## 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 $\Delta H_h^\circ$ 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 $\Delta X_t$ (X = G, H, S) from pure state to aqueous solution and the thermodynamic partial molar properties $\phi_j$ (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 $\Delta G_h^\circ$ and $\Delta S_h^\circ$ values with a unique and proper choice of the standard states, (*ii*) relating the values of the $\Delta X_h^\circ$ and $\phi_j$ 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.

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## 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 $\mu$m 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 hexa-amminecadmium(II) complex. An emphasis may be made upon the bond length variation of copper(II) ammine complexes with changing numbers of ammo-

nia molecules combined. The tetraamminecopper(II) complex has four ammonia molecules at the equatorial position and two water molecules at the axial one. The Cu–NH₃ bond distance within the complex is *longer* by 0.1 Å than the Cu–OH₂ distance within the aqua complex. On the contrary, the axial Cu–OH₂ bond within the tetraamminecopper(II) complex shortens by *ca.* 0.1 Å. In a higher copper(II)–ammine complex formed by the addition of a large excess of ammonia to the solution (although the composition of the complex is not determinable either $Cu(NH_3)_5(OH_2)^{2+}$ or $Cu(NH_3)_6^{2+}$ by the present method), the length of the Cu–NH₃ bond at the equatorial position within the complex *shortens* to 1.94 Å, whereas the length of the Cu–NH₃ bond at the axial position is remained practically unchanged by replacement of the water molecule(s) within the tetraamminecopper(II) complex with ammonia. Such complicated changes in the bond lengths within the copper ammine complexes are not explained by simple theories of coordination chemistry.

The diamminesilver(I) complex has a linear structure, which is similar to the structure of the aqua silver(I) complex. However, the bond length between the silver atom and the ammonia molecules within the diammine complex is much shorter than the corresponding metal–ligand distance within the aqua complex. Free solvent molecules are not found in the region less than 3 Å from the central silver atom of the both complexes.

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## Classical Ionic Fluids in the Mean Spherical Approximation

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The analytical solution of the mean spherical approximation (MSA) has been used to calculate excess thermodynamic properties of aqueous and non-aqueous solutions of 1–1, 1–2, 1–3, 1–n electrolytes. For some solutions and a few molten salts also structure functions and pair correlation func-

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tions have been obtained. The possibility of use of MSA to simulate systems of primary interest in the framework of enhanced oil recovery is also discussed. Finally, MSA pair correlation functions are compared with the Debye–Hückel correlation functions in an attempt to compute higher order graph contributions beyond the ring diagrams which yield the D–H approximation.

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## Polymer Attached Catalysts

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Homogeneously catalyzed reactions usually take place at low temperatures and pressures and with high selectivity. Heterogeneous catalysts however have many engineering advantages.

A practical limitation to performing homogeneously catalyzed reactions in liquid phase is the difficulty of separating the product from the catalysts. To overcome this difficulty homogeneous catalysts have been attached to a variety of insoluble supports, with the aim of acquiring the properties of insolubility while maintaining the reactivity exhibited in solution.

The liquid phase, however, plays an important role in polymer supported catalysts and the solvent–substrate–support interactions have a large influence on the catalytic activity and selectivity of this type of catalysts. This property associated with the high dependence of the reduction rate on size and rigidity of the substrate suggests that reduction takes place within the resin, where the active sites are located, rather than at its surface, and that the catalyst could 'remember' conditions used during the synthesis.

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## Catalytic Red–Ox Reactions of Small Molecules with Participation of Solvent Protons

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Small molecules such as $C_2H_2$, CO, $CO_2$, $N_2$ *etc.* can be reduced in protic media in the presence of