

The Covalent Bond

To gain a deeper understanding of the covalent bond, or shared electron bond, let's look at a simple example, the hydrogen molecule:



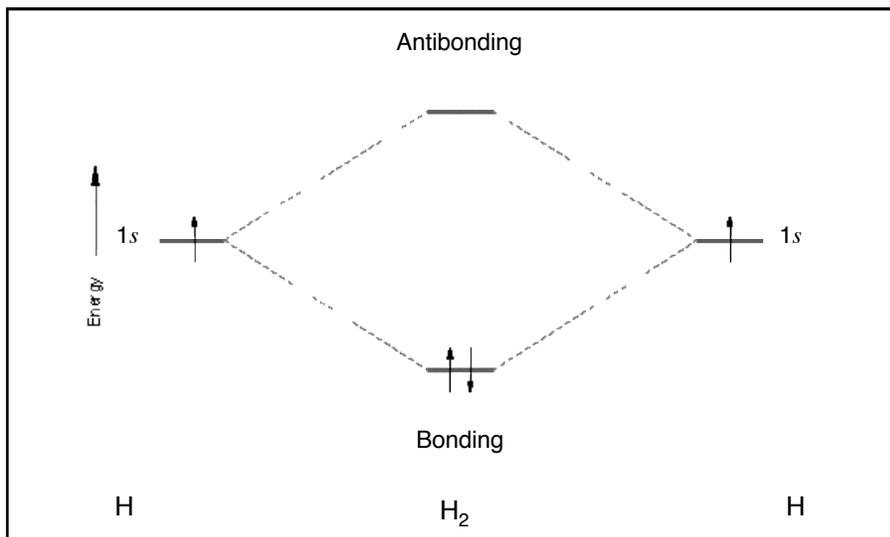
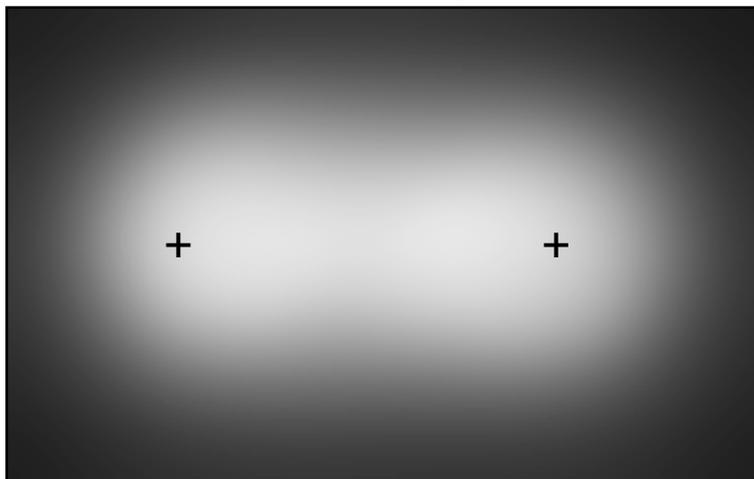
The two nuclei of the hydrogen molecule are strongly held together, about 0.74 \AA apart, by their covalent bond. This bond consists of the electrostatic attraction for the nuclei by the shared electrons (balancing the mutual repulsion of the protons). The bond energy (the energy required to split H_2 into H and H) is 432 kJ mole^{-1} .

The bond is created by overlap of the two $1s$ orbitals. As pictured at right the electrons occupy the space around both nuclei with their motion largely concentrated in the space between the nuclei.

The electron waves resonate between the two nuclei. Before bonding, there were two $1s$ atomic orbitals, and after bonding there will be two **molecular orbitals**.

The bond exists when the electron pair is located in the one of lower energy of these two molecular orbitals, a *symmetric, bonding* orbital. The other molecular orbital as shown in the *molecular orbital diagram* of H_2 at right

