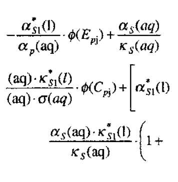
Apparent molar isentropic compressions and expansions of solutions†



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Isentropic compressibilities of solutions κ_S are readily calculated using the Newton–Laplace equation together with measured speeds of sound and densities. The result is an apparent molar isentropic compression for a given solute-j, $\phi(K_{Sj};\ \mathrm{def})$ and a limiting property, $\phi(K_{Sj};\ \mathrm{def})^\infty$. This review examines the definition and calculation of $\phi(K_{Sj};\ \mathrm{def})$ and $\phi(K_{Sj};\ \mathrm{def})^\infty$, commenting on the related isentropic expansions, $\phi(E_{Sj};\ \mathrm{def})$ and $\phi(E_{Sj};\ \mathrm{def})^\infty$. We describe the thermodynamics which underpins the use of isentropic properties in the study of solute–solvent and solute–solute interactions.

1 Introduction

This review explores the definition and calculation of isentropic compressibilities and, to a lesser extent, isentropic expansibilities of solutions. We direct attention to the extensive chemical

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† Electronic supplementary information (ESI) is available: derivations of several key equations cited in the review. See http://www.rsc.org/suppdata/cs/a9/a908547e/

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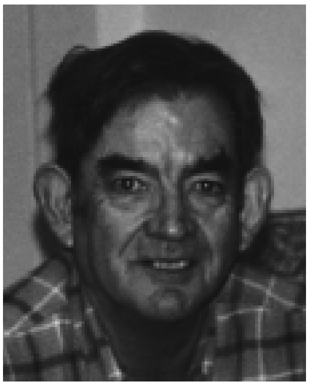

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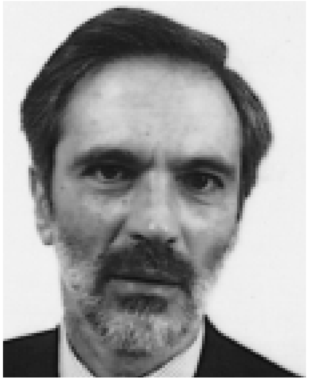

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literature describing these properties of aqueous solutions. We develop thermodynamic equations starting from the macroscopic properties of solutions; *e.g.* Gibbs energy, volume, compression and expansion. These properties are linked to partial molar properties and apparent molar properties of solutes in solution. Isentropic compressions of solutions have an interesting history. Recently published papers still refer to the classic monograph written by Harned and Owen.[1] We draw particular attention to their definition of apparent molar isentropic compressions.

2 Thermodynamic background

For a closed system containing n_1 and n_2 moles of chemical substances 1 and 2 the Gibbs energy is a dependent variable; the variables $[T,p,n_1,n_2]$ are the independent variables. Temperature T is the thermal potential. Pressure p is the mechanical variable. The number of composition variables is established using the Gibbs Phase Rule. For closed systems (at defined T and p) at thermodynamic equilibrium the composition (organisation) is represented by ξ^{eq} and the affinity for spontaneous change A is zero consistent with the Gibbs energy being a minimum; eqn. (1).

$$A^{\mathrm{eq}} = (\partial G/\partial \xi)^{\mathrm{eq}}_{T,p} = 0 \qquad (1)$$

The Gibbs energy, volume and entropy of a solution at equilibrium are state variables. We draw a contrast with those properties which are associated with a process (pathway). Thus we contrast the state variable V with an unspecified compression K of a solution where we need to define the path followed by the system when the pressure is changed. The Gibbs energy of a system at thermodynamic equilibrium where the affinity for spontaneous change is zero and where the molecular composition/organisation is ξ^{eq}, is characterised by eqn. (2).

$$G = G[T,p,n_1,n_2,A = 0] \qquad (2)$$

The same state is characterised by the equilibrium volume and equilibrium entropy by eqn. (3) and eqn. (4).

$$V = V[T,p,n_1,n_2,A = 0] \qquad (3)$$

$$S = S[T,p,n_1,n_2,A = 0] \qquad (4)$$

A common feature is the use of the two intensive variables, temperature and pressure, in the definition of extensive variables G, V and S. When pressure is increased by finite increments from p to $(p + \Delta p)$ the volume changes in finite increments from V to $(V + \Delta V)$. For an important pathway, the temperature is constant. However, to satisfy the condition that the affinity for spontaneous change A is zero, the molecular organisation/composition ξ changes but continues to represent equilibrium conditions. The volume at pressure $(p + \Delta p)$ is defined using eqn. (5).

$$V = V[T,p + \Delta p,n_1,n_2,A = 0] \qquad (5)$$

In principle we plot volume as a function of pressure at constant temperature, n_1, n_2 and at '$A = 0$'. The gradient of the plot at the point defined by eqn. (3) yields the equilibrium isothermal compression, K_T $(A = 0)$; eqn. (6).

$$K_T(A = 0) = -(\partial V/\partial p)_{T,A = 0} \qquad (6)$$

$K_T(A = 0)$ characterises the state defined by the set of variables, $[T,p,n_1,n_2,A = 0]$; *cf.* eqn. (2)–(4). We turn our attention to another property starting with the system having a volume defined by eqn. (3). The system is perturbed by a change in pressure from p to $(p + \Delta p)$ in an equilibrium displacement. However on this occasion we require that it is the entropy which remains constant at the value defined by eqn. (4). In principle we plot volume V as a function of pressure at constant n_1, n_2, at '$A = 0$' and at a constant entropy equal to that defined by eqn. (4). The gradient of the plot at the point where the volume is defined by eqn. (3) yields the equilibrium isentropic compression, $K_S(A = 0)$; eqn. (7); isentropic = adiabatic and at equilibrium.

$$K_S(A = 0) = -(\partial V/\partial p)_{S,A = 0} \qquad (7)$$

The equilibrium state characterised by $K_S(A = 0)$ is defined by the variables $[T,p,n_1n_2,A = 0]$. In other words an isentropic volumetric property describes a solution defined in part by the intensive variables, T and p. Significantly the condition on the partial derivative in eqn. (7) is the extensive variable, entropy. For a stable phase, K_S is positive. Both K_T and K_S are state variables.

The arguments outlined above are repeated with respect to both isobaric $E_p(A = 0)$ and isentropic $E_S(A = 0)$ equilibrium expansions; eqn. (8) and eqn. (9).

$$E_p(A = 0) = (\partial V/\partial T)_{p,A = 0} \qquad (8)$$

$$E_S(A = 0) = (\partial V/\partial T)_{S,A = 0} \qquad (9)$$

$E_p(A = 0)$ and $E_S(A = 0)$ characterise a solution described by the variables $[T,p,n_1,n_2,A = 0]$. The set of independent variables of the type $[T,p,n_1,n_2]$ is called Gibbsian in recognition of the unique contribution made by J. W. Gibbs to chemical thermodynamics. The importance of the set of independent variables $[T,p,n_1,n_2]$ and hence of the Gibbs energy is clarified by drawing a comparison with other thermodynamic potential functions.[2]

With reference to the set of independent variables $[S,V,n_1,n_2]$ chemical equilibrium at constant S and constant V, corresponds to a minimum in thermodynamic energy, U. With reference to the set of independent variables $[S,p,n_1,n_2]$ thermodynamic equilibrium at constant S and p occurs at the state where the enthalpy H is a minimum. The sets of independent variables, $[S,p,n_1,n_2]$, $[S,V,n_1,n_2]$ and $[T,V,n_1,n_2]$ are 'non-Gibbsian'.

