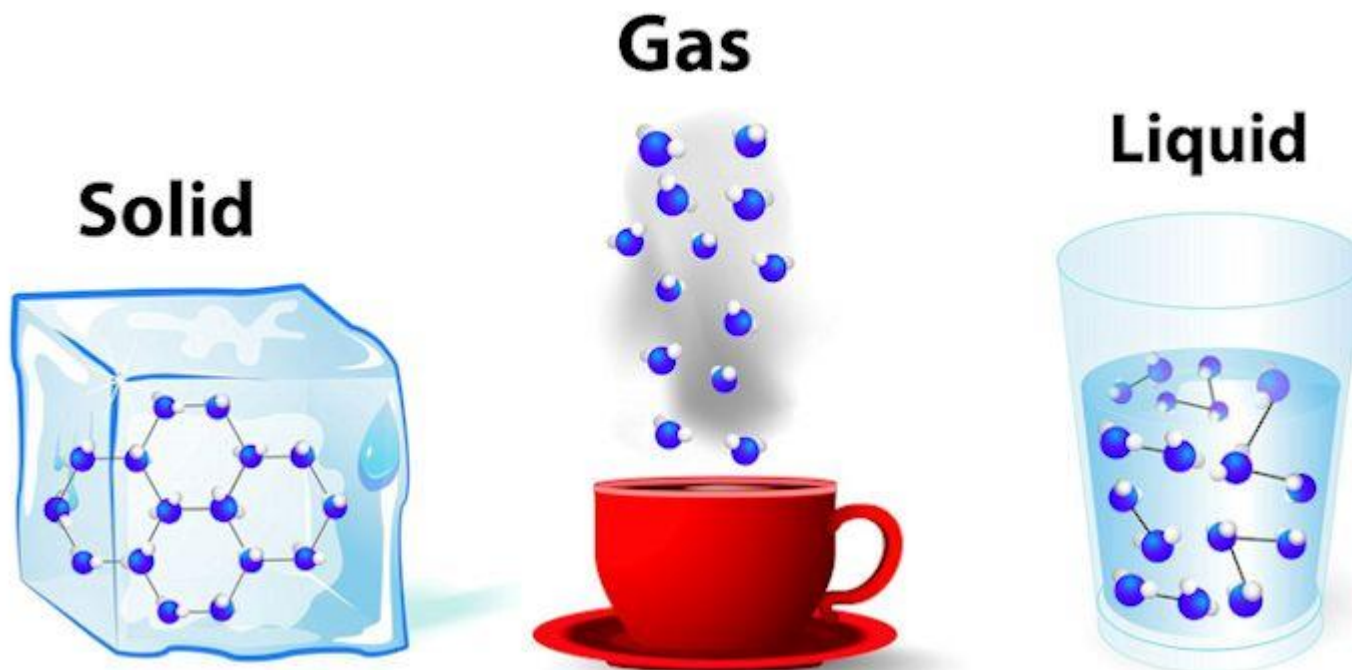


# State of matter



**Molecules to exist as aggregates in gases, liquids and solids, *intermolecular forces must exist.*** Like *intramolecular* bonding energies found in covalent bonds, *intermolecular* bonding is largely governed by electron orbital interactions. Cohesion, or the attraction of like molecules, and adhesion, or the attraction of unlike molecules, are manifestations of intermolecular forces.

Repulsion is a reaction between two molecules that forces them apart. For molecules to interact, these forces must be balanced in an energetically favored arrangement. Briefly, the term energetically favored is used to describe the intermolecular distances and intramolecular conformations where the energy of the interaction is maximized on the basis of the balancing of attractive and repulsive forces. At this point, if the molecules are moved slightly in any direction, the stability of the interaction will change by either a decrease in attraction (when moving the molecules away from one another) or an increase in repulsion (when moving the molecules toward one another).

## **Repulsive and attractive forces**

**When molecules interact, both repulsive and attractive forces operate.**

**As 2 atoms or molecules are brought closer together, the opposite charges and binding forces in the 2 molecules are closer together than the similar charges and forces, causing the molecules to attract one another.**

**The negatively charged electron clouds of the molecules largely govern the balance (equilibrium) of forces between the 2 molecules. When the molecules are brought so close that the outer charge clouds touch, they repel each other like rigid elastic bodies.**

Thus, attractive are necessary for molecules to cohere, whereas repulsive forces act to prevent the molecules from interpenetrating each other.

Moelwyn Hughes pointed to analogy between human behavior and molecular phenomena: Just as the actions of humans are often influenced by a conflict of loyalties, so too is molecular behavior governed by attractive and repulsive forces.