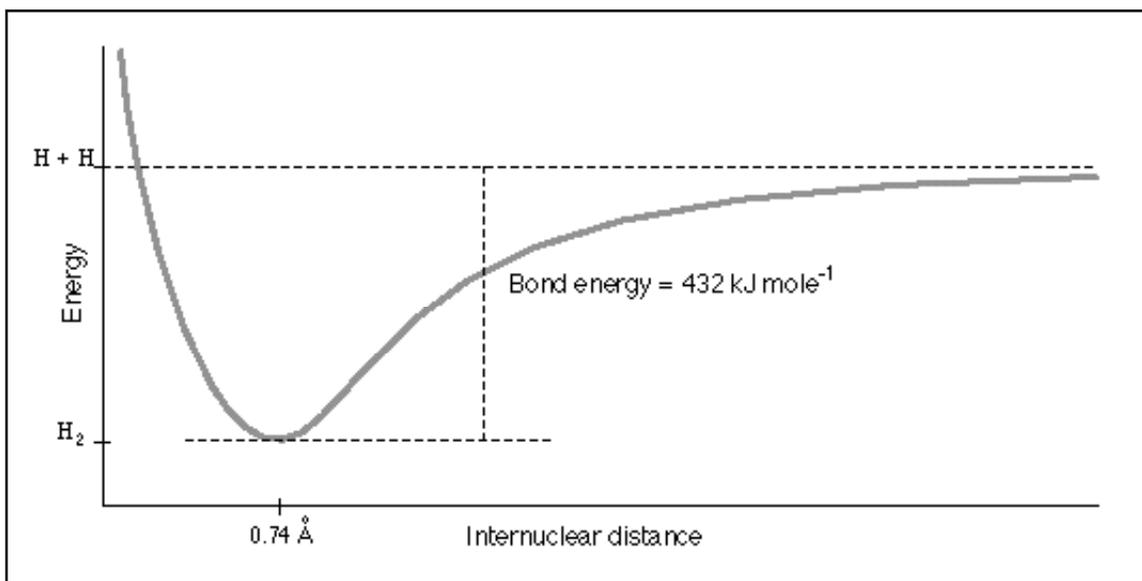
This orbital exists along with the bonding orbital, but the space occupied by the antibonding orbital is beyond the internuclear space (not between the nuclei). If both electrons were to occupy such an orbital, the hydrogen nuclei would both repel one another and be attracted to the electrons. Imagine a covalent bond between two helium atoms, in which case the antibonding orbital would be filled in addition to the bonding orbital, and you can see why two helium atoms show only a weak attraction.



Note that like atomic orbitals, molecular orbitals obey the Pauli exclusion principle (giving a maximum of two electrons per orbital), the aufbau principle (which states that lowest energy orbitals fill first), and Hund's rule (which governs the filling of orbitals of equal energy).

Molecular Orbital Theory and the Oxygen Molecule

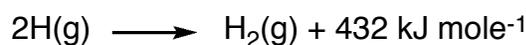
Like hydrogen, pure oxygen most often exists as a diatomic molecule. However, the elec-



Above we have the energy diagram for the formation of a hydrogen molecule from two hydrogen atoms. As the atoms approach from a distance (right to left on the graph), a covalent bond forms between the mutually attracting atoms. It should be familiar to you that closure of separation between two mutually attracting components of a system indicates a loss of potential energy. A person in the laboratory would witness the evolution of some amount of energy (heat or work) equal to the potential energy lost as such bonds form. The law of conservation of energy explains why the formation of the hydrogen molecule from two hydrogen atoms is exothermic.

Potential energy is lowest for two hydrogen atoms whose internuclear distance is 0.74 \AA . At this point, energy would be required from outside the system either to shorten or lengthen the separation of the atoms. (At distances shorter than 0.74 \AA , the force of repulsion of the protons for each other is greater than the force of attraction by the electron cloud between the nuclei. Notice also that to move the atoms to a distance greater than 0.74 \AA , requires work against the bond.) This potential energy minimum is the reason for the stability of molecules.

The difference in energy between the product compound and the reactants is called the **heat of formation** ($-\Delta H$) of the compound. The reaction expressing the formation of hydrogen molecule from the elemental form of hydrogen is as follows:



The symbol ΔH refers to the **enthalpy** of the reaction, which in this case would be equal to $-432 \text{ kJ mole}^{-1}$. It is common practice in chemistry, however, to refer to the enthalpy of H_2 as being 0 kJ mole^{-1} . This is because the *molecular* form, not the atomic form, of hydrogen is the *standard state* of the element, meaning that hydrogen almost always appears in elemental form as H_2 molecules. Chemistry data tables therefore refer to the enthalpy of *atomic* hydrogen as 216 kJ mole^{-1} , as the purpose of such tables is to state how much energy is absorbed or evolved in the formation of a certain substance from the elements in their standard states.