3 Volume intensive variables

The (equilibrium) volume intensive compressibilities, κ_T and κ_S are defined[†] by eqn. (10) and eqn. (11).

$$\kappa_T = -(\partial V/\partial p)_T/V = K_T \cdot V^{-1} \qquad (10)$$

$$\kappa_S = -(\partial V/\partial p)_S/V = K_S \cdot V^{-1} \qquad (11)$$

Eqn. (8) and eqn. (9) define two (equilibrium) expansions leading to the volume intensive properties, α_S and α_p; eqn. (12) and eqn. (13).

$$\alpha_S = (\partial V/\partial T)_S/V = E_S \cdot V^{-1} \qquad (12)$$

$$\alpha_p = (\partial V/\partial T)_p/V = E_p \cdot V^{-1} \qquad (13)$$

Rowlinson and Swinton have stated that the latter property α_S is 'of little importance'.[3] The isobaric heat capacity per unit volume σ is the ratio, C_P/V. A quantity that is important is the difference δ between compressibilities; eqn. (14).

$$\delta = \kappa_T - \kappa_S = T \cdot [\alpha_p]^2 \cdot V/C_p = T \cdot [\alpha_p]^2/\sigma \qquad (14)$$

In the chemical literature the property σ is given different symbols and names; *e.g.* volumetric specific heat.[4] We identify σ as the thermal (or, heat) capacitance. The symbol ε is the difference between isobaric and isentropic expansibilities; eqn. (15).

$$\varepsilon = \alpha_p - \alpha_S = \kappa_T \cdot \sigma/T \cdot \alpha_p \qquad (15)$$

The Newton–Laplace equation[5] is the starting point for the determination of isentropic compressibilities [*cf.* eqn. (11)] of solutions using speed of sound u and density ρ; eqn. (16).

$$u^2 = (\kappa_S \cdot \rho)^{-1} \qquad (16)$$

In fact the speed of sound at zero frequency is a thermodynamically defined quantity.[3,5] Densities and speed of sound[6] u

(at low frequency, *e.g.* 1 MHz) can be precisely measured. The isentropic condition on κ_S means that as a sound wave passes through a liquid the pressure and temperature fluctuate within each microscopic volume but the entropy remains constant. The isentropic compressibility of water (l) at ambient T and p can be calculated using either the speed of sound κ_S^*(l;acoustic) or using κ_T^*(l), α_p^*(l) and σ^*(l) to yield [see eqn. (14)] κ_S^*(l;thermodyn). The two estimates agree lending support to the practice of calculating isentropic compressibilities of solutions using the Newton–Laplace equation. We can equate the isentropic condition with adiabatic, provided that the compression and relaxation process is microscopically reversible.

4 Solutions; partial molar properties

For a solution prepared using n_1 moles of solvent-1 and n_j moles of solute-j, at defined T and p the extensive thermodynamic property Q [= $G, H, S, V\ldots$] is related to the partial molar properties Q_1 [= $(\partial Q/\partial n_1)_{T,p,n(j)}$] and Q_j [= $(\partial Q/\partial n_j)_{T,p,n(l)}$]; eqn. (17).

$$Q = n_1 \cdot Q_1 + n_j \cdot Q_j \qquad (17)$$

Equations relating partial properties with the internal energy U, its natural variables S and V, and its Legendre transforms (*e.g.* Helmholtz energy, enthalpy and Gibbs energy) together with T and p must have the same structure as in the general thermodynamic description of a phase. Such partial molar properties are called Lewisian.[7] Lewis sought properties which play a role thermodynamically identical to molar properties such as molar volumes and molar isobaric heat capacities of pure substances and which are used in equations identical in form with those used for pure substances. Nevertheless the formalism involving partial molar properties, $Q_j(T,p)$ in general must be established in each case. Partial molar expansions $E_{pj}(T,p)$ and compressions K_{Tj} (T,p) are Lewisian, but partial molar isentropic compressions $K_{Sj}(T,p)$ are not; see Section 9.

For real aqueous solutions, both V_1(aq) and V_j(aq) depend on the composition of a solution. However, V_1(aq) and V_j(aq) do not change independently, as the composition of the solution is changed. The Gibbs–Duhem equation leads, for systems at constant temperature and pressure, to the following condition.

$$n_1 \cdot \mathrm{d}V_l + n_j \cdot \mathrm{d}V_j = 0 \qquad (18)$$

A further important set of variables is called ‘apparent molar’. For a given aqueous solution, the thermodynamic property Q(aq) is related to the molar property of the solvent, water $Q_1{}^*$(l) and the apparent molar property of the solute $\phi(Q_j)$; eqn. (19).

$$Q(\mathrm{aq}) = n_1 \cdot Q_1^* + n_j \cdot \phi(Q_j) \qquad (19)$$

Apparent $\phi(Q_j)$ and partial molar Q_j(aq) thermodynamic properties are similar and become identical in the limit of infinite dilution. In an ideal solution, each solute molecule exerts an influence on the properties of the solution independent of all other solute molecules in the solution. The solute molecules are *effectively* an infinite distance apart leading to the useful concept of the infinitely dilute solution.

In even a cursory investigation of the properties of solutions, a key consideration is the distance between solute molecules. For a simple solute (*e.g.* urea) in aqueous solutions at concentration c_j the average distance apart, d, is given by $(N_A \cdot c_j)^{-1/3}$ where N_A is the Avogadro constant. Then, if $c_j = 10^{-2}$ mol dm^{-3}, d equals 5.5 nm.

Links between the macroscopic properties of a closed multicomponent system, and the variables that describe properties attributed to the individual chemical components, are created through chemical potentials.[8] For a system at equilibrium, chemical potentials have all the characteristics of state variables. Chemical potentials are similar in this respect to volume V, entropy S and enthalpy H; all are first derivatives of the Gibbs energy.

For a neutral solute-j in aqueous solution at fixed T and p the chemical potential, μ_j(aq) is related to the molality m_j using eqn. (20) where γ_j is the activity coefficient of solute-j; $m^0 = 1$ mol kg^{-1}.

$$\mu_j(\mathrm{aq}) = \mu_j^0(\mathrm{aq}) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0) \qquad (20)$$

By definition, at all T and p, limit$(m_j \rightarrow 0)\gamma_j = 1$; μ_j^0(aq) is the chemical potential of solute-j in an ideal solution where $m_j = m^0 = 1$ mol kg^{-1}. For an ideal solution, γ_j is unity at all molalities. A key consideration in formulating equations for the dependence of partial molar properties on composition is the limit that molality m_j tends to zero; *e.g.* with reference to eqn. (20), limit$(m_j \rightarrow 0)\mu_j(\mathrm{aq;id}) = -\infty$. In other words, the solute is increasingly stabilised as the solution is diluted (at fixed T and p). The Gurney model for solutions identifies cospheres of solvent around each solute molecule. Hence solute–solute interactions as described by activity coefficient γ_j can be understood in part in terms of cosphere–cosphere interactions. The extent to which the properties of a given neutral solute-j deviate from the state defined as thermodynamically ideal reflects to a large part the hydrophobic–hydrophilic character of solute molecules.

For an aqueous salt solution[9] containing a 1 : 1 salt (*e.g.* NaCl), the analogue of eqn. (20) takes the following form where μ_j(aq) is the chemical potential of salt-j in aqueous solution.

$$\mu_j(\mathrm{aq}) = \mu_j^0(\mathrm{aq}) + 2 \cdot R \cdot T \cdot \ln(m_j \cdot \gamma_\pm / m^0) \qquad (21)$$

In eqn. (21) $\gamma_\pm$ is the mean ionic activity coefficient of salt-j in solution. At all T and p, limit$(m_j \rightarrow 0)\gamma_\pm = 1$; μ_j^0(aq) is the chemical potential of salt-j in an ideal aqueous solution having unit molality. As for simple solutes, in the limit of infinite dilution the chemical potential of a salt in solution is minus infinity. We anticipate that μ_j^0(aq) is given by the sum of ionic properties μ_+^0(aq) and μ_-^0(aq) which are determined in part by cation–water and anion–water interactions respectively, *i.e.* ionic hydration.

The mean activity coefficient $\gamma_\pm$ describes ion–ion interactions in solution. The classic analysis in this context was given by Debye and Hückel; see, for example, reference 10. For very dilute solutions, the result is the famous Debye–Hückel Limiting Law, often simply expressed as DHLL. The algebra is simplified by defining a quantity S_γ which is characteristic of the solvent, temperature and pressure through the corresponding dependences of solvent density ρ_1^*(l) and relative permittivity, ε_r.

Hence
$$\ln(\gamma_\pm = -|z_+ \cdot z_-| \cdot S_\gamma \cdot [m_j/m^0]^{1/2} \qquad (22)$$

Therefore, limit$(m_j \rightarrow \mathrm{zero})\ln(\gamma_\pm) = 0$; $\gamma_\pm = 1$. In other words, for very dilute solutions $\ln(\gamma_\pm)$ is a linear function of $(m_j/m^0)^{1/2}$ the gradient being defined by eqn. (22). According to the DHLL, the chemical potential of salt-j in a real solution is lower than in the corresponding ideal solution.

