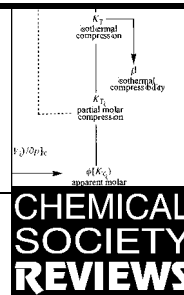# Equilibrium, frozen, excess and volumetric properties of dilute solutions

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The properties of aqueous solutions can be analysed in several ways leading to the identification of, for example, frozen, equilibrium, relaxational, complex, sophisticated, delphic, isodelphic, ideal and excess contributions. These terms are examined and illustrated in terms of increasing orders of partial differentials of Gibbs energies, volumes, expansions and compressions.

1 Introduction

The volume of a closed system is an important and, indeed, comprehensible thermodynamic function of state defined,[1a] for example, for a single phase by the set of independent variables temperature T, pressure p and amount of each chemical substance j, n_j; eqn. (1-1); equations are numbered according to the section in which they appear.

$$V = V[T, p, n_i] \qquad (1\text{-}1)$$

We note that temperature T and pressure p are intensive variables. With reference to eqn. (1-1), the symbol n_i represents the set describing the amounts of all chemical substances in the system. Chemists are challenged by eqn. (1-1) in several interesting ways. There is the problem of understanding the contributions made to volume V by each chemical substance j in the system. One way of tackling this problem probes the change in volume δV when δn_j moles of substance j are added leading to the definition of a partial molar volume V_j. The consequence of switching from a closed to an open system in this formalism is not discussed here although it is an interesting point.[1b] For the most part we confine our attention to aqueous solutions prepared by adding n_j moles of substance j (*e.g.* urea) to n_1 moles of liquid water. We also confine our attention to solutes which do not undergo solvolysis reactions. In order to probe, therefore, the role of solute–solute, solute–solvent and solvent–

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solvent interactions in determining the volume $V(\text{aq})$ of a solution a useful procedure identifies the corresponding volume $V(\text{aq;id})$ in the event that the properties of this solution are ideal. The difference $[V(\text{aq}) - V(\text{aq;id})]$ defines an excess volume.

In the context again of eqn. (1-1), another challenge concerns understanding the dependences of volume V on temperature and on pressure. These dependences are described in terms of expansion E, compression K, expansivity α and compressibility κ. Closely linked to this new set of properties are the corresponding instantaneous (frozen) and equilibrium properties.

2 Gibbs energies

The set of independent variables $[T, p, n_i]$ used in eqn. (1-1) also defines the function of state called the Gibbs energy which for systems at fixed T and p is the thermodynamic potential. For a closed system at equilibrium the Gibbs energy is a minimum. Chemistry is based on the assumption that across the whole range of possible compositions (and organisations—see below), the minimum in Gibbs energy G is unique.[2] (All experience based on experiment supports this assumption.) If the state defined by eqn. (1-1) is not at this minimum, spontaneous chemical reaction/reorganisation takes place, driven by the affinity for spontaneous change A, the product of A and extent of chemical reaction being positive;[1c] $A\,\mathrm{d}\xi \geqslant 0$, De Donder's inequality where $A = -(\delta G/\delta\xi)_{T,p}$.

Conceptually, we freeze-frame the thermodynamic state defined by eqn. (1-1) in, by definition, state (I) where the affinity for spontaneous change is $A(\text{I})$ and the composition is $\xi(\text{I})$. Again, conceptually, we perturb the system into a nearby state by changes in pressure δp, temperature δT and amount of substance j δn_j. There are two interesting constraints which we impose on this perturbation.

(A) Perturbation is to a near neighbouring state such that affinity A remains constant.

(B) Perturbation is to a near neighbouring state at constant extent of reaction; *i.e.* at constant composition/organisation where ξ is constant.

We are interested in the differential change in, for example, volume V under these two conditions. In fact, we direct our attention to equilibrium states perturbed such that either (*a*) $A = A^{\text{eq}} = 0$, or (*b*) $\xi = \xi^{\text{eq}}$.

The keyword in the above two paragraphs is spontaneous. In a typical kinetics experiment n_i moles of reactants are added to an aqueous solution at time $t = 0$ (at fixed T and p). Spontaneous chemical reaction driven by the affinity for change leads the system to a minimum in Gibbs energy. The rate at which this process occurs is examined using the formalism of chemical kinetics. Similarly, when an aliquot of a solution containing micelles formed by an ionic surfactant is injected into water, the micellar aggregates break up as the system spontaneously moves towards a minimum in Gibbs energy.[3]

3 Partial molar volumes

The distinction between the two types of perturbation is illustrated using the following examples. A given closed

aqueous solution of benzoic acid at specified temperature and pressure (close to ambient) contains at equilibrium (G = minimum, $A = 0$ and $\xi = \xi^{eq}$) n_1^{eq} moles of water, n^{eq} (PhCOOH) moles of benzoic acid, n^{eq} (H^+) moles of hydrogen ions and n^{eq} (PhCOO$^-$) moles of benzoate anions. Then the analogue of eqn. (1-1) has the following form.

$$V = V[T,p,n_1^{eq}, n^{eq}(PhCOO^-), n^{eq}(H^+)] \qquad (3\text{-}1)$$

This volume V is readily measured by direct measurements of density ρ and mass w. To this system we rapidly add δn(PhCOOH) moles of benzoic acid with consequent change in volume from V to $(V + \delta V)$. The two limiting conditions identified in the previous section are now considered. The system is frozen such that the amount of benzoic acid in the new system is $[n^{eq}(PhCOOH) + \delta n(PhCOOH)]$. In other words, the change in volume δV occurs at fixed extent of reaction ξ^{eq}, the perturbation being characterised by $[\delta V/\delta n(PhCOOH)]_{T,p,\xi eq}$. The latter quantity is the frozen partial molar volume of PhCOOH in this aqueous solution; if $j \equiv$ PhCOOH, the defined quantity is $V_{j,T,p,\xi eq}$ (aq). By adding δn(PhCOOH) moles of benzoic acid the system is taken away from a minimum in G and the affinity for spontaneous acid dissociation increased. Spontaneous (and, in this case, fast) chemical reaction allows the system to regain after time Δt, an equilibrium state where A is zero. So an alternative name for the frozen partial molar volume is an instantaneous partial molar volume.

In the other class of perturbations, the system responds such that in the new state chemical equilibrium is established, the amounts of benzoate and hydrogen ions increasing. The increase in amount of PhCOOH in the solution when δn(PhCOOH) moles are added is moderated. [Moderation is not, however, universally true despite the widespread application of Le Chatelier's principle—see ref. 1(d)]. In other words, the change in volume δV occurs at constant affinity A, actually at '$A = 0$' so that the perturbation is characterized by the partial quantity $[\delta V/\delta n(PhCOOH)]_{T,p,A = 0}$. This is the equilibrium partial molar volume of PhCOOH in this aqueous solution.

