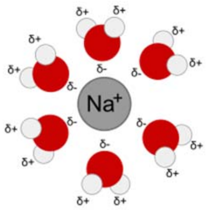
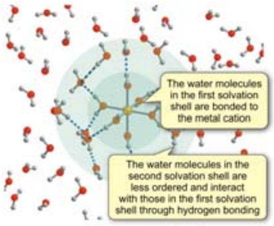




Physical & Interfacial Electrochemistry 2013

Lecture 2.

Electrolyte Solutions : Ion/solvent interactions: ionic solvation.

Module JS CH3304 MolecularThermodynamics and Kinetics

Ionics: the physical chemistry of ionic solutions.

In previous lecture courses at the Freshman level we presented a rather general introduction to electrochemical systems and concepts. In this lecture course we begin the study of physical electrochemistry in earnest and set the ball rolling by discussing Ionics, the physical chemistry of electrolyte solutions.

We recall that electrolyte solutions are solutions which can conduct electricity. We recall from basic general chemistry that in solutions solutes can exist in a number of possible forms:

- Molecular units: solution is non-conducting, normal colligative properties exhibited, XRD analysis indicates discrete molecular units in the solid.
- Molecular units plus ions: solution is weakly conducting, colligative properties indicate slightly more than expected numbers of particles present, XRD analysis indicates discrete molecular units in the solid.

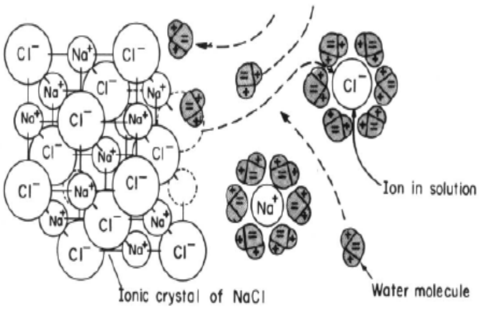
We now begin the study of physical electrochemistry in earnest and consider the solvation of ions in electrolytic solutions . In particular in this lecture we shall focus on ion - solvent interactions , and discuss the progress that has been made in the understanding of the nature and structure of solvated ions . Our main emphasis will be on aqueous solutions .

In recent years many advances have been made both in experimental techniques (spectroscopic and diffraction methods) and in computational simulation protocols (such as molecular dynamics MD, especially as applied to biologically important molecules) which may be used as tools for the study of ionic solvation processes .

The term electrolyte is of particular importance here. Now electrolytes may be defined as a class of compounds , which, upon dissolution in a polar solvent , dissociate at least partially into ions . If we zero in on the concept of dissociation , or the splitting apart to form ions , and concentrate on the extent to which dissociation takes place, then we can distinguish between two types of electrolytes . These two designations are termed true and potential . A true electrolyte implies complete dissociation into ions, whereas for a potential electrolyte only limited dissociation takes place . Thus sodium chloride NaCl is a true electrolyte whereas acetic acid CH_3COOH is a potential electrolyte . These statements are well known from basic freshman chemistry. The mechanism of ion formation is different for both of these electrolyte types.

A slightly older designation which is still in current use are the terms strong and weak electrolytes . Note that solutes giving in solution molecular units are termed non-electrolytes, those generating both molecular units plus ions, weak electrolytes and those forming ions only, strong electrolytes.

NaCl is an ionic compound consisting of Na^+ and Cl^- ions joined together via electrovalent bonds in a crystal lattice . When solid NaCl is put in contact with a solvent such as water , the solvent molecules rapidly attack the lattice , disrupt and break the ionic bonds and thereby generate hydrated ions $Na^+(aq)$ and $Cl^-(aq)$ as outlined schematically below. Here we see ion/solvent interactions very much at work.



Dissolution of crystal by action of solvent.

Significant (complete) Dissociation/ionization. Ion/solvent interaction Strong.

A different situation pertains for acetic acid. The latter is a neutral organic compound. In this case a specific reaction between the solute and solvent, a proton transfer reaction, results in the generation of acetate $CH_3CO_2^-$ and hydronium ions H_3O^+ ions. A proton is transferred from the organic acid (a proton donor) to a water molecule (a proton acceptor) outlined below. We have a Bronsted-Lowry acid/base reaction . Now the latter process only proceeds to a limited extent . Typically the degree of dissociation is ca. 10^{-3} .

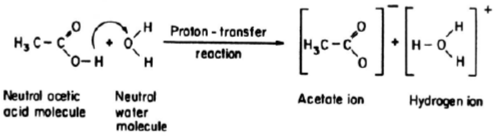
$$HA + H_2O \rightleftarrows H_3O^+(aq) + A^-$$

$$K_A = \frac{[H_3O^+][A^-]}{[HA]}$$

Weak acid
K_A small.

Refer to Bronsted-Lowry Acid/Base Behaviour discussed in JF CH1101.

Chemical method: proton transfer reaction.



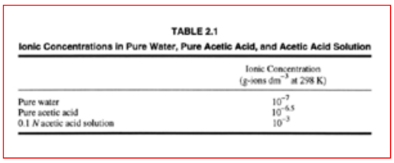


TABLE 2.1

Ionic Concentrations in Pure Water, Pure Acetic Acid, and Acetic Acid Solution

	Ionic Concentration (g-ions dm^{-3} at 298 K)
Pure water	10^{-7}
Pure acetic acid	$10^{-6.5}$
0.1 *N* acetic acid solution	10^{-3}

Degree of dissociation small, 0.1 %.

The structure of water , the ubiquitous medium .

Water is of course the most generally used solvent system in electrochemistry . However for some applications non aqueous solvents must be used (e.g. in high density lithium battery systems). As a general rule , an electrochemically useful solvent must be able to dissolve a reasonable amount of an inorganic electrolyte (ca. at least 10^{-3} mol dm^{-3}) .

Bockris & Reddy, Modern Electrochemistry
2^{nd} edition, Kluwer, New York, 1998,
Vol.1 Ionics, Ch.2.

We see that when compared with other solvents, liquid water exhibits several distinctive properties . For instance , water has a high relative permittivity (e_r = 78) , high surface tension (72 mN m^{-1}), high thermal capacity (75 J $mol^{-1}K^{-1}$) and thermal conductivity (0.6 J $s^{-1}m^{-1}K^{-1}$). Also , its molar volume is the smallest of all the common solvents and so it will exhibit the highest particle density . A further point to note is that the enthalpy of vaporization is greater that the enthalpy of fusion in contrast to the situation observed for non polar solvents where the latter quantities are of similar magnitudes . The surface tension of water is also considerably larger than other solvents. The same can be said for the molar heat capacity . Finally , considering the magnitude of the molar mass of water , we note that its viscosity is anomalously high. Hence these bulk properties of liquid water suggest that the latter must be quite highly ordered and that considerable *molecular association is present . Furthermore we can conclude that intermolecular attractive interactions are stronger in liquid water than in other solvents* .

The structure of water and ice depend on the geometry exhibited by a single water molecule . Molecular structure determines macroscopic properties . We know from Freshman Chemistry that a single H_2O molecule has eight valence electrons (six from oxygen and one each from the two hydrogen atoms). The demands of individual atomic valencies dictate that the oxygen atom is covalently bonded to each of the hydrogen atoms and that two lone pairs of electrons reside on the oxygen atom . Hence in the language of quantum mechanics , the oxygen atom is sp^3 hybridised . Water exhibits a tetrahedral stereochemistry . The HOH bond angle is 104.5 ° . The molecule acts as a dipole and the lp electrons may enter into hydrogen bonding with hydrogens on neighboring water molecules . In this way a three dimensional network structure may be generated .

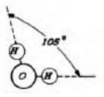


Fig. 2.5. A water molecule is nonlinear.

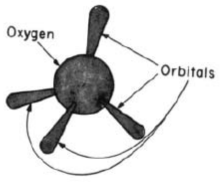


Fig. 2.6. The hybrid orbitals of an oxygen atom.

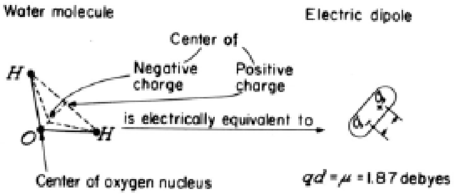


Fig. 2.7. A water molecule can be considered electrically equivalent to a dipole.

Methods of structural analysis such as XRD, ND, NMR, IR and Raman spectroscopy applied to liquid water have indicated that under normal conditions ca. 70% of water molecules exist in "ice floes" (clusters of ca. 50 molecules exhibiting a structure similar to that of ice) . The mean lifetime of such *networked structures* is ca. 10^{-11} s .

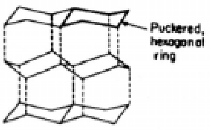


Fig. 2.8. The oxygen atoms in ice, which are located at the intersections of the lines in the diagram, lie in a network of open puckered hexagonal rings.

And what of the structure of ice ? The best experimental evidence suggests that the latter material consists of a network of open puckered hexagonal rings joining oxygen atoms together . Each oxygen atom is tetrahedrally surrounded by four other oxygen atoms . Also, in between any two oxygen atoms is located a hydrogen atom which is associated to the adjacent oxygen atoms via hydrogen bonding . Hence each oxygen atom has two hydrogen atoms near it at an estimated distance of ca. 0.175 nm . Now such a network structure of associated water molecules contains interstitial regions located between the tetrahedra , which typically are larger than the dimension of a water molecule . Hence it appears that a free non-associated water molecule can enter the interstitial regions without generating any disruption of the network structure .

We can therefore say that liquid water under most conditions is described in terms of a somewhat broken down, slightly expanded form of the ice lattice . In short, liquid water partly retains the tetrahedral bonding and resultant network structure characteristic of the crystalline structure of ice . Hence by analogy with the ice structure one has associated network water and structurally free non associated water located in the interstitial regions in the network .