5 Volumes of solutions: partial and apparent molar volumes

The isothermal differential dependence of the chemical potential μ_j (aq) on pressure leads to the partial molar volume for solute-j, V_j(aq). From eqn. (20), for a neutral solute

$$V_j(\mathrm{aq}) = V_j^0(\mathrm{aq}) + R \cdot T \cdot [\partial \ln(\gamma_j)/\partial_p]_T \qquad (23)$$

Accordingly limit$(m_j \rightarrow 0)V_j(\mathrm{aq}) = V_j^0(\mathrm{aq}) = V_j^\infty$ (aq). Here V_j^∞(aq) is the limiting (infinite dilution) partial molar volume of solute-j in aqueous solution. The limiting partial molar volume of a solute in a given solution (at defined T and p) is characteristic in part of solute–solvent interactions.

The volume of an aqueous solution prepared using m_j moles of solute-j and 1 kg of water is given by eqn. (24), where M_1 is the molar mass of the solvent.

$$V(\mathrm{aq};\ w_1/\mathrm{kg} = 1) = M_1{}^{-1}\cdot V_1(\mathrm{aq}) + m_\mathrm{j}\cdot V_\mathrm{j}(\mathrm{aq}) \qquad (24)$$

For real solutions, $V_1(\mathrm{aq})$ and $V_\mathrm{j}(\mathrm{aq})$ cannot be immediately calculated from the measured density, $\rho(\mathrm{aq})$ of an aqueous solution because both $V_1(\mathrm{aq})$ and $V_\mathrm{j}(\mathrm{aq})$ depend on molality m_j. An apparent molar volume of solute-j, $\phi(V_\mathrm{j})$, is defined; eqn. (25).

$$V(\mathrm{aq};w_1/\mathrm{kg} = 1) = M^{-1}\cdot V_1^*(\mathrm{l}) + m_\mathrm{j}\cdot\phi(V_\mathrm{j}) \qquad (25)$$

Lewis and Randall commented[9] that 'apparent molal quantities have little thermodynamic utility', a statement repeated in the second[8] but not the third[10] edition of this classic monograph. A further comment concerns two plots;[11] (i) $V(\mathrm{aq};\ w_1 = 1\ \mathrm{kg})$ against m_j, and (ii) $[V(\mathrm{aq};w_1 = 1\ \mathrm{kg}) - (1/M_1)\cdot V_1^*(\mathrm{l})]$ against m_j. Then $V_\mathrm{j}(\mathrm{aq})$ is the gradient of the tangent to the curve in plot type (i) at the specified molality m_j; $\phi(V_\mathrm{j})$ is the gradient of the line in plot type (ii) joining the origin and $[V(\mathrm{aq};w_1 = 1\ \mathrm{kg}) - (1/M_1)\cdot V_1^*(1)]$ at molality m_j.

By definition, $\mathrm{limit}(m_\mathrm{j} \to 0)\phi(V_\mathrm{j}) = \phi(V_\mathrm{j})^\infty = V_\mathrm{j}^\infty(\mathrm{aq})$; the limit of $\phi(V_\mathrm{j})$ at infinite dilution equals the limiting partial molar volume of the solute $V_\mathrm{j}^\infty(\mathrm{aq})$. Partial and apparent molar volumes are related by eqn. (26).

$$V_\mathrm{j}(\mathrm{aq}) = \phi(V_\mathrm{j}) + m_\mathrm{j}\cdot[\partial\phi(V_\mathrm{j})/\partial m_\mathrm{j}]_{T,p} \qquad (26)$$

$\phi(V_\mathrm{j})$ is usually calculated using the densities of solvent $\rho_\mathrm{j}^*(1)$ and solution $\rho(\mathrm{aq})$ at the same T and p together with the composition of the solution; *e.g.* eqn. (27) where c_j is the concentration of solute-j.

$$\phi(V_\mathrm{j}) = \{[\rho_1^*(1) - \rho(\mathrm{aq})]/c_\mathrm{j}\cdot\rho_1^*(1)\} + [M_\mathrm{j}/\rho_1^*(1)] \qquad (27)$$

For dilute solutions containing simple neutral solutes, $\phi(V_\mathrm{j})$ is usually adequately described by a linear function of m_j such that $\phi(V_\mathrm{j})^\infty$ and V_j^∞ are readily obtained; eqn. (28).

$$\phi(V_\mathrm{j}) = \phi(V_\mathrm{j})^\infty + b_v\cdot(m_\mathrm{j}/m^0) \qquad (28)$$

The partial molar volume for a given 1 : 1 salt $V_\mathrm{j}(\mathrm{aq})$ is related to the differential dependence of $\ln(\gamma_\pm)$ on pressure at fixed T and molality m_j; *cf.* eqn. (21).

$$V_\mathrm{j}(\mathrm{aq}) = V_\mathrm{j}^\infty(\mathrm{aq}) + 2\cdot R\cdot T\cdot[\partial\ln(\gamma_\pm)/\partial p]_T \qquad (29)$$

From the definition of $\gamma_\pm$ $\mathrm{limit}(m_\mathrm{j} \to 0)V_\mathrm{j}(\mathrm{aq}) = V^\infty_{\mathrm{j(aq)}}$. Hence in the limit of infinite dilution the partial molar volume is a real quantity.

According to the DHLL for a 1 : 1 salt,

$$V_\mathrm{j}(\mathrm{aq}) = V_\mathrm{j}^\infty(\mathrm{aq}) - 2\cdot R\cdot T\cdot S_V\cdot(m_\mathrm{j}/m^0)^{1/2} \qquad (30)$$

By definition, $S_V = (\partial S_\gamma/\partial p)_T$; S_V is negative. According therefore to the DHLL, $V_\mathrm{j}(\mathrm{aq})$ is a linear function of $(m_\mathrm{j}/\mathrm{m}^0)^{1/2}$ (at fixed T and p). According to the DHLL the dependence of apparent molar volume $\phi(V_\mathrm{j})$ on molality m_j is given by eqn. (31) where V_j^∞ equals $\phi(V_\mathrm{j})^\infty$.

$$\phi(V_\mathrm{j}) = \phi(V_\mathrm{j})^\infty - (4/3)\cdot R\cdot T\cdot S_V\cdot(m_\mathrm{j}/m^0)^{1/2} \qquad (31)$$

For 1 : 1 salts in aqueous solutions having molality 0.05 mol kg^{-1} at 298 K the difference $\phi(V_\mathrm{j}) - \phi(V_\mathrm{j})^\infty$ does not follow the pattern required by the DHLL. Rather the deviations can be understood in terms of charge–charge interactions as described by the DHLL together with cosphere–cosphere interactions between hydration cospheres described by an additional term linear in salt concentration.[12]

At this point we highlight the theme being developed in this review. For a given aqueous solution at defined T and p and at equilibrium containing a single solute-j; (*e.g.* urea) the Gibbs energy G is a state variable; *cf.* eqn. (1). The solute-j in this solution can be characterised by its chemical potential, $\mu_\mathrm{j}(\mathrm{aq})$; eqn. (20) and eqn. (21). Then μ_j (aq) is related to the molality m_j using eqn. (20) in which $\mu_\mathrm{j}^0(\mathrm{aq})$ is in part determined by solute–solvent interactions and γ_j characterises solute–solute interactions in a real solution. In the next stage the isothermal dependence of $\mu_\mathrm{j}(\mathrm{aq})$ on pressure leads to the partial molar volume $V_\mathrm{j}(\mathrm{aq})$. Densities of solutions are used to estimate the apparent molar volume $\phi(V_\mathrm{j})$ using eqn. (27). In turn the limiting (infinite dilution) volumetric property is obtained. The next task involves identifying those properties of solute and solvent which determine $V_\mathrm{j}^\infty(\mathrm{aq})$. One approach assumes that $V_\mathrm{j}^\infty(\mathrm{aq})$ is given by the sum of two contributions, $V_\mathrm{j}(\mathrm{intrinsic})$ and $V_\mathrm{j}(\mathrm{cosphere})$; *cf.* reference 12. Thus $V_\mathrm{j}(\mathrm{intrinsic})$ reflects the 'size' of the solute molecule-j whereas $V_\mathrm{j}(\mathrm{cosphere})$ represents the impact of solute–solvent interactions; *i.e.* the hydration of solute-j in aqueous solution.

$$\text{Hence } V_\mathrm{j}^\infty(\mathrm{aq}) = V_\mathrm{j}(\mathrm{intrinsic}) + V_\mathrm{j}(\mathrm{cosphere}) \qquad (32)$$

Unfortunately there is no unambiguous method which allows us to calculate the two component volumes identified in eqn. (32). Nevertheless we speculate that $V_\mathrm{j}(\mathrm{intrinsic})$ is independent of temperature and pressure such that the temperature and pressure derivatives of $V_\mathrm{j}^\infty(\mathrm{aq})$ offer a method for probing the hydration of solutes in aqueous solution *via* $V_\mathrm{j}(\mathrm{cosphere})$. We stress the word 'speculate' in this context. Therefore the isothermal compressibility κ_T describing the (equilibrium) dependence of volume on pressure at constant temperature might seem the property which should command most of our attention. Unfortunately isothermal compressions of solutions are not readily measured. Similarly, determination of partial molar expansions of a solute-j requires careful determination of densities of solutions as a function of both temperature and composition. Hence the amount of published information is not extensive. At first sight it is surprising that the most extensively measured property of solutions in this context is the isentropic compressibility, κ_S. A less commonly quoted volumetric property of aqueous solutions is the isentropic expansion, $E_S(\mathrm{aq})$. There is an interesting link between the isentropic compressions and expansions; section 10.