One more example is relevant. Consider an aqueous solution at specified T and p prepared using n_1 moles of liquid water (l) and n_u moles of urea(s). The volume of this system is specified by eqn. (3-2); cf. eqn. (1-1).

$$V = V[T,p,n_1, n_u]^{eq} \qquad (3\text{-}2)$$

The superscript 'eq' (plus conditions that G = minimum and $A = 0$) indicates that the organisation of the solution described by ξ^{eq} characterising water–water, water–urea and urea–urea interactions is unique to the system defined by eqn. (3-2). Conceptually, we add δn_u moles of urea producing a change in volume δV. The frozen (or instantaneous) partial molar volume of urea, $(\delta V/\delta n_j)_{T,p,n_1,\xi eq}$ describes the change in volume where these intermolecular interactions remain unchanged. In contrast, the equilibrium partial molar volume $(\delta V/\delta n_j)_{T,p,n_1,A = 0}$ characterises the change in volume, urea–urea, urea–water and water–water interactions changing in order to hold the system at equilibrium where '$A = 0$'; see, for example, data in ref. 4. In the latter case, although the Gibbs energies are different before and after addition of δn_j moles of urea, the Gibbs energies are at minima in both states.

The above argument centres on volumes and partial molar volumes. But the question is raised as to which thermodynamic variables and related partial molar properties need be classified along similar lines, namely frozen (instantaneous) and equilibrium.

4 Gibbs energies and potentials

Returning to eqn. (1-1) we replace variable V by the Gibbs energy G; eqn. (4-1).

$$G = G[T,p,n_i] \qquad (4\text{-}1)$$

We assert that eqn. (4-1) is valid over the range of compositions/organisations described by the variable ξ.

The system described by eqn. (4-1) is perturbed by a change in pressure δp. Two limiting perturbations of the Gibbs energy are envisaged; (i) at constant affinity A, and (ii) at constant ξ, linked by the following calculus operation. At constant temperature eqn. (4-2) holds.

$$\left(\frac{\partial G}{\partial p}\right)_A = \left(\frac{\partial G}{\partial p}\right)_\xi - \left(\frac{\partial A}{\partial p}\right)_\xi \left(\frac{\partial \xi}{\partial A}\right)_p \left(\frac{\partial G}{\partial \xi}\right)_p \qquad (4\text{-}2)$$

The latter equation applied to the state where G is a minimum (i.e. at equilibrium) and '$A = 0$'. But[1e] the affinity A equals $-(\delta G/\delta \xi)_T$. In other words, at equilibrium, $(\delta G/\delta \xi)_{T,p}$ is zero. Moreover, the partial differential $(\delta G/\delta p)_T$ equals volume V. Hence eqn. (4-3).

$$V(A = 0) = (\partial G/\partial p)_{T,A = 0} = (\partial G/\partial p)_{T,\xi eq} = V(\xi^{eq}) \qquad (4\text{-}3)$$

Therefore the equilibrium and frozen volumes are the same which is not unexpected because volume V is a function of state being a property which is not path dependent; 'volume' is 'volume'. Similar transformations [cf. eqn. (4-2)] with respect to the dependences on temperature of G and G/T (at fixed pressure) confirm that (a) $S(A = 0) = S(\xi^{eq})$ and (b) $H(A = 0) = H(\xi^{eq})$; thus entropy S and enthalpy H are functions of state;[4] Fig. 1.
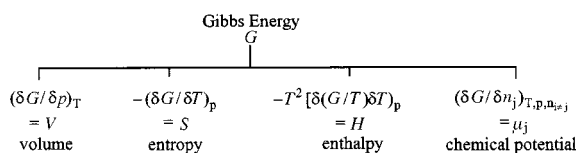

Fig. 1 Functions of state

An important first differential of the Gibbs energy G is with respect to the amount of substance j, namely $(\delta G/\delta n_j)$ at fixed T, p and $n_{i \neq j}$. This important partial differential is the chemical potential of chemical substance j. We return to eqn. (4-1) and consider a freeze-frame description of the system at defined T and p prepared with composition n_i^0; the superscript '0' refers to time zero. Spontaneous chemical reaction occurs driven by the affinity for spontaneous change. We freeze-frame the system where the composition is ξ and the affinity equals A. This system is perturbed by adding δn_j moles of substance j, one of the i-substances. The analogue of eqn. (4-2) has the following form (at defined T and p): eqn. (4-4).

$$\left(\frac{\partial G}{\partial n_j}\right)_A = \left(\frac{\partial G}{\partial n_j}\right)_\xi - \left(\frac{\partial A}{\partial n_j}\right)_\xi \left(\frac{\partial \xi}{\partial A}\right)_p \left(\frac{\partial G}{\partial \xi}\right)_{n_j} \qquad (4\text{-}4)$$

We consider the case where the system being perturbed was at equilibrium where '$A = 0$', G is a minimum and, significantly $(\delta G/\delta \xi)$ is zero. Therefore eqn. (4-5) holds.

$$\mu_j(A = 0) = (\partial G/\partial n_j)_{A = 0} = (\partial G/\partial n_j)_{\xi eq} = \mu_j(\xi^{eq}) \qquad (4\text{-}5)$$

In other words, the chemical potential μ_j for substance j in this system at '$A = 0$' equals the chemical potential μ_j for the condition $\xi = \xi^{eq}$. Thus frozen (instantaneous) and equilibrium chemical potentials are equal, placing chemical potentials on a par with the function of state H, V and S in the thermodynamic hierarchy, these being first derivatives of the Gibbs energy; Fig. 1. Hammett reached the same conclusion by noting, in his terms, that 'sophisticated' and 'primitive' chemical potentials[5] are equal. In the context of describing the properties of solutions, Grunwald uses the terms[6] isodelphic to describe the partial molar properties of substance j when addition of δn_j moles of solute j does not change the organisation of the solvent network; lyodelphic describes the difference between isodelphic and equilibrium partial molar properties. The lyodelphic contribution to the chemical potential of solute j is zero, [cf. eqn. (4-4)]. In other words, the equilibrium chemical potential of solute j is equal to the isodelphic chemical potential.[7] In a similar context, Ben-Naim[8] uses the terms

'freeze' and 'release' in treating the thermodynamics of aggregation.

