quad \text{miscible}

$$\Delta S_{mix} > 0$$

$$\Delta V_{mix} = 0$$

$$\Delta H_{mix} = 0$$

$$V = n \left( \frac{\partial V}{\partial n} \right) + n \left( \frac{\partial V}{\partial n_i} \right)$$

Constants for ideal solutions, not constant for non ideal solutions
Ideal Binary Solutions

For a binary solution with components 1 and 2 the total vapor pressure is,

\[ P_{\text{total}} = P_1 + P_2 - x_1 P^*_1 + (1 - x_1) P^*_2 - P^*_1 + (P^*_1 - P^*_2 x_1) \]

Where \( x_i \) = mole fraction in solution, \( P^*_i \) vapor pressure of pure liquid \( i \); \( x_1 \) and \( x_2 \).

Mole fraction of each component in the gaseous phase be \( y_1 \) and \( y_2 \):

\[ y_1 = \frac{x_1 P^*_1}{P_1 - P_2} \quad \Rightarrow \quad x_1 = \frac{y_1 P^*_2}{P_2'} \]

Composition of liquid and gaseous phases, \( x_i \) and \( y_i \), are not the same in the 2-phase region at a given \( P^*_2 \):

\[ x_i = \frac{P_{\text{vap}(i)} - P^*_i}{P_1 - P_2} \quad y_i = \frac{P_{\text{vap}(i)} - P^*_i}{P^*_2} \]

For benzene, \( P^*_B \) and \( P^*_n \).
For a binary mixture of \( i \) and \( j \)

**Average composition** \( Z_i \)

\[
Z_i = \frac{n_i^n + n_j^n}{n_i + n_j} = \frac{n_i}{n_{total}}
\]

*liq. and vap. coexistence region*

**Average composition** refers to the average from all relevant phases, liquid and/or vapor phases.

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**Phase rule** for an ideal solution of two components (\( C=2 \)) and three independent state variables (\( P, T \) and \( Z_{benzene} \)).

\[
F = C - p + 2 \quad F = 4 - p
\]

At \( b, c \); two phase system, composition in phases would change; tie line.

At the extremities of the tie line; \( x_{benzene} < x_{toluene} \), vapor enriched with benzene.

*Always more of volatile component in vapor phase.*
Relative Amounts of Materials in the two Phases

For benzene

\[ n_b^* = n_b^\text{liq} + n_b^\text{vap} \]

\[ \beta_b = n_b^\text{vap} - n_b^\text{liq} = \frac{\gamma_b}{\gamma_b} \frac{n_b^\text{vap}}{n_b^\text{liq}} = \frac{n_b^\text{vap} - n_b^\text{liq}}{n_b^\text{liq}} \]

multiplication, followed by subtraction:

\[ n_b^\text{liq}(\beta_b - x_b) = n_b^\text{vap}(y_b - Z_b) \]

Lever Rule!!

Fractional Distillation: Temperature-Composition Diagram

A separation technique based on the fact that vapor phase above a solution is richer in the more volatile component.

The temperature-composition diagram: temperature of the solution (and vapor) vs. the average system composition, for a given total vapor pressure.
Non-Ideal Solutions: Real Solutions (Binary)

Non-similar intermolecular forces of solvent and solute (a) \(A - B > A - A = B - B\) or (b) \(A - B < A - A = B - B\) would produce non-ideal solutions. \(T_b vs x\) plots show solutions with azeotropic mixtures, (a) with maximum and (b) minimum boiling points.

Azeotropic mixture is a liquid mixture with a constant (minimum or maximum boiling point). Such a mixture will distill without decomposition and fixed mole ratio.