6 Thermal expansions of solutions: isobaric properties

The isobaric differential dependence of the volume, V, on temperature (at equilibrium where $A = 0$) is given by eqn. (8). The isobaric expansion $E_p(\mathrm{aq})$ for an aqueous solution containing solute-j is related to the partial molar expansions of solute and solvent; *cf.* eqn. (17).

$$E_p(\mathrm{aq}) = n_1\cdot E_{p1}(\mathrm{aq}) + n_\mathrm{j}\cdot E_{p\mathrm{j}}(\mathrm{aq}) \qquad (33)$$

Similarly from eqn. (19) for $Q \equiv V$,

$$[\partial V(\mathrm{aq})/\partial T]_p = n_1\cdot[\partial V_1^*(\mathrm{l})/\partial T]_p + n_\mathrm{j}\cdot[\partial\phi(V_\mathrm{j})/\partial T]_p \qquad (34)$$

$$\text{Thus,} \quad E_p(\mathrm{aq}) = n_1\cdot E_{p1}^*(\mathrm{l}) + n_\mathrm{j}\cdot\phi(E_{p\mathrm{j}}) \qquad (35)$$

Here $\phi(E_{p\mathrm{j}}) = [\partial\phi(V_\mathrm{j})/\partial T]_\mathrm{p}$, the (equilibrium) apparent molar isobaric expansion for solute-j. Further, $\phi(E_{p\mathrm{j}})$ is related to $\alpha_p(\mathrm{aq})$ and $\alpha_{p1}^*(\mathrm{l})$ using eqn. (36); *cf.* eqn. (27).

$$\phi(E_{p\mathrm{j}}) = [\alpha_p(\mathrm{aq}) - \alpha_{p1}^*(\mathrm{l})]\cdot(c_\mathrm{j})^{-1} + \alpha_{p1}^*(\mathrm{l})\cdot\phi(V_\mathrm{j}) \qquad (36)$$

Thus $\phi(E_{p\mathrm{j}})$ is obtained for a solution having concentration c_j.

7 Isentropic expansions of solutions

Generally little interest has been shown in either partial or apparent molar isentropic expansions of solutes. Complications are encountered in understanding isentropic expansions without the redeeming feature of practical accessibility *via* an analogue of the Newton–Laplace equation (Section 3). The isentropic expansion $E_S(\mathrm{aq})$ is defined by eqn. (9). The constraint on this partial differential refers to the entropy of the solution. The straightforward schemes described in eqn. (34)-(36) cannot be carried over to a consideration of E_S(aq) because as we change the amount of solute n_j for a fixed temperature, pressure and amount of solvent n_1, so both V(aq) and S(aq) change yielding a new isentropic thermal expansion E_S(aq) at a new entropy S(aq). Then for a series of solutions having different molalities, comparison of E_S(aq) is not straightforward because entropy S(aq) is itself a function of solution composition. Further comparison cannot be readily drawn with the isentropic thermal expansion of the pure solvent E^*_{S1}(l); eqn. (37).

$$E^*_{S1}(1) = [\partial V^*_1(1)/\partial T] \text{ at constant } S^*_1(1) \tag{37}$$

Thus E_S(aq) is a non-Gibbsian property. Consequently, familiar thermodynamic relationships involving partial molar properties are not valid in the case of partial molar isentropic (thermal) expansions which are non-Lewisian properties. We describe $[\partial V_j(\text{aq})/\partial T]$ for solute-j in aqueous solution at constant S(aq) as a semi-partial molar property.

Then for a solution having entropy S(aq), two partial molar isentropic thermal expansions are defined for the solvent and solute. Thus at S(aq) characterised by T, p, n_1 and n_j,

$$E_{S1}(\text{aq;def}) = [\partial E_S(\text{aq})/\partial n_1] \text{ at fixed } T, p \text{ and } n_1 \tag{38}$$

$$E_{Sj}(\text{aq;def}) = [\partial E_S(\text{aq})/\partial n_j] \text{ at fixed } T, p \text{ and } n_1 \tag{39}$$

So that, $$E_S(\text{aq}) = n_1 \cdot E_{S1}(\text{aq;def}) + n_j \cdot E_{Sj}(\text{aq;def}) \tag{40}$$

Eqn. (40) relates E_S(aq) to the partial molar intensive isentropic properties of both solvent and solute.

We find a similar dichotomy in defining an apparent molar isentropic expansion for solute-j, $\phi(E_{Sj})$. We might assert that $\phi(E_{Sj})$ is defined by the isentropic differential dependence $\phi(V_j)$ on temperature. Alternatively, we use an equation by analogy to those used to relate, for example, V(aq) to V^*_1 and $\phi(V_j)$.

Differentiation of eqn. (19) with $V \equiv Q$ at constant entropy again raises the problem that the molar entropy S(aq) does not equal the molar entropy of the pure solvent, S^*_1(l) However, by analogy with the definition of $\phi(E_{pj})$ we define a quantity $\phi(E_{Sj}$; def) using eqn. (41); *cf.* eqn. (35).

$$E_S(\text{aq}) = n_1 \cdot E^*_{S1}(\text{l}) + n_j \cdot \phi(E_{Sj};\text{def}) \tag{41}$$

In eqn. (41) E^*_{S1}(l) is the molar intensive property of the solvent. Thus, the isentropic expansion of the solution at entropy S(aq) is linked with that of the pure solvent at entropy S^*_1(l). Further

$$\phi(E_{Sj};\text{def}) = [\alpha_S(\text{aq}) - \alpha^*_{S1}(\text{l})] \cdot (c_j)^{-1} + \alpha^*_{S1}(\text{l}) \cdot \phi(V_j) \tag{42}$$

Interesting equations link isobaric and isentropic expansions; Section 10.

8 Isothermal compressions and compressibilities of solutions

The differential dependence of V(aq) on pressure (at constant temperature) yields an equation for the isothermal (equilibrium) compression of a solution; *cf.* eqn. (24),

$$K_T(\text{aq}) = n_1 \cdot K_{T1}(\text{aq}) + n_j \cdot K_{Tj}(\text{aq}) \tag{43}$$

Partial molar compressions K_{T1}(aq) and K_{Tj}(aq) are Lewisian properties of solute and solvent respectively. The analogue of eqn. (41) has the following form where $\phi(K_{Tj})$ is the apparent molar (isothermal) compression of solute-j.

$$K_T(\text{aq}) = n_1 \cdot K^*_{T1}(\text{l}) + n_j \cdot \phi(K_{Tj}) \tag{44}$$

where $$\phi(K_{Tj}) = -[\partial \phi(V_j)/\partial p]_T \tag{45}$$

$\phi(K_{Tj})$ is related to the concentration of solute c_j and the apparent molar volume, $\phi(V_j)$.

$$\phi(K_{Tj}) = [\kappa_T(\text{aq}) - \kappa^*_{T1}(\text{l})] \cdot (c_j)^{-1} + \kappa^*_{T1}(\text{l}) \cdot \phi(V_j) \tag{46}$$

The latter equation resembles the equations for $\phi(E_{pj})$ and $\phi(E_{Sj};\text{def})$ as a function of the concentration of solute c_j and $\phi(V_j)$. Both $\phi(K_{Tj})$ and K_{Tj}(aq) depend on the molality of the solute. K_{Tj}(aq) is related to the second differential of the solute activity coefficient with respect to pressure; *cf.* eqn. (23).

$$K_{Tj}(\text{aq}) = K^\infty_{Tj}(\text{aq}) - R \cdot T \cdot [\partial^2 \ln(\gamma_j)/\partial p^2]_T \tag{47}$$

One might have anticipated an extensive scientific literature reporting K^∞_{Tj}(aq) for a wide range of solutes. Unfortunately, direct measurement of isothermal compressibilities is difficult; at least to the precision required for determining K^∞_{Tj}(aq). Under these circumstances two procedures have been adopted, one commendable and the other perhaps less so. In both cases, the chosen route uses the isentropic compressibilities of solutions calculated from densities and speed of sound (Section 3).