5 Chemical equilibria

Using an approach based on Henry's Law, the chemical potential of a neutral solute j [$e.g.$ urea(s)] in aqueous solution is related to the molality m_j using eqn. (5-1) where γ_j is the activity coefficient; $m^0 = 1$ mol kg^{-1}.

$$\mu_j(aq;T;p) = \mu_j(aq;id;m_j = m^0;T;p) + RT\ln(m_j\gamma_j/m^0) \quad (5\text{-}1)$$

By definition, limit ($m_j \to 0$; $m_i \to 0$) γ_j equals 1.0 at all temperatures and pressures; $\mu_j(aq;id;m_j = m^0;T;p)$ is the chemical potential of solute j in an ideal solution ($\gamma_j = 1.0$) having unit molality.

Granted that $\mu_j(aq;T;p)$ is the same for frozen ξ^{eq}, and equilibrium properties, the question arises—does this same condition apply to $\mu_j^\#(aq;T;p)$ [$\equiv\mu_j(aq;id;m_j = m^0;T;p)$]?

Consider an aqueous solution prepared using n_x^0 moles of chemical substance X where again superscript '0' indicates at time zero. Experimental evidence indicates that two chemical substances, $X(aq)$ and $Y(aq)$ exist in chemical equilibrium (at G = minimum where A = 0 at defined T and p). Such experimental evidence often arises because the two solutes have quite different UV–VIS absorption spectra. At equilibrium eqn. (5-2) holds.

$$\mu_X^{eq}(aq) = \mu_Y^{eq}(aq) \quad (5\text{-}2)$$

Eqn. (5-2) offers the link with the argument developed in conjunction with the chemical potential of substance X. For this aqueous solution we would record the same increment in Gibbs energy G when δn_X moles of substance X are added irrespective of whether only substance X is present in the solution or substance X is in equilibrium with substance Y. Using Hammett's terminology[5] the primitive and sophisticated chemical potentials of solute X are identical.

Using the primitive description of the above system, the chemical potential of substance $X(aq)$ is related to the composition of the solution using the following equation [$cf.$ eqn. (5-1)] for fixed T and p: eqn. (5-3).

$$\mu_X(aq) = \mu_X^\#(aq;prim) + RT\ln[m_X^0\gamma_X(prm)/m^0] \quad (5\text{-}3)$$

Using the sophisticated description of the solution wherein the composition is described by molalities $m_X^{eq}(soph)$ and m_Y^{eq}(soph), combination of eqn. (5-1) and (5-2) yields eqn. (5-4) for the solution at fixed T and p.

$$\mu_X^\#(aq;soph) + RT\ln[m_X^{eq}(soph)\gamma_X^{eq}(soph)/m^0]$$
$$= \mu_Y^\#(aq;soph) + RT\ln[m_Y^{eq}(soph)\gamma_r^{eq}/m^0] \quad (5\text{-}4)$$

By definition, equilibrium constant K is given by eqn. (5-5).

$$K = m_Y^{eq}(soph)\gamma_Y^{eq}(soph)/m_X^{eq}(soph)\gamma_X^{eq}(soph) \quad (5\text{-}5)$$

But $m_X^0 = [m_Y^{eq}(soph) + m_X^{eq}(soph)]$ so that $m_X^0 = \{1 + [K\gamma_X^{eq}(soph)/\gamma_Y^{eq}(soph)]\} m_X^{eq}(soph)\gamma_X^{eq}(soph)$.

Then using the formulations for the chemical potential of substance X in solution we obtain eqn. (5-6).

$$\mu_X^\#(aq;prim) = \mu_X^\#(aq;soph)$$
$$- RT\ln[\{1 + [K\gamma_X^{eq}(soph)/\gamma_Y^{eq}(soph)]\}/\gamma IRX(prim)] \quad (5\text{-}6)$$

In the limit that the solutions have ideal properties under both descriptions we obtain eqn. (5-7).

$$\mu_X^\#(aq;prim) = \mu_X^\#(aq;soph) - RT\ln[1 + K] \quad (5\text{-}7)$$

Therefore the reference chemical potentials for a given solute are not identical. Consequently, all other reference partial molar quantities ($e.g.$ limiting partial molar volumes and limiting partial molar enthalpies) characterising solutes in sophisticated and primitive descriptions also differ.

6 Limiting partial molar properties and excess properties

According to eqn. (5-1), the chemical potential of solute j in a solution, molality m_j is related to the activity coefficient γ_j and

a reference chemical potential $\mu_j^\#(aq)$ at fixed temperature and pressure. In the event that the solution is ideal such that there are no solute–solute interactions, $\gamma_j = 1.0$ and the chemical potential for solute j, $\mu_j(aq;id)$ is given by eqn. (6-1).

$$\mu_j(aq;id) = \mu_j^\#(aq) + RT\ln(m_j/m^0) \quad (6\text{-}1)$$

Interestingly in the limit that m_j tends to zero, $\mu_j(aq;id)$ [and $\mu_j(aq)$ for real solutions] tends to minus infinity.[9] This means that solute j is increasingly stabilised as the solution becomes more dilute. This is the thermodynamic reason for the problems faced by industries which require solvents having very high purity. To remove the last trace of solute presents an awesome task. Eqn. (5-1) and (6-1) are important equations because they provide the basis for equations which describe the dependences on composition of other partial molar properties. For example, the partial molar volume $V_j(aq)$ of solute j is given by the partial derivative $(\partial\mu_j/\partial p)_T$. Thus from eqn. (5-1) for simple solute j we obtain eqn. (6-2).

$$V_j(aq) = V_j^\#(aq) + RT(\partial\ln\gamma_j/\partial p)_T \quad (6\text{-}2)$$

Therefore from the definition of γ_j, limit ($m_j \to 0$) $V_j(aq)$ equals $V_j^\#(aq)$ which we may also write as $V_j^\infty(aq)$, the limiting partial molar volume. We make one further point in this connection because it is always advisable to examine these and comparable equations in terms of what happens in certain limits.[9] For example, the partial molar entropy S_j of solute j is given by the partial derivative $-(\partial\mu_j/\partial T)_p$. Then eqn. (6-3) holds.

$$S_j(aq) = S_j^\#(aq) - R\ln(m_j\gamma_j/m^0) - RT(\partial\ln\gamma_j/\partial T)_p \quad (6\text{-}3)$$

Therefore from the definition of γ_j, limit ($m_j \to 0$) $S_j(aq)$ equals $+\infty$. In other words, the term $S_j^\infty(aq)$ has no practical meaning whereas $V_j^\infty(aq)$ does.

