Topic 1440

Expansions: Isobaric: Binary Liquid Mixtures

The isobaric (equilibrium) expansion of a liquid, volume V, is defined by equation (a).

\[ E_p = \left( \frac{\partial V}{\partial T} \right)_p \]  

(a)

Both \( E_p \) and V are extensive properties of a mixture. Therefore it is convenient to refer to the molar property, \( E_{pm}(\text{mix}) \).

Thus \[ E_{pm}(\text{mix}) = \left( \frac{\partial V_m(\text{mix})}{\partial T} \right)_p \]  

(b)

At fixed T and p, \( V_m(\text{mix}) \) for a binary liquid mixture is related to the partial molar volumes of the two components.

\[ V_m(\text{mix}) = x_1 \cdot V_1(\text{mix}) + x_2 \cdot V_2(\text{mix}) \]  

(c)

From equation (b)

\[ E_{pm}(\text{mix}) = x_1 \cdot \left( \frac{\partial V_1(\text{mix})}{\partial T} \right)_p + x_2 \cdot \left( \frac{\partial V_2(\text{mix})}{\partial T} \right)_p \]  

(d)

For a binary mixture having molar volume \( V_m(\text{mix}) \) and density \( \rho(\text{mix}) \),

\[ \rho(\text{mix}) = \frac{(x_1 \cdot M_1 + x_2 \cdot M_2)}{V_m(\text{mix})} \]  

(e)

Here \( M_1 \) and \( M_2 \) are the molar masses of liquids 1 and 2 respectively.

\[ V_m(\text{mix}) = \frac{(x_1 \cdot M_1 + x_2 \cdot M_2)}{\rho(\text{mix})} \]  

(f)

Hence,

\[ \frac{\partial V_m(\text{mix})}{\partial T} = -\frac{[(x_1 \cdot M_1 + x_2 \cdot M_2)/\rho(\text{mix})] \cdot [\partial \ln(\rho(\text{mix}))]/\partial T}{\rho(\text{mix})} \]  

(g)

\( E_{pm}(\text{mix}) \) is obtained for a given mixture from the isobaric dependence of density on temperature. There is merit in considering equations for \( E_{pm}(\text{mix};id) \) of a binary mixture having ideal thermodynamic properties and hence for the related excess molar expansion \( E_{pm}^E \).

With, 

\[ E_{pm}(\text{mix};id) = x_1 \cdot E_1^*(\ell) + x_2 \cdot E_2^*(\ell) \]  

(h)

\[ E_{pm}^E = E_{pm}(\text{mix}) - E_{pm}(\text{mix};id) \]  

(i)

\( E_{pm}(\text{mix};id) \) is the mole fraction weighted sum of the isobaric expansions of the pure liquid components at the same T and p. The isobaric
expansibility of an ideal binary liquid mixture $\alpha_p^{\text{mix};\text{id}}$ is given by equation (j).

$$\alpha_p^{\text{mix};\text{id}} = \frac{x_1 \cdot E_{p1}^*(\ell) + x_2 \cdot E_{p2}^*(\ell)}{x_1 \cdot V_{p1}^*(\ell) + x_2 \cdot V_{p2}^*(\ell)}$$

(\text{j})

Or, $\alpha_p^{\text{mix};\text{id}} = \frac{x_1 \cdot E_{p1}^*(\ell)}{x_1 \cdot V_{p1}^*(\ell) + x_2 \cdot V_{p2}^*(\ell)} + \frac{x_2 \cdot E_{p2}^*(\ell)}{x_1 \cdot V_{p1}^*(\ell) + x_2 \cdot V_{p2}^*(\ell)}$  

(k)

Hence, $\alpha_p^{\text{mix};\text{id}} = \frac{x_1 \cdot V_{p1}^*(\ell) \cdot \alpha_{p1}^*(\ell)}{x_1 \cdot V_{p1}^*(\ell) + x_2 \cdot V_{p2}^*(\ell)} + \frac{x_2 \cdot V_{p2}^*(\ell) \cdot \alpha_{p2}^*(\ell)}{x_1 \cdot V_{p1}^*(\ell) + x_2 \cdot V_{p2}^*(\ell)}$

(l)

Hence, expansibility $\alpha_p^{\text{mix};\text{id}}$ can be expressed in terms of the volume fractions of the corresponding ideal binary liquid mixture.

$$\alpha_p^{\text{mix};\text{id}} = \phi_1^{\text{mix};\text{id}} \cdot \alpha_{p1}^*(\ell) + \phi_2^{\text{mix};\text{id}} \cdot \alpha_{p2}^*(\ell)$$

(m)

The excess (equilibrium) isobaric expansivity $\alpha_p^E^{\text{mix}}$ is given by equation (n) [1].

