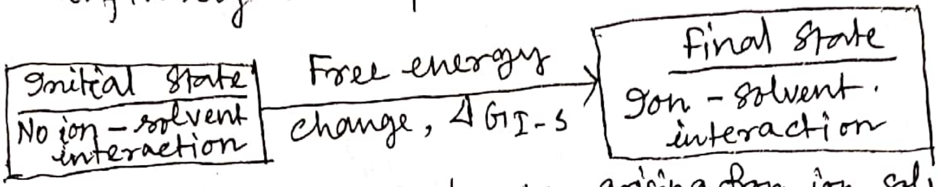
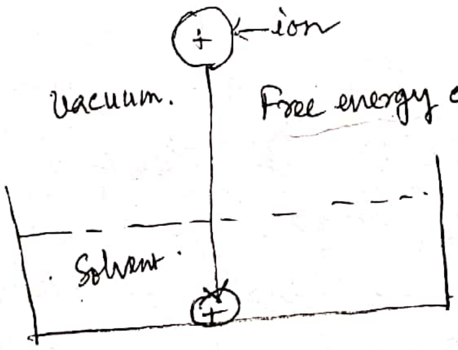
~~To~~ Theory of solvent interaction

Ion - Solvent interaction

Let us consider a problem of the free-energy change for transfer of ions from vacuum to solution. The initial state, therefore, is that of ions in vacuum at an infinitely low pressure.



The free-energy change arising from ion-solvent interactions.



Free energy change = free energy of ion - Solvent interactions

ΔG_{I-S} per mole of ion $= N_A \times$ reversible work done to transfer an ion from vacuum into solvent.

An example of a very crude and approximate model for ion-solvent interactions is that suggested by Born in 1920. In the Born model, the ~~assumptions~~ main features are

① an ion is viewed as a rigid sphere (of radius r_i) bearing ~~a~~ a charge $z_i e_0$ (e_0 is the electronic charge). ~~Therefore, only the charge on the ion is responsible~~ for ~~ion-solvent interaction~~

② The solvent is a structureless dielectric ~~continuum~~ continuum having dielectric constant ϵ.

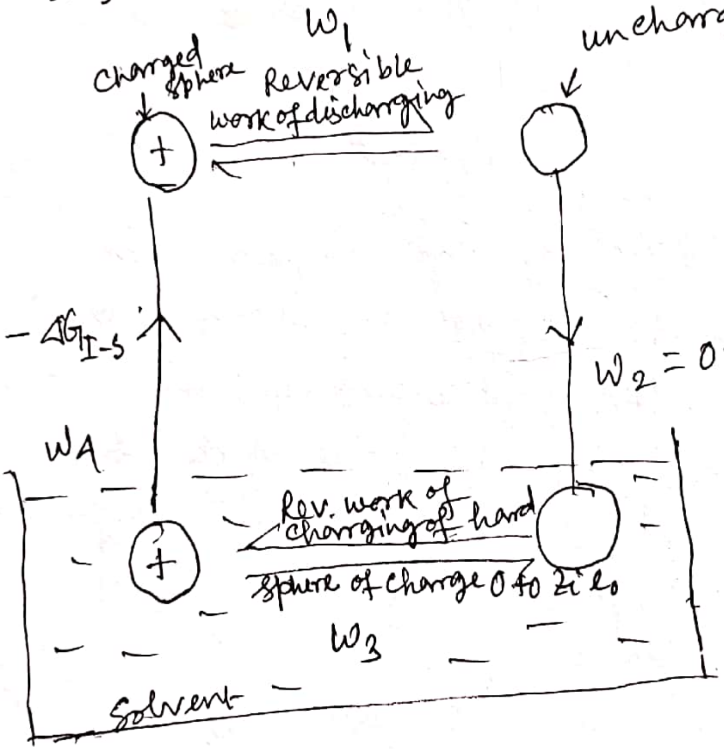
③ Only the charge on the ion is responsible for ion-solvent interaction.

Therefore, the present problem of ion-solvent interaction can be assumed ~~no~~ as the work done in transferring a charged sphere from vacuum into a continuum.

By considering a charged sphere equivalent to an ion, the Born model is assuming that it is only the charge on the ion (or charged sphere) that is responsible for ion - solvent interactions. The interactions between the solvent and the ion are considered to be solely electrostatic in origin.