As preparation for some of the subject matter discussed in the following sections we set down the basis of a definition for the excess Gibbs energy of an aqueous solution containing the single solute, chemical substance j. For a solution with ideal properties (at fixed T and p), the chemical potential of solute j is given by eqn. (5-1) with $\gamma_j = 1.0$. Then eqn. (6-4) holds.

$$\mu_j^E(aq) = \mu_j(aq) - \mu_j(aq;id) = RT\ln\gamma_j \quad (6\text{-}4)$$

For the solvent water in this solution the chemical potential $\mu_1(aq)$ is related to m_j and the practical osmotic coefficient ϕ using eqn. (6-5) where $\mu_1^*(\ell)$ is the chemical potential of water at the same time T and p, eqn. (6-5) applies.

$$\mu_1(aq) = \mu_1^*(\ell) - \phi RTM_1 m_j \quad (6\text{-}5)$$

For an ideal solution $\phi = 1$ and $\gamma_j = 1$. The excess Gibbs energy is defined by eqn. (6-6) for a solution prepared using 1 kg of solvent and m_j moles of solvent.

$$G^E = m_j RT[1 - \phi + \ln\gamma_j] \quad (6\text{-}6)$$

G^E is an intensive property of the solution because it refers to a thermodynamic property of a solution prepared using a fixed mass of solvent. The link between the dependence of ϕ and γ_j on molality m_j is provided by the Gibbs–Duhem equation.

7 Volumes

In Section 3 we commented on the significance of equilibrium and frozen partial molar properties using volumetric properties of solutions as examples. Here we take up the story again but develop the argument along the lines given in Section 5. The broad sweep of our analysis is set out in Fig. 2 starting with the function of state, volume V.

We consider a solution prepared using n_j moles of substance j ($e.g.$ urea) and n_1 moles of water (ℓ). The analogue of eqn. (4-2) describes the change in volume δV when δn_j moles of chemical substance j are added to the solution (i) at constant affinity A and (ii) at constant extent of reaction ξ, both at constant T, p and n_1, eqn. (7-1).

$$\left(\frac{\partial V}{\partial n_j}\right)_A = \left(\frac{\partial V}{\partial n_j}\right)_\xi - \left(\frac{\partial A}{\partial n_j}\right)_\xi \left(\frac{\partial \xi}{\partial A}\right)_{n_j} \left(\frac{\partial V}{\partial \xi}\right)_{n_j} \quad (7\text{-}1)$$
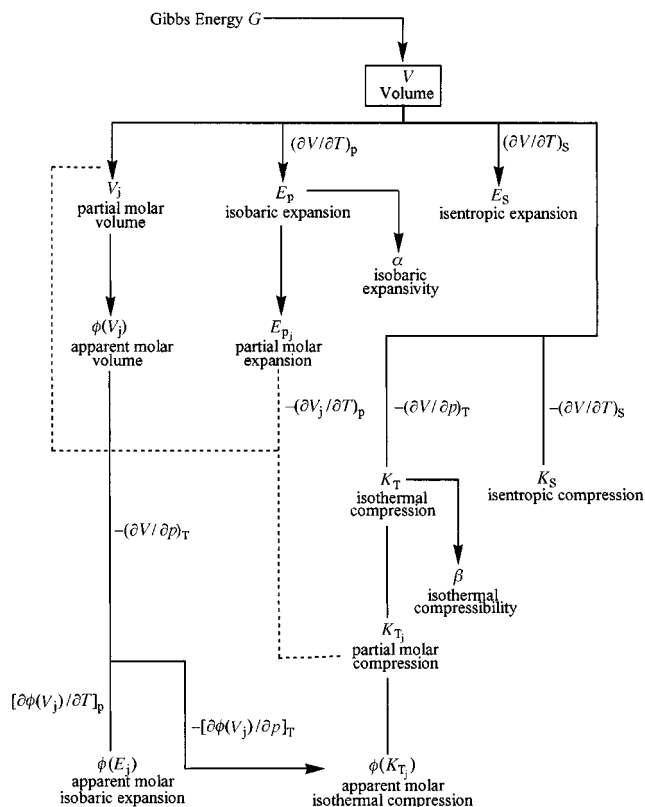
Fig. 2

But $(\partial V/\partial \xi)_{n_j}$ is not zero and so the equilibrium partial molar volume of substance j, $V_j(A = 0)$ is not equal to the frozen partial molar volume, $V_j(\xi^{eq})$. We recall our discussion in Section 2 of the volumetric properties of urea(aq).

The volume of an aqueous solution comprising n_1 moles of water and n_j moles of solute j is related to the equilibrium partial molar volumes $V_j(aq)$ and $V_1(aq)$ using eqn. (7-2).

$$V(aq) = n_1 V_1(aq) + n_j V_j(aq) \qquad (7-2)$$

However, an alternative form of eqn. (7-2) defines $V(aq)$ in terms of the apparent molar volume[10] $\phi(V_j)$, eqn. (7-3).

$$V(aq) = n_1 V_1^*(\ell) + n_j \phi(V_j) \qquad (7-3)$$

If the properties of the solution are ideal, eqn. (7-4).

$$V(aq;id) = n_1 V_1^*(\ell) + n_j \phi(V_j)^\infty \qquad (7-4)$$

Here $\phi(V_j)^\infty$ [$= V_j^\infty(aq)$] is the limiting (indinite dilution) partial molar volume of solute j.

Another form of eqn. (7-3) describes the volume of a solution prepared using 1 kg of water. So we have eqn. (7-5) where eqn. (7-6) holds.

$$V(aq) = (1/M_1)V_1^*(\ell) + m_j \phi(V_j) \qquad (7-5)$$
$$V(aq;id) = (1/M_1)V_1^*(\ell) + m_j \phi(V_j)^\infty \qquad (7-6)$$

Therefore the excess volume V^E is given by eqn. (7-7).

$$V^E(aq) = m_j[\phi(V_j) - \phi(V_j)^\infty] \qquad (7-7)$$

An advantage of the latter equation is that V^E is an intensive variable. Eqn. (7-3) forms the basis of the experimental determination of $\phi(V_j)$. The mass of the aqueous solution w equals $(w_1 + w_j)$ or $(w_1 + n_j M_j)$ where M_j is the molar mass of the solute. The densities of the solution and the solvent are $\rho(aq)$ [$= w/V(aq)$] and $\rho_1^*(\ell)$ respectively. Hence[11a] eqn. (7-8) holds.

$$\phi(V_j) = (m_j)^{-1}[\rho(aq)^{-1} - \rho_1^*(\ell)^{-1}] + (M_j/\rho) \qquad (7-8)$$

Eqn. (7-8) does not determine the dependence of $\phi(V_j)$ on m_j; the dependence is characteristic of the solution. In fact, the form of

this dependence[12] is not defined by thermodynamics although, in many cases, the dependence of $\phi(V_j)$ on m_j for dilute solutions is linear. [For salt solutions, the Debye–Hückel limiting law prompts analysis in the form of a dependence of $\phi(V_j)$ on $(m_j)^{\frac{1}{2}}$.]