Drawing a Lewis Electron Dot Diagram of a Molecule

Lewis diagrams are useful tools to understand the chemical bonds in molecules because they conveniently represent the sharing of valence electrons. In most cases, drawing a Lewis diagram is a simple matter if you follow the following steps.

Let us take as our example the carbonate ion CO_3^{2-} .

Step 1 Determine the total number of valence electrons for the molecule by counting all the valence electrons for each atom in the molecule. Also, if the molecule is a polyatomic ion, add the number of negative charges to the total (subtract if it is a positive ion).

C: 4 valence electrons	4
+ O: 6 valence electrons X 3	18
+ ion charge gives 2 electrons	2
<hr/>	
	= 24 electrons

Step 2 Draw the skeleton structure of the molecule. Remember that the element whose symbol appears first in the formula is usually the central atom and that the most symmetrical form is probably the right one.



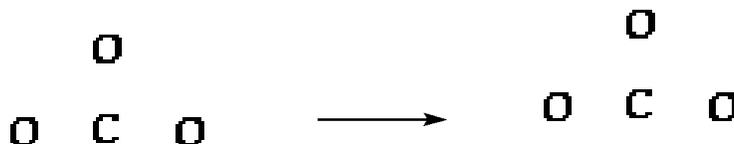
Step 3 Place a pair of electrons between the bonded atoms



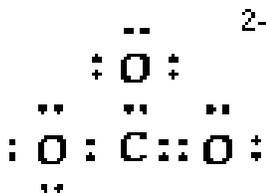
Step 4 Distribute electrons to complete the octets of the atoms surrounding the central atom:



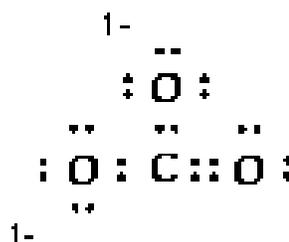
Step 5 Calculate how many electrons are left over and place them in pairs around the central atom to complete its octet. In the case of CO_3^{2-} , we have none left over at this point to form the octet on carbon. This indicates the presence of a **double bond**:



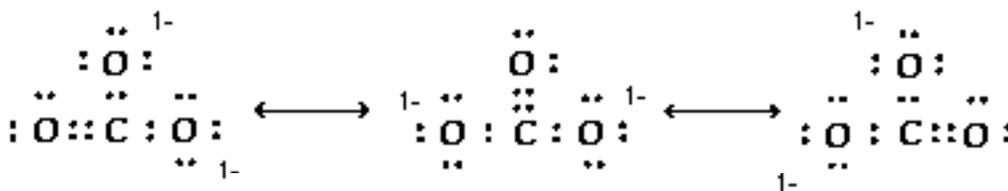
Here is the Lewis electron dot formula for CO_3^{2-} :



We calculate the **formal charge** on each atom by first calculating the sum of the number of unshared electrons plus 1/2 the number of shared electrons. We then subtract this sum from the number of valence electrons the atom would possess in atomic form. Indicating formal charge on our Lewis formula for CO_3^{2-} gives us:

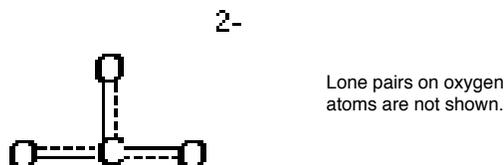


Sometimes you will encounter molecules for which more than one Lewis dot formula can be constructed. This is the case with CO_3^{2-} . Two other dot formulas are possible. All are equally acceptable:



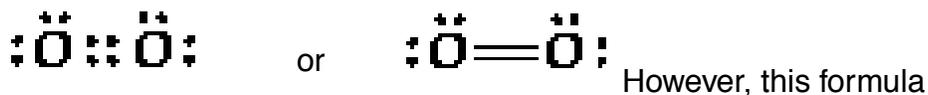
A molecule for which two or more dot formulas are available is said to exhibit **resonance**. The true bonding of our molecule is somewhere between the three forms above. CO_3^{2-} is a **resonance hybrid** of the three. It is not necessary in resonance that all possible forms contribute equally to the actual structure, but in the case of CO_3^{2-} they do.

Using dashes for our bonds, we can represent this situation by **delocalization** of bonding electrons:



Based on observations of many compounds, we know the average C—O single bond distance to be 1.43 \AA , and the average C=O double bond distance is 1.22 \AA . The bond distance in our molecule, CO_3^{2-} , is intermediate at 1.29 \AA .