Repulsion is due to the interpenetration of the electronic clouds of molecules and increases Exponentially with a decrease in distance between the molecules. At a certain equilibrium distance, about  $3 \text{ to } 4 \times 10^{-8}$  (3-4 angstroms), the repulsive and attractive forces are equal.

**At this position, the potential of the 2 molecules is a minimum and the system is most stable.**

This principle of minimum potential energy applies not only to molecules, but also to atoms and to large objects as well.

The effect of repulsion on the intermolecular three-dimensional structure of a molecule is well illustrated in considering the conformation of the two terminal methyl groups in butane, where they are energetically favored in the *trans* conformation because of a minimization of the repulsive forces. It is important to note that the arrangement of the atoms in a particular stereoisomer gives the *configuration* of a molecule. On the other hand, *conformation* refers to the different arrangements of atoms resulting from rotations about single bonds.

## Van der Waals Forces

Van der Waals forces relate to nonionic interactions between molecules, yet they involve charge–charge interactions .

numerous reactions like nucleophilic substitutions are introduced where one molecule may carry a partial positive charge and be attractive for interaction with a partially negatively charged nucleophilic reactant. These partial charges can be permanent or be induced by neighboring groups, and they reflect the polarity of the molecule.

The presence of these polarities in molecules can be similar to those observed with a magnet. For example, dipolar molecules frequently tend to align themselves with their neighbors so that the negative pole of one molecule points toward the positive pole of the next. Thus, large groups of molecules may be associated through weak attractions known as dipole–dipole or Keesom forces. Permanent dipoles are capable of inducing an electric dipole in nonpolar molecules (which are easily polarizable) to produce dipole-induced dipole, or Debye, interactions, and nonpolar molecules can induce polarity in one another by induced dipole-induced dipole, or London, attractions.



The dispersion or London force is sufficient to bring about the condensation of nonpolar gas molecules so as to form liquids and solids when molecules are brought quite close to one another. In all three types of van der Waals forces, the potential energy of attraction varies inversely with the distance of separation,  $r$ , raised to the sixth power,  $r^6$ . The potential energy of repulsion changes more rapidly with distance. This accounts for the potential energy minimum and the resultant equilibrium distance of separation,  $r_e$ .

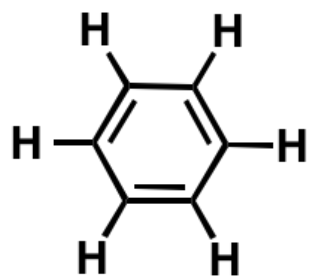
**Table 2-1 Intermolecular Forces and Valence Bonds**

<b>Bond Type</b>	<b>Bond Energy (approximately) (kcal/mole)</b>
Van der Waals forces and other intermolecular attractions	
Dipole-dipole interaction, orientation effect, or Keesom force	
Dipole-induced dipole interaction, induction effect, or Debye force	1-10
Induced dipole-induced dipole interaction, dispersion effect, or London force	
Ion-dipole interaction	
Hydrogen bonds: $\text{O}-\text{H} \cdots \text{O}$	6
$\text{C}-\text{H} \cdots \text{O}$	2-3
$\text{O}-\text{H} \cdots \text{N}$	4-7
$\text{N}-\text{H} \cdots \text{O}$	2-3
$\text{F}-\text{H} \cdots \text{F}$	7
Primary valence bonds	
Electrovalent, ionic, heteropolar	100-200
Covalent, homopolar	50-150

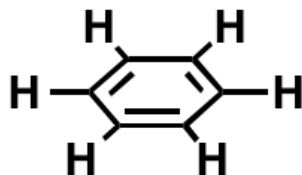
## Orbital overlap

An important *dipole–dipole* force is the interaction between pi-electron orbitals in systems. For example, aromatic–aromatic interactions can occur when the double-bonded pi-orbitals from the two rings overlap (Fig. 2-3).<sup>2</sup> Aromatic rings are dipolar in nature, having a partial negative charge in the pi-orbital electron cloud above and below the ring and partial positive charges residing at the equatorial hydrogens, as illustrated in Figure

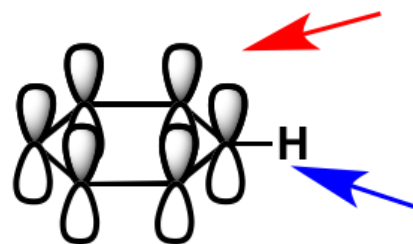
### How p Orbitals Contribute to Aromaticity in Benzene



benzene  
(top view)



benzene  
(side view)