8 Isochoric conditions

An interesting set of independent variables defines the Helmholtz energy of a system, F; *cf.* eqn. (1-1): eqn. (8-1).

$$F = F[T,V,n_i] \qquad (8-1)$$

Then all spontaneous processes under isochoric–isothermal conditions lower spontaneously the Helmholtz energy of a closed system. We do not develop this point further except to note that in contrast to the set of independent variables given in eqn. (1-1) and (4-1), the set in eqn. (8-1) involves two extensive variables, volume and amounts, n_i. The isochoric condition has aroused controversy[13–16] in analysis of kinetic data with respect to the calculation of isochoric activation parameters.[14,17,18] The controversy centres on answers to the simple question—which volume is held constant?[13] The issue remains unresolved.

9 Isobaric expansions and isobaric expansibilities

We return to a consideration of thermodynamic variables defined by the set of independent variables specified in eqn. (1-1) and (4-1). The volume of an aqueous solution having defined composition (*e.g.* n_1 moles of water and n_j moles of solute j) depends on temperature at fixed pressure. There are two limiting ways in which the volume of this solution may change as a result of a change in temperature; (*a*) at constant affinity A, and (*b*) at constant extent of reaction/organisation ξ. These two limiting changes are related (at defined T and p), eqn. (9-1).

$$\left(\frac{\partial V}{\partial T}\right)_A = \left(\frac{\partial V}{\partial T}\right)_\xi - \left(\frac{\partial A}{\partial T}\right)_\xi \left(\frac{\partial \xi}{\partial A}\right)_T \left(\frac{\partial V}{\partial \xi}\right)_T \qquad (9-1)$$

In particular case of a system at equilibrium we identify two limiting expansions; the equilibrium isobaric expansion $E_p(A = 0)$ [$= (\partial V/\partial T)_{p;A=0}$] and the frozen isobaric expansion $E_p(\xi^{eq})$ [$= (\partial V/\partial T)_{p;\xi eq}$]. Further for the condition '$A = 0$' then $(\partial V/\partial T)_{p;\xi}$ equals[1f] $T (\partial H/\partial \xi)_{T,p}$. Hence eqn. (9-2).

$$E_p(A = 0) = E_p(\xi^{eq}) - T^{-1} (\partial \xi/\partial A)_{T,p} (\partial V/\partial \xi)_{T,p} (\partial H/\delta \zeta)_{T,p} \qquad (9-2)$$

Equilibrium isobaric thermal expansions of aqueous solutions can be directly measured dilatometrically.[19] The analogue of eqn. (7-1) in which enthalpy H replaces volume V is a key equation with respect to the temperature-jump fast reaction technique.[20] Although at equilibrium $(\partial A/\partial \xi)_{T;p}$ is negative, the sign of the product, $(\partial V/\partial \xi)_{T;p} (\partial H/\partial \xi)_{T;p}$ is not predetermined. Therefore, the sign of $E_p(A = 0)$ is not fixed. In fact, for water below 277 K at ambient pressure, the temperature of maximum density (TMD), $E_p(A = 0)$ is negative;[21] a similar feature is shown for many aqueous solutions[22,23] in the region of 277 K. As written in eqn. (9-2), $E_p(A = 0)$ and $E_p(\xi^{eq})$ are extensive variables but not functions of state because they characterise pathways. We divide by the volume, an extensive function of state (see above), to define an isobaric equilibrium expansibility $\alpha(A = 0)$ [$= V^{-1} E_p(A = 0)$] and an isobaric frozen expansivity $\alpha(\xi^{eq})$ [$= V^{-1} E_p(\xi^{eq})$], two volume intensive properties of a solution, eqn. (9-3).

$$\alpha(A = 0) = \alpha(\xi^{eq}) - (VT)^{-1}(\partial \xi/\partial A)_{T,p}(\partial V/\partial \xi)_{T,p}(\partial H/\partial \xi)_{T,p} \qquad (9-3)$$

In these terms $\alpha(\xi^{eq})$ represents the volumetric response of a system to a thermal shock as the temperature is increased in an infinitesimal time. The extended product term describes the relaxation of the system[24] to the state characterised by $\alpha(A = 0)$.

For the aqueous solution described in eqn. (7-4), the isobaric thermal expansion is described by eqn. (9-4).

$$E_p(A = 0) = \left(\frac{\partial V}{\partial T}\right)_{P;A=0} = N_1 \left(\frac{\partial V_1^*(\ell)}{\partial T}\right)_{P;A=0} + n_j \left(\frac{\partial \phi(V_j)}{\partial T}\right)_{p;A+0} \tag{9-4}$$

We define an apparent equilibrium molar isobaric expansion of solute j, $\phi(E_j)$ by the partial differential $(\partial \phi(V_j)/\partial T)_{p;A=0}$, an intensive property of solute j. Similarly, for the solvent water, $E_1^*(\ell;A = 0)$ equals $[\partial V_1^*(\ell)/\partial T]_{p;A=0}$. Hence for a solution prepared using 1 kg of solvent, where both $E_1^*(\ell;A = 0)$ and $\phi(E_j)$ are intensive variables we have eqn. (9-5).

$$E_p(A = 0;aq;w_1 = 1 \text{ kg}) = (1/M_1)E_1^*(\ell;A = 0) + m_j\phi(E_j) \tag{9-5}$$

For the corresponding ideal solution we have eqn. (9-6).

$$E_p(A = 0;aq;w_1 = 1 \text{ kg};id) = (1/M_1)E_1^*(\ell;A = 0) + m_j\phi(E_j)^\infty \tag{9-6}$$

The equilibrium partial molar expansion of solute j $E_j(aq)$ and of solvent water $E_1(aq)$ are defined by $[\partial V_j(aq)/\partial T]_p$ and $[\partial V_1(aq)/\partial T]_p$. These quantities are normally calculated from measured dependences of $V_j(aq)$ and $V_1(aq)$ [cf. eqn. (7-8) using $\phi(V_j)$] on composition at a series of fixed temperatures. For urea(aq) $\phi(E_j)$ and $\phi(E_j)^\infty$ are positive[4] at ambient pressure over the range $0 \leqslant m_j \leqslant 10.0$ mol kg^{-1}. For 2-methylpropan-2-ol(aq) in very dilute solutions,[12] the dependence of $E_j(aq)$ on m_j and temperature is complicated. The second differential, $[\partial^2 V_j^\infty(aq)/\partial T^2]_p$ has been used to classify solutes on the basis of their effect on water–water interactions.[25] An (intensive—based on fixed mass of solvent) excess equilibrium isobaric expansion E_p^E is defined by eqn. (9-7); cf. eqn. (6-6).