Note that the mean oxygen-oxygen bond distance in ice is 0.276 nm whereas in liquid water it is 0.292 nm . Furthermore, the number of oxygen nearest neighbours in ice is 4 and in water is between 4.4 and 4.6 .

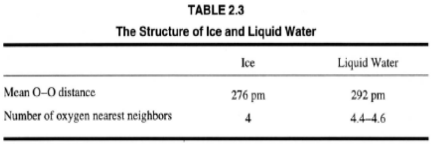


TABLE 2.3

The Structure of Ice and Liquid Water

	Ice	Liquid Water
Mean O–O distance	276 pm	292 pm
Number of oxygen nearest neighbors	4	4.4–4.6

It is important to note that this distinction between network and free water is not a static one . Networks can break down : more free water molecules can be formed . Free water molecules may combine to form clusters (typically ca. 50 water molecules joined together) . The situation is therefore quite dynamic . Free water can be transformed into network water and vice versa . This picture (icelike labile clusters and monomeric water molecules) was initially proposed some time ago by Frank and Wen .

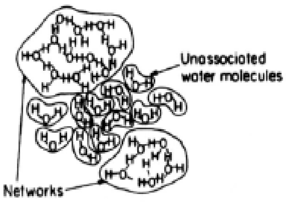


Fig. 2.10. Schematic diagram to show that in liquid water there are networks of associated water molecules and also a certain fraction of free, unassociated water molecules.

One expects that solvents such as MeOH and formic acid should also exhibit considerable association via hydrogen bonding and that a certain degree of order should be present . However as noted by Desnoyers and Jolicoeur [2] the details of solvent-solvent interactions in polar liquids is generally unknown at the present time , water being the only exception . Solvent-solvent interactions can and do play an important part in ionic solvation . However their effect is very difficult to establish in non-aqueous solutions . In this course we will concentrate mainly on water , since the latter has been well characterised experimentally and is best understood .

Solvent / solvent interactions can involve dipole / dipole , dipole / induced dipole , induced dipole / induced dipole (dispersion) and dipole/ quadrupole interactions .

How many water molecules must be joined together before the bulk properties of water are observed ? Put another way , we ask how many water molecules does it take before the cluster shows the properties of wetness or before the dielectric properties approach that of bulk water ? This is not a philosophical question : the answer leads one to the forefront of research . A single water molecule will not suffice : this much we know . A recent textoook author has quoted a value of ca. 6 molecules . This is clearly far too low .

Simonson has recently calculated using Molecular Dynamics (MD) techniques a value for the static dielectric constant of water using a simple model system consisting of a microscopic droplet of water in a vacuum . The idea behind this approach is as follows .

Almost all computational studies to date have been based on simulations of bulk water either using so called periodic boundary conditions (more about these later on) or by combining a finite spherical microscopic region with an outer bulk region modelled as a dielectric continuum. Such computations are difficult, time consuming and hence very expensive to do . Lots of long range interactions have to be taken into account and this causes convergence problems when the computation is done . Optimal computational strategies are still being pursued .

On the other hand using a model such as a spherical water droplet imbedded in a vacuum , one can dispense with long range interactions and one can readily compute all the interactions within the droplet whose size can be chosen . Simonson has shown that very good agreement (e_r in the range 77 - 87) with the experimental bulk dielectric constant of water is obtained for a droplet of 1963 TIP3P water molecules (sphere 2.4 nm radius) at T = 292 K after a simulation time of 1000 ps . Hence from this work it is clear that a cluster of some 2000 water molecules can mimic the behavior of the bulk liquid .

We now move on and consider some simple approaches used for quantifying what happens when an ion enters from the gas phase into a polar solvent such as water and becomes solvated (or hydrated). In particular we shall consider the energetics of the interaction between an ion and the solvent .

We shall initially adopt a very simple first order approach and assume that the solvent medium does not have a molecular structure , but instead can be regarded as a dielectric continuum . In this approach we assume that the interactions between the ion and the solvent are electrostatic in origin and we view the ion as a charged sphere of radius r and the solvent as a dielectric continuum of dielectric constant e_r.

The solvent is the medium in which the solute exists. It is often called
A dielectric. A dielectric can be thought of in terms of an insulator, which is
A substance which stops or tends to stop the flow of charge., in other
words to stop a current passing through it.
If a substance which acts as an insulator is placed between two charges it
Reduces

- the field strength
- the force acting between the charges
- the electrostatic potential energy of interaction between the charges

And the factor by which it reduces these quantities is called the
relative permittivity ε_r.
It is important to note that this definition of relative permittivity is
independent of any assumption as to what the dielectric is made of.
In particular it is independent of any assumption that the dielectric is
composed of atoms and molecules, and so requires no discussion of the
medium at a microscopic level.
In effect the dielectric constant is just a proportionality constant
characteristic of the medium.

Solvation: Solute-solvent interactions.

Introduction.

We focus attention on charged solutes (ions) in polar solvents. Much work has been done in this area of Physical Electrochemistry both from a theoretical and an experimental viewpoint. The topic is also of considerable importance in biophysical chemistry when the solvation of macromolecular protein molecules is addressed.

Firstly with respect to the theoretical analysis we consider two distinct approaches to solute/solvent interactions.

- Non-structural treatment.

This is based on viewing the solvent as a structureless dielectric continuum into which the ion is embedded as a charged sphere. The methodology of classical electrostatics is used in the detailed analysis of the energetics of the problem.

The energetics of salvation is expressed in terms of thermodynamic cycles and the pertinent thermodynamic quantities such as ΔG_S, ΔH_S and ΔS_S are determined in the context of simple electrostatic models.

The non-structural approach is based on the original model developed by Born (1920). This type of analysis is very approximate but is still being used with some success.

Good agreement between theory and experiment is obtained via the introduction of empirical fitting parameters which serve to quantify the ionic radius in the solvent.

The non-structural Born approach has been generalised in recent years to examine the salvation energetics of macromolecules, and is so a topic of considerable current interest in biophysical chemistry.

- Structural treatment.

This defines the modern approach. Here we view the solvent as a molecular entity with a well defined structure (as indeed it has). We need a model of the solvent in the immediate vicinity of the ion. Again the solvation energetics are quantified in terms of the thermodynamic entities ΔG_S, ΔH_S and ΔS_S. The theoretical analysis is again based on electrostatic models but these are more elaborate and include ion/dipole and ion/quadrupole interactions. The structural treatments based on the early work of Bernal and Fowler (1933). The results obtained are encouraging but a fully satisfactory theoretical model has yet to be developed.

In contrast the experimental analysis of solvation is quite well developed.

Structural information on the environment of a solvated ion is obtained from:

- diffraction methods: X-ray, neutron and electron diffraction, EXAFS etc.
- spectroscopic studies : uv/vis, ir, nmr, raman spectroscopies etc.

Diffraction methods provide direct information about the environment surrounding the ion in solution, whereas indirect structural information is provided from spectroscopic methods.

One difficulty is that dilute solutions need to be examined in order to focus in on ion/solvent interactions. If more concentrated solutions are used then ion/ion interactions come into play and cloud the issue.

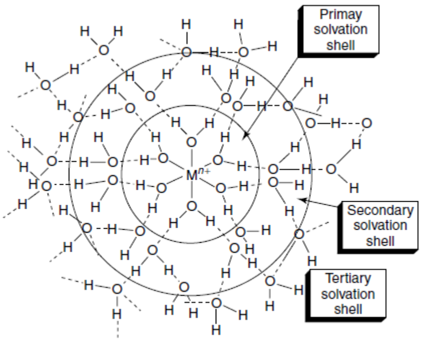
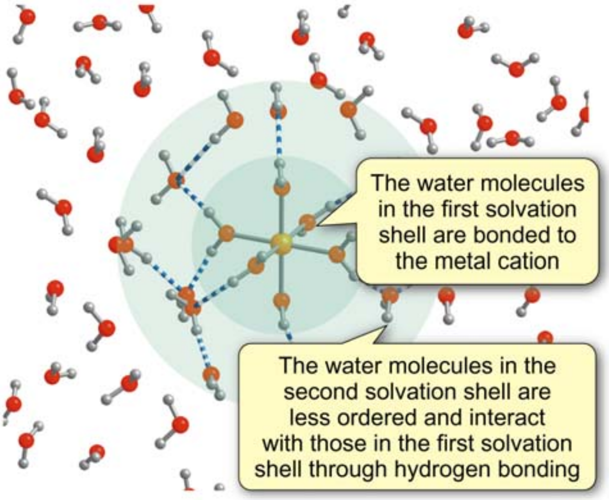


Figure 6. The localized structure of a hydrated metal cation in aqueous solution, the metal ion being assumed to have a primary hydration number of six.



The water molecules in the first solvation shell are bonded to the metal cation

The water molecules in the second solvation shell are less ordered and interact with those in the first solvation shell through hydrogen bonding

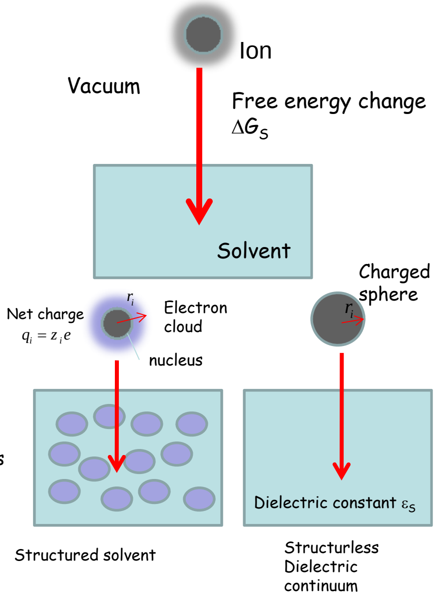
In this section we discuss an approach developed by Born which can be used to model the energetics of ion/solvent interactions in a convenient manner . This approach may have its origins over sixty years ago and is certainly limited, but it can , and has yielded a large number of qualitative and semi-quantitative insights . Now this approach is limited and has had its detractors . However this continuum approach represents a simple, easily interpretable, and computationally inexpensive physical model that does not involve many adjustable parameters . The major problem with this approach is that the concept of a macroscopic dielectric response is applied to a molecular system.