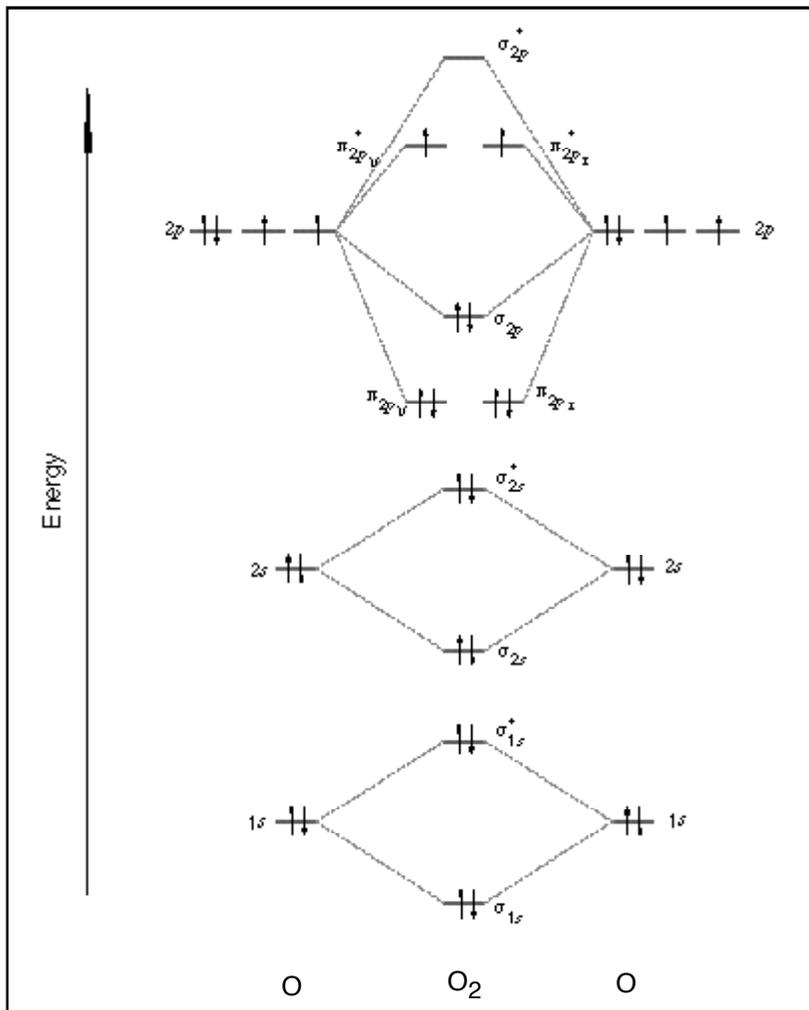
tronic structure of molecular oxygen is unusual. We could easily arrive at the following Lewis structure:



describes oxygen as diamagnetic, but we know from experiment that it is paramagnetic.* Let's examine the molecular orbital diagram of oxygen to see what the Lewis dot formula isn't telling us:

We can see that there are two unpaired electrons in the anti-bonding orbitals $\pi_{2p_y}^*$ and $\pi_{2p_z}^*$. These unpaired electrons are the source of the paramagnetism of O_2 . Note that it would be impossible to represent these two unpaired electrons in a Lewis dot formula.

When referring to a bond between two atoms, the **bond order** refers to the number of pairs of electrons in the bond as seen in the Lewis structure. In molecular orbital theory, we can arrive at bond order by taking one half the difference between the number of bonding electrons and the number of antibonding electrons. In both cases we see that the bond order in molecular oxygen is 2, a double bond.



The Lewis formula of nitrogen:

As you can see, the bond between the atoms is of the third order, a triple bond. Test your understanding of molecular orbital theory by imagining the diagram above for nitrogen (atomic number 7). Is molecular nitrogen diamagnetic or paramagnetic?



The valence-shell electron-pair repulsion (VSEPR) model

* There are three main types of magnetic behavior in substances (molecular or atomic) : **diamagnetism**, **paramagnetism**, and **ferromagnetism**.

