

Full paper

A Concise Equation of State for Aqueous Solutions of Electrolytes Incorporating Thermodynamic Laws and Entropy

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Abstract: Recently, the author suggested a simple and composite equation of state by incorporating fundamental thermodynamic properties like heat capacities into her earlier concise equation of state for gases based on free volume and molecular association / dissociation. This work brings new results for aqueous solutions, based on the analogy of the equation of state for gases and solutions over wide ranges of pressures (for gases) and concentrations (for solutions). The definitions of entropy and heat energy through the equation of state for gases also hold for solutions.

Key words: concise equation of state for solutions, gas-solution analogy, partial dissociation, electrolytes, thermodynamic laws, entropy and heat

1. Concise equation of state for aqueous solutions

The recent paper [1] on a concise equation of state for gases incorporating thermodynamic laws and entropy, was based on van't Hoff's ideal law analogy found valid [2] for higher pressures (for gases) and concentrations (for solutions). For aqueous solutions, the following concise equation of state was established for strong electrolytes like NaCl(aq) for all concentrations [2],

$$\pi(V_A - V_h)/i = \pi V_f = RT \quad (1)$$

where π and V_A are the osmotic pressure and total volume of water (A) respectively of a solution containing one mole (consisting of one molecular weight) of solute at temperature T , R is the molar gas constant, V_h is the volume of water held as hydration by one mole of solute, $i = [1 + (v - 1)\alpha]$ is the van't Hoff factor representing the actual number of moles of solute due to partial dissociation of one mole of the electrolyte into $v\alpha$ ions and $(1 - \alpha)$ ion pairs, α is the degree of dissociation, v is the number of moles into which one mole of solute dissociates at infinite dilution and V_f is the free (subscript f) volume of solvent per mole of solute. For a non-electrolyte like sucrose in water, $i = 1$. The values of π , V_h and i can be evaluated from the available data on osmotic coefficients as described in [2].

Note that equation (1) is not the ideal law, $\pi V = RT$ (although similar in mathematical form) but with V_f in place of V , the total volume of solution. As $\pi \rightarrow 0$, $i \rightarrow v$ and $\pi V_f \rightarrow RT$ (ideal law). The equations presented earlier for gases [1], also hold for solutions (with subscript s, and with osmotic pressure π in place of pressure P for gases). For an easier comparison with the equations established for gases [1], this paper is written in a similar way.

2. Equation of state incorporating heat capacities

The above equation (1) can be combined with the heat capacity at constant osmotic pressure (C_{π_f}) and constant volume (C_{V_f}) respectively, defined here on the free volume per mole basis. The ideal heat capacity difference is equal to the gas constant. Since the ideal law and equation (1) here are of the same form with V_f in place of V , the heat capacity difference is substituted here for R in equation (1) to obtain a new composite equation of state based on π , V , T and thermodynamic quantities,

$$\pi V_f = (C_{\pi_f} - C_{V_f})T = RT \quad (2)$$

Small changes $d\pi$, dV_f and dT of π , V_f and T in equation (2) are related by,

$$\pi dV_f + V_f d\pi = (TdC_{\pi_f} + C_{\pi_f}dT) - (TdC_{V_f} + C_{V_f}dT) \quad (3a)$$

$$\pi dV_f + V_f d\pi = (C_{\pi_f} - C_{V_f})dT = RdT \quad (3b)$$

where $dC_{\pi_f} = d(C_{V_f} + R) = dC_{V_f}$, $C_{V_f}dT = dE_s$ is the change in internal energy (E_s) of the solution, $\pi dV_f = -dA_s = RTd\ln V_f$ is the work of expansion (dilution, for solution), denoted as change in Helmholtz free energy (A_s) for the solution, $C_{\pi_f}dT = dH_s$ is the change in enthalpy (H_s), and $-V_f d\pi = -dG_s = -RTd\ln \pi$ is the work of compression, denoted as the change in Gibbs free energy (G_s). Thus,

$$-dA_s + dG_s = dH_s - dE_s = RdT \quad (4)$$

3. Equation of state, heat, entropy and partition function

On rearranging the terms in equations (3), one finds that

$$\pi dV_f + C_{Vf}dT = C_{\pi f}dT - V_f d\pi = dQ_s \quad (5a)$$

$$-dA_s + dE_s = dH_s - dG_s = d(TS) = dQ_s \quad (5b)$$

where dQ_s , the amount of heat energy absorbed by the solution, causes a temperature change dT and volume change dV_f at osmotic pressure π , or osmotic pressure change $d\pi$ at volume V_f , as per Helmholtz's definition, $E_s - A_s = TS$, where S is the entropy. Thus, equations (5) are the energy conservation laws in accordance with the 1st law of thermodynamics.

