Topic1510

Expansions; Isentropic; Liquid Mixtures

A given binary liquid mixture has mole fraction $x_1 [= 1 - x_2]$ at temperature $T$ and pressure $p$. The system is at equilibrium at a minimum in Gibbs energy where the affinity for spontaneous change is zero. The molar volume and molar entropy of the mixtures are given by equations (a) and (b).

$$V_m = V_m[T,p,x_1] \quad (a)$$
$$S_m = S_m[T,p,x_1] \quad (b)$$

These two equations describe the properties of the system in the T-p-composition domain; i.e. a Gibbsian description. We consider two dependences of the volume on temperature under the constraint that the affinity for spontaneous change remains at zero; i.e equilibrium expansions. The isobaric expansion is defined by equation (c).

$$E_p(mix) = \left(\frac{\partial V(mix)}{\partial T}\right)_p \quad (c)$$

The isentropic expansion is defined by equation (d)

$$E_s(mix) = \left(\frac{\partial V(mix)}{\partial T}\right)_s \quad (d)$$

In the latter case the system tracks a path with increase in temperature where the affinity for spontaneous change remains at zero and the entropy remains the same at that defined by equation (b). [NB $E_p(mix)$ and $E_s(mix)$ as defined by equations (c) and (d) are extensive properties.] The two expansions are related through the (equilibrium) isobaric heat capacity $C_p(mix)$ and the (equilibrium) isothermal compression $K_T(mix)$ [1].

Thus

$$E_s(mix) = E_p(mix) - \frac{C_p(mix) \cdot K_T(mix)}{T \cdot E_p(mix)} \quad (e)$$

In the context of the property $E_p(mix)$, the entropy of the system changes with an increase in temperature at constant pressure. But by definition the entropy does not change for an isentropic expansion, $E_s(mix)$.

For a binary liquid mixture having ideal thermodynamic properties,

$$E_s(mix;id) = E_p(mix;id) - \frac{C_p(mix;id) \cdot K_T(mix;id)}{T \cdot E_p(mix;id)} \quad (f)$$
In this comparison we note that $E_{p}(\text{mix})$ and $E_{p}(\text{mix};\text{id})$ refer to the same pressure but the entropies referred to in $E_{S}(\text{mix})$ and $E_{S}(\text{mix};\text{id})$ are not the same. The same contrast arises when we set out the two equations describing expansions of the pure liquids.

$$E_{S_{1}}^{*}(\ell) = E_{p_{1}}^{*}(\ell) - \frac{C_{p_{1}}^{*}(\ell) \cdot K_{T_{1}}^{*}(\ell)}{T \cdot E_{p_{1}}^{*}(\ell)} \quad (g)$$

$$E_{S_{2}}^{*}(\ell) = E_{p_{2}}^{*}(\ell) - \frac{C_{p_{2}}^{*}(\ell) \cdot K_{T_{2}}^{*}(\ell)}{T \cdot E_{p_{2}}^{*}(\ell)} \quad (h)$$

The subject is complicated by the galaxy of entropies implied by the phrase ‘at constant entropy’.

**Footnote**

[1] Using a calculus operation,

$$\left( \frac{\partial V}{\partial T} \right)_{S} = \left( \frac{\partial V}{\partial T} \right)_{p} - \left( \frac{\partial S}{\partial T} \right)_{p} \cdot \left( \frac{\partial V}{\partial S} \right)_{T} \cdot \left( \frac{\partial V}{\partial p} \right)_{T} \quad (a)$$

We note two Maxwell equations.

From $U = U[S,V]$, \( \partial^{2}U/\partial S \cdot \partial V = \partial^{2}U/\partial V \cdot \partial S \)

Then \( \left( \frac{\partial T}{\partial V} \right)_{S} = -\left( \frac{\partial p}{\partial S} \right)_{V} \)

We invert the latter equation. Hence

$$E_{S} = \left( \frac{\partial V}{\partial T} \right)_{S} = -\left( \frac{\partial S}{\partial p} \right)_{V} = \left( \frac{\partial V}{\partial S} \right)_{p} \cdot \left( \frac{\partial S}{\partial V} \right)_{p} \quad (b)$$

$$= -K_{S} \cdot \left( \frac{\partial S}{\partial T} \right)_{p} \cdot \left( \frac{\partial V}{\partial T} \right)_{p} = -K_{S} \cdot C_{p} / T \cdot E_{p}$$

Similarly \( \partial^{2}G/\partial T \cdot \partial p = \partial^{2}G/\partial p \cdot \partial T \quad (c) \)

Then, \( E_{p} = \left( \frac{\partial V}{\partial T} \right)_{p} = -\left( \frac{\partial S}{\partial p} \right)_{T} \)

Also at equilibrium, \( S = -\left( \frac{\partial G}{\partial T} \right)_{p} \)

But \( G = H - T \cdot S \). Then \( H = G - T \cdot \left( \frac{\partial G}{\partial T} \right)_{p} \)

$$\frac{\partial H}{\partial T} = \frac{\partial G}{\partial T} - T \cdot \left( \frac{\partial^{2}G}{\partial T^{2}} \right) - \frac{\partial G}{\partial T}$$
Further, \[ \left( \frac{\partial H}{\partial T} \right)_p = C_p = -T \cdot \left( \frac{\partial^2 G}{\partial T^2} \right)_p = T \cdot \left( \frac{\partial S}{\partial T} \right)_p \] (d)

Based on equation (a), \[ E_S = E_p - C_p \cdot K_t / T \cdot E_p \]