Max Born was one of the founding fathers of modern quantum mechanics having proposed the probability interpretation of the wavefunction for which he ultimately obtained a belated Nobel Prize .

In the Born approach a blend of classical electrostatics and thermodynamic cycles is adopted . The object of the exercise is to evaluate , from first principles, the Gibbs energy change ΔG_S associated with the process of ionic solvation , where one considers the transfer of an ion from a gaseous vapour at low partial pressure to the desired solvent (i.e. water) in the absence of any ion/ion interactions . In simple terms the work of transfer of an ion from vacuum to a solvent is equated with the Gibbs energy of solvation . Hence the formidable task of quantifying the energetics of ionic solvation in a structured solvent is reduced using this approximate approach to answering the question : what is the work done in transferring a charged sphere from vacuum into a dielectric continuum ?

Energetics of ionic solvation : Non-structural Treatment. Born Model (1920)

We consider the following situation.
Initial state: no ion/solvent interactions.
This corresponds to ion in vacuum.
Final State: ion/solvent interactions operative.
This corresponds to ion in solution.
Thermodynamics states that for reversible
Process taking place at const. T & P,
Free Energy change ΔG equals net work
(other than PV work) done on system.
We need to calculate the work done in
Transferring an ion from vacuum into a solvent.



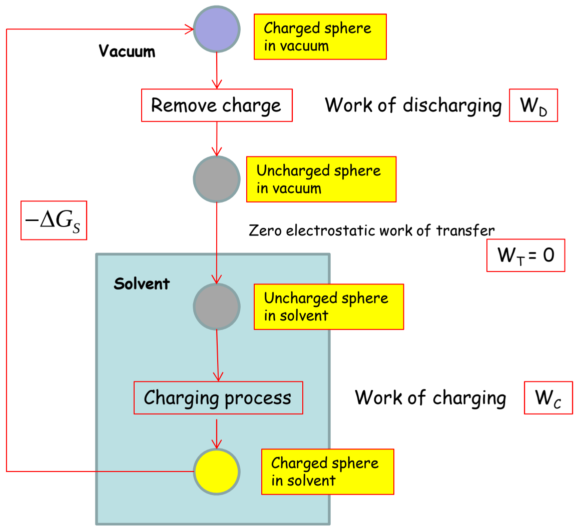
A solvent such as water has a complex structure. To simplify our analysis we dispense with structure and regard the solvent as a structurless dielectric continuum. This medium has a dielectric constant given by ε_S The ion also has structure (ion + associated hydration sheath). We represent the ion as a charged sphere of net charge $q_i = z_i e$ and radius r_i.

Gibbs energy of solvation computed via a thermodynamic cycle.

Born Model : Thermodynamic cycle to calculate the work done in transferring a charged sphere from vacuum into the solvent.

Main assumption:
Only charge on ion is Responsible for ion/solvent interaction.
Hence ion/solvent interactions are solely electrostatic in nature.

The following thermodynamic cycle is developed. The ion i , represented as a charged sphere of radius R,is considered in to be initially located in a vacuum, and the work W_d required to strip the ion of its charge $q = z_i e$ is determined . Then this uncharged sphere is transferred into the solvent dielectric medium . We assume that this transfer process involves no work . Then the charge on the sphere inside the solvent is restored to its full value $q = z_i e$ and the work done in charging W_c is determined . Finally, the ion is transferred from the solvent back into vacuum . The work done in this transfer process is - ΔG_s .



Vacuum

Charged sphere in vacuum

Remove charge

Work of discharging W_D

Uncharged sphere in vacuum

$-\Delta G_S$

Zero electrostatic work of transfer

$W_T = 0$

Solvent

Uncharged sphere in solvent

Charging process

Work of charging W_C

Charged sphere in solvent

In a thermodynamic cycle the algebraic Sum of all the work terms is zero.

$$\boxed{\begin{aligned} &W_d + W_{tr} + W_c - \Delta G_s = 0 \\ &\Delta G_s = W_c + W_d \end{aligned}}$$

We now evaluate the work done in charging a sphere of radius R from $q = 0$ to $q = z_i e$, where z_i denotes the valence of ion i and e is the fundamental electronic charge . To do this we start off with an uncharged sphere and add infinitesimal amounts dq to the sphere until the final charge level is attained .The product of electrostatic potential ψ and the charge increment dq gives the work increment dw.

$$\boxed{dw = \psi\, dq}$$

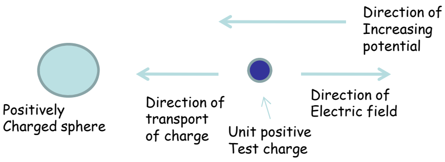
The total work done in charging the sphere is obtained by summing over all the little increments dw.

$$\boxed{W_c = \int_0^{z_i e} dw = \int_0^{z_i e} \psi dq}$$

ε_0 = permittivity of vacuum = 8.854×10^{-12} $C^2N^{-1}m^{-2}$

From fundamental electrostatics we recall that the electrostatic potential at a certain point in space is defined as the work done to transport a unit positive charge from infinity to that specific point . Now the electrostatic potential at a point located a distance r from a charged sphere ψ (r) is given by the product of the electric field strength E(r) (which defines the electric force per unit charge) acting on the moving test charge and the distance r through which the charge is carried .

$$\boxed{\psi(r) = -\int_\infty^R E(r)dr = -\frac{1}{4\pi\varepsilon_0}\int_\infty^R \frac{q}{r^2}dr = \frac{q}{4\pi\varepsilon_0 R}}$$



Direction of Increasing potential

Positively Charged sphere

Direction of transport of charge

Unit positive Test charge

Direction of Electric field

Total charging work W_c

$$\boxed{\begin{aligned} W_c &= \int_0^{z_i e} \psi(r = R)dq = \frac{1}{4\pi\varepsilon_0}\int_0^{z_i e} \frac{q}{R}dq \\ &= \frac{1}{4\pi\varepsilon_0}\left\{\frac{(z_i e)^2}{2R}\right\} \end{aligned}}$$

Work done in discharging sphere is negative of charging work, $W_d = - W_c$

$$W_d = -\frac{1}{4\pi\varepsilon_0}\left\{\frac{(z_i e)^2}{2R}\right\}$$

The recharging work done when the sphere is present in the <u>solvent dielectric</u> is modified by the macroscopic dielectric constant of the medium ε_r.

$$W_c = \frac{1}{4\pi\varepsilon_0}\left\{\frac{(z_i e)^2}{2\varepsilon_r R}\right\}$$

Born expression for Gibbs energy of Solvation.

$$\Delta G_s = W_d^{\,vac} + W_c^{\,diel} = -\frac{1}{4\pi\varepsilon_0}\left\{\frac{(z_i e)^2}{2R}\right\}\left[1-\frac{1}{\varepsilon_r}\right]$$

Note that in the expression for ΔG_s there is a negative sign heading the rhs . Now since the dielectric constant $\varepsilon_r > 1$ always and so $1/\varepsilon_r < 1$ then ΔG_s will always be negative . The solvation proceeds spontaneously : ions prefer to be solvated than to be in vacuum . Hence <u>solvation is thermodynamically favourable</u>. The Born equation also predicts that the smaller the ion (smaller R) and the larger the dielectric constant , the greater will be the solvation free energy .

The Entropy and enthalpy of solvation are readily evaluated. Note that ΔH_S is a quantity readily compared with experiment.

$$\Delta H_s = \Delta G_s + T\Delta S_s$$

$$\Delta S_s = -\left(\frac{\partial \Delta G_s}{\partial T}\right)_P = \frac{N_A}{4\pi\varepsilon_0}\frac{z_i^2 e^2}{2R}\frac{1}{\varepsilon_r^2}\frac{\partial\varepsilon_r}{\partial T}$$

$$\Delta H_s = -\frac{N_A}{4\pi\varepsilon_0}\frac{z_i^2 e^2}{2R}\left\{1-\frac{1}{\varepsilon_r}-\frac{T}{\varepsilon_r^2}\frac{\partial\varepsilon_r}{\partial T}\right\}$$

Molar Gibbs Energy of solvation

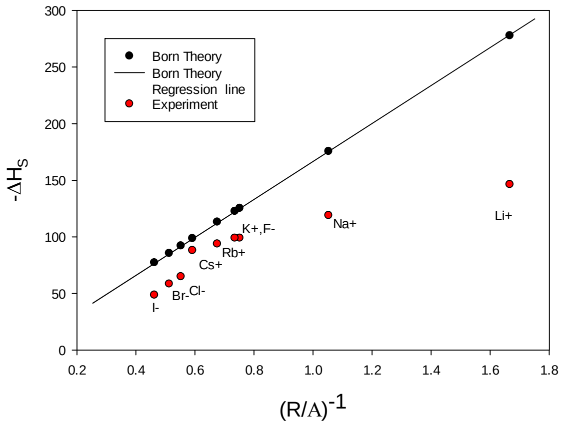
$$\Delta G_s = -\frac{N_A}{4\pi\varepsilon_0}\left\{\frac{(z_i e)^2}{2R}\right\}\left[1-\frac{1}{\varepsilon_r}\right] = -\frac{N_A}{4\pi\varepsilon_0}\left\{\frac{q^2}{2R}\right\}\left[1-\frac{1}{\varepsilon_r}\right]$$

A clear prediction is that the solvation free energy should vary inversely with ion size R

Born Model : Comparing theory and Experiment

P.W. Atkins, A.J. MacDermott, J. Chem. Ed.59 (1982) 359-360

We note that the Born model makes predictions which suggest that the ion solvent interaction is much stronger than it actually is . We readily see this if we compare experimentally determined ΔH_s values for the alkali metal ions and the halide ions with that evaluated via the Born expression . If one plots ΔH_s versus the inverse of the Pauling crystal radius we note that the linear relationship between ΔH_s and 1/R predicted by the Born expression is not observed . The experimental data points are all much lower than the theoretical Born equation line . In general the use of ionic radii leads to an overestimate of the solvation energies of anions and in particular the calculated solvation energy of cations can be almost 100 kcal mol^{-1} greater than experimental values . In any event it is quite remarkable that such a crude electrostatic model works at all ! In fact what is measured is the enthalpy of solvation of a salt not that of an individual ion .