The Gibbs-Duhem Equation

In a binary solution the chemical potentials of the two components are related. This is an important result, because it allows the chemical potential of a nonvolatile solute (with near zero vapor pressure) be determined. For a binary solution, starting with:

\[
dG = \int \left( \frac{\partial G}{\partial n_1} \right)_{T,P} \, dn_1 + \int \left( \frac{\partial G}{\partial n_2} \right)_{T,P} \, dn_2
\]

At constant \(T, P\)

\[
dG = \mu_1 dn_1 + \mu_2 dn_2
\]

For a solution made by mixing components 1 and 2, starting from nothing and ending with \(n_1\) and \(n_2\) moles, Gibbs energy changes from 0 to \(G\) (say).

\[
\int G = \mu_1 n_1 + \mu_2 n_2
\]

Colligative Properties

Colligative properties considered are:

- Freezing point depression of the solution
- Boiling point elevation of the solution
- Osmotic pressure of the solution

Colligative properties of solutions depend on the amount of the non-volatile solute molecules or ions dissolved in a solvent, and does not depend on their molecular structure/nature.

**Dissolution of a solute in a solvent makes the solution more stable w.r.t. the pure solvent due to the loss of Gibbs free energy resulting from the increase in entropy.** The solid phase formed at the freezing point and the vapor phase remain unchanged as no solute is present in the solid and no non-volatile solute is present in the vapor phase.
\[ d\mu = -S_m dT + V_m dP \]

\[ \left( \frac{d\mu}{dT} \right)_P = -S_m \]

Slopes:
\[ S_{solv} > S_{sol} > S_{solid} \]

With \( T \) increase, \( s \to l \to g \)

At a given temperature the phase with the lowest \( \mu \) is the most stable.

Only the liquid chemical potential is affected due to the formation of the solution.

Expansions - Chemical Potential Plots at constant \( P \)
At f.p. the solution is in equilibrium with the pure solidified solvent, therefore;
\[ \mu_{\text{solution}} = \mu^*_{\text{solid}} \]
\[ \frac{\mu_{\text{solution}}}{RT} + RT \ln x_{\text{solution}} = \mu^*_{\text{solid}} \]

Rearranging:
\[ \ln x_{\text{solution}} = \frac{-\Delta G_{\text{fus}}}{RT} \]
Because, \( s \rightarrow l \) (melting/fusion)
\[ \Delta G = \mu^*_{\text{solid}} - \mu^*_{\text{solution}} \]
\[ \left( \frac{\partial T}{\partial x_{\text{solution}}} \right)_p = \frac{\partial T}{\partial \Delta G_{\text{fus}}} \]
\[ \left( \frac{\partial T}{\partial x_{\text{solution}}} \right)_p = \left( \frac{\partial \ln x_{\text{solution}}}{\partial x_{\text{solution}}} \right)_p \]

Freezing point depression of the solution
At f.p. the solution is in equilibrium with the pure solid (solvent), therefore;
\[ \mu_{\text{solution}} = \mu^*_{\text{solid}} \]
\[ \frac{\mu_{\text{solution}}}{RT} + RT \ln x_{\text{solution}} = \mu^*_{\text{solid}} \]
If the molality of the solute is \( m_{\text{solute}} \); 1 kg of solvent contains \( m \) moles of solute.

\[
\ln x_{\text{solute}} = \ln \left( \frac{m_{\text{solute}}}{m_{\text{solute}} + m_{\text{solvent}}} \right)
\]

\[
m_{\text{solute}} = \frac{1000 \times m_{\text{solute}}}{M_{\text{solvent}}}
\]

\[
m_{\text{solvent}} = \frac{m_{\text{solvent}} \times M_{\text{solvent}}}{1000}
\]

\[
\ln x_{\text{solute}} = \ln \left( \frac{1}{1 + \frac{m_{\text{solvent}} \times M_{\text{solvent}}}{M_{\text{solvent}}}} \right) = -\ln (1 + m_{\text{solvent}} M_{\text{solvent}})
\]

\[
-\ln (1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - x \quad (x < 1)
\]
Boiling point elevation of the solution

The boiling point elevation can be calculated using the logic with the appropriate enthalpy and free energy term and the temperature at which f->g phase equilibrium occur at 1 atm pressure (standard pressure).

\[ \Delta T_b = \frac{\Delta H_{solution}}{\Delta H_{vaporization}} \times n_{solute} = K_b m_{solute} \]

Osmotic pressure of the solution

Semipermeable membrane allows movement of small solvent molecules but do not permit larger solutes to pass through it. When a pod made from a semipermeable membrane containing a solute that do not pass through the membrane is immersed in the pure solvent, the solvent diffuses into the pod at the start. Eventually this diffusion ends when equilibrium is established.