The commendable route combines the measured isentropic compressibilities, densities and isobaric heat capacities C_p(aq) in order to calculate isothermal compressibilities; *cf.* eqn. (14) for a given solution having molality m_j. An excellent example of this approach is described by Bernal and Van Hook[13] who used the Desnoyers–Philip equation (see Section 10) to calculate $\phi(K_{Tj})^\infty$ for glucose, sucrose and fructose in aqueous solutions at 348 K. In a similar manner, Hedwig *et al.* used the Desnoyers–Philip equation (Section 10) to obtain estimates of limiting apparent molar isothermal compressions of glycyl dipeptides in aqueous solutions at 298 K.[14]

The less commendable but, under the circumstances, understandable route uses a measured κ_S as being effectively the same as κ_T. Hence $\phi(K_{Sj};\text{def})$ is often taken as a satisfactory estimate of $\phi(K_{Tj})$. We return to this point in Section 9 because there are further problems which we need to address.

For neutral solutes $\phi(K_{Tj})$ is satisfactorily expressed as a linear function of the concentration c_j.

Thus $$\phi(K_{Tj}) = \phi(K_{Tj})^\infty + a_K \cdot c_j \tag{48}$$

For aqueous salt solutions the apparent molar compression, $\phi(K_{Tj})$ is often a linear function of the square root of the salt concentration.[15]

Thus $$\phi(K_{Tj}) = \phi(K_{Tj})^\infty + S_K \cdot c_j^{\frac{1}{2}} \tag{49}$$

9 Isentropic compressions and compressibilities of solutions

We turn to the definition of a property that, by analogy to $\phi(K_{Tj})$, is the apparent molar isentropic compression of the solute $\phi(K_{Sj})$ which, again by analogy, is related to a partial molar isentropic compression K_{Sj} of solute-j. For reasons given below, we write the apparent property $\phi(K_{Sj};\text{def})$.

These isentropic properties emerge from consideration of eqn. (3) and eqn. (4). The assertion is made that an aqueous solution can be perturbed, by a small change in pressure δp, to a neighbouring state having the same entropy; *cf.* eqn. (4). Then the equilibrium isentropic compression is defined by eqn. (50).

$$K_S(\text{aq}) = -[\partial V(\text{aq})/\partial p]_{S(\text{aq}} \tag{50}$$

The constraint on this partial differential refers to ‘at constant S(aq)’. Thus the definition of K_S(aq) uses non-Gibbsian independent variables. Isentropic parameters do not arise naturally from the formalism which expresses the Gibbs energy in terms of independent variables in the case of, for example, a simple solution, $[T,p,n_1,n_j]$.

The isothermal compression of a solution K_T(aq) and partial molar isothermal compressions of both solvent K_{T1}(aq) and solute K_{Tj}(aq) are defined using Gibbsian independent variables; *e.g.* eqn. (43)-(45). Unfortunately these equations cannot be simply carried over to the isentropic property $K_S(\text{aq})$. Indeed the isentropic pressure dependence of the volume may be expressed as in eqn. (51). The equation emphasises that the entropy which remains constant is that of the solution.

$$K_S(\text{aq}) = -n_1 \cdot [\partial V_l(\text{aq})/\partial p]_{S(\text{aq});A=0} - n_\text{j} \cdot [\partial V_\text{j}(\text{aq})/\partial p]_{S(\text{aq});A=0} \tag{51}$$

On the other hand, K_S (aq) may also be re-expressed using Euler's theorem.

$$\text{Then, } K_S(\text{aq}) = n_1 \cdot [\partial K_S(\text{aq})/\partial n_1]_{T,p,n(\text{j})} + n_\text{j} \cdot [\partial K_S(\text{aq})/\partial n_\text{j}]_{T,p,n(1)} \tag{52}$$

But $K_S(\text{aq})$ is defined using non-Gibbsian independent variables. As a consequence two inequalities follow.

$$-[\partial V_1(\text{aq})/\partial p]_{S(\text{aq})} \neq [\partial K_S(\text{aq})/\partial n_1]_{T,p,n(\text{j})} \tag{53}$$

$$-[\partial V_1(\text{aq})/\partial p]_{S(\text{aq})} \neq [\partial K_S(\text{aq})/\partial n_\text{j}]_{T,p,n(1)} \tag{54}$$

$[\partial K_S(\text{aq})/\partial n_1]_{T,p,n(\text{j})}$ and $[\partial K_S(\text{aq})/\partial n_1]_{T,p,n(1)}$ are respectively the partial molar properties of the solvent and solute. Because partial molar properties should describe the effects of a change in composition on the properties of a solution, we write eqn. (52) for an aqueous solution[7] in the following form.

$$K_S(\text{aq}) = n_1 \cdot K_{S1}(\text{aq;def}) + n_\text{j} \cdot K_{S\text{j}}(\text{aq;def}) \tag{55}$$

$$\text{Hence,} \quad K_{S\text{j}}(\text{aq;def}) \neq -[\partial V_\text{j}(\text{aq})/\partial p]_{S(\text{aq})} \tag{56}$$

Therefore $K_{S\text{j}}(\text{aq;def})$ is a non-Lewisian partial molar property. We might define a molar isentropic compression of solute j as (minus) the isentropic differential dependence of partial molar volume on pressure. This alternative definition is consistent with eqn. (51) expressing a summation rule analogous to that used for partial molar properties. However some other thermodynamic relationships involving partial molar properties would not be valid in this case. Therefore, $-[\partial V_\text{j}(\text{aq})/\partial p]_{S(\text{aq})}$ is a semi-partial property. A similar problem is encountered in defining an apparent molar compression for solute-j, $\phi(K_{S\text{j}})$ in a solution having volume $V(\text{aq})$; *cf.* eqn. (56). We might assert that $\phi(K_{S\text{j}})$ is related to the isentropic differential dependence of $\phi(V_\text{j})$ on pressure, $-[\phi(V_\text{j})/\partial p]_{S(\text{aq})}$. Alternatively, using as a guide the apparent molar properties $\phi(E_{p\text{j}})$ and $\phi(K_{T\text{j}})$, we could define $ø(K_{S\text{j}};\text{def})$ using eqn. (57).

$$K_S(\text{aq}) = n_1 \cdot K^*_{S1}(\text{l}) + n_\text{j} \cdot \phi(K_{S\text{j}};\text{def}) \tag{57}$$

$K_{S\text{j}}(\text{aq;def})$ as given by eqn. (52) and $\phi(K_{S\text{j}};\text{def})$ are linked; eqn. (58).

$$K_{S\text{j}}(\text{aq;def}) = \phi(K_{S\text{j}};\text{def}) + n_\text{j} \cdot [\partial \phi(K_{S\text{j}};\text{def})/\partial n_\text{j}]_{T,p,n(1)} \tag{58}$$

This equation is of the general form encountered for other apparent and partial molar properties; *cf.* eqn. (26). This form is also valid in the case of partial and apparent molar isobaric expansions, isothermal compressions and isobaric heat capacities. On the other hand, the semi-partial isentropic compression defined by $-[\partial V_\text{j}(\text{aq})/\partial p]_{S(\text{aq})}$ and the semi-apparent isentropic compression defined by $-[\partial \phi(V_\text{j})/\partial p]_{S(\text{aq})}$ are related. Thus the isentropic pressure dependence of $V_\text{j}(\text{aq})$ is given by eqn. (59).

$$-[\partial V_\text{j}(\text{aq})/\partial p]_{S(\text{aq})} = -[\partial \phi(V_\text{j})/\partial p]_{S(\text{aq})} - n_\text{j} \cdot \{\partial[\partial \phi(V_\text{j})/\partial n_\text{j}]_{T,p,n(1)}/\partial p\}_{S(\text{aq})} \tag{59}$$

$$\text{Hence, } \{\partial[\partial \phi(V_\text{j})/\partial n_\text{j}]_{T,p,n(1)}/\partial p\}_{S(\text{aq})} \neq \{\partial[\partial \phi(V_\text{j}\}/\partial p]_{S(\text{aq})}/\partial n_\text{j}\}_{T,p,n(1)} \tag{60}$$

Hence, the analogue of eqn. (58) does not hold for these 'semi' properties. The inequalities (53) and (54) highlight the essence of non-Lewisian properties. Their origin is a combination of properties defined in terms of Gibbsian and non-Gibbsian independent variables as in eqn. (51) and eqn. (52). This combination is also the reason for the inequality (60). We stress that the isentropic condition in eqn. (51) and eqn. (52) refers to the entropy $S(\text{aq})$ of the solution defined as is the volume $V(\text{aq})$ by the Gibbsian independent variables $[T,p,n_1 n_\text{j}]$. But this is not the entropy $S^*_1(\text{l})$ of the pure solvent having volume $V^*_1(\text{l})$. $S(\text{aq})$ at fixed composition is not simply related to $S^*_1(\text{l})$ as, for example, linear functions of temperature and pressure.