Born theory suggests that ion/solvent interactions are much stronger than experiment shows them to be.
Need to use effective dielectric constant of solvent region near ion rather than bulk value (ca. 80 for water).

Continuum Solvation Models: Recent Developments.

Rashin & Honig Model : J. Phys. Chem., 89 (1985) 5588-5593.
In original Born model R was chosen as the ionic radius derived from crystallographic measurements. This leads to quite considerable deviations between experiment and theory. Born Equation estimates (using crystallographic ion radii) of the enthalpy of solvation are considerably higher than values derived from experimental measurements. For example:
Li^+ :R = 0.60Å, $\Delta H_{S,calc}$ = - 277.7 kcal/mol, $\Delta H_{S,expt}$ = - 146.3 kcal/mol.
Na^+: R = 0.95 Å. $\Delta H_{S,calc}$ = - 175.5 kcal/mol, $\Delta H_{S,expt}$ = - 118.9 kcal/mol.

Rashin & Honig suggested that R should be replaced by the parameter R_C termed the cavity radius. Transferring the uncharged ion intothe solvent produces a cavity. The size of this cavity should be used in calculations involving the Born equation. The cavity radius is defined as the distance from the nucleus at which the electron density of the surrounding medium becomes significant.

The cavity radius is a rather arbitrary concept, but it has been suggested that the covalent radii of cations and the ionic radii of anions provide a useful first approximation to the cavity radius.

B. Honig, K. Sharp, A-S Yang, J. Phys. Chem., 97 (1993) 1101-1109

Rashin & Honig Model : J. Phys. Chem., 89 (1985) 5588-5593.

$$\Delta G_s = -\frac{N_A}{(4\pi\varepsilon_0)}\frac{z_i^2 e^2}{2R_{ic}}\left\{1-\frac{1}{\varepsilon_r}\right\}$$

$$\Delta H_s = -\frac{N_A}{4\pi\varepsilon_0}\frac{z_i^2 e^2}{2R_{IC}}\left\{1-\frac{1}{\varepsilon_r}-\frac{T}{\varepsilon_r^2}\frac{\partial\varepsilon_r}{\partial T}\right\}$$

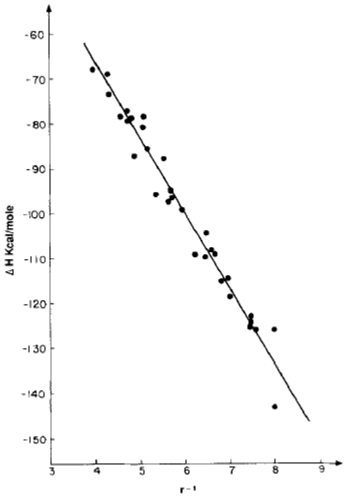


FIGURE 1. Comparison of experimental (*dots*) and predicted (*solid line*) enthalpies of ion hydration. The enthalpies are given per unit charge. The experimental values are given for the following ions: Li^+, Na^+, K^+, Rb^+, Cs^+, F^-, Cl^-, Br^-, I^-, Cu^+, Ag^+, Cu^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}, Al^{+3}, Sc^{+3}, Y^{+3}, La^{+3}, Ce^{+3}, Ce^{+4}, Ga^{+3}, In^{+3}, NH_4^+, OH^-, S^{-2}, SH^-.

Predicted and experimental ΔH_s values are in good agreement, with the error typically being in the region of 7 % .

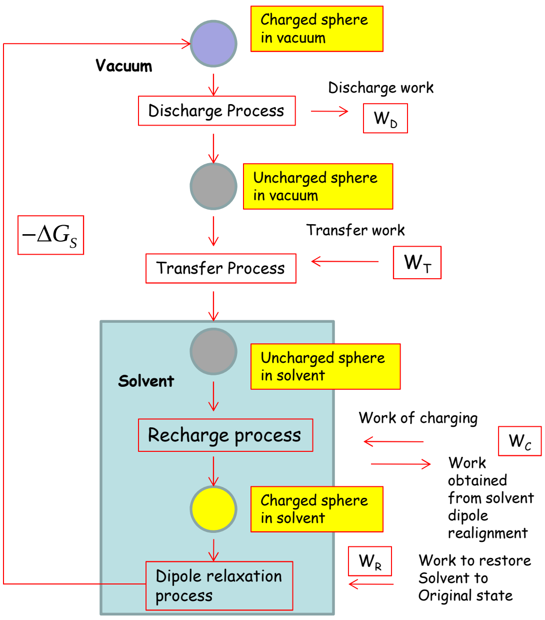
The agreement between theory and experiment is quite good, the calculated values are consistently larger than the experimental values by some 10 - 15 kcal mol^{-1}.

Bontha & Pintauro Model. J. Phys. Chem., 96 (1992) 7778-7782.

Bontha & Pintauro developed a modified Born thermodynamic cycle . It was presumed that the total free energy change associated with the transfer of an ion from vacuum to a polarizable solvent was equal to the sum of the work terms associated with the following processes :

- discharge of the ion in vacuum (W_d) ,
- transfer of the neutral species from vacuum into the solvert (W_{tr}) ,
- re-charging the species in the solvent (W_c),
- restoring the solvent to its original state (W_R)
- transferring the charged ion back into vacuum .

The W_R term is an important addition to the Born approach . During the recharging of an ion in a polarizable solvent it is to be expected that the solvent dipoles are orientated in the electric field generated by the ion . This will result in a decrease in the potential energy of the solvent . Hence, when the Born cycle is completed an amount of work W_R must be added to the solvent in order to restore the rotational and translational motion of the solvent molecules i.e. the aligned solvent dipoles must undergo relaxation .


Charged sphere in vacuum

Vacuum

Discharge Process

Discharge work

W_D

Uncharged sphere in vacuum

$-\Delta G_S$

Transfer work

Transfer Process

W_T

Solvent

Uncharged sphere in solvent

Work of charging

Recharge process

W_C

Work obtained from solvent dipole realignment

Charged sphere in solvent

W_R

Work to restore Solvent to Original state

Dipole relaxation process

The net free energy of solvation ΔG_s is given by

$$\boxed{\Delta G_s = -\left(W_D + W_T + W_c + W_R\right)}$$

W_D= work done in discharging ion in vacuum

W_T = work done in transferring neutral species to solvent

W_C = work done in charging neutral species in solvent

W_R = work done in restoring solvent to original state (relaxation of aligned solvent dipoles).

It was also assumed that the solvent was a polarizable dielectric medium, which implies that the dielectric constant varies with electric field strength and that dielectric saturation effects must be considered.

Hence the dielectric constant near an ion will be <u>much less </u>than the dielectric constant of the bulk solvent

All four work terms can be calculated using Classical electrostatics.

Detailed analysis can show that

$$W_D = -\frac{q^2}{8\pi\varepsilon_0 a}$$

$$W_T = ma + c$$

$$W_C = \varepsilon_0 \int_V dV \int_0^{\bar{D}} \bar{E} \bullet d\bar{D}$$

$$= \varepsilon_0 \int_V dV \int_0^{\bar{E}} \varepsilon_r \bar{E} \bullet d\bar{E} + \varepsilon_0 \int_V dV \int_{\varepsilon_r(\infty)}^{\varepsilon_r(r)} \bar{E}^2 d\varepsilon_r$$

$$W_S = -\varepsilon_0 \int_V dV \int_{\varepsilon_r(\infty)}^{\varepsilon_r(r)} \bar{E}^2 d\varepsilon_r$$

$q =$ charge

$\bar{E} =$electric field vector, $\bar{E} = \nabla \psi, \psi =$electrostatic potential

$\bar{D} = \varepsilon_0 \varepsilon_r \bar{E} =$electric displacement vector

$\varepsilon_r = \varepsilon_r\left(\bar{E}\right)$dielectric constant is function of electric field strength.

The total Gibbs energy of solvation is Outlined across.

$$\Delta G_s = -\frac{q^2}{8\pi\varepsilon_0 a} + W_T + \varepsilon_0 \int_V dV \int_0^{\bar{E}} \varepsilon_r(r)\,\bar{E}\bullet d\bar{E}$$

In order to evaluate the double integral, the interrelationship between the radially dependent electric field and solvent permittivity surrounding an ion must be determined over the entire ion charging process. This is done by simultaneously solving the modified Laplace equation of the electrostatic potential in a polarizable dielectric medium and the Booth equation which describes the variation in the solvent permittivity with electric field strength.