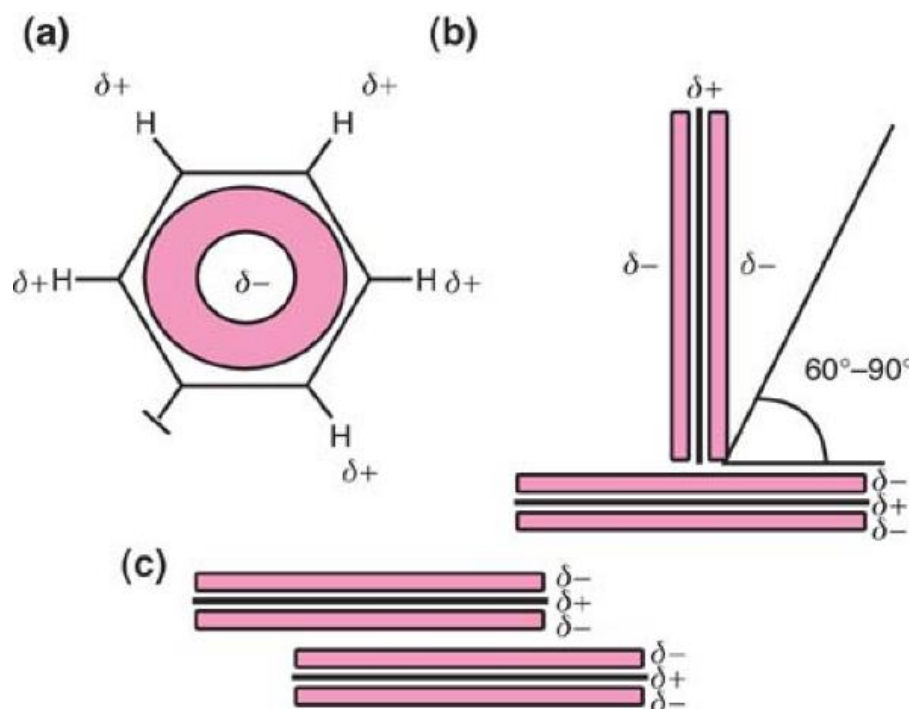


benzene  
(showing p orbitals)

Each p orbital  
contains one electron  
(six total  $\pi$  electrons)

Note that C-H bonds  
are at 90° to the  
pi system  
(only one C-H  
shown, for clarity)

Therefore, a dipole–dipole interaction can occur between two aromatic molecules. In fact, at certain geometries aromatic–aromatic interaction can stabilize *inter*- and/or *intramolecular* interactions with the highest energy interactions occurring when the rings are nearly perpendicular to one another

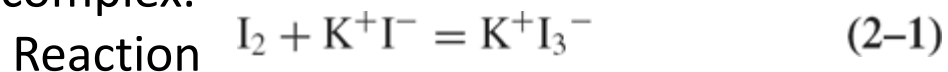


Aromatic stacking can also occur in the solid state, and was first identified as a stabilizing force in the structure of small organic crystals.

### ***Ion–Dipole and Ion-Induced Dipole Forces***

In addition to the dipolar interactions known as van der Waals forces, other attractions occur between polar or nonpolar molecules and ions. These types of interactions account in part for the solubility of ionic crystalline substances in water; the cation, for example, attracts the relatively negative oxygen atom of water and the anion attracts the hydrogen atoms of the dipolar water molecules.

Ion-induced dipole forces are presumably involved in the formation of the iodide complex.



accounts for the solubility of iodine in a solution of potassium iodide. This effect can clearly influence the solubility of a solute and may be important in the dissolution process.

## ***Ion–Ion Interactions***

Another important interaction that involves charge is the ion–ion interaction. An ionic, electrovalent bond between two counter ions is the strongest bonding interaction and can persist over the longest distance. However, weaker ion–ion interactions, in particular salt formations, exist and influence pharmaceutical systems.

Ion–ion interactions are normally viewed from the standpoint of attractive forces: A cation on one compound will interact with an anion on another compound, giving rise to an *intermolecular* association. Ion–ion interactions can also be repulsive when two ions of like charge are brought closely together. The repulsion between the like charges arises from electron cloud overlap, which causes the *intermolecular* distances to increase, resulting in an energetically favored dispersion of the molecules. Clearly, the strength of ion–ion interactions will vary according to the balancing of attractive and repulsive forces between the cation- and anion-containing species. It is important to keep in mind that ion–ion interactions are considerably stronger than many of the forces described in this section and can even be stronger than covalent bonding when an ionic bond is formed.