Thermodynamic Properties of Non-charged Molecules in Aqueous Solution

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In the years from 1960 to 1975 a great deal of reviews has been published on the thermodynamic properties of aqueous non-ionic solutions. The interest in these properties is justified from their usefulness in connection with: (*a*) solubilities of non-charged molecules in water; (*b*) effects of the hydration on chemical equilibria; (*c*) understanding of some phenomena typical of biochemical systems; (*d*) calculation of thermodynamic functions of hydration ΔH_h° for ionic species; (*e*) calculation of non-electrostatic contribution in theories of ionic solutions; (*f*) test of theories on water and aqueous solutions.

The recent investigations on the thermodynamics of non-ionic aqueous solutions present two main aspects, on one hand a strong impetus in collecting data concerning the thermodynamic functions of transfer ΔX_t ($X = G, H, S$) from pure state to aqueous solution and the thermodynamic partial molar properties ϕ_j ($j = v, c_p, E, k$) for various classes of compounds and in a wide range of temperature and concentration, and on the other some attempts in giving a rational framework to the collected material along the following lines: (*i*) expressing the ΔG_h° and ΔS_h° values with a unique and proper choice of the standard states, (*ii*) relating the values of the ΔX_h° and ϕ_j properties to the molecular structures through their description in terms of group contributions, (*iii*) expressing the solute–solute interactions in the frame of the McMillan–Mayer solution theory.

In this lecture a survey will be given of what has been done in the topics mentioned above. A short account will also be devoted to the courses taken by the theories on water and aqueous solutions.

Solute–Solvent Interactions as Required for the Existence of a Liquid

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The exclusive consideration of interactions between solvent molecules does not provide an understanding of a pure liquid [1]. It is known that any real liquid contains solutes. For example any 'non-aqueous solvent' contains traces of dissolved water and gases that cannot be removed completely. Any solute acts as nucleating and structure regulating center [2]. Water purged of all foreign particles produces its own ions. This process of self-ionization has been ascribed as resulting from cooperative processes [3]. Such ions as well as any other solute particles are enriched in the boundary areas. With decreasing drop size the self ionization constant is expected to increase, the effects being remarkable below 10 μm diameter, when water is known to freeze below –39 °C irrespective of its environment [4]. The structural features have been interpreted as evidence for the domination of cooperative processes. This is in agreement with its enhanced reactivity, as shown by its ability to dissolve silica or calcium fluoride [5].

References

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A Comparison between Structures of Aqua and Ammine Complexes in Solution as Studied by an X-Ray Diffraction Method

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The structures of aqua and ammine complexes of some divalent transition metals and silver(I) in aqueous solutions were determined by the X-ray diffraction method at 25 °C.

All of the aqua complexes of the transition metals from manganese(II) to zinc(II) have six water molecules in their first coordination shell. The bond distances between the central metals and hydrated water molecules are changed so as to be expected from the crystal stabilization field energies of the complexes. The Jahn–Teller distortion of the aqua copper(II) complex in solution is recognized by this method. Silver(I) ion has two water molecules in the linear form.

In ammoniacal aqueous solutions, zinc(II) ion combines with, at most, four ammonia molecules to form a tetrahedral structure. On the other hand, cadmium ion forms the regularly octahedral hexaamminecadmium(II) complex. An emphasis may be made upon the bond length variation of copper(II) ammine complexes with changing numbers of ammo-