These equations (outlined across) are quite complicated and must be solved numerically using a finite difference technique on a computer.

$$\nabla \bullet \left\{ \varepsilon_r(r) \nabla \psi(r) \right\} = 0$$

$$\varepsilon_r(r) = n^2 + \frac{3\left(\varepsilon_r(\infty) - n^2\right)}{\beta \nabla \psi(r)} \left\{ \coth\left[\beta \nabla \psi(r)\right] - \frac{1}{\beta \nabla \psi(r)} \right\}$$

$$\beta = \frac{5\mu}{2k_B T}\left(n^2 + 2\right)$$

n = optical refractive index of solvent

μ = dipole moment of solvent molecule

k_B = Boltzmann constant

r = radial co-ordinate measured from centre of ion

Boundary Conditions

$$r \to \infty \quad \psi \to 0 \quad \varepsilon_r \to \varepsilon_r(\infty)$$

$$r = a \quad \frac{d\psi}{dr} = -\frac{\sigma}{\varepsilon_0 \varepsilon_r (r = a)}$$

σ= surface charge density C m^{-2}

Bontha & Pintauro Model. J. Phys. Chem., 96 (1992) 7778-7782.

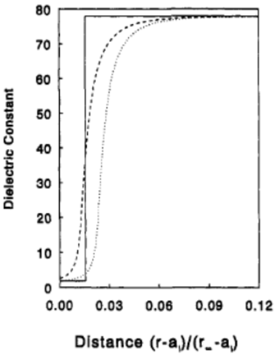


Figure 5. Radial variation in the predicted solvent dielectric profile for univalent cations in water at 298 K: (···) Li$^+$; (- -) Cs$^+$; (—) one-layer profile of Abraham and Lizzi.[8]

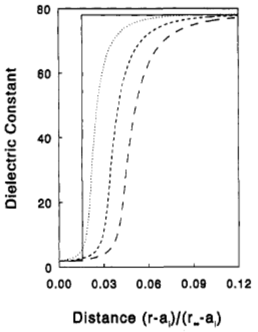


Figure 6. Radial variation in the predicted solvent dielectric profile for uni- and multivalent cations in water at 298 K: (···) Na$^+$; (- -) Ca^{2+}; (– –) Y^{3+}; (—) one-layer profile of Abraham and Lizzi.[8]

Firstly, the variation of local dielectric constant with distance for various extents of surface charging in the range 40 to 100 % is outlined. We note that the distance from the ion surface over which dielectric saturation is observed gets larger the greater the extent of surface charging. The computed variation in the dielectric constant of water (at 298 K) as a function of radial distance from the ion surface for two univalent ions with different radii (Li^+ and Cs^+) and for cations of similar radius and different charge (Na^+, Ca^{2+} and Y^{3+}) are presented. We also show the computed variation expected using the one layer dielectric model of Abraham and Lizzi in these figures . The Abraham-Lizzi model predicts that the dielectric constant remains at its bulk value until a certain critical distance. After that, the value drops to a very low level . Hence the Abraham-Lizzi model does not differentiate between ions of different charges and size . It does approximate well the computed variation in dielectric constant with radial distance for univalent ions of large radius , but only poorly approximates the variation expected for small univalent and for all divalent and trivalent ions .

Bontha & Pintauro Model. J. Phys. Chem., 96 (1992) 7778-7782.

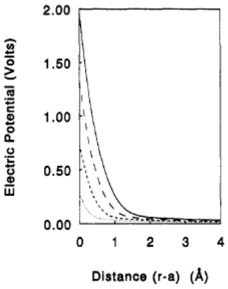


Figure 2. Effect of fractional surface charge density on computed electric potential profiles for K^+ in water at 298 K: (···) 40% (of final surface charge); (- -) 60%; (– –) 80%; (—) 100%.

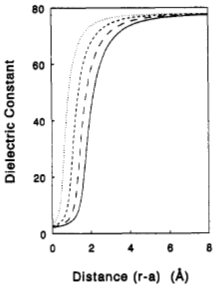


Figure 3. Effect of fractional surface charge density on the computed solvent dielectric profiles for K^+ in water at 298 K: (···) 40% (of final surface charge); (- -) 60%; (– –) 80%; (—) 100%.

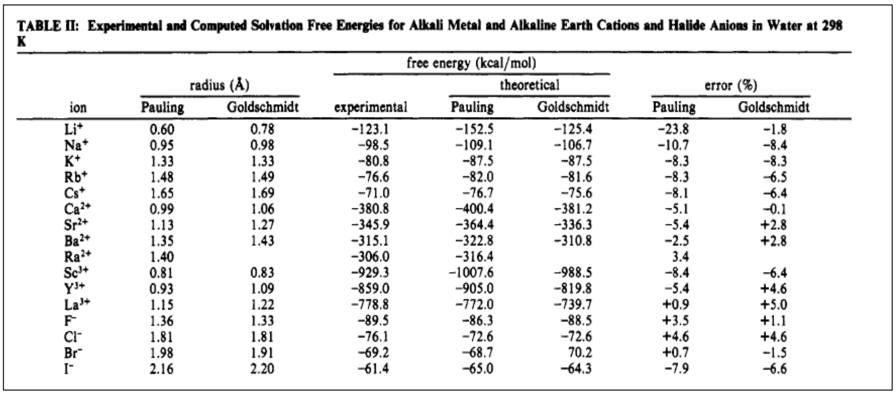


TABLE II: Experimental and Computed Solvation Free Energies for Alkali Metal and Alkaline Earth Cations and Halide Anions in Water at 298 K

	radius (Å)		free energy (kcal/mol)				
				theoretical		error (%)	
ion	Pauling	Goldschmidt	experimental	Pauling	Goldschmidt	Pauling	Goldschmidt
Li^+	0.60	0.78	−123.1	−152.5	−125.4	−23.8	−1.8
Na^+	0.95	0.98	−98.5	−109.1	−106.7	−10.7	−8.4
K^+	1.33	1.33	−80.8	−87.5	−87.5	−8.3	−8.3
Rb^+	1.48	1.49	−76.6	−82.0	−81.6	−8.3	−6.5
Cs^+	1.65	1.69	−71.0	−76.7	−75.6	−8.1	−6.4
Ca^{2+}	0.99	1.06	−380.8	−400.4	−381.2	−5.1	−0.1
Sr^{2+}	1.13	1.27	−345.9	−364.4	−336.3	−5.4	+2.8
Ba^{2+}	1.35	1.43	−315.1	−322.8	−310.8	−2.5	+2.8
Ra^{2+}	1.40		−306.0	−316.4		3.4	
Sc^{3+}	0.81	0.83	−929.3	−1007.6	−988.5	−8.4	−6.4
Y^{3+}	0.93	1.09	−859.0	−905.0	−819.8	−5.4	+4.6
La^{3+}	1.15	1.22	−778.8	−772.0	−739.7	+0.9	+5.0
F^-	1.36	1.33	−89.5	−86.3	−88.5	+3.5	+1.1
Cl^-	1.81	1.81	−76.1	−72.6	−72.6	+4.6	+4.6
Br^-	1.98	1.91	−69.2	−68.7	70.2	+0.7	−1.5
I^-	2.16	2.20	−61.4	−65.0	−64.3	−7.9	−6.6

In table above we show the computed and experimental ionic solvation Gibbs energies calculated using the Bontha - Pintauro model for a range of cations and anions in water at 298 K . Goldschmidt values of the ionic radii were adopted in the calculation . Agreement between theory and experiment is quite good .

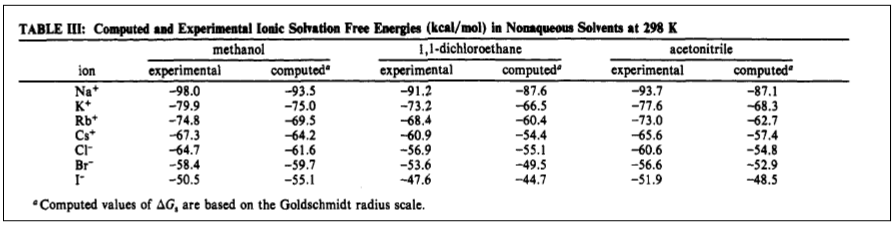


TABLE III: Computed and Experimental Ionic Solvation Free Energies (kcal/mol) in Nonaqueous Solvents at 298 K

	methanol		1,1-dichloroethane		acetonitrile	
ion	experimental	computed[a]	experimental	computed[a]	experimental	computed[a]
Na^+	−98.0	−93.5	−91.2	−87.6	−93.7	−87.1
K^+	−79.9	−75.0	−73.2	−66.5	−77.6	−68.3
Rb^+	−74.8	−69.5	−68.4	−60.4	−73.0	−62.7
Cs^+	−67.3	−64.2	−60.9	−54.4	−65.6	−57.4
Cl^-	−64.7	−61.6	−56.9	−55.1	−60.6	−54.8
Br^-	−58.4	−59.7	−53.6	−49.5	−56.6	−52.9
I^-	−50.5	−55.1	−47.6	−44.7	−51.9	−48.5

[a] Computed values of ΔG_s are based on the Goldschmidt radius scale.

The analysis can also be extended to non aqueous solvents . In table above we show some results for three solvents : methanol, 1,1-dichloroethane and acetonitrile . Again excellent agreement is obtained between theory and experiment . The model predictions are typically within 10 % of the experimental solvation energy values .