From the relation between partition function (f) and molar entropy [3],

$$S = R \ln W = E_s/T + R \ln f = (E_s - A_s)/T \quad (6)$$

where W is the maximum probability of existence at the given π , V , T and the last term comes from the Helmholtz relation. Note that $E_s = RT^2(d \ln f / dT)_V$ and $dE_s = C_{Vf}dT$ from equations (5), $-A_s = RT \ln f$ and $-dA_s = RT d \ln f = RT d \ln V_f$. The partition function is [1]

$$f = V_f / V_{dB} = RT / \pi V_{dB} \quad (7)$$

where $V_{dB} = (\Lambda_{dB})^3$, $\Lambda_{dB} = (h/p)$ is the de Broglie wavelength [4], h is the Planck constant and p is the linear momentum of the solute.

Thus, from equations (5), Q_s , the heat energy, can be defined as in the case of gases [1] (*for the first time*) as,

$$Q_s = E_s - A_s = H_s - G_s = TS = RT \ln W = \pi V_f \ln W \quad (8)$$

This shows that the solution at any given π , V , T has a heat energy, Q_s and it is related to the internal energy E_s , enthalpy H_s , the free energies A_s and G_s and entropy S as shown by equation (8). At $T = 0$, $Q = 0$ (and S is chosen as zero at $T = 0$, as per the 3rd law). Since the above quantities have standard values (E° , H° , A° , G° and S°) at STP, the standard value of $Q^\circ = E^\circ - A^\circ = H^\circ - G^\circ = T^\circ S^\circ$ at STP. In the case of NaCl(aq), $S^\circ = 115.48 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ at 25 °C as per the data in [5]. This allows one to obtain Q° as $T^\circ S^\circ = 34.43 \text{ kJ} \cdot \text{mol}^{-1}$. The difference in Q_s in any two states, $\Delta Q_s = Q - Q^\circ = \Delta E - \Delta A = \Delta H - \Delta G = \Delta(TS)$.

4. Equation of state, entropy and reversibility

In a *reversible* process consisting of isothermal expansion (dV_f) at temperature T_1 accompanied by a heat change $dQ_\pi = \pi d(V_f \ln W) = T_1 dS$ (see equation (8)) followed by isothermal compression ($d\pi$) at T_2 accompanied by a heat change $dQ_{vf} = V_f d(\pi \ln W) = T_2 dS$, (as in a Carnot cycle), the *net change* $dQ_\pi - dQ_{vf} = 0$, but

$$dQ_\pi/T_1 - dQ_{vf}/T_2 = dS - dS = 0 \quad (9)$$

Thus the ratio dQ/T is of significance for a reversible process [and it gave rise to the notion of entropy as $dQ/T = S$ (instead of dS !) and that $S - S = 0$ for a reversible process (2nd law of thermodynamics). Note the inconsistency that S is also sometimes defined as $\delta Q/T$ or q_{rev}/T].

It is to be noted that dQ is the sum of two terms:

$$dQ = TdS + SdT \quad (10)$$

The free energy terms in equations (5) depend on dS and dT as follows:

$$-dA_s = \pi dV_f = dQ - C_{vf}dT = TdS + (S - C_{vf})dT \quad (11a)$$

$$dG_s = V_f d\pi = C_{\pi f}dT - dQ = (C_{\pi f} - S)dT - TdS \quad (11b)$$

For an isothermal process, $dT = 0$ and $dA_\pi = dG_\pi = -TdS = dQ_\pi$.

Thus, entropy, heat capacities and the thermodynamic laws are integral parts of the new equation of state, equation (2).

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