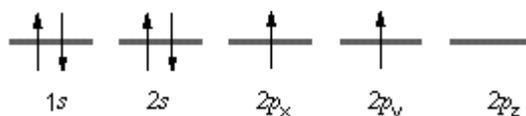
A **diamagnetic** substance (molecular or atomic) is not attracted by a magnetic field (it may be slightly repelled by such a field). This property generally means that the substance has only paired electrons.

A **paramagnetic** substance is weakly attracted by a magnetic field, which generally results from having unpaired electrons. This gives the substance a net spin magnetic moment.

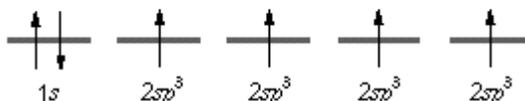
A **ferromagnetic** substance, such as iron, can be strongly magnetized due to the fact that the atomic (not spin) magnetic moments achieve parallel alignment within the material.

Orbital Hybridization

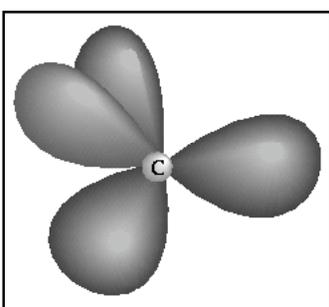
The electron configuration of atomic carbon shows its six electrons with four of them arranged into two pairs. Two electrons are unpaired:



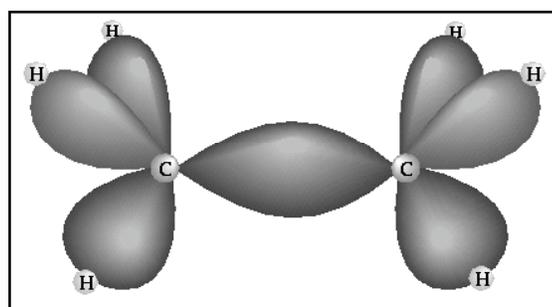
The concept of **orbital hybridization** has been proposed to explain the fact that carbon often forms four covalent bonds which arrange themselves around carbon in a tetrahedral fashion. The idea of covalent bonds as simple combinations of preexisting atomic orbitals would lead one to conclude that carbon would form only two covalent bonds with its two unpaired electrons. In reality, the four orbitals in the L shell of carbon transform into resonance hybrid orbitals. When this occurs, the four electrons in the L shell are of equal energy and unpaired:



This is called **sp^3 hybridization**. The resultant orbitals have 25% s character and 75% p character. sp^3 orbitals are arranged in a *tetrahedral* fashion around carbon.

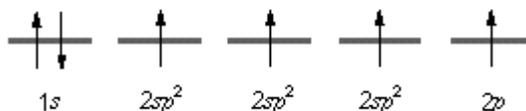


sp^3 orbitals exist when carbon enters into only **single bonds**. A single bond contains one pair of electrons. We call the four bonds around each carbon **sigma (σ) bonds**, meaning that



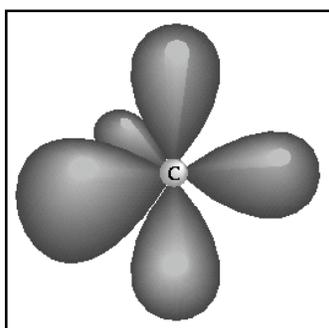
electron density is greatest along the axis between the nuclei.

When carbon enters into a **double bond**, the orbitals containing its four valence electrons

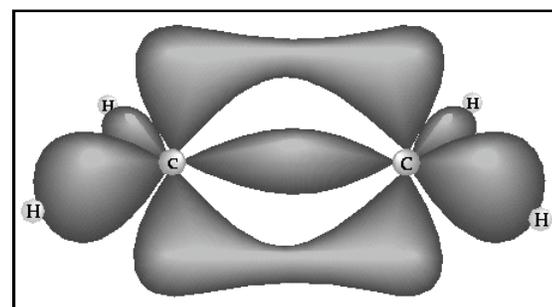


assume a different configuration called **sp^2 hybridization**:

In sp^2 hybridization, only two of the p orbitals enter into the process of hybridization. The resultant orbitals have 33% s character and 67% p character. sp^2 orbitals are arranged in a *trigonal planar* fashion