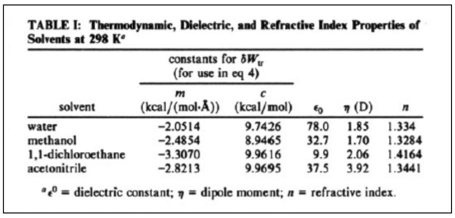


TABLE I: Thermodynamic, Dielectric, and Refractive Index Properties of Solvents at 298 K[a]

	constants for δW_{tr} (for use in eq 4)				
solvent	m (kcal/(mol·Å))	c (kcal/mol)	ϵ_0	η (D)	n
water	−2.0514	9.7426	78.0	1.85	1.334
methanol	−2.4854	8.9465	32.7	1.70	1.3284
1,1-dichloroethane	−3.3070	9.9616	9.9	2.06	1.4164
acetonitrile	−2.8213	9.9695	37.5	3.92	1.3441

[a] ϵ^0 = dielectric constant; η = dipole moment; n = refractive index.

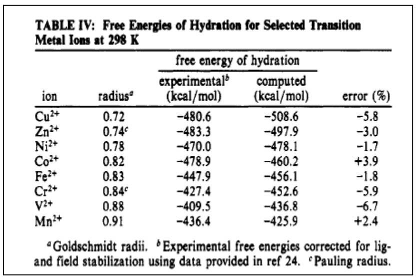


TABLE IV: Free Energies of Hydration for Selected Transition Metal Ions at 298 K

		free energy of hydration		
ion	radius[a]	experimental[b] (kcal/mol)	computed (kcal/mol)	error (%)
Cu^{2+}	0.72	−480.6	−508.6	−5.8
Zn^{2+}	0.74[c]	−483.3	−497.9	−3.0
Ni^{2+}	0.78	−470.0	−478.1	−1.7
Co^{2+}	0.82	−478.9	−460.2	+3.9
Fe^{2+}	0.83	−447.9	−456.1	−1.8
Cr^{2+}	0.84[c]	−427.4	−452.6	−5.9
V^{2+}	0.88	−409.5	−436.8	−6.7
Mn^{2+}	0.91	−436.4	−425.9	+2.4

[a] Goldschmidt radii. [b] Experimental free energies corrected for ligand field stabilization using data provided in ref 24. [c] Pauling radius.

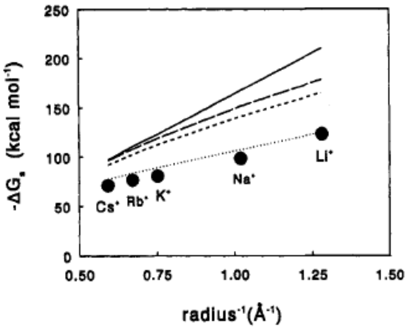


Figure 4. Comparison of hydration free energies for alkali metal ions at 298 K: (●) experimental data (from ref 22); (···) present theory; (- -) theory of Markin and Volkov;[13] (——) theory of Laidler and Pegis;[14] (—) Born theory.[1]

Results from theory agree quite Well with experiment. Typically Error is in region of 2=6%. This is a good result given nature of assumptions made (solvent is dielectric continuum).

What are the advantages of the Bontha-Pintauro model ? The model contains no adjustable parameters , and specifically considers the effect of dielectric saturation in the vicinity of the solvated ion . Agreement between theory prediction and experimental measurements is quite good, typically within 10 %. The Bontha-Pintauro approach is the most recent elaboration on the original Born model developed over 70 years ago , and may be used as a convenient computational protocol to evaluate Gibbs energies of solvation . However the model is still firmly based on continuum electrostatics and does not view the solvent as a structured entity. This is a major disadvantage , of this and all other Born type continuum electrostatic approaches .

Some elaborations on the structural theory of solvation.

The theoretical models discussed in the previous sections have neglected the important fact that water has a very well defined structure , and that this structure will have a very large part to play in the solvation of a particular ion . Details of water structure have been presented in a previous slide.We recall that in liquid water there are networks of associated (via hydrogen bonding interactions) water molecules and also a certain fraction of free unassociated water molecules . We now proceed on and ask the question : what happens to the structure of water when ions enter the solvent ?

At this point we introduce a centrally important idea . We saw that water molecules can be represented as dipoles . Hence one might expect that the intruding ions will interact with the dipolar hosts . This interaction is not gentle and causes major changes in the structure of water . The spherically symmetric electric field of the ion can tear water dipoles out of the water lattice and make them point or orient with the appropriate charged end towards the central ion .

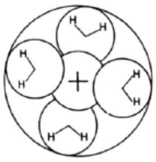


Fig. 2.11. An ion enveloped by a sheath of oriented solvent molecules.

Consequently, we arrive at a picture of ion / dipole forces as providing the principal basis of ionic solvation . Because of the operation of these ion/dipole forces, we can imagine that a certain number of water molecules in the immediate vicinity of the ion may be trapped and orientated in the ionic field . We arrive at a picture of ions enveloped by a solvent sheath of orientated, immobilised water molecules. These immobilised water molecules move with the ion as it moves through the solvent medium . The fate of these immobilised solvent molecules is tied up with that of their partner ion . The ion and its solvent sheath form a single kinetic entity .

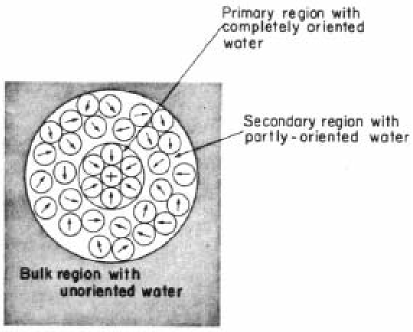
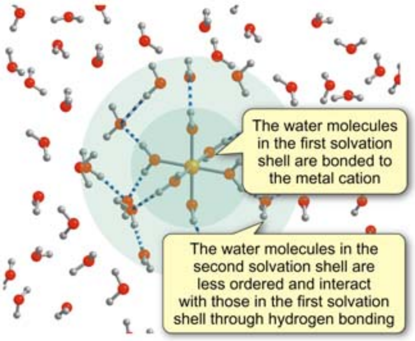


Fig. 2.12. The neighborhood of an ion may be considered to consist of three regions with differing solvent structures: (1) the primary or structure-forming region, (2) the secondary or structure-breaking region, and (3) the bulk region.

What of the situation far away from the ion ? At a large enough distance from the ion, the electric field is negligible and the solvent structure will be unaffected by the ionic field . Here the bulk water structure will pertain . The solvent molecules will not realise that the ion is there at all .



The water molecules in the first solvation shell are bonded to the metal cation

The water molecules in the second solvation shell are less ordered and interact with those in the first solvation shell through hydrogen bonding

In the region between the solvation sheath (where the electric field of the ion determines the water orientation) and the bulk water (where the orientation of the water molecules is uninfluenced by the electric field of the ion) , the orientating influences of the ion and the water network operate in a microscopic tug of war . The former tries to align the water dipoles parallel to the spherically symmetric electric field of the ion, whereas the water network tries to make the water molecules in this "in between" region continue adopting the tetrahedral bonding arrangement required for membership of the network structure . Hence caught between the two types of influences, the water in this in between region seeks to adopt a compromise structure that is neither completely orientated nor disorientated . In this intermediate region the water structure is said to be partially broken down as outlined across.

Let us therefore summarise the situation . We can describe three regions near an ion : (i) the primary or structure enhanced region located next to the ion where the water molecules are immobilised and orientated by the electric field of the ion, (ii) the secondary or structure broken region where the normal bulk structure of water is broken down to various degrees , and (iii) the bulk solvent region where the water structure is unaffected by the ion and the tetrahedrally bonded network characteristic of bulk water is exhibited . These regions are illustrated in the previous slide.

It should be realised that these regions differ in their degree of sharpness . The primary solvation sheath is reasonable well defined .

We have noted that both the central ion and its immobilised layer of water molecules form a single kinetic entity . The number of water molecules associated with the ion during its translational motion is termed the primary solvation (hydration) number n_h . We must distinguish the solvation number from the coordination number . The latter defines the number of solvent molecules in contact with the ion and is determined by geometric considerations .

It is important to note that solvation numbers determined via different experimental techniques can give different answers due to the ambiguity inherent in the definition of the solvation number concept . In contrast, the in between region of secondary solvation is not as well defined . The regions of primary and secondary solvation define the region over which ion-solvent interactions operate .

We now examine a simple structural model invoking ion-dipole interactions which may be used to provide a quantitative estimate of the energetics of ionic solvation .

We now present an account of a very simple simple model of ionic solvation in which the structural details (although described at a very basic level) of the solvent is considered . This account will again dwell on the energetics of solvation and is based on the work reported many years ago by Bernal and Fowler , Eley and Evans , and Frank and Evans .

Again we resort to a simple thought experiment (which is a favourite pursuit of physical electrochemists) to help clarify the situation . The essentials are presented in across and follow the essential idea of Bernal and Fowler.

We set the ball rolling by assuming that the primary solvation shell occupies a certain volume corresponding to n primary solvent molecules *plus* one more to make room for the bare ion . As a consequence of this supposition a volume corresponding to n+1 solvent molecules must be made available in the solvent for the immersion of a primary solvated ion . We therefore remove n+1 solvent molecules and transfer them to vacuum . A *cavity* is left in the solvent as a result of this process . We let W_{CF} denote the work done in cavity formation . We assume of course that the size of an un-solvated ion is the same as that of a solvent molecule . This approximation is reasonable for some ions .

Bernal Fowler Model

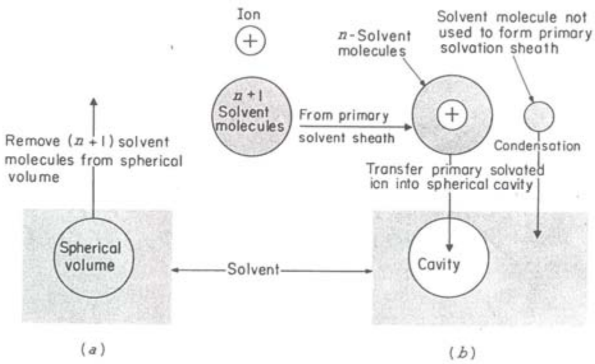


Fig. 2.29. A thought experiment to separate out various aspects of ion–solvent interactions.