At equilibrium the pressure is higher in the pod than in the surrounding solvent. The process of diffusion through the membrane would dilute the solution is osmosis. The excess pressure in the solution with respect to the solvent is termed osmotic pressure.
At equilibrium,

\[ \mu_{\text{solute}}^* (T, P, x_{\text{solute}}) = \mu_{\text{solute}}^* (T, P) \]

\[ \mu_{\text{solute}}^* (T, P + \pi, x_{\text{solute}}) = \mu_{\text{solute}}^* (T, P + \pi) + RT \ln x_{\text{solute}} \]

\[ \mu_{\text{solute}}^* (T, P) = \mu_{\text{solute}}^* (T, P + \pi) + RT \ln x_{\text{solute}} \]

\[ \mu_{\text{solute}}^* (T, P + \pi, x_{\text{solute}}) = \mu_{\text{solute}}^* (T, P + \pi) + RT \ln x_{\text{solute}} \]

\[ \Rightarrow \mu_{\text{solute}} < \mu_{\text{solute}}^* \]

Naturally, \( \mu_{\text{solute}} \) is less compared to \( \mu_{\text{solute}}^* \) (solution side more stable). Thus given the opportunity to come to equilibrium by separating them via a semipermeable membrane there will be a movement of molecules from the solvent side to solution side.

Movement to stability (to reach equilibrium) is to equalize the potentials. This is achieved by developing a higher pressure on the solution side brought about by the movement of solvent molecules through the semipermeable membrane.

Because \( dG = -SdT + VdP \) and \( d\mu = dG_m = -S_mdT + V_m dP \):

\[ d\mu = -S_mdT + V_m dP \]

\[ \int_{\text{solvent}} d\mu = \int_{\text{solute}} \left( -S_mdT + \frac{V_m dP}{P} \right) \]

\[ \mu_{\text{solute}}^* (T, P + \pi, x) - \mu_{\text{solute}}^* (T, P) = V_m \pi \]

\[ \Rightarrow \mu_{\text{solute}}^* (T, P) = \mu_{\text{solute}}^* (T, P + \pi) + RT \ln x_{\text{solute}} \]

\[ \mu_{\text{solute}}^* (T, P + \pi, x) - \mu_{\text{solute}}^* (T, P + \pi) + RT \ln x_{\text{solute}} = V_m \pi \]

\[ -RT \ln x_{\text{solute}} = V_m \pi \]

\[ \ln x_{\text{solute}} = \ln (1 - x_{\text{solute}}) \approx -x_{\text{solute}} \]

for dilute solutions

\[ \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} \approx \frac{n_{\text{solute}}}{n_{\text{solvent}}} \]

for dilute solutions

Therefore \( RT \frac{n_{\text{solute}}}{n_{\text{solvent}}} = V_m \pi \Rightarrow RT n_{\text{solute}} = n_{\text{solvent}} V_m \pi = V \pi \)

\[ \pi = \frac{n_{\text{solute}} RT}{V} \]

vart Hoff Equation \( [\pi V = n_{\text{solute}} RT] \)
Non-Ideal Solutions: Real Solutions (Binary – volatile components)

Non-similar intermolecular forces of solvent and solute (a) A-B < A-A = B-B (positive deviation) or (b) A-B > A-A = B-B (negative deviation) would produce non-ideal solutions, however they may be miscible.