$$\alpha_p^E^{\text{mix}} = \frac{1}{V_m^{\text{mix}}} \left[ \left( \frac{\partial V_m^E^{\text{mix}}}{\partial T} \right)_p - V_m^E \alpha_p^{\text{mix};\text{id}} \right]$$

(n)

From another standpoint the thermal expansion of a binary liquid mixture is analysed in terms of the differential dependence of rational activity coefficients on temperature and pressure. For liquid component 1 at temperature $T$ and pressure $p$,

$$\mu_1^{\text{mix}} = \mu_1^0(\ell) + R \cdot T \cdot \ln(x_1 \cdot f_1) + \int_p^0 V_1^*(\ell) \cdot dp$$

(o)

Then $V_1^{\text{mix}} = V_1^*(\ell) + R \cdot T \cdot [\partial \ln(f_1)/\partial p]_T$  

(p)

At temperature $T$,

$$E_{p1}^{\text{mix}} = E_{p1}^{\text{mix};\text{id}} + R \cdot \partial [\ln(f_1)/\partial p]_T + R \cdot T \left[ \frac{\partial}{\partial T} \left( \frac{\partial \ln(f_1)}{\partial p} \right) \right]_{T,p}$$

(q)

$$E_{p2}^{\text{mix}} =$$

$$E_{p2}^{\text{mix};\text{id}} + R \cdot \partial [\ln(f_2)/\partial p]_T + R \cdot T \left[ \frac{\partial}{\partial T} \left( \frac{\partial \ln(f_2)}{\partial p} \right) \right]_{T,p}$$

(r)

Two equations follow for the excess partial molar isobaric expansions of the components of the mixture.
\[ E_{p_1}^E (\text{mix}) = R \cdot \left[ \partial \ln(f_1) / \partial p \right]_T + R \cdot T \cdot \left[ \frac{\partial}{\partial T} \left( \frac{\partial \ln(f_1)}{\partial p} \right) \right]_{T,p} \]  

\[ E_{p_2}^E (\text{mix}) = R \cdot \left[ \partial \ln(f_2) / \partial p \right]_T + R \cdot T \cdot \left[ \frac{\partial}{\partial T} \left( \frac{\partial \ln(f_2)}{\partial p} \right) \right]_{T,p} \]  

Therefore for the mixture,

\[ E_{p_m}^E (\text{mix}) = x_1 \cdot E_{p_1}^E (\text{mix}) + x_2 \cdot E_{p_2}^E (\text{mix}) \]

**Footnotes**

[1] For a binary liquid mixture at defined \( T \) and \( p \),

\[ V_m (\text{mix}) = V_{m_{\text{mix;id}}} + V_m^E \]

\[ \alpha_p (\text{mix}) = \frac{1}{V_m (\text{mix})} \cdot \frac{\partial}{\partial T} \left[ V_{m_{\text{mix;id}}} + V_m^E \right] \]

Or, \( \alpha_p (\text{mix}) = \frac{1}{V_m (\text{mix})} \cdot \frac{\partial V_{m_{\text{mix;id}}}}{\partial T} + \frac{1}{V_m (\text{mix})} \cdot \frac{\partial V_m^E}{\partial T} \)

But, \( \alpha_p (\text{mix;id}) = \frac{1}{V_{m_{\text{mix;id}}}} \cdot \frac{\partial V_{m_{\text{mix;id}}}}{\partial T} \)

By definition, \( \alpha_p^E = \alpha_p (\text{mix}) - \alpha_p (\text{mix;id}) \)

\[ \alpha_p^E (\text{mix}) = \left[ \frac{1}{V_m (\text{mix})} - \frac{1}{V_{m_{\text{mix;id}}}} \right] \cdot \frac{\partial V_{m_{\text{mix;id}}}}{\partial T} + \frac{1}{V_m (\text{mix})} \cdot \frac{\partial V_m^E}{\partial T} \]

\[ \alpha_p^E (\text{mix}) = \left[ \frac{V_m (\text{mix}) - V_{m_{\text{mix;id}}}}{V_m (\text{mix}) \cdot V_{m_{\text{mix;id}}}} \right] \cdot \frac{\partial V_m (\text{mix;id})}{\partial T} + \frac{1}{V_m (\text{mix})} \cdot \frac{\partial V_m^E}{\partial T} \]

\[ \alpha_p^E (\text{mix}) = \left[ \frac{V_m^E}{V_m (\text{mix})} \right] \cdot \alpha_p (\text{mix;id}) + \frac{1}{V_m (\text{mix})} \cdot \frac{\partial V_m^E}{\partial T} \]

Hence, \( \alpha_p^E (\text{mix}) = \frac{1}{V_m (\text{mix})} \cdot \left[ \frac{\partial V_m^E}{\partial T} \right]_{T,p} - V_m^E \cdot \alpha_p (\text{mix;id}) \)