The Born model suggests a simple thought process for calculating the free energy ΔG_{I-S} of ion - solvent interactions i.e. the work of transferring an ion from vacuum into the solvent. A thermodynamic cycle ~~was used which obey of~~ where law of conservation of energy is maintained ~~was~~ was used. If we starts with an ion in vacuum and then goes through a hypothetical cycle of changes, ending with the starting condition (i.e. ion in vacuum), then algebraic sum of all the energies involved in the various steps must be zero. The particular cycle that will be used is the following: (1) The ion (or ~~chor~~ charged sphere) is first considered in vacuum and the work W_1 of stripping of its charge z_ie_0 is computed (2) This uncharged sphere is slipped into the solvent; this process ~~will~~ will involve no work, i.e. $W_2 = 0$ because the interactional work is assumed to arise from the charge on the ion. (3) The charge on the sphere inside the solvent is restored to the full value z_ie_0 and the charge work W_3 is computed.

4) Finally, the ion is transferred from the solvent to vacuum. Since this transfer process is opposite to that involved ~~was~~ in the definition of the free energy ΔG_{I-S} of ion-solvent interactions, the work W_4 associated with this last step of the cycle i.e. the transfer of ion from the solvent to vacuum yields $-\Delta G_{I-S}$



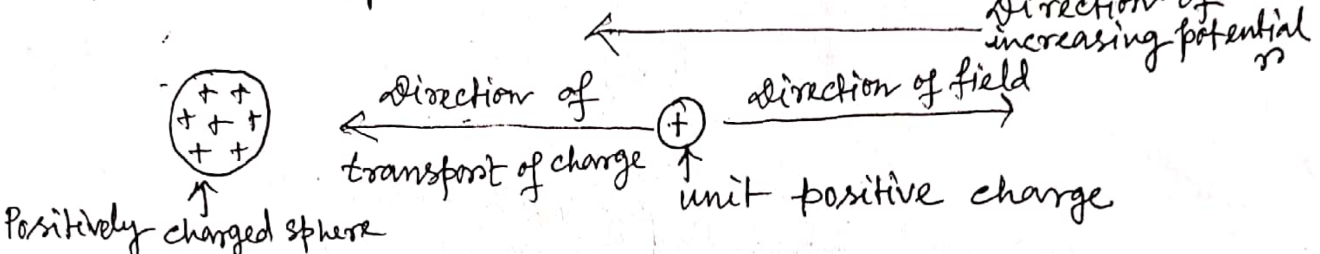
Now, if the algebraic sum of the work terms associated with the cycle is set equal to ~~zero~~ zero

$$W_1 + W_2 + W_3 + W_4 = 0$$

or
$$\underset{(W_1)}{\text{work of discharging ion in vacuum}} + 0 + \underset{(W_3)}{\text{work of charging ion in solvent}} - \Delta G_{I-S} = 0$$

or,
$$\Delta G_{I-S} = W_1 + W_3$$
$$= \text{Work of discharging in vacuum} + \text{Work of charging ion in solvent.}$$

The electrostatic potential ψ_r, at a distance r from a charged sphere is the work done to transport a unit positive charge from infinity up to a distance r from the sphere.



Total work $= \int_0^{z_i e_0} \psi_r \, dq$.

The sign of the potential ψ_r will be determined as follows. Suppose the sphere is charged positively. Then it exerts a repulsive force on the unit positive charge, and the potential ψ_r, the work which has to be done by an external agency in transporting the unit positive charge i.e. overcoming the repulsive interaction, will be taken to be positive. But the electric force of the charged ~~species~~ sphere on the unit positive charge i.e. the field, acts in the direction opposite to that in which the charge is being moved. Since both the field and the direction of transport are vectors (the pdt. of two vectors A & B is AB $\cos\theta$. Here vectors are in opposite directions $\theta = \pi$, & $\cos\theta = -1$ $\therefore$ the pdt. is $-AB$) and since the vectors point in opposite ways, their product is negative.

$$\therefore \psi_r = -\int_{\infty}^{r} F \, dx = -\int_{\infty}^{r} \frac{q.1}{\epsilon x^2} \, dx .$$

or, $\Psi_r = \left(\frac{q}{\epsilon x}\right)_{\infty}^{r}$

$= \frac{q}{\epsilon r}$

$\therefore \Psi_r = \frac{q}{\epsilon r}$.

