1. Various Properties of $N$ components in a Single Phase

$V =$ total volume of the phase

$v = \frac{V}{n_1 + \cdots n_N} =$ molar volume of the phase

$v_i = v \bigg|_{n_j \neq i} = 0 =$ molar volume if phase contains only pure component $i$

$\bar{V}_i = \left( \frac{\partial V}{\partial n_i} \right)_{T,P,n_j \neq i} =$ partial molar volume of component $i$

2. Relationships at fixed $T$ and $P$

$V_{T,P} = \sum_{i=1}^{N} n_i \bar{V}_i$

$v_{T,P} = \sum_{i=1}^{N} x_i \bar{V}_i$

$\frac{dV_{T,P}}{dT} = \sum_{i=1}^{N} \bar{V}_i \frac{dn_i}{dT} : \text{from taking differentials}$

$0 = \sum_{i=1}^{N} n_i \frac{d\bar{V}_i}{dT} = \sum_{i=1}^{N} x_i \frac{d\bar{V}_i}{dT} : \text{Gibbs-Duhem}$
Example 1: After mixing various moles of component $A$ with $B$ (at a fixed $T$ and $P$) resulted in the following regression equation for molar volume:

$$v(x_A) = (ax_A^3 + bx_A^2 + cx_A + d) \text{ cm}^3 \text{ mol}^{-1}$$

$$a = 0.3; \quad b = 0.9; \quad c = -1.6; \quad d = 1$$

Evaluate/check the following under the conditions specified:

a) $V$ and $\nu$ for a mixture of 30 mol $A$ and 50 mol $B$

b) $\nu_B$

c) $\bar{V}_A$ and $\bar{V}_B$ as a function of $x_A$

d) $\bar{V}_A$ and $\bar{V}_B$ for a mixture of 30 mol $A$ and 50 mol $B$

e) Verify that $V = n_A \bar{V}_A + n_B \bar{V}_B$ using results from items a) and d)

f) $\Delta V$ after adding 10 moles of $A$ and 5 moles of $B$ to conditions in item a)

g) Verify Gibbs-Duhem relation for $\bar{V}_A$ and $\bar{V}_B$ using result from item c)

3. Properties Change of Mixing

Thought experiment:
Consider two types of spheres, $A$ and $B$, having equal density but volume($A$) = 2 volume($B$). Take different quantities of each type but summing up to the same total pieces, e.g. 1000 piece total. Shake together until well-mixed and measure the volume of the mixture.

$\rightarrow$ Packing will impact the volume:
Possible outcome:

Notes:

1. Molar volume at ① is for pure \( B \) and at ④ for pure \( A \).
2. At ③, additional \( B \) will reduce the molar volume of the mixture (as \( x_A \) is reduced).
3. Mixing based on simple averaging is represented by a straight line connecting \( v_A \) and \( v_B \).
4. Since \( B \) might be filling voids resulting in tighter packing, the resulting volume is expected to be less than just a simple weighted average.
5. For a system of molecules, other effects may come to play, e.g. intermolecular attractive or repulsive forces.

Let \( \Delta_{mix}v \) be the difference between the actual \( v(x_A) \) from the ideal mixing (i.e. simple average),

\[
\Delta_{mix}v = v - \sum_{i=1}^{N} x_i v_i
\]

(Note that the term \( \sum_{i=1}^{N} x_i v_i \) is in a line (for binary system) or plane (for a ternary system) with vertices at properties of pure components)

Alternatively,

\[
\Delta_{mix}v = \sum_{i=1}^{N} x_i \bar{V}_i - \sum_{i=1}^{N} x_i v_i = \sum_{i=1}^{N} x_i (\bar{V}_i - v_i)
\]
Also, if we multiply $\Delta_{mix} v$ by $n_T = \sum_{i=1}^{N} n_i$,

$$
\Delta_{mix} V = n_T \Delta_{mix} v \\
= n_T \left( v - \sum_{i=1}^{N} x_i v_i \right) \\
= V - \sum_{i=1}^{N} n_i v_i
$$

Alternatively,

$$
\Delta_{mix} V = \sum_{i=1}^{N} n_i \bar{v}_i - \sum_{i=1}^{N} n_i v_i = \sum_{i=1}^{N} n_i (\bar{v}_i - v_i)
$$

**Example 2:** Consider the binary system consisting $A$ and $B$ given in example 1

$$
v(x_A) = (a x_A^3 + b x_A^2 + c x_A + d) \frac{cm^3}{mol}
$$

$a = 0.3; b = 0.9; c = -1.6; d = 1$

Find $\Delta_{mix} v(x_A)$.

Solution:

$$
v_A = v(1) = a + b + c + d = 0.6 \frac{cm^3}{mol}
$$

$$
v_B = v(0) = d = 1 \frac{cm^3}{mol}
$$

$$
\Delta_{mix} v(x_A) = v(x_A) - [x_A v_A + (1 - x_A) v_B]
= v(x_A) - [(x_A)(0.6) + (1 - x_A)(1)]
= v(x_A) - [1 - 0.4 x_A]
= 0.3 x_A^3 + 0.9 x_A^2 - 1.2 x_A
$$