The isentropic condition is involved in the definitions of isentropic compression, $K^*_{S1}(\text{l})$ and isentropic compressibility $\kappa^*_{S1}(\text{l})$ of the solvent.

$$K^*_{S1}\ (\text{l}) = -[\partial V^*_1(\text{l})/\partial p] \text{ at constant } S^*_1(\text{l}) \tag{61}$$

$$\kappa^*_{S1}(\text{l}) = K^*_{S1}(\text{l})/V^*_1(\text{l}) = -[\partial V^*_1(\text{l})/\partial p]/V^*_1(\text{l}) \text{ at constant } S^*_1(\text{l}) \tag{62}$$

The different isentropic conditions in eqn. (50) and in eqn. (61) and eqn. (62) signal a complexity in the isentropic differentiation of eqn. (25) with respect to pressure.

Interest in the isentropic compresssibilities of solutions was stimulated by Gucker[15] and, in particular, by Harned and Owen.[1] The latter authors *defined* a (practical) property of the solute, here called $\phi(K_{S\text{j}};\text{def})$ using eqn. (63) where the composition of a given aqueous solution is expressed using concentration c_j.

$$\phi(K_{S\text{j}};\text{def}) \equiv [\kappa_\text{S}(\text{aq}) - \kappa^*_{S1}(\text{l})] \cdot [c_\text{j}]^{-1} + \kappa^*_{S1}(\text{l}) \cdot \phi(V_\text{j}) \tag{63}$$

Also

$$\phi(K_{S\text{j}};\text{def}) \equiv [\kappa_\text{S}(\text{aq}) \cdot \rho^*_1(\text{l}) - \kappa^*_{S1}(\text{l}) \cdot \rho(\text{aq})] \cdot [c_\text{j} \cdot \rho^*_1(\text{l})]^{-1} + \kappa^*_{S1}(\text{l}) \cdot M_\text{j} \cdot [\rho^*_1(\text{l})]^{-1} \tag{64}$$

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

$$\phi(K_{S\text{j}};\text{def}) \equiv [\kappa_\text{S}(\text{aq}) - \kappa^*_{S1}(\text{l})] \cdot [m_\text{j} \cdot \rho^*_1(\text{l})]^{-1} + \kappa_S(\text{aq}) \cdot \phi(V_\text{j}) \tag{65}$$

$$\phi(K_{S\text{j}};\text{def}) \equiv [\kappa_\text{S}(\text{aq}) \cdot \rho^*_1(\text{l}) - \kappa^*_{S1}(\text{l}) \cdot \rho(\text{aq})] \cdot [m_\text{j} \cdot \rho(\text{aq}) \cdot \rho^*_1(\text{l})]^{-1} + \kappa_S(\text{aq}) \cdot M_\text{j} \cdot [\rho(\text{aq})]^{-1} \tag{66}$$

These last four defining equations are rigorously equivalent. A crucial feature of eqn. (63)–(66) is the equivalence symbol (*i.e.* ≡). In this sense Harned and Owen[1] defined an apparent isentropic compression of solute-j in terms of the quantities on the rhs of eqn. (63). They recognised that $\phi(K_{S\text{j}};\text{def})$ does not have thermodynamic basis. Unfortunately many authors refer to the proposals by Harned and Owen[1] without noting the significance of the symbol, ≡. The target quantity is the apparent molar isentropic compression defined by eqn. (57) which, however, is not a description of an isentropic process as its name might suggest. In fact $\phi(K_{S\text{j}};\text{def})$ is a measure of the change in the isentropic compression of a solution when solute-j is added under isothermal-isobaric conditions. The equivalence symbol in eqn. (63)–(66) is important.[16]

The impression is often given that eqn. (63)–(66) are thermodynamic. Some authors do, however, indicate reservations especially when the estimates of $\phi(K_{S\text{j}};\text{def})$ are discussed, particularly the dependence of $\phi(K_{S\text{j}};\text{def})$ on solution composition. Franks and co-workers[17] recognised the lack of isobaric heat capacity data which forces the adoption of the approach in which $\phi(K_{S\text{j}};\text{def})$ is effectively assumed equal to $\phi(K_{T\text{j}})$. Owen and Simons[18] estimate that overlooking the difference between $\kappa_S(\text{aq})$ and $\kappa_T(\text{aq})$ causes errors of approximately 7.5% in estimates of $\phi(K_{T\text{j}})^\infty$ for NaCl(aq) and KCl(aq) at 298 K.

Interesting patterns emerge for the dependences of $\phi(K_{S\text{j}};\text{def})$ on molality m_j and on solute-j. Further, these dependences are readily extrapolated (geometrically) to infinite dilution to yield estimates of $\phi(K_{S\text{j}};\text{def})^\infty$. These comments apply to solutions of neutral solutes in both aqueous and non-aqueous solutions; *e.g.* solutions in propylene carbonate.[19]

For dilute solutions of neutral solutes $\phi(K_{S\text{j}};\text{def})$ is often a linear function of the molality m_j.

$$\text{Thus} \quad \phi(K_{S\text{j}};\text{def}) = \phi(K_{S\text{j}};\text{def})^\infty + b_{KS} \cdot (m_\text{j}/m^0) \tag{67}$$

For aqueous solutions containing ureas, acetamides and α,ω-alkanediols, the slope b_{KS} is positive and characteristic of the solute.[20] Sakurai *et al.*[21] report the results of a detailed investigation into the isentropic compression of alcohols in dilute solutions over the range from 5 to 45 Celsius. Interestingly $\phi(K_{S\mathrm{j}};\mathrm{def})^\infty$ is generally smaller than the molar property of the pure liquid-j. Galema and Høiland[22] use eqn. (65) to analyse speed of sound data for several carbohydrates in aqueous solutions at 298 K. They comment on the calculation of $K_{S\mathrm{j}}(\mathrm{aq;def})$ for solute-j using eqn. (68).

$$K_{S\mathrm{j}}(\mathrm{aq;def}) = \phi(K_{S\mathrm{j}};\mathrm{def}) + m_\mathrm{j}\cdot[\partial\phi(K_{S\mathrm{j}};\mathrm{def})/\partial m_\mathrm{j}]_{T,p} \quad (68)$$

This study confirmed the importance of the stereochemistry of carbohydrates on their hydration. A clear contrast is drawn between those solutes where the hydrophilic groups match and mismatch[23] into the three dimensionally hydrogen-bonded structure of liquid water.

Desnoyers *et al.*[24] used eqn. (65) to probe micelle formation by alkyldimethylamine oxides. Eqn. (65) was used to analyse the isentropic compressibilities of micellar aqueous solutions containing sodium octanoate and ethoxylated alcohols.[25] Iqbal and Verrall[26] use eqn. (66) in an examination of the compressibilities of glycyl peptides in aqueous solutions at 298 K. The dependence of $\phi(K_{S\mathrm{j}};\mathrm{def})$ on molality m_j is linear leading to estimates $\phi(K_{S\mathrm{j}};\mathrm{def})^\infty$. For amino acids in aqueous solution at 298 K, the calculated $\phi(K_{S\mathrm{j}};\mathrm{def})$ is a linear function[27] of the molality of the neutral amino acid yielding estimates of $\phi(K_{S\mathrm{j}};\mathrm{def})^\infty$.

For salt solutions, the dependence of $\phi(K_{S\mathrm{j}};\mathrm{def})$ on the molality of the salt is generally examined in the light of equations describing the role of ion–ion interactions (see Section 4). For dilute solutions eqn. (69) forms the basis for examining the dependence of $\phi(K_{S\mathrm{j}};\mathrm{def})$ on $(m_\mathrm{j})^{1/2}$ where m_j is the molality of the salt-j.