If, therefore, one starts with an uncharged sphere of radius r_i in a vacuum and slowly builds up the charge from zero to a final value $z_i e_0$, then the total work consists of all the little elements of work dw i.e.

$$W_{charging} = \int dw = \int_0^{z_i e_0} \Psi_r \, dq$$

$$= \int_0^{z_i e_0} \frac{q}{\epsilon r} \, dq.$$

Obviously, the work of discharging a charged sphere in vacuum is the negative of the charging work because, in the discharging process one is taking away charge from a charged sphere

$$W_{discharge} = \int_{z_i e_0}^{0} \frac{q}{r} \, dq.$$

$$\therefore \Delta G_{I-S} = \int_0^{z_i e_0} \frac{q}{\epsilon r} \, dq + \int_{z_i e_0}^{0} \frac{q}{r} \, dq.$$

$$= \left(\frac{q^2}{2\epsilon r}\right)_0^{z_i e_0} + \left(\frac{q^2}{2r}\right)_{z_i e_0}^{0}$$

$$= \frac{z_i^2 e_0^2}{2\epsilon r} - \frac{z_i^2 e_0^2}{2r}.$$

$$= -\frac{z_i^2 e_0^2}{2r}\left(1 - \frac{1}{\epsilon}\right)$$

$$\therefore \boxed{\Delta G_{I-S} \text{ per mole of ion} = -\frac{N_A z_i^2 e_0^2}{2r}\left(1-\frac{1}{\epsilon}\right)}$$

This is known as Born equation.

$$\Delta S_{I-S} = -\left[\frac{\partial(\Delta G_{I-S})}{\partial T}\right]_P$$

$$= \frac{N_A z_i^2 e_0^2}{2r}\left(\frac{1}{\epsilon^2}\right)\left(\frac{\partial \epsilon}{\partial T}\right)$$

$$\therefore \boxed{\Delta S_{I-S} = \frac{N_A z_i^2 e_0^2}{2r}\,\frac{1}{\epsilon^2}\left(\frac{\partial \epsilon}{\partial T}\right)_P}$$

$$\Delta H_{IS} = \Delta G_{I-S} + T\,\Delta S_{I-S}$$

$$= -\frac{N_A z_i^2 e_0^2}{2r}\left(1-\frac{1}{\epsilon}\right) + T.\frac{N_A z_i^2 e_0^2}{2r}\left(\frac{1}{\epsilon^2}\right)\left(\frac{\partial \epsilon}{\partial T}\right)_P$$

$$\text{or, } \boxed{\Delta H_{I-S} = -\frac{N_A z_i^2 e_0^2}{2r}\left[1-\frac{1}{\epsilon}-\frac{T}{\epsilon^2}\left(\frac{\partial \epsilon}{\partial T}\right)_P\right]}$$

If $\epsilon > 1$, $\frac{1}{\epsilon}$ = fraction.

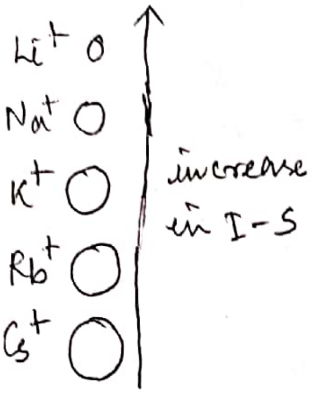
$\therefore \left(1-\frac{1}{\epsilon}\right) = +ve$

$\therefore \Delta G_{I-S} = -ve$ quantity

It's significance is that ion prefers solvent compared to vacuum.

If z_i is large (provided size is same) greater the valency, greater is the $-ve$ value of ΔG. So greater stability in solvent.

Na^+
Ca^{2+} $\downarrow$ increases in I-S. Charge density on ion increases on the surface.
Al^{3+}



Born model gives ~50% higher value than experimental value.

Problems in Born model and solutions.

1) Proper dielectric const ϵ_{bulk} should be used instead of ϵ.
In presence of ion, solvent molecules are oriented. We take local dielectric constant around the ion instead of taking bulk dielectric constant

2) Radius.
Crystallographic radius is the radius of bare ion which is taken in Born equation. But while interaction occurs, ions are surrounded by solvent ions. There is a bulk unit.
We should take the radius of solvated ion instead of bare ion. Then the radius will be increased. So ΔG_{I-S} for calculation will reduce and reach near the ΔG_{I-S} actual.

3) Structure consideration
Consideration of different interactions present in ion will give exact value of ΔG_{I-S}.

All these problems were modified in Eley Evans model.