

Ionic Bonds

The energy of ionic bonds can be related by Coulomb's law to the work required to bring two charges separated by an infinite distance to some finite distance of separation, r . For two molecules, A and B:

$$F = \frac{q_1 q_2}{Dr^2}$$

Where $q_1 = Z_A e$ which is equal to the product of the number of charges on A and the charge of one electron, e . Similarly, $q_2 = Z_B e$ and r is the distance between the centers of charge and D is the dielectric constant.

Ionic

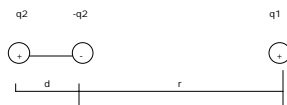
Instead of work the relation of the charges may be expressed as the potential energy of the system:

$$V = \frac{q_1 q_2}{Dr}$$

In the case of Na^+Cl^- , and given the distance of separation of the Na^+ and Cl^- ions in a crystal and the charge of an electron and assuming that $D = 1$ in the crystal, a value for the bond energy of 120 kcal/mole is obtained.

Ion - Dipole

Covalent bonds may have a partial ionic nature due to unequal electronegativity of the joined atoms. These dipoles may interact with ions or with other dipoles. If a positive ion interacts with a simple linear dipole, the situation exists:



Where d is the distance of separation of the atom and the dipole and r is the distance the ion is separated from the dipole.

Ion - Dipole

Then

$$V = \frac{q_1 \mu}{Dr^2}$$

It is observed that the energy of interaction is proportional to a constant for the covalent molecule, its dipole moment, and the charge of the ion. It is inversely proportional to the dielectric constant and to the distance of separation squared.

Dipole-Dipole Interactions

When two dipoles approach each other they may repel or attract depending on the arrangement of charges. In general, if there is freedom of movement, the forces will align to become attractive. By substituting a dipole for an ion it can be shown that:

$$V = \frac{\mu_1 \mu_2}{Dr^3}$$

Hydrogen Bonds

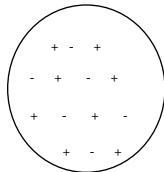
In proteins, as in water, the most important dipole-dipole interactions involve molecules that contain hydrogen.

This leads to a discussion of the hydrogen bond which is a special form of the dipole-dipole interaction.

The hydrogen atom consists of only a single proton and an electron.

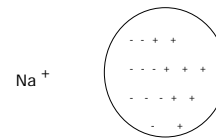
Induced Dipoles

The electron clouds around some molecules are so nearly symmetrical that no dipole moment exist. The charge distribution around such a molecule can be represented as



Induced Dipoles

If a charged group is placed near the molecule a change in the charge distribution may be induced and thus a dipole moment may be caused to exist such as:



Induced Dipoles

The interaction of the ion with the individual dipole would then be:

$$V = \frac{\alpha q}{D^2 r^4}$$

Such interactions are very dependent upon the distance of separation and also upon the dipole moment of the medium.

Dipole Induced Dipoles

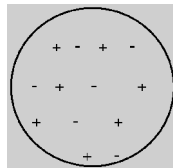
A permanent dipole also has a charge that can induce an attractive electrical interaction in nearby molecules. The strength of the interaction can be shown to be equal to:

$$V = \frac{-2\alpha q^2}{D^2 r^6}$$

These forces are operative over only very short distances.

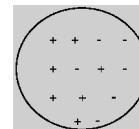
London Forces

For a symmetrical molecule there will be no permanent dipole. The distribution of charges will look something like:



London

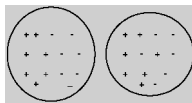
This is an average situation. At any given instant, the distribution may be less evenly distributed:



This is a transient dipole

Induced Dipole

If this transient dipole is near to another molecule, it may induce a dipole moment.



If they are close enough, they will reinforce each other and become relatively stable.

Bonds

Kind	Form	Kcal
Ion	$V = \frac{qq_2}{Dr}$	10-200
Ion-dipole	$V = -\frac{q\mu}{Dr^2}$	2 - 10
Dipole-Dipole	$V = -\frac{\mu_1\mu_2}{Dr^3}$	0 - 1 1 - 10

Bonds

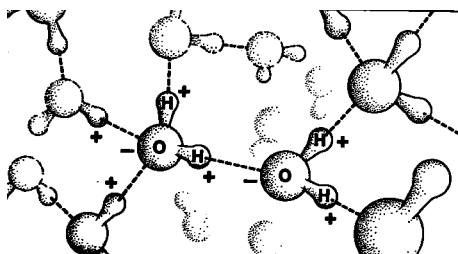
Kind	Form
Ion-Induced	$V = -\frac{\alpha q^2}{D^2 r^4}$
Transient-Induced	$V = -\frac{2\alpha q^2}{D^2 r^6}$

Energy of Transfer

Group	H	G
CH ₄ (benzene) - CH ₄ (H ₂ O)	-2.8	+2.6
CH ₄ (ether) - CH ₄ (H ₂ O)	-2.4	+3.3
CH ₄ (CCl ₄) - CH ₄ (H ₂ O)	-2.5	+2.9

What is the entropy change? Is the system becoming more or less ordered?

Structure of Water



Solvation

U_{12} is the attraction of the solute for the solvent
 U_{11} is the attraction of the solvent for the solvent
 U_{22} is the attraction of the solute for the solute

$$U_{Net} = U_{12} - \frac{1}{2}U_{11} - \frac{1}{2}U_{22}$$

If U_{net} is negative, solvation occurs

Solvation

Solvation should not be considered in terms of permanent bonding of a solute by a solvent.

A solvent molecule merely stays longer near a solute than it would in $U_{\text{net}} = 0$

The difference may be 10^{-9} S instead of 10^{-12} S

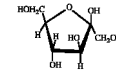
If $U_{\text{net}} > 0$ there is negative solvation

Types of Solutes

Ions or ionic groups Na^+ Cl^-

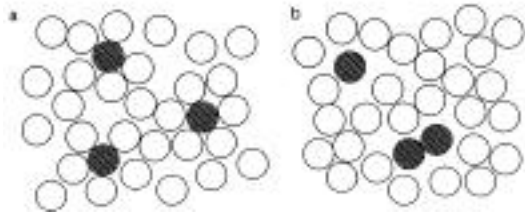
Strong dipoles $\text{C}=\text{O}$ NH

Somewhat polar groups

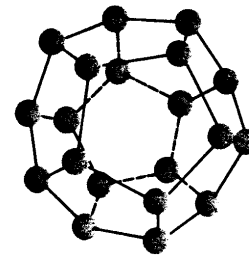


Nonpolar groups $\text{C}_{18}\text{H}_{36}$

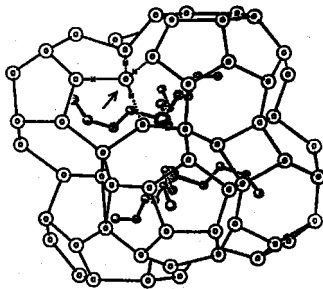
Solvation



Clathrate Structure



Hydrophobic in Water



Hydrophobic Entropy

The entropy change from the ordering of the hydrophobic groups is not as great as the change that results from the ordering of water molecules. This causes the hydrophobic groups to associate away from the aqueous phase.

Most bonds are less stable at higher than lower temperatures. For hydrophobic bonds, the entropy in the bonded state is higher. The higher the temperature, the more favorable the entropy difference.

Hydrophobic bonds strengthen a temperature increases.

Temperature Effects

