**Topic770**

**Compressions: Isentropic: Solutions ;General Comments**

At fixed \( T \) and \( p \), the equilibrium state for an aqueous solution is a minimum in Gibbs energy, \( G^{\text{eq}} \). The first derivative of \( G^{\text{eq}} \) with respect to temperature at constant pressure yields the equilibrium enthalpy \( H^{\text{eq}} \). The first derivative of \( H^{\text{eq}} \) with respect to temperature also at constant pressure yields the equilibrium isobaric heat capacity \( C_p^{\text{eq}} \).

Alternatively we can track the pressure derivatives of \( G^{\text{eq}} \). The first derivative of \( G^{\text{eq}} \) with respect to pressure at fixed temperature is the equilibrium volume \( V^{\text{eq}} \). The first derivative of \( V^{\text{eq}} \) with respect to pressure at fixed temperature yields the equilibrium isothermal compression \( K_T^{\text{eq}} \), the ratio \( K_T^{\text{eq}}/V^{\text{eq}} \) yielding the equilibrium isothermal compressibility \( \kappa_T^{\text{eq}} \). Concentrating attention on equilibrium properties of aqueous solutions, an extensive literature concerns \( V(\text{aq}) \) in terms of the corresponding densities, \( \rho(\text{aq}) \). An extensive literature describes isobaric heat capacities \( C_p(\text{aq}) \), effectively the second derivative of \( G(\text{aq}) \). Rather less literature describes \( \kappa_T(\text{aq}) \), a second derivative of \( G(\text{aq}) \) with respect to pressure. However an extensive literature reports isentropic compressibilities, \( \kappa_S(\text{aq}) \); equation (a).

\[
\kappa_S = -(1/V) \cdot (\partial V/\partial p)_S = K_S \cdot V^{-1} \quad (a)
\]

This perhaps surprising observation is accounted for by the fact that speeds of sound (at low frequency, e.g. 1 MHz) in aqueous solutions are conveniently and precisely measured using either the ‘sing-around; [1] or ‘pulse-echo-overlap’ [2] methods (for a summary of the ‘History of Sound’ see reference 3.) Then using the Newton-LaPlace equation \( \kappa_S(\text{aq}) \) is obtained [5]; equation (b).

\[
u^2 = (\kappa_S \cdot \rho)^{-1} \quad (b)
\]

The speed of sound at zero frequency is a thermodynamically defined property [5,6]. The isentropic compressibility of water (\( \ell \)) at ambient \( T \) and \( p \) can be calculated using either the speed of sound \( \kappa_S^*(\ell; \text{acoustic}) \) or using \( \kappa_T^*(\ell), \alpha_p^*(\ell) \) and \( \sigma^*(\ell) \) to yield \( \kappa_S^*(\ell; \text{thermodynamic}) \). The two estimates agree lending support to the practice of calculating isentropic compressibilities of solutions using the Newton-Laplace equation.

We equate the isentropic condition with adiabatic, provided that the compression is reversible.

An important quantity is the difference \( \delta \) between compressibilities; equation (c).

\[
\delta = \kappa_T - \kappa_S = T \cdot (\alpha_p)^2 / \sigma \quad (c)
\]

The property \( \sigma \) is given a number of different names but here we use the term, heat (or, thermal) capacitance. The ratio of isothermal to isentropic compressions equals the ratio of isobaric to isochoric heat capacities [8].
Interest in the isentropic compressibilities of solutions was stimulated by Gucker and co-workers [9,10] and, in particular, by Harned and Owen [11]. The latter authors defined a property of the solute, here called \( \phi(K_{S_j}; \text{def}) \) using equation (e) where the composition of a given aqueous solution is expressed using concentration \( c_j \).

\[
\phi(K_{S_j}; \text{def}) \equiv [\kappa_S(aq) - \kappa_{SI}(\ell)] \cdot [c_j]^{-1} + \kappa_{SI}^*(\ell) \cdot \phi(V_j)
\]

