**Topic1300**

*“Excess” Thermodynamic Properties*

Description of the thermodynamic properties of both solutions and liquid mixtures in terms of excess properties has considerable merit. However care has to be exercised in defining excess properties [1-3]. It is not sufficient, for example, to argue that all properties of a given binary liquid mixture would be linear functions of mole fraction composition in the event that the properties of this mixture are “ideal”. There is of course no rule that states one is forbidden from doing this. But it is not allowed to identify immediately deviations “ideal” with those features responsible for deviation from thermodynamically defined ideal based on, for example, Gibbs energies of mixing. Similarly it is not good practice to use an arbitrary definition of the properties of ideal solutions and to account for deviations from ideal directly in terms of fraction responsible for deviations in the thermodynamic properties of the solution from ideal.

Care has to be exercised in anticipating patterns in the properties of solutions which can be claimed as ideal from a thermodynamic viewpoint. We illustrate the point with reference to expansivities in the context of binary liquid mixtures. A given liquid mixture is prepared at defined T and p using \( n_1 \) moles of water and \( n_2 \) moles of liquid 2.

Then, \( V_{\text{mix}} = n_1 \cdot V_1^{\text{mix}} + n_2 \cdot V_2^{\text{mix}} \) \hspace{1cm} (a)

At fixed pressure (and at ‘A = 0’),

\[
\left[ \frac{\partial V_{\text{mix}}}{\partial T} \right]_p = n_1 \cdot \left[ \frac{\partial V_1^{\text{mix}}}{\partial T} \right]_p + n_2 \cdot \left[ \frac{\partial V_2^{\text{mix}}}{\partial T} \right]_p \hspace{1cm} (b)
\]

We divide through by \( V_{\text{mix}} \) and incorporate new terms.

\[
\left[ \frac{1}{V_{\text{mix}}} \right] \left[ \frac{\partial V_{\text{mix}}}{\partial T} \right]_p = \left[ \frac{n_1 \cdot V_1^{\text{mix}}}{V_{\text{mix}}} \right] \left[ \frac{\partial V_1^{\text{mix}}}{\partial T} \right]_p + \left[ \frac{n_2 \cdot V_2^{\text{mix}}}{V_{\text{mix}}} \right] \left[ \frac{\partial V_2^{\text{mix}}}{\partial T} \right]_p \hspace{1cm} (c)
\]
The term \( \left[ n_1 \cdot V_1(\text{mix})/V(\text{mix}) \right] \) is an effective volume fraction for substance 1, \( \phi_1 \); similarly for \( \phi_2 \). We define effective component expansibilities, \( \alpha_1 \) and \( \alpha_2 \).

Thus,
\[
\alpha_1 = \left[ 1/V_1(\text{mix}) \right] \left[ \partial V_1(\text{mix})/\partial T \right]_p \quad \text{(d)}
\]
and
\[
\alpha_2 = \left[ 1/V_2(\text{mix}) \right] \left[ \partial V_2(\text{mix})/\partial T \right]_p \quad \text{(e)}
\]

Hence (using equation (c))
\[
\alpha_p(\text{mix}) = \phi_1(\text{mix}) \cdot \alpha_1(\text{mix}) + \phi_2(\text{mix}) \cdot \alpha_2(\text{mix}) \quad \text{(f)}
\]

For an ideal mixture, \( V(id:\text{mix}) = n_1 \cdot V_1^i(\ell) + n_2 \cdot V_2^i(\ell) \quad \text{(g)} \)

Since \( \phi_1(id) = n_1 \cdot V_1^i(\ell)/V(id:\text{mix}) \), the volume fraction for the ideal mixture [similarly for \( \phi_2(id) \)], then
\[
\alpha_p(id : \text{mix}) = \phi_1(id) \cdot \alpha_{p1}^i(\ell) + \phi_2(id) \cdot \alpha_{p2}^i(\ell) \quad \text{(h)}
\]

An excess (isobaric) thermal expansivity is given by equation (i).
\[
\alpha_p(E) = \alpha_p(\text{mix}) - \alpha_p(id : \text{mix}) \quad \text{(i)}
\]

Equation (h) confirms that
\[
\alpha_p(id : \text{mix}) \neq x_1 \cdot \alpha_{p1}^i(\ell) + x_2 \cdot \alpha_{p2}^i(\ell) \quad \text{(j)}
\]

In other words the definition of an ideal property using the otherwise conventional form in equation (j) is invalid.

**Footnotes**