Expansions Isentropic; Solutions: Apparent and Partial Molar

A given solution is prepared using $n_1$ moles of solvent (water) and $n_j$ moles of solute $j$. The volume of the system is defined by equation (a).

$$ V = V[T, p, n_1, n_j] \quad (a) $$

We consider the case where the closed system is at equilibrium and hence where the affinity for spontaneous change is zero. The entropy of the system (at equilibrium) is defined by the same set of independent variables.

Thus $$ S = S[T, p, n_1, n_j] \quad (b) $$

The system is perturbed at constant pressure by a change in temperature. The path followed by the system is such that the affinity for spontaneous change remains at zero (i.e. at equilibrium) and that the entropy of the system $S(aq)$ remains constant at that given by equation (b).

The equilibrium isentropic expansion of the system is defined by equation (c).

$$ E_s(A = 0) = \left( \frac{\partial V}{\partial T} \right)_{S(aq), A = 0} \quad (c) $$

$E_s(A=0)$ is an extensive property of the system. Nevertheless it is convenient to consider an intensive property. For example, $E_s(aq; A=0; w_1 = 1 \text{ kg}; m_j)$ is the equilibrium isentropic expansion of a solution molality $m_j$ prepared using 1 kg of water($\ell$).

For a system comprising pure solvent at defined $T$ and $p$ we define a molar (equilibrium) isentropic expansion, $E^*_s(\ell)$; equation (d).

$$ E^*_s(\ell; A = 0) = \left( \frac{\partial V^*_s(\ell)}{\partial T} \right)_{S^*_s(\ell), A = 0} \quad (d) $$

The volume of a solution, molality $m_j$, prepared using 1 kg of water($\ell$) is related to the composition using either equations (e) or (f).

$$ V(aq; w_1 = 1 \text{ kg}) = \left(\frac{1}{M_1}\right) \cdot V^*_1(\ell) + m_j \cdot \phi(V_j) \quad (e) $$

$$ V(aq; w_1 = 1 \text{ kg}) = \left(\frac{1}{M_1}\right) \cdot V_1(aq) + m_j \cdot V_j(aq) \quad (f) $$

A key problem emerges. We note that the conditions on the partial differential in equation (c) relate to the entropy of the aqueous solution. The latter condition is not the same as that invoked in equation (d) which refers to the molar entropy of the pure solvent. We could of course differentiate equation (e) with respect to
temperature at fixed entropy $S(aq)$. However we would encounter a term
\[
\left( \frac{\partial V^*_i(\ell)}{\partial T} \right)_{S(aq)}.
\]
This is a complicated derivative where we might have hoped for
a term \[
\left( \frac{\partial V^*_i(\ell)}{\partial T} \right)_{S^*_i(\ell)}.
\] The way forward is to accept the problem and define a
property, by analogy with the corresponding isobaric property, a property
$\phi(E_{S_j}; \text{def})$ which has the appearance of proper thermodynamic apparent
property.

Then, \[E_S(aq; A = 0; w_1 = 1 \text{ kg}) = (1/M_1) \cdot E_{S_1}^*(\ell; A = 0) + m_j \cdot \phi(E_{S_j}; \text{def}) \] (g)
There is a subtle problem with respect to equation (f) which can be
differentiated with respect to $T$ at constant $S(aq)$ as defined by equation (b).

Then \[E_S(aq; w_1 = 1 \text{ kg}) = (1/M_1) \left( \frac{\partial V_1(aq)}{\partial T} \right)_{S(aq)} + m_j \cdot \left( \frac{\partial V_j(aq)}{\partial T} \right)_{S(aq)} \] (h)
Partial molar isentropic expansions $E_{S_1}(aq)$ and $E_{S_j}(aq)$ are defined by the
following equations.

\[
E_{S_1}(aq) = \left( \frac{\partial E_S(aq)}{\partial n_1} \right)_{T,p,n(j)} \] (i)

\[
E_{S_j}(aq) = \left( \frac{\partial E_j(aq)}{\partial n_j} \right)_{T,p,n(l)} \] (j)

But $E_{S_1}$ and $E_{S_j}$ are non-Lewisian partial molar properties. Hence

\[
E_{S_1}(aq) \neq \left( \frac{\partial V_1(aq)}{\partial T} \right)_{S(aq)} \] (k)

\[
E_{S_j}(aq) = \left( \frac{\partial V_j(aq)}{\partial T} \right)_{S(aq)} \] (l)