Also

\[
\phi(K_{S_j}; \text{def}) \equiv [\kappa_S(aq) - \kappa_{SI}^*(\ell) \cdot \rho(aq)] \cdot [c_j \cdot \rho_j^*(\ell)]^{-1} + \kappa_{SI}(\ell) \cdot M_j \cdot [\rho_j^*(\ell)]^{-1}
\]

Similar equations relate \( \phi(K_{S_j}; \text{def}) \) to the molality of the solute, \( m_j \).

\[
\phi(K_{S_j}; \text{def}) \equiv [\kappa_S(aq) - \kappa_{SI}^*(\ell)] \cdot [m_j \cdot \rho_j^*(\ell)]^{-1} + \kappa_S(aq) \cdot \phi(V_j)
\]

The latter four equations are stated by analogy with those relating \( \phi(K_T) \) to the composition of a solution. In these terms equations (e) to (h) are said to describe the same property of a given solute. A crucial feature of equations (e) - (h) is the equivalence symbol (i.e. \( \equiv \)). In this sense Harned and Owen [11] defined an apparent isentropic compression of solute-j in terms of the quantities on the r.h.s. of equation (a). They recognised that \( \phi(K_{S_j}; \text{def}) \) does not have thermodynamic basis. The target quantity is the apparent molar isentropic compression defined by equation (i) which, however, is not a description of an isentropic process as its name might suggest.

\[
\phi(K_{S_j}; \text{def}) = (1 / n_j) \cdot K_S(aq; T; p) - (n_j / n_j) \cdot K_{SI}^*(\ell; T; p)
\]

In fact \( \phi(K_{S_j}; \text{def}) \) is a measure of the change in the isentropic compression of a solvent when solute j is added under isothermal-isobaric conditions. The equivalence symbol in equations (e) - (h) is important [12,13]. In fact reservations are often expressed especially when estimates of \( \phi(K_{S_j}; \text{def}) \) are discussed, particularly the dependence of \( \phi(K_{S_j}; \text{def}) \) on solution composition. Franks and co-workers [14] recognised that the lack of isobaric heat capacity data forces the adoption of an approach in which \( \phi(K_{S_j}; \text{def}) \) is often effectively assumed equal to \( \phi(K_T) \). Owen and Simons [15] comment that overlooking the difference between \( \kappa_S(aq) \) and \( \kappa_T(aq) \) causes errors of approximately 7.5% in estimates of \( \phi(K_T) \) for NaCl(aq) and KCl(aq) at 298 K.
In terms of the development of the theory, a problem is encountered with the differential dependence of the molar volume of the solvent on pressure at constant entropy of the solution. The task is to describe how the molar volume of the solvent would depend on pressure if it were held at the same entropy of the solution.

Footnotes
[8] We use several calculus operations. Thus,
\[(\partial V / \partial p)_T = -(\partial T / \partial p)_V \cdot (\partial V / \partial T)_p = -((\partial T / \partial p)_V \cdot (\partial V / \partial S)_p \cdot (\partial S / \partial T)_p)
\]
And,
\[(\partial V / \partial p)_S = -(\partial S / \partial p)_V \cdot (\partial V / \partial S)_p = -((\partial T / \partial p)_V \cdot (\partial V / \partial S)_p \cdot (\partial S / \partial T)_V)
\]
Then,
\[(\partial V / \partial p)_T / (\partial V / \partial p)_S = (\partial S / \partial T)_p / (\partial S / \partial T)_V
\]
Further \[H = G + T \cdot S\] and \[S = - (\partial G / \partial T)_p\]
Hence, \[H = G - T \cdot (\partial G / \partial T)_p\]
Then \[(\partial H / \partial T)_p = C_p = -T \cdot (\partial^2 G / \partial T^2)_p = T \cdot (\partial S / \partial T)_p\]
Similarly \[(\partial U / \partial T)_V = C_V = T \cdot (\partial S / \partial T)_V\]
Therefore, \[K_T / K_S = C_p / C_V\]