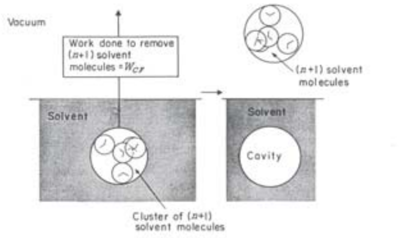


Fig. 2.30. The formation of a cavity in the solvent by the removal of $n + 1$ solvent molecules.

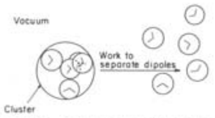


Fig. 2.31. Dissociation of a cluster of $n + 1$ molecules by breaking the bonds holding them together.

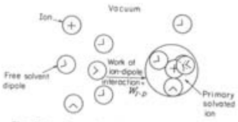


Fig. 2.33. Formation of a primary solvated ion.

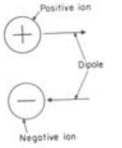


Fig. 2.32. The minimum interaction-energy orientation of a dipole to an ion.

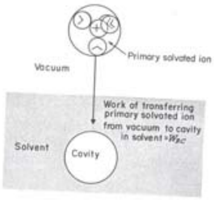


Fig. 2.34. Transfer of a primary solvated ion from vacuum into a cavity in the solvent.

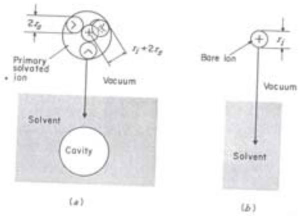


Fig. 2.35. The difference between the Born charging process in (a) the ion–dipole model of solvation in which a primary solvated ion of radius $r_i + 2r_s$ is transferred into the solvent (Section 2.3.3) and in (b) the nonstructural model of Born (*cf.* Section 2.2.5) in which a bare ion of radius r_i is involved.

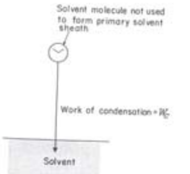


Fig. 2.37. The condensation of a water molecule left behind in vacuum because it was not used to form the primary solvent sheath.

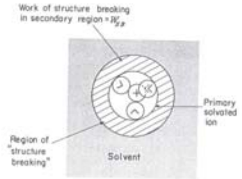


Fig. 2.36. The introduction of a primary solvated ion into the cavity causes disturbance to the structure of the solvent in the immediate vicinity of the solvated ion.

Now before the n+1 solvent molecules can orient around the ion in vacuum , the water cluster must firstly dissociate into n+1 separate molecules . We set W_D as representing the work done in this dissociation process .

Ion-dipole bonds are then made between n solvent molecules and the target ion . A primary solvation sheath is formed . We must determine the work W_{ID} done in this process . In short the interaction energy between an ion and a dipole must be evaluated .

Then, the ion along with its primary solvation sheath is transferred from vacuum into the cavity within the solvent . The work done in this case is equal to the Born enthalpy of solvation W_B . We note that the radius of the solvated ion R + $2r_s$ is used in the Born expression previously derived .

The introduction of the primary solvated ion into the cavity causes disturbance of the solvent structure in the immediate neighbourhood of the solvated ion . As a result of this a structure breaking work term W_{SB} must also be included .

Finally we may ask is the story complete . Has everything been accounted for ? The answer must be no . What about our extra solvent molecule left in vacuum ? This species must finally be transferred from vacuum into the solvent . The work done in this process is W_c , the work of condensation .

Now this thought experiment or thermodynamic cycle may appear to be quite complicated , but it really is the most simple one that we may devise . More complicated situations may be enumerated as done by Bockris and Saluja . Implicit in our simple model is that the coordination number and solvation number are the same . Also we proposed that only the ion- dipole interaction need be considered . Both of these restrictive assumptions may be removed and more elaborate models developed . We have also not really considered the region of secondary solvation (the second "in between" layer in any specific detail , we merely specify some work W_{SB} . Again this limitation may be dispensed with in a more detailed analysis .

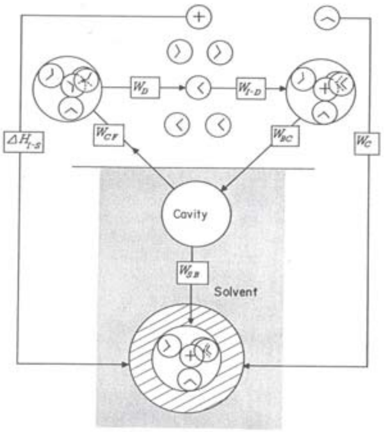


Fig. 2.38. How the total heat ΔH_{I-S} of ion–solvent interactions has been separated in a thought experiment into the various steps of cavity formation W_{CF}, cluster dissociation W_D, formation of primary solvated ion W_{I-D}, Born charging W_{BC}, structure breaking W_{SB}, and condensation, W_C.

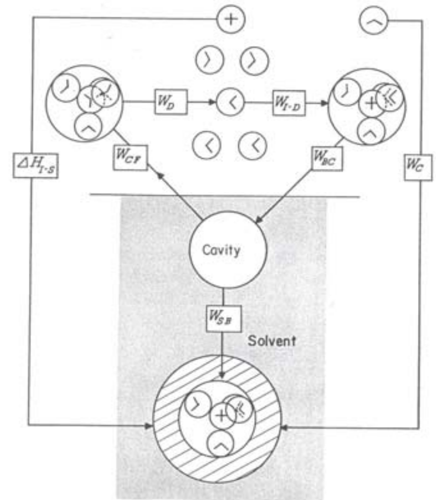


Fig. 2.38. How the total heat ΔH_{I-S} of ion–solvent interactions has been separated in a thought experiment into the various steps of cavity formation W_{CF}, cluster dissociation W_D, formation of primary solvated ion W_{I-D}, Born charging W_{BC}, structure breaking W_{SB}, and condensation, W_C.

We set the ball rolling by assuming that the primary solvation shell occupies a certain volume corresponding to n primary solvent molecules plus one more to make room for the bare ion . As a consequence of this supposition a volume corresponding to n+1 solvent molecules must be made available in the solvent for the immersion of a primary solvated ion . We therefore remove n+1 solvent molecules and transfer them to vacuum . A cavity is left in the solvent as a result of this process . We let W_{CF} denote the work done in cavity formation .
We assume of course that the size of an un-solvated ion is the same as that of a solvent molecule . This approximation is reasonable for some ions .

We can calculate the enthalpy of solvation by adding together all of the component work terms enumerated previously .

$$\begin{aligned}\Delta H_s &= W_{CF} + W_D + W_{ID} + W_B + W_{SB} + W_C \\ &= \left(W_{CF} + W_D + W_{SB} + W_C\right) + W_{ID} + W_B \\ &= W_\Sigma + W_{ID} + W_B\end{aligned}$$

Here we have differentiated between the electrostatic terms W_{ID} and W_B and the other work terms which have all been lumped together into a composite work term W_Σ . We now must evaluate all of these work terms . The electrostatic work terms W_B and W_{ID} are readily evaluated . The former quantity is obtained directly from the Born theory.

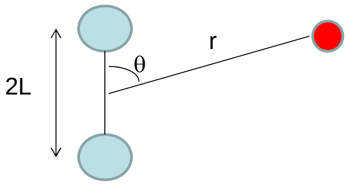
$$W_B = -\frac{N_A (z_i e)^2}{4\pi\varepsilon_0}\frac{1}{2(R+2r_s)}\left\{1 - \frac{1}{\varepsilon_r} - \frac{T}{\varepsilon_r^2}\left(\frac{\partial\varepsilon_r}{\partial T}\right)_p\right\}$$

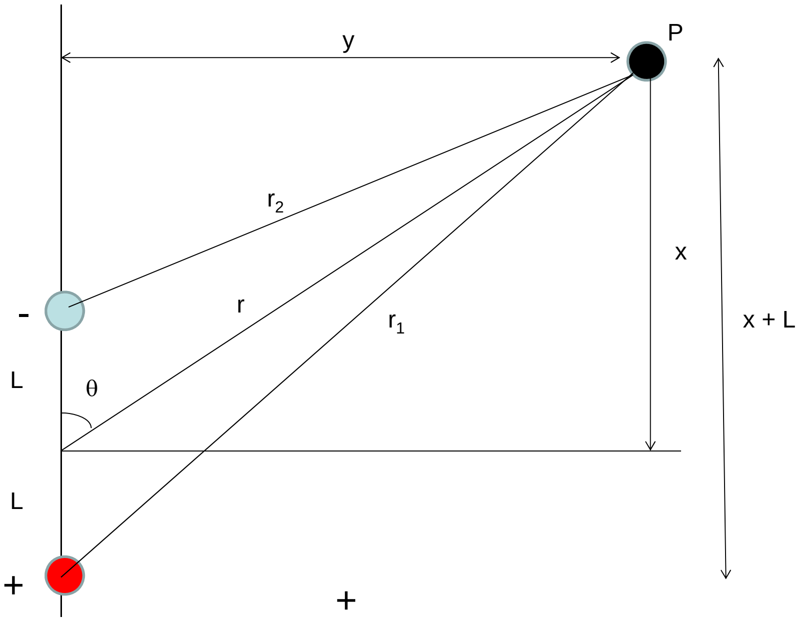
Here R denotes the unsolvated ionic radius and r_s denotes the radius of a water molecule . Hence the quantity R + $2r_s$ represents the radius of a primary solvated ion . In deriving this equation we again consider a Born type transfer process but in this case we are moving a primary solvated ion from vacuum into a cavity within the solvent . We also use the bulk dielectric constant of water in this expression since we assume for the sake of simplicity that the water structure outside the cavity is normal and undisturbed .