Then, \[E_S(aq; w_1 = 1 \text{ kg}) = (1/M_1) \cdot E_{S_1}(aq) + m_j \cdot E_{S_j}(aq) \] (m)
In practical terms equation (n) follows from equation (g),

\[
\phi(E_{S_j}; \text{def}) = (1/m_j) \cdot [E_S(aq; A = 0; w_1 = 1 \text{ kg}) - (1/M_1) \cdot E_{S_1}^*(\ell; A = 0)] \] (n)
Two practical equations follow from equation (n) allowing $\phi(E_{S_j}; \text{def})$ to be
calculated from the isentropic expansibilities of solutions and solvent, both
volume intensive variables [1].
\[ \phi(E_{Sj}; \text{def}) = [m_j \cdot \rho_j^*(\ell)]^{-1} \cdot [\alpha_s(aq) - \alpha_{Sj}^*(\ell)] + \alpha_s(aq) \cdot \phi(V_j) \quad (o) \]
\[ \phi(E_{Sj}; \text{def}) = [c_j]^{-1} \cdot [\alpha_s(aq) - \alpha_{Sj}^*(\ell)] + \alpha_{Sj}^*(\ell) \cdot \phi(V_j) \quad (p) \]
where \( \alpha_s(aq) = \frac{1}{V(aq)} \cdot \left( \frac{\partial V(aq)}{\partial T} \right)_{S(aq)} \quad (q) \)
\[ \alpha_{Sj}^*(\ell) = \frac{1}{V_j^*(\ell)} \cdot \left( \frac{\partial V_j^*(\ell)}{\partial T} \right)_{S_j^*(\ell)} \quad (r) \]

**Footnotes**

[1] From equation (n),
\[ \phi(E_{Sj}; \text{def}) = (1/m_j) \cdot [E_s(aq; w_i = 1 \text{ kg}) \cdot (1/M_1) \cdot E_{Sj}^*(\ell)] \quad (a) \]
We use equation (m) for a solution prepared using 1 kg of water.
\[ E_s(aq; w_i = 1 \text{ kg}) = (1/M_1) \cdot E_{Sj}(aq) + m_j \cdot E_{Sj}(aq) \]
Then \( \phi(E_{Sj}; \text{def}) = (1/m_j) \cdot [(1/M_1) \cdot E_{Sj}(aq) + m_j \cdot E_{Sj}(aq) - (1/M_1) \cdot E_{Sj}^*(\ell)] \)
Or, \( \phi(E_{Sj}; \text{def}) = E_{Sj}(aq) + (1/m_j) \cdot (1/m_j) \cdot [E_{Sj}(aq) - E_{Sj}^*(\ell)] \)
Hence using equation (m),
\[ \phi(E_{Sj}; \text{def}) = (1/m_j) \cdot E_s(aq; w_i = 1 \text{ kg}) - (1/M_1) \cdot (1/m_j) \cdot E_{Sj}^*(\ell) \]
Using equations (q) and (r),
\[ \phi(E_{Sj}; \text{def}) = (1/m_j) \cdot \alpha_s(aq) \cdot V(aq; w_i = 1 \text{ kg}) - (1/M_1) \cdot (1/m_j) \cdot \alpha_{Sj}^*(\ell) \cdot V_j^*(\ell) \]
\[ \phi(E_{Sj}; \text{def}) = (1/m_j) \cdot \alpha_s(aq) \cdot [(1/M_1)V_j^*(\ell) + m_j \cdot \phi(V_j)] \]
Or,
\[ -(1/M_1) \cdot (1/m_j) \cdot \alpha_{Sj}^*(\ell) \cdot V_j^*(\ell) \]

Or \( \phi(E_{Sj}; \text{def}) = (V_j^*(\ell) / m_j \cdot M_1) \cdot [\alpha_s(aq) - \alpha_{Sj}^*(\ell)] + \alpha_s(aq) \cdot \phi(V_j) \)
Or \( \phi(E_{Sj}; \text{def}) = [m_j \cdot \rho_j^*(\ell)]^{-1} \cdot [\alpha_s(aq) - \alpha_{Sj}^*(\ell)] + \alpha_s(aq) \cdot \phi(V_j) \)
Also \( [m_j \cdot \rho_j^*(\ell)]^{-1} = [1/c_j] - \phi(V_j) \)
Then, \( \phi(E_{Sj}; \text{def}) = [(1/c_j) - \phi(V_j)] \cdot [\alpha_s(aq) - \alpha_{Sj}^*(\ell)] + \alpha_s(aq) \cdot \phi(V_j) \)

Or, \( \phi(E_{Sj}; \text{def}) = (1/c_j) \cdot [\alpha_s(aq) - \alpha_{Sj}^*(\ell)] \)
Hence, \( \phi(E_{Sj}; \text{def}) = (1/c_j) \cdot [\alpha_s(aq) - \alpha_{Sj}^*(\ell)] + \phi(V_j) \cdot \alpha_{Sj}^*(\ell) \)
For further details see----