Then, $$\phi(K_{S\mathrm{j}};\mathrm{def}) = \phi(K_{S\mathrm{j}};\mathrm{def})^\infty + S_{KS}\cdot(m_\mathrm{j}/m^0)^{1/2} \quad (69)$$

For a large range of 1 : 1 salts, that $\phi(K_{S\mathrm{j}};\mathrm{def})^\infty$ is negative is attributed to electrostriction by the ionic charges. $\phi(K_{S\mathrm{j}};\mathrm{def})^\infty$ is more negative for solutions in D_2O, than in H_2O, as a consequence of more intense electrostriction in D_2O.[28] Further, on the basis of the Desnoyers–Philip equation (see Section 10), the difference $\phi(K_{S\mathrm{j}};\mathrm{def}) - \phi(K_{T\mathrm{j}})^\infty$ is small but not negligible, amounting to approximately 10%. For alkylammonium ions in aqueous solutions $\phi(K_{S\mathrm{j}};\mathrm{def})^\infty$ decreases with increase in the hydrophobic power, matching a general increase in $\phi(V_j)^\infty$.[29]

Generally the property S_{KS} cannot be evaluated because the isentropic dependence of the relative permittivity of the solvent is required.[28] Further, the DHLL for $\phi(K_{S\mathrm{j}};\mathrm{def})$ is itself a complicated function of salt molality.[30] However for many dilute salt solutions $\phi(K_{S\mathrm{j}};\mathrm{def})$ is approximately a linear function of $(m_\mathrm{j}/m^0)^{1/2}$; *cf.* eqn. (69). Indeed $\phi(K_{S\mathrm{j}};\mathrm{def})$ is approximately a linear function of $(m_\mathrm{j}/m^0)^{1/2}$ for a wide range of aqueous and non-aqueous salt solutions; *e.g.* tetraalkylammonium salts in cyanomethane and benzonitrile.[31] $\phi(K_{S\mathrm{j}};\mathrm{def})$ for copper(I) and sodium perchlorates in cyanobenzene, pyridine and cyanomethane show almost no dependence on salt molality.[31]

Determination of $\phi(K_{S\mathrm{j}};\mathrm{def})$ for amino acids,[32,33] proteins, nucleic acids and nucleotides[34] has attracted enormous interest. Interesting patterns emerge pointing to the complexity of both solute–water and solute–solute interactions in these systems.

In terms of the development of the theory, the problem is concerned with the differential dependence of $V_1^*(\mathrm{l})$ on pressure at constant $S(\mathrm{aq})$ describing how the volume of the solvent would depend on pressure if it were held at the same entropy as the solution.[16]

Thus

$$-[(\partial\phi(V_\mathrm{j})/\partial p]_{S(\mathrm{aq})} = [\kappa_S(\mathrm{aq}) - \kappa_{S1}^*(\mathrm{l})]\cdot[m_\mathrm{j}\cdot\rho_1^*(\mathrm{l})]^{-1} + \kappa_S(\mathrm{aq})\cdot\phi(V_\mathrm{j}) + [m_\mathrm{j}\cdot\rho_1^*(\mathrm{l})]^{-1}\cdot T\cdot\alpha_1(\mathrm{l})\cdot\{[\alpha_p/\sigma(\mathrm{aq})] - [\alpha_{p1}^*(\mathrm{l})/\sigma_1^*(\mathrm{l})]\} \quad (70)$$

The latter equation is thermodynamically correct. No assumptions have been made in its derivation. We adopt the procedure used by Harned and Owen.[1]

$$-[(\partial\phi(V_\mathrm{j})/\partial p]_{S(\mathrm{aq})} = \phi(K_{S\mathrm{j}};\mathrm{def}) + [m_\mathrm{j}\cdot\rho_1^*(\mathrm{l})]^{-1}\cdot T\cdot\alpha_{p1}^*(\mathrm{l})\cdot\{[\alpha_p(\mathrm{aq})/\sigma(\mathrm{aq})] - [\alpha_{p1}^*(\mathrm{l})/\sigma_1^*(\mathrm{l})]\} \quad (71)$$

Consequently the difference between $-[\partial\phi(V_\mathrm{j})/\partial p]_{S(\mathrm{aq})}$ and $\phi(K_{S\mathrm{j}};\mathrm{def})$ is determined by the difference $\Delta\phi$; eqn. (72).

$$\Delta\phi = \{[\alpha_p(\mathrm{aq})/\sigma(\mathrm{aq})] - [\alpha_{p1}^*(\mathrm{l})/\sigma_1^*(\mathrm{l})]\} \quad (72)$$

However, $\Delta\phi/m_\mathrm{j}$ is indeterminate at infinite dilution. But using L'Hospital's rule,

$$\mathrm{limit}\ (m_\mathrm{j} \longrightarrow 0)\Delta\phi/m_\mathrm{j} = [\rho_1^*(\mathrm{l})\cdot\alpha_{p1}^*(\mathrm{l})/\sigma_1(\mathrm{l})]\{[\phi(E_{p\mathrm{j}})^\infty/\alpha_{p1}^*(\mathrm{l})] - [\phi(C_{p\mathrm{j}})^\infty/\sigma_1^*(\mathrm{l})]\} \quad (73)$$

Nevertheless, despite the thermodynamic polish given to the analysis of isentropic compressions of solutions, there is an underlying problem. The latter again emerges in eqn. (70) which needs to refer to compressions at constant entropies for solutions and the pure solvent. In fact rarely is this feature acknowledged. Indeed one purpose of this review is to point out this feature.

10 Apparent molar isothermal and isentropic compressions and expansions: infinite dilution

Expansions and compressions of solutions under a combination of isothermal, isobaric and isentropic constraints are intimately linked.[35] The most frequently quoted relationship is the Desnoyers–Philip equation[4] linking $\phi(K_{T\mathrm{j}})$ and $\phi(K_{S\mathrm{j}};\mathrm{def})$. We noted that the extrapolated limiting value $\phi(K_{T\mathrm{j}})^\infty$ offers information about the hydration of a solute. Nevertheless in the face of experimental problems the favoured approach examines isentropic compressibilities. The apparent molar isothermal compression for solute-j $\phi(K_{T\mathrm{j}})$ is related to the solute concentration c_j using eqn. (46). The corresponding apparent molar isentropic compression of solute-j $\phi(K_{S\mathrm{j}};\mathrm{def})$ is related to the concentration using eqn. (63). Hence $\phi(K_{T\mathrm{j}})$ and $\phi(K_{S\mathrm{j}};\mathrm{def})$ are related by the following eqn. (74).

$$\phi(K_{T\mathrm{j}}) - \phi(K_{S\mathrm{j}};\mathrm{def}) = (c_\mathrm{j})^{-1}\cdot[\delta(\mathrm{aq}) - \delta_1^*(\mathrm{l})] + \delta_1^*(\mathrm{l})\cdot\phi(V_\mathrm{j}) \quad (74)$$

The difference $[\phi(K_{T\mathrm{j}}) - \phi(K_{S\mathrm{j}};\mathrm{def})]$ depends on the concentration of the solute c_j. Further $[\delta(\mathrm{aq}) - \delta_1^*(\mathrm{l})]$ is not zero. Thus from eqn. (14),

$$\delta(\mathrm{aq}) - \delta_1^*(\mathrm{l}) = \{T\cdot[\alpha_p(\mathrm{aq})]^2/(\mathrm{aq})\} - \{T\cdot[\alpha_{p1}^*(\mathrm{l})]^2/\sigma_1^*(\mathrm{l})\} \quad (75)$$

Using the technique of adding and subtracting the same quantity, eqn. (75) can be re-expressed as follows.

$$\delta(\mathrm{aq}) - \delta_1^*(\mathrm{l}) = \{\delta(\mathrm{aq})/[\alpha_p(\mathrm{aq})]^2\}\cdot[\alpha_p(\mathrm{aq}) + \alpha_{p1}^*(\mathrm{l})]\cdot\alpha_p(\mathrm{aq}) - \alpha_{p1}^*(\mathrm{l})] - [\delta_1^*(\mathrm{l})/\sigma(\mathrm{aq})]\cdot[\sigma(\mathrm{aq}) - \sigma_1^*(\mathrm{l})] \quad (76)$$

The difference, $[\alpha_p(\mathrm{aq}) - \alpha_{p1}^*(\mathrm{l})]$ is related to $\phi(E_{p\mathrm{j}})$ using eqn. (36). Similarly, $[\sigma(\mathrm{aq}) - \sigma_1^*(\mathrm{l})]$ is related to $\phi(C_{p\mathrm{j}})$ using eqn. (77).