$$E_p^E(A = 0) = E_p(A = 0;aq;w_1 = 1 \text{ kg}) - E_p(A = 0;w_1 = 1 \text{ kg};aq;id) \tag{9-7}$$

Therefore eqn. (9-8) holds.

$$E_p^E = m_j[\phi(E_j) - \phi(E_j)^\infty] \tag{9-8}$$

In other words, the excess expansion $E_p^E(A = 0)$ is a well-defined property given by the product of solute molality m_j and a difference in real and ideal apparent molar expansions. However, a similar clear definition does not emerge if we turn our attention to expansibilities. The starting point is the definition given above for $\alpha_T(A = 0)$ [$= V^{-1}E_p(A = 0)$]. Then using eqn. (9-4) we have eqn. (9-9).

$$\alpha_p(A = 0) = n_1[V_1^*(\ell)/V(aq)][V_1^*(\ell)]^{-1}E_p^*(\ell;A = 0) + n_j[\phi(V_j)/V(aq)][\phi(V_j)]^{-1}\phi(E_j) \tag{9-9}$$

If for the pure solvent, $\alpha_p^*(A = 0)$ equals $[V_1^*(\ell)]^{-1}E_p^*(A = 0;\ell)]$, then the isobaric expansibility of the solution $\alpha_p^*(A = 0)$ is given by eqn. (9-10).

$$\alpha_p(A = 0) = n_1[V_1^*(\ell)/V(aq)]\alpha_p^*(\ell) + [n_j/V(aq)]\phi(E_j) \tag{9-10}$$

The property of the solution $\alpha_p(A = 0)$ is given by an equation which only partly resembles eqn. (7-3) with the added complexity of a volumetric ratio $[V_1^*(\ell)/V(aq)]$. There is no obvious quantity which could be described as an apparent molar isobaric expansivity of the solute j. Consequently, there is no obvious route leading in an elegant manner to an excess isobaric expansibility of the solution; cf. eqn. (9-8).

We end this section by returning to eqn. (9-9) written as eqn. (9-11).

$$\alpha_p(A = 0)V = n_1V_1^*(\ell)\alpha_1^*(A = 0) + n_j\phi(E_j) \tag{9-11}$$

The latter equation forms the starting point for the derivation of eqn. (9-12) which shows how $\phi(E_j)$ is calculated using measured $\alpha_p(A = 0)$ for a solution molality m_j.

$$\phi(E_j) = [m_j\rho(aq)\rho_1^*(\ell)]^{-1} \{[\rho_1^*(\ell)\alpha_p(aq;A = 0)] - [\rho(aq)\alpha_1^*(\ell;A = 0)]\} + [\alpha(aq)M_j/\rho(aq)] \tag{9-12}$$

This equation closely resembles eqn. (7-9) and is a member of the same family of volumetric equations (see below).

10 Isothermal compression and compressibility

In addition to isobaric expansion, the other major component of Fig. 2 describes compressions and compressibilities of solutions. There are two limiting ways in which the volume of a solution may change as a result of a change in pressure (at fixed temperature); (i) at constant affinity A, and (ii) at constant extent of reaction/organisation ξ. Thus, at fixed temperature,

$$\left(\frac{\partial V}{\partial p}\right)_A = \left(\frac{\partial V}{\partial p}\right)_\xi - \left(\frac{\partial A}{\partial p}\right)_\xi \left(\frac{\partial \xi}{\partial A}\right)_p \left(\frac{\partial V}{\partial \xi}\right)_p \tag{10-1}$$

The partial differential $(\partial A/\partial p)_{T;\xi}$ equals[1g] $-(\partial V/\partial \xi)_{T;p}$. In the case where the system was at equilibrium, the partial differential $-(\partial V/\partial p)_{T;A=0}$ is the equilibrium isothermal compression $K_T(A = 0)$ whereas $-(\partial V/\partial p)_{T;\xi eq}$ is the frozen compression $K_T(\xi^{eq})$. Hence from eqn. (10-1) we have eqn. (10-2).

$$K_T(A = 0) = K_T(\xi^{eq}) - (\partial \xi/\partial A)_{T;p}^{eq}[\partial V/\partial \xi]_{T;p}^{eq}]^2 \tag{10-2}$$

The compressions $K_T(A = 0)$ and $K_T(\xi^{eq})$ are extensive properties of a solution. The volume intensive properties are isothermal compressibilities $\kappa_T(A = 0)$ and $\kappa_T(\xi^{eq})$ defined by eqn. (10-3) and (10-4).

$$\kappa_T(A = 0) = -(1/V)(\partial V/\partial p)_{T;A=0} = +V^{-1}K_T(A = 0) \tag{10-3}$$

$$\kappa_T(\xi^{eq}) = -(1/V)(\partial V/\partial p)_{T;\xi eq} = +V^{-1}K_T(\xi^{eq}) \tag{10-4}$$

Then from eqn. (10-2) we have (10-5).

$$\kappa_T(A = 0) = \kappa_T(\xi^{eq}) - (\partial \xi/\partial A)_{T;p}^{eq}[(\partial V/\partial \xi)_{T;p}^{eq}]^2 \tag{10-5}$$

But $(\partial A/\partial \xi)_{T;p}$ is negative for all stable phases. Hence, irrespective of the volume of reaction $(\partial V/\partial \xi)_{T;p}^{eq}$, $\kappa_T(A = 0)$ is always greater than $\kappa_T(\xi^{eq})$. In fact, eqn. (10-5) is the key equation for the pressure-jump fast reaction technique,[20] the second (large) term on the right-hand side of eqn. (10-5) being the relaxational term.