Non ideal solutions do not follow the Raoult’s Law. $P_i = x_i P^*$

The partial and total pressures above a real (non-ideal) solution differ considerably from that predicted by Raoult’s law. From the thermodynamic point of view the characteristics of real solutions are as follows:

- $\Delta G_{\text{mix}} < 0$: miscible
- $\Delta S_{\text{mix}} > 0$: (positive or negative for non-ideal solutions)
- $\Delta H_{\text{mix}} = 0$: (partial molar quantity)

$$V^\text{mix} = x(V^*_1 + (1-x)W^*_1)$$
$$V^\text{ideal} = xV^*_1 + (1-x)W^*_1$$
$$\Delta V_{\text{mix}} - V^\text{ideal} \neq 0$$

Concept of partial molar quantities (partial molar volume)

Partial molar volumes:

- Add $V_{n_1}, n_2$
- $V_{\text{mix}} = x_1 \left( \frac{\partial V}{\partial n_1} \right) + x_2 \left( \frac{\partial V}{\partial n_2} \right)$ real solution
- $\left( \frac{\partial V}{\partial n_1} \right), \left( \frac{\partial V}{\partial n_2} \right)$ - molar volumes of 1 and 2 at constant T,P.

These gradients are not constants for 'real solutions'.

Molar volumes in real solutions are dependent on the composition,

$$V(P,T,n_1,n_2) = \frac{\partial V}{\partial n_1}$$ partial molar volume

For a binary solution of general composition $n_1$ and $n_2$,

$$V_{\text{mix}} = x_1 V^*(P,T,n_1) + x_2 V^*(P,T,n_2)$$
$$\Delta V_{\text{mix}} = (n_1 V^*_1(P,T,n_1) + n_2 V^*_2(P,T,n_2)) - V_{\text{ideal}} \neq 0$$

Partial molar volumes ($V$) depend on the concentration of all components therefore the total volume of the mixture ($V$) is composition dependent (non linear).
Example: Chloroform/acetone mixtures

Changes in the partial molar volumes with concentration – small and not negligible.

As $V_1$ increases $V_2$ decreases and vice versa. Partial molar volumes are related in the same way as the chemical potentials are related in the Gibbs-Duhem equation.

Gibbs-Duhem Equation

\[ n_1 \, d\mu_1 + n_2 \, d\mu_2 = 0 \quad \text{or} \quad x_1 \, d\mu_1 + x_2 \, d\mu_2 = 0 \]

In terms of the partial molar volumes, the Gibbs-Duhem equation takes the form:

\[ x_1 \, dV_1 + x_2 \, dV_2 = 0 \quad \Rightarrow \quad dV_1 = \frac{x_2}{x_1} \, dV_2 \]
Ideal Dilute Solution:

Real solution $\rightarrow$ Ideal solution (can be described precisely).

$\mu_i^{\text{solvent}} = \mu_i^{*} + RT \ln \frac{P_i}{P_i^*}$ (* refers to the pure component $i$.

$P = x_i P^*$

For real solutions (non-ideal) $P_i \neq x_i P_i^*$,

$P = x_i P_i^*$; $x_i = \frac{P_i}{P_i^*}$, $i = \text{solute}$

define activity, $a_i = \frac{P_i}{P_i^*}$ (for ideal solution $a_i = x_i$)

and activity coefficient, $\gamma_i = \frac{a_i}{x_i}$

activity coefficient, $\gamma_i = \frac{a_i}{x_i}$; $\gamma_i = \gamma_i^{\text{solvent}}$

$\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$ (or $x_{\text{solute}} \rightarrow 0$)

As $P_{\text{ideal}} \rightarrow 0$, $x_{\text{solute}} \rightarrow 0$; real $\rightarrow$ ideal

As $P_{\text{ideal}} \rightarrow P_{\text{ideal}}$, $x_{\text{solute}} \rightarrow 1$; real $\rightarrow$ ideal

$\gamma$ has no molecular model, should be considered as a correction (fudge) factor to account for the deviation from ideality.

$\mu_i^{\text{solvent}} = \mu_i^{*} + RT \ln \gamma_i$ for real solutions, all components.