Internal Pressure; Liquid Mixtures; Excess Property

The thermodynamic equation of state takes the form shown in equation (a).

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p
\]  

(a)

The partial differential \(\partial U / \partial V\)_T is the internal pressure, \(\pi_{\text{int}}\) (with units, N m\(^{-2}\)). A calculus operation relates three interesting partial derivatives in the context of p-V-T properties; equation (b).

\[
\frac{\partial p}{\partial T}_V = -\left( \frac{\partial V}{\partial T} \right)_p \cdot \left( \frac{\partial p}{\partial V} \right)_T
\]  

(b)

For a given liquid at defined T and p, the isobaric (equilibrium) thermal expansion, \(E_p\) equals \(\partial V / \partial p\)_T. The isothermal (equilibrium) compression \(K_T\) is defined by \(\partial V / \partial p\)_T. According to equations (a) and (b), \(\pi_{\text{int}}\) is given by equation (c).

\[
\pi_{\text{int}} = (T \cdot E_p / K_T) - p
\]  

(c)

For the purpose of the analysis described here, equation (c) describes the equilibrium molar properties of a given binary liquid mixture at temperature T and pressure p. The internal pressure is a non-Gibbsian property of a liquid. Nevertheless it is interesting to compare internal pressures of real and the corresponding ideal binary liquid mixture [1]. In other words we require an equation for the internal pressure of binary liquid mixture \(\pi_{\text{int}}^\text{id}\) having thermodynamic properties which are ideal. Marczak[1] uses equation (c) in which the corresponding molar properties of the mixture, mole fraction composition \(x_2\), \(E_{\text{pm}}^\text{id}(x_2)\) and \(K_{\text{Tm}}^\text{id}(x_2)\) are given by the mole fraction weighted properties of the pure liquids.

\[
E_{\text{pm}}^\text{id}(x_2) = \sum_{i=1}^{i=2} x_i \cdot E_{\text{pm}}^i(\ell)
\]  

(d)

\[
K_{\text{Tm}}^\text{id}(x_2) = \sum_{i=1}^{i=2} x_i \cdot K_{\text{Tm}}^i(\ell)
\]  

(e)

Equations (d) and (e) can be generalised to multi-component liquid mixtures. From equation (c) for a binary liquid mixture having thermodynamic properties which are ideal, the internal pressure \(\pi_{\text{int}}^\text{id}(x_2)\) is given by equation (f).

\[
\pi_{\text{int}}^\text{id}(x_2) = T \cdot \frac{E_{\text{pm}}^\text{id}(x_2)}{K_{\text{Tm}}^\text{id}(x_2)} - p
\]  

(f)
Or using equations (d) and (e), \( \pi_{\text{int}}^d(x_2) = \frac{\sum_{i=1}^{i=2} T \cdot x_i \cdot E_{pi}^* (\ell)}{\sum_{i=1}^{i=2} x_i \cdot K_{Ti}^* (\ell)} - p \) (g)

Equation (g) is re-written to establish \( \pi_{\text{int},i}^* (\ell) \) as a term on the r.h.s. of the latter equation for \( \pi_{\text{int}}^d(x_2) \).

\[
\pi_{\text{int}}^d(x_2) = -p + \sum_{i=1}^{i=2} x_i \cdot \frac{[\pi_{\text{int},i}^* (\ell) + p] \cdot K_{Ti}^* (\ell)}{\sum_{i=1}^{i=2} x_i \cdot K_{Ti}^* (\ell)} 
\] (h)

But according to equation (c), for the pure liquid \(-i\),

\[
\pi_{\text{int},i}^* (\ell) + p = T \cdot E_{pi}^* (\ell) / K_{Ti}^* (\ell) 
\] (i)

Hence from equation (h),

\[
\pi_{\text{int}}^d(x_2) = -p + \sum_{i=1}^{i=2} x_i \cdot [\pi_{\text{int},i}^* (\ell) + p] \cdot K_{Ti}^* (\ell) 
\] (j)

In other words,

\[
\pi_{\text{int}}^d(x_2) = -p + \frac{x_1 \cdot \pi_{\text{int},1}^* (\ell) \cdot K_{Ti}^* (\ell)}{\sum_{i=1}^{i=2} x_i \cdot K_{Ti}^* (\ell)} + \frac{x_2 \cdot \pi_{\text{int},2}^* (\ell) \cdot K_{T2}^* (\ell)}{\sum_{i=1}^{i=2} x_i \cdot K_{Ti}^* (\ell)} + \frac{x_2 \cdot p \cdot K_{T2}^* (\ell)}{\sum_{i=1}^{i=2} x_i \cdot K_{Ti}^* (\ell)} 
\] (k)

Hence, \( \pi_{\text{int}}^d(x_2) = \frac{\sum_{i=1}^{i=2} x_i \cdot \pi_{\text{int},i}^* (\ell) \cdot K_{Ti}^* (\ell)}{\sum_{i=1}^{i=2} x_i \cdot K_{Ti}^* (\ell)} \) (l)

By definition [1], for liquid component \(k\),

\[
\psi_k = \frac{x_k \cdot K_{Tk}^* (\ell)}{\sum x_i \cdot K_{Ti}^* (\ell)} 
\] (m)

In other words, \( \pi_{\text{int}}^d(x_2) = \sum_{i=1}^{i=2} \psi_i \cdot \pi_{\text{int},i}^* (\ell) \) (n)
The corresponding excess internal pressure at mole fraction \( x_2 \), \( \pi^E_{\text{int}}(x_2) \) is defined by equation (o).

\[
\pi^E_{\text{int}}(x_2) = \pi_{\text{int}}(x_2) - \sum_{i=1}^{i=2} \psi_i \cdot \pi^*_{\text{int},i}(\ell) \quad (o)
\]

Marczak [1] reports \( \pi^E_{\text{int}}(x_2) \) as a function of mole fraction \( x_2 \) for two binary liquid mixtures at 298.15 K; (a) methanol + propan-1-ol, and (b) tribromomethane + n-octane.

Footnotes