For an aqueous solution the isothermal equilibrium compression $K_T(A = 0)$ is related to the isothermal differential of eqn. (7-3) with respect to pressure, eqn. (10-6).

$$K_T(A = 0) = -(\partial V/\partial p)_{T;A=0} = -n_1\left(\frac{\partial V_1^*(\ell)}{\partial p}\right)_{T;A=0} - n_j\left(\frac{\partial \phi(V_j)}{\partial p}\right)_{T;A=0} \tag{10-6}$$

Thus $K_T(A = 0)$ is an extensive property of a solution. It is convenient to define an equilibrium apparent molar isothermal compression $\phi(K_{Tj})$ $\{ = -(\partial \phi(V_j)/\partial p)_{T;A=0}\}$. For an aqueous solution prepared using 1 kg of solvent we relate the intensive compression $K_T(A = 0;aq;w_1 = 1 \text{ kg})$ to the composition using eqn. (10-7).

$$K_T(A = 0;aq;w_1 = 1 \text{ kg}) = (1/M_1)K_{1T}^*(\ell;A = 0) + m_j\phi(K_{Tj}) \tag{10-7}$$

For the solution whose properties are ideal, eqn. (10-8) applies.

$$K_T(A = 0;aq;w_1 = 1 \text{ kg}) = (1/M_1)K_{1T}^*(\ell;A = 0) + m_j\phi(K_{Tj})^\infty \tag{10-8}$$

Then the excess compression K_T^E is defined by eqn. (10-9).

$$K_T^E = m_j[\phi(K_{Tj}) - \phi(K_{Tj})^\infty] \tag{10-9}$$

Interestingly, the form of eqn. (10-9) resembles those for the excess volumes [eqn. (7-8)] and excess isobaric expansions [eqn. (9-8)]. The general form of eqn. (10-7) describes the extensive compression of a solution containing n_j moles of solute j and n_1 moles of water eqn. (10-10).

$$K_T(A = 0) = n_1K_{1T}(\ell;A = 0) + n_j\phi(K_{Tj}) \tag{10-10}$$

Calculation of $\phi(E_j)$ from compressibilities uses eqn. (10-11) which is derived in a manner analogous to that used to obtain eqn. (9-12).

$$\phi(K_{Tj}) = [m_j\rho(aq)\rho_1^*(\ell)]^{-1}\{[\rho_1^*(\ell)\kappa_T(aq;A=0)]$$
$$- [\rho(aq)\kappa_1^*(\ell);A=0)]\} + [\kappa_T(aq);A=0]M_j/\rho(aq)\} \quad (10\text{-}11)$$

Further, just as for expansibilities, an elegant equation similar to that used for excess volumes [eqn. (7-8)] cannot be used to define an excess isothermal compressibility. Similarly, there is no analogue of a partial molar volume which can be identified as a partial molar compressibility. Direct measurement of isothermal compressibilities of aqueous systems is, nevertheless, not straightforward bearing in mind that $\kappa(aq)$ depends on composition, temperature and pressure.

11 Isentropic compression and isentropic compressibilities

Data describing equilibrium isothermal compressibilities of aqueous solutions are not extensive. It may at first sight seem surprising, therefore, that information concerning equilibrium isentropic compressibilities (*i.e.* compression at constant entropy, κ_S) is more extensive. The reason for this state of affairs is the Newton–La Place equation relating isentropic compressibility to the density of a solution ρ and the velocity of sound u in the solution; $\kappa_S = (u^2\rho)^{-1}$. If the frequency of the sound wave is low (*e.g.* in the MHz range), the calculated quantity is the equilibrium isentropic compressibility $\kappa_S(A=0)$. In other words, each microscopic volume of a solution is compressed at constant entropy. Moreover, these compressibilities can be precisely measured.[26,27]

The isentropic condition raises problems from the standpoints of both thermodynamic theory and the interpretation of derived parameters. From the outset we have to change the basis of the thermodynamic treatment. Thus in reviewing equilibrium isobaric expansions $E_p(A=0)$ and isothermal compressions $K_T(A=0)$, the analysis developed in a straightforward manner from the function of state called volume defined using eqn. (1-1). In the latter case, our interests centred on the T–p composition domain for which the thermodynamic potential function is the Gibbs energy. In order to understand the significance of isentropic compressibilities κ_S and isentropic compressions K_S, we switch interests into the S-p-composition domain. This is not a trivial switch. All spontaneous processes in closed systems at fixed entropy and pressure lower the enthalpy H of a system such that thermodynamic equilibrium corresponds to a minimum in enthalpy where the affinity for spontaneous change is zero. Thus the enthalpy of a closed system is defined[1e] by eqn. (11-1).

$$H = H[S, p, \xi] \quad (11\text{-}1)$$

The volume of the system is given by the partial differential, $(\partial H/\partial p)_{S;\xi}$. The analogue of eqn. (1-1) is eqn. (11-2).

$$V = V[S, p, n_i] \quad (11\text{-}2)$$

In other words, we have switched the set of independent variables defining the volume from $[T, p, n_i]$ to $[S, p, n_i]$, a switch from 'Lewisian' to 'non-Lewisian' independent variables.[28] The key point to note is that in one set, T and p are both intensive variables whereas in the other set [*cf.* eqn. (11-1) and (11-2)] the independent variable S is extensive making two extensive variables in this definition. This contrast between the two sets is not trivial indicating that the choice of independent variables is more than a matter of convenience.

Two equilibrium quantities are of interest in this section; (*i*) the equilibrium isentropic compression, $K_S(A=0)$ and (*ii*) the equilibrium isentropic compressibility $\kappa_S(A=0)$. The corresponding instantaneous properties are $K_S(\xi^{eq})$ and $\kappa_S(\xi^{eq})$. The difference between these equilibrium and instantaneous properties is at the heart of the ultrasonic fast reaction technique.[20,29] At low rates of compression (*i.e.* change in pressure) at constant entropy, solvent–solvent, solvent–solute and solute–solute interactions within each microscopic volume of an aqueous solution change in order to keep the system at a minimum in enthalpy. The differential dependence of volume V on pressure at constant temperature and affinity is related to the differential

dependence of volume V on pressure at constant entropy and affinity using eqn. (11-3).

$$\left(\frac{\partial V}{\partial p}\right)_{S;A} = \left(\frac{\partial V}{\partial p}\right)_{T;A} - \left(\frac{\partial S}{\partial p}\right)_{T;A}\left(\frac{\partial T}{\partial S}\right)_{p;A}\left(\frac{\partial V}{\partial T}\right)_{p;A} \quad (11\text{-}3)$$

We use eqn. (11-3) with the constraint that constant affinity A is at '$A=0$'. The last partial derivative in eqn. (11-3) is, therefore, the isobaric equilibrium expansion $E_p(A=0)$; *cf.* eqn. (9-2). A Maxwell relationship[1g] shows that $(\partial S/\partial p)_{T;A=0}$ equals $-(\partial V/\partial T)_{p;A=0}$, which is $-E_p(A=0)$. Further, the partial differential $(\partial S/\partial T)_{p;A=0}$ equals[1h] the ratio of the equilibrium isobaric heat capacity to the temperature, $C_p(A=0)/T$. Moreover, $E_p(A=0)$ equals $\alpha_p(A=0)V$; *cf.* eqn. (9-3). Therefore,[30]

$$K_S(A=0) = K_T(A=0) - \{[\alpha_p(A=0)V]^2T/C_p(A=0)\} \quad (11\text{-}4)$$

Thus by definition the equilibrium isentropic compression $K_S(A=0)$ equals $-(\partial V/\partial p)_{S;A=0}$. In eqn. (11-4), $K_S(A=0)$, $K_T(A=0)$, V and $C_p(A=0)$ are extensive properties of the solution. The ratio $[C_p(A=0)/V]$ is the equilibrium isobaric heat capacity per unit volume of the solution, $\sigma(A=0)$. Then we have eqn. (11-5).