$$\phi(C_{p\mathrm{j}}) = [\sigma(\mathrm{aq}) - \sigma_1^*(\mathrm{l})]\cdot(c_\mathrm{j})^{-1} + \sigma_1^*(\mathrm{l})\cdot\phi(V_\mathrm{j}) \quad (77)$$

Then using eqn. (76), we express eqn. (74) in the following manner.

$$\phi(K_{T\mathrm{j}}) - \phi(K_{Sj};\mathrm{def}) = [\delta(\mathrm{aq})/\alpha_p(\mathrm{aq})]\cdot\{1 + [\alpha_{p1}^*(\mathrm{l})\alpha_p(\mathrm{aq})]\}\cdot\phi(E_{p\mathrm{j}}) - [\delta_1^*(\mathrm{l})/\sigma(\mathrm{aq})]\cdot\phi(C_{p\mathrm{j}}) + \{\delta_1^*(\mathrm{l}) - [\delta(\mathrm{aq})\cdot\alpha_{p1}^*(\mathrm{l})/\alpha_p(\mathrm{aq})]\}\cdot\phi(V_\mathrm{j}) \quad (78)$$

Eqn. (78) was obtained by Desnoyers and Philip[4] although a proof was not given. Desnoyers and Philip showed that if $\phi(K_{T\mathrm{j}})^\infty$ and $\phi(K_{S\mathrm{j}};\mathrm{def})^\infty$ are the limiting (infinite dilution) apparent molar properties, the difference is given by eqn. (79).

$$\phi(K_{T\mathrm{j}})^\infty - \phi(K_{S\mathrm{j}};\mathrm{def})^\infty = \delta_1^*(\mathrm{l})\cdot\{[2\cdot\phi(E_{p\mathrm{j}})^\infty/\alpha_{p\mathrm{j}}^*(\mathrm{l})] - [\phi(C_{p\mathrm{j}})^\infty/\sigma_1^*(\mathrm{l})]\} \quad (79)$$

Using eqn. (63), $\phi(K_{S\mathrm{j}};\mathrm{def})$ is plotted as a function of c_j across a set of different solutions having different entropies. Then limit($c_\mathrm{j} \rightarrow 0$)$\phi(K_{S\mathrm{j}};\mathrm{def})$ defines $\phi(K_{S\mathrm{j}};\mathrm{def})^\infty$. Granted two limiting quantities, $\phi(E_{p\mathrm{j}})^\infty$ and $\phi(C_{p\mathrm{j}})^\infty$ are available for the solution at the same T and p, eqn. (79) is used to calculate $\phi(K_{T\mathrm{j}})^\infty$ using $\phi(K_{S\mathrm{j}};\mathrm{def})^\infty$.

An alternative form of eqn. (78 refers to a solution, molality m_j.[30]

Thus, $\phi(K_{T\mathrm{j}}) - \phi(K_{S\mathrm{j}};\mathrm{def}) = \delta_1^*(\mathrm{l})\cdot\{[2\cdot\phi(E_{p\mathrm{j}})/\alpha_{p1}^*(\mathrm{l})] - [\phi(C_{p\mathrm{j}})/\sigma_1^*(\mathrm{l})] + [\rho_1^*(\mathrm{l})\cdot m_\mathrm{j}\cdot[\phi(E_{p\mathrm{j}})]^2/[\alpha_{p1}^*(\mathrm{l})]^2]\}\cdot\{1 + [\rho_1^*(\mathrm{l})\cdot m_\mathrm{j}\cdot\phi(C_{p\mathrm{j}})/\sigma_1^*(\mathrm{l})]\}^{-1}$ (80)

The apparent molar expansions, $\phi(E_{p\mathrm{j}})$ and $\phi(E_{p\mathrm{j}};\mathrm{def})$ are linked by eqn. (81).

$$\begin{aligned}\phi(E_{p\mathrm{j}}) - \phi(E_{S\mathrm{j}};\mathrm{def}) = &-\frac{\varepsilon_1^*(\mathrm{l})}{\alpha_p(\mathrm{aq})}\cdot\phi(E_{p\mathrm{j}}) + \frac{\varepsilon(\mathrm{aq})}{\kappa_T(\mathrm{aq})}\cdot\phi(K_{T\mathrm{j}}) \\ &+ \frac{\varepsilon(\mathrm{aq})\cdot\kappa_T^*(\mathrm{l})}{\kappa_T(\mathrm{aq})\cdot\sigma(\mathrm{aq})}\cdot\phi(C_{p\mathrm{j}}) \\ &+ \left[\varepsilon_1^*(\mathrm{l})\cdot\left(1+\frac{\alpha_{p1}^*(\mathrm{l})}{\alpha_p(\mathrm{aq})}\right) - \frac{\varepsilon(\mathrm{aq})\cdot\kappa_{T1}^*(\mathrm{l})}{\kappa_T(\mathrm{aq})}\cdot\left(1+\frac{\sigma_1^*(\mathrm{l})}{\sigma(\mathrm{aq})}\right)\right]\cdot\phi(V_j)\end{aligned} \qquad (81)$$

where $\varepsilon_1^*(\mathrm{l})$ and $\varepsilon(\mathrm{aq})$ are defined by eqn. (15). In the limit of infinite dilution,

$$\frac{\phi(E_{p\mathrm{j}})^\infty - \phi(E_{S\mathrm{j}};def)^\infty}{\varepsilon_1^*(\mathrm{l})} = -\frac{\phi(E_{p\mathrm{j}})^\infty}{\alpha_{p1}^*(\mathrm{l})} + \frac{\phi(K_{T\mathrm{j}})^\infty}{\kappa_{T1}^*(\mathrm{l})} + \frac{\phi(C_{p\mathrm{j}})^\infty}{\sigma_1^*(\mathrm{l})} \qquad (82)$$

On the rhs of eqn. (82) each term is the ratio of a limiting apparent molar property of solute-j to the corresponding volume intensive property of the solvent. An allied set of equations incorporate terms relating to isentropic compressions. Thus

$$\begin{aligned}\phi(E_{S\mathrm{j}};\mathrm{def}) = &-\frac{\alpha_{S1}^*(\mathrm{l})}{\alpha_p(\mathrm{aq})}\cdot\phi(E_{p\mathrm{j}}) + \frac{\alpha_S(\mathrm{aq})}{\kappa_S(\mathrm{aq})}\cdot\phi(K_{S\mathrm{j}};\mathrm{def}) + \\ &\frac{\alpha_S(\mathrm{aq})\cdot\kappa_{S1}^*(\mathrm{l})}{\kappa_S(\mathrm{aq})\cdot\sigma(\mathrm{aq})}\cdot\phi(C_{p\mathrm{j}}) + \left[\alpha_{S1}^*(\mathrm{l})\cdot\left(1+\frac{\alpha_{p1}^*(\mathrm{l})}{\alpha_p(\mathrm{aq})}\right) - \right. \\ &\left.\frac{\alpha_S(\mathrm{aq})\cdot\kappa_{S1}^*(\mathrm{l})}{\kappa_S(\mathrm{aq})}\cdot\left(1+\frac{\sigma_1^*(\mathrm{l})}{\sigma(\mathrm{aq})}\right)\right]\cdot\phi(V_j)\end{aligned} \qquad (83)$$

Then in the limit of infinite dilution,

$$\frac{\phi(E_{S\mathrm{j}};\mathrm{def})^\infty}{\alpha_{S1}^*(l)} = -\frac{\phi(E_{p\mathrm{j}})^\infty}{\alpha_{p1}^*(l)} + \frac{\phi(K_{S\mathrm{j}};\mathrm{def})^\infty}{\kappa_{S1}^*(l)} + \frac{\phi(C_{p\mathrm{j}})^\infty}{\sigma_1^*(\mathrm{l})} \qquad (84)$$

Finally, ‘semi’ apparent molar isentropic expansions (section 7) and compressions (Section 9) are linked; eqn. (85).

$$[\partial\phi(V_\mathrm{j})]\partial T]_{S(\mathrm{aq})}/\alpha_S(\mathrm{aq}) = -[\partial\phi(V_\mathrm{j})/\partial p]_{S(\mathrm{aq})}/\kappa_S(\mathrm{aq}) \qquad (85)$$

Therefore in an analogous fashion to the pattern shown by eqn. (82) and eqn. (84) an interesting pattern emerges in the form of the terms in eqn. (85).

These fascinating equations illustrate the power of thermodynamics in drawing together the properties of a given solution. Indeed this has been one of the themes of this review.

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