Ion-dipole work.

In the R denotes the unsolvated ionic radius and r_s denotes the radius of a water molecule . Hence the quantity R + $2r_s$ represents the radius of a primary solvated ion . In deriving this expression we again consider a Born type transfer process but in this case we are moving a primary solvated ion from vacuum into a cavity within the solvent . We also use the bulk dielectric constant of water in this expression since we assume for the sake of simplicity that the water structure outside the cavity is normal and undisturbed .

The other electrostatic term is concerned with the interaction between the ion and the n free solvent dipoles in vacuum to form the primary solvated ion in vacuum . This is a standard problem in electrostatics and the mathematical details are not difficult to follow . Our problem is to calculate the interaction energy between a dipole and an ion placed at a distance r from the dipole center We assume that the dipole is orientated at an angle θ to the line joining the centers of the ion and the dipole . We assume that the dipole is of length 2L .





Now the ion-dipole interaction energy U_{ID} is equal to the product of the ionic charge $q_i = z_i e$ and the electrostatic potential y(r) due to the dipole . We recall from basic electrostatic theory that the potential due to an assembly of charges is given by the sum of the potentials due to each charge constituting the assembly . Since the dipole consists of the charges + q and - q which are located at distances r_1 and r_2 from the point P defining the position of the ion (see figure on previous slide) , hence the total electrostatic potential is given by :

$$\psi(r) = \frac{q}{4\pi\varepsilon_0}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \qquad (1)$$

From basic geometrical considerations we note that :

$$r_1^2 = (x+L)^2 + y^2$$
$$r_1 = \sqrt{(x+L)^2 + y^2} = \sqrt{x^2 + y^2 + L^2 + 2xL} \qquad (2)$$

Also we note that

$$x^2 + y^2 = r^2 \text{ and } x = r\cos\theta$$

. Hence eqn.2 reduces to

$$r_1 = \sqrt{r^2 + L^2 + 2rL\cos\theta} = r\sqrt{1 + \left(\frac{L}{r}\right)^2 + \frac{2L}{r}\cos\theta} \qquad (3)$$

Inverting this expression we obtain

$$\frac{1}{r_1} = \frac{1}{r}\left\{1 + \left(\frac{L}{r}\right)^2 + \frac{2L}{r}\cos\theta\right\}^{-1/2} \qquad (4)$$

We now make the point dipole approximation and assume that P is located very far away from the dipole and so r » 2L . We can then expand the rhs of eqn.4 using the Binomial theorem to obtain :

$$\frac{r}{r_1} \cong 1 - \frac{1}{2}\left\{\frac{L^2}{r^2} + \frac{2L}{r}\cos\theta\right\} + \frac{3}{8}\left\{\frac{L^2}{r^2} + \frac{2L}{r}\cos\theta\right\}^2 - \frac{15}{16}\left\{\frac{L^2}{r^2} + \frac{2L}{r}\cos\theta\right\}^3 + ... \qquad (5)$$

If we now neglect terms of order higher than L^2/r^2 we obtain :

$$\frac{1}{r_1} \cong \frac{1}{r} - \frac{L}{r^2}\cos\theta + \frac{L^2}{2r^3}\left(3\cos^2\theta - 1\right) \quad (6)$$

In a similar manner we may show that :

$$\frac{1}{r_2} = \frac{1}{r}\left\{1 + \left(\frac{L}{r}\right)^2 - \frac{2L}{r}\cos\theta\right\}^{-1/2}$$
$$\cong \frac{1}{r} + \frac{L}{r^2}\cos\theta + \frac{L^2}{2r^3}\left\{3\cos^2\theta - 1\right\} \quad (7)$$

If we substitute eqn.6 and eqn.7 into eqn.1 we obtain the following expression for the electrostatic potential at the ion due to the presence of the dipole :

$$\psi(r,\theta) = -\frac{2Lq}{4\pi\varepsilon_0 r^2}\cos\theta = -\frac{p}{4\pi\varepsilon_0 r^2}\cos\theta \quad (8)$$

In the latter p = 2Lq denotes the dipole moment . We can replace the distance r by the sum R + r_s to obtain the following expression.

$$\psi = -\frac{p}{4\pi\varepsilon_0 (R + r_s)^2}\cos\theta \quad (9)$$

We note from eqn.9 that the potential due to a dipole falls off approximately as the square of the distance r, whereas the potential due to a single point charge varies only as r^{-1} . This observation is readily explained . The difference in the behavior of the potential at large distances arises from the fact that the charges in a dipole appear close together for an observer located at some distance away from the dipole and their fields cancel more and more as the distance r increases . We also note that the electrostatic potential also depends on the orientation angle θ .

It is clear for maximum interaction we set θ = π and so cos θ = 1 and eqn. 9 reduces to

$$\psi = -\frac{z_i e p}{4\pi\varepsilon_0 (R + r_s)^2} \quad (10)$$

We assume that n solvent molecules surround the ion in the primary hydration sheath . Hence per mole of ions the ion-dipole work term is given by :

$$W_{ID} = -\frac{N_A}{4\pi\varepsilon_0}\frac{n z_i e p}{(R + r_s)^2} \quad (11)$$

This result may also be obtained in a mathematically more rigorous manner which we will not describe here but involves Legendre Polynomials which are only suitable for real black belt electrochemists at the Graduate level!!!

We can also look at more complex electrostatic interactions. For example we can look at the ion/water Quadrupole interaction.
The latter may be calculated using the methods of electrostatics and the following expression may be derived.

$$W_{IQ} = -\frac{N_A n z_i e \mu}{4\pi\varepsilon_0 (r_i + r_s)^2} \pm \frac{N_A n z_i e p}{2(4\pi\varepsilon_0)(r_i + r_s)^3}$$

In latter expression μ represents the Dipole moment and p is the quadrupole moment and n is the coordination number.
For water.
The positive sign in second term on rhs corresponds to cations and
the negative sign to anions. Hence in a more
Sophisticated nalaysis we should replace
W_{ID} by W_{IQ}.

Ion-induced Dipole work

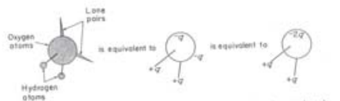


Fig. 2.45. The electrical equivalence between a water molecule and a quadrupole.

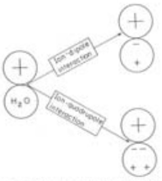


Fig. 2.46. Improvement in the calculation of the ion–water molecule interactions by altering the model of the water molecule from a dipole to a quadrupole.

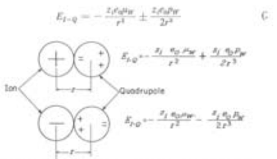
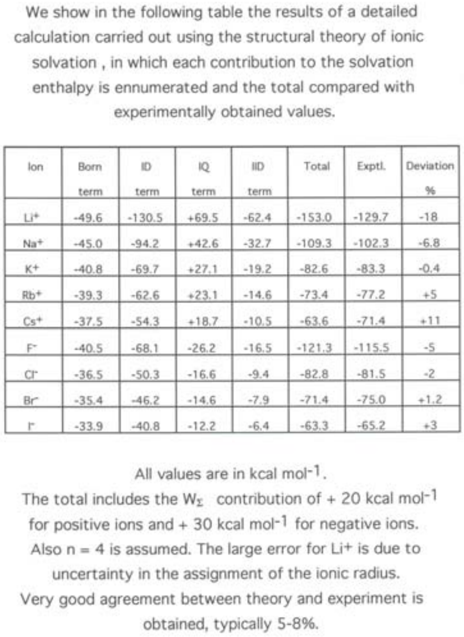


Fig. 2.47. The symmetrical orientation of a quadrupole to an ion.

We also may have to account for ion/induced
dipole interaction work W_{IID} .
This term arises from the fact that when The water molecule is in contact with the ion, the electric field of the ion tends to distort the charge distribution (quantified in terms of deformation polarizability α in the water molecule and so *induces* a dipole moment on the water molecule.

$$W_{IID} = -\frac{N_A}{\left(4\pi\varepsilon_0\right)^2}\frac{n\alpha\left(z_i e\right)^2}{2\left(r_i + r_s\right)^4}$$



We show in the following table the results of a detailed calculation carried out using the structural theory of ionic solvation , in which each contribution to the solvation enthalpy is ennumerated and the total compared with experimentally obtained values.

Ion	Born term	ID term	IQ term	IID term	Total	Exptl.	Deviation %
Li^+	-49.6	-130.5	+69.5	-62.4	-153.0	-129.7	-18
Na^+	-45.0	-94.2	+42.6	-32.7	-109.3	-102.3	-6.8
K^+	-40.8	-69.7	+27.1	-19.2	-82.6	-83.3	-0.4
Rb^+	-39.3	-62.6	+23.1	-14.6	-73.4	-77.2	+5
Cs^+	-37.5	-54.3	+18.7	-10.5	-63.6	-71.4	+11
F^-	-40.5	-68.1	-26.2	-16.5	-121.3	-115.5	-5
Cl^-	-36.5	-50.3	-16.6	-9.4	-82.8	-81.5	-2
Br^-	-35.4	-46.2	-14.6	-7.9	-71.4	-75.0	+1.2
I^-	-33.9	-40.8	-12.2	-6.4	-63.3	-65.2	+3

All values are in kcal mol^{-1}.
The total includes the W_{Σ} contribution of + 20 kcal mol^{-1} for positive ions and + 30 kcal mol^{-1} for negative ions.
Also n = 4 is assumed. The large error for Li^+ is due to uncertainty in the assignment of the ionic radius.
Very good agreement between theory and experiment is obtained, typically 5-8%.