$$K_S(A=0) = K_T(A=0) - \{[\alpha_p(A=0)]^2VT/\sigma(A=0)\} \quad (11\text{-}5)$$

Similarly, in terms of isentropic compressibilities, eqn. (11-6).

$$\kappa_S(A=0) = \kappa_T(A=0) - \{[\alpha_p(A=0)]^2T/\sigma(A=0)\} \quad (11\text{-}6)$$

In the next stage we return to an equation for the volume of an aqueous solution prepared using n_1 moles of solvent water and n_j moles of solute j; eqn. (7-3). The isobaric compression $K_T(A=0)$ is given by eqn. (10-6) in terms of the equilibrium isobaric compression of the solvent $K_{1T}^*(\ell)$ and an equilibrium partial differential isothermal dependence of $\phi(V_j)$ on pressure. Thus we have eqn. (11-7).

$$K_T(aq;A=0) = n_1K_{1T}^*(\ell;A=0) - n_j[\partial\phi(V_j)/\partial p]_{T;A=0} \quad (11\text{-}7)$$

The task at this stage is to write down a satisfactory equation for the isentropic equilibrium compression of the solution. In the context of treating the thermodynamic properties of binary liquid mixtures, the way forward was signalled by Benson and Kumaran,[31] by Reis[28] and by Douhéret, Moreau and Viallard[32] particularly in developing equations describing excess compressibilities and excess compressions. Here we comment on the equilibrium isentropic compressions of aqueous solutions. Thus it follows from eqn. (11-4) that for the pure solvent, water: eqn. (11-8).

$$K_{1T}^*(\ell;A=0) = K_{S1}^*(\ell;A=0)$$
$$+ \{[\alpha_{1p}^*(\ell;a=0)V_1^*(\ell)]^2T/C_{p1}^*(\ell;A=0)\} \quad (11\text{-}8)$$

For the solution, according to eqn. (11-4) we have eqn. (11-9).

$$K_T(aq;A=0) = K_S(aq;A=0)$$
$$+ \{[\alpha_p(aq;A=0)V(aq)]^2T/C_p(A=0;aq)\} \quad (11\text{-}9)$$

In eqn. (11-8), $K_{1T}^*(\ell;A=0)$ and $K_{S1}^*(\ell;A=0)$ refer to a mole of liquid water whereas in eqn. (11-9) $V(aq)$ and $C_p(A=0;aq)$ are extensive properties of the solution described in eqn. (11-7) having compression $K_T(aq;A=0)$. The analytical problem is highlighted by eqn. (11-8) and (11-9). The isentropic condition on $K_{S1}^*(\ell;A=0)$ is understandable in terms of the condition associated with compression by the sound wave. The isothermal conditions on $K_{1T}^*(\ell;A=0)$ and $K_T(aq;A=0)$ are understandable in terms of the isothermal condition associated with measuring the dependence of volumes on pressure. Thus we can arrange experimentally for these two temperatures to be the same in order to compare the isothermal compressions of water and an aqueous solution having defined molality. Unfortunately, we cannot ensure in a comparison of $K_{1S}^*(A=0)$ for water and $K_S(aq;A=0)$ for an aqueous solution that the two

entropies are the same. In each case, the compression is isentropic (*cf.* the Newton–Laplace equation) but we cannot be sure that the properties of solution and solvent are compared at the same entropy. Furthermore, in examining the dependence of $K_S(\text{aq};A = 0)$ on the composition of a solution (*e.g.* on molality of solute *j*), we cannot be sure that comparisons can be made of the properties of these solutions at the same entropy.

There is merit in defining an apparent equilibrium isentropic compression of solute *j*, $\phi(K_{Sj})$ in terms of $-[\partial\phi(V_j)/\partial p]_{S;A = 0}$. Similarly, $\phi(K_{Tj}) = -[(\partial\phi(V_j)/\delta p]_{T;A = 0}$. Granted therefore that experiment yields $\kappa_S(\text{aq};A = 0)$ for an aqueous solution (at defined *T* and *p*) and $\kappa_{S1}^*(\ell;A = 0)$ for the pure solvent water, eqn. (11-10) yields the apparent molar isentropic compression of the solute $\phi(K_{Sj})$.

$$\phi(K_{Sj}) = [1/m_j\rho_1^*(\ell)][\kappa_S(\text{aq};A = 0) - \kappa_{S1}^*(\ell;A = 0)] \\ + \kappa_S(\text{aq};A = 0)\phi(V_j) \qquad (11\text{-}10)$$

Indeed, this is a classic equation used by many authors who cite as the key reference the monograph by Harned and Owen,[12b] confidence being boosted by the strong similarity with equations for $\phi(V_j)$, $\phi(E_{pj})$ and $\phi(K_{pj})$ as described in the previous sections. So common practice has been to use eqn. (11-10) as a method of determining the apparent property of $\phi(K_{Sj})$ from measured $\kappa_S(\text{aq};A = 0)$ for a solution molality m_j.

Then the patterns which emerge are discussed in the conceptually simpler context of isothermal compression. Lara and Desnoyers note[33] that for 2-butoxyethanol(aq) at 298 K, 'isothermal and isentropic compressibilities are quite similar and reflect the same kind of interactions'. Franks and co-workers[34] discuss the dependence of $\phi(K_j)$ on composition and structure for various sugars in aqueous solutions in terms of solute-hydration and solute–solute interactions although the measured quantity was $\phi(K_{Sj})$. In the context of aqueous salt solutions, for example, Criss and co-workers[35] compare $\phi(K_{Si})^\infty$ for ion *i* with the trend predicted by the Born equation for the isothermal property. Quite generally, therefore, measured isentropic properties are understood in terms of models based on isothermal properties. This approach has obvious practical merit. Nevertheless, this author has reservations concerning what seems a somewhat cavalier approach to the isentropic condition. Perhaps there is a need for a new approach to the task of understanding the significance of isentropic compressibilities of solution.

12 Acknowledgements

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