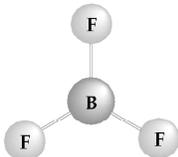
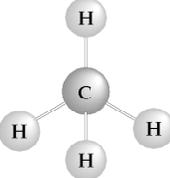
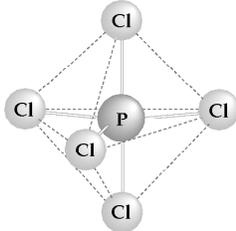
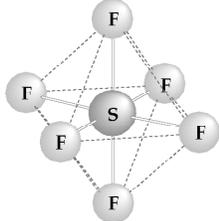


around carbon with the remaining p orbital breaking the plane, perpendicular to the others. sp^2 orbitals are formed when carbon enters into a double bond, as pictured in ethylene at right. In ethylene, each carbon is singly

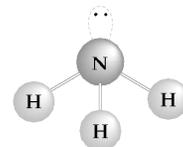


bonded to two hydrogen atoms and doubly bonded to the other carbon. One component of the double bond is created by overlap between two sp^2 orbitals, represented in the picture of ethylene by the electron density on the axis between the two carbon atoms, a sigma (σ)

The VESPR model predicts the shapes of molecules and ions. The main principle is that valence-shell electron pairs are arranged about the atoms of a compound so that there is maximum separation among electrons, thus minimizing electron repulsions. Here is a table showing variation of molecular geometry with number of regions of electron density around a central atom.

Electron Pairs	Molecular Geometry	Angles	
2	Linear	180°	
3	Trigonal planar	120°	
4	Tetrahedral	109°	
5	Trigonal bipyramidal	90°, 120° 180°	
6	Octahedral	90°, 180°	

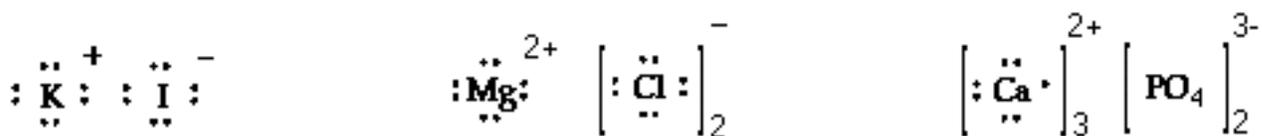
Above we have pictured only molecules whose central atoms have attained their maximum number of covalent bonds with other atoms. Remember that unbonded pairs of electrons also constitute regions of electron density and occupy a position in the predicted geometry. At right is NH_3 . Having four pairs of valence electrons around its central atom, the form of NH_3 is based upon the tetrahedron. The geometry is called trigonal pyramidal. Also note that lone pair - lone pair and lone pair - bonded pair repulsions are stronger than bonded pair - bonded pair repulsions. So the H-N-H angle will be a little less than 109° (107°).



Ionic Compounds

An ionic bond occurs when electrons are *transferred* from the valence shell of one atom to the valence shell of another. The atom that loses electrons becomes a **cation** (a positive ion), while the atom that gains electrons becomes an **anion** (a negative ion). The **ionic bond** is constituted by the attraction between the ions.

Ionic compounds are formed between the metals in groups I and II (low ionization energy) and the nonmetals in the upper right corner of the periodic table (high electron affinity). Also, the anions of certain acids, especially the oxygen acids, can form ionic compounds with group I and II metals. Here are some examples of ionic compounds:

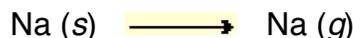


When atoms react to form ionic compounds, they either lose or gain electrons so that they attain the electron configuration of the nearest noble gas. In other words, the octet rule applies to the formation of ionic compounds.

The Born-Haber cycle

To understand the energy of formation of an ionic compound, the **Born-Haber cycle** is a useful tool, in which we imagine the events occur in a series of steps. We can do this because of the law of conservation of energy, which applied to chemical reactions is called **Hess's law of heat summation**. This law states that the net value of the enthalpy change for an overall chemical process is merely the sum of all the enthalpy changes that take place along the way. The Born-Haber cycle for the formation of sodium chloride NaCl would proceed as follows:

Step 1: Sodium in its solid state is vaporized to produce gaseous sodium (sublimation). We must begin with the solid because that is the *standard state* of pure sodium, and we need to reach the gas because the atoms are essentially isolated in that state and thus prepared to react. The energy required for this *endothermic* process is 25.8 kcal mole⁻¹ ($\Delta H = +25.8$ kcal).



Step 2: 1/2 mole of molecular chlorine is dissociated to produce 1 mole of chlorine atoms. This process is also *endothermic* (positive enthalpy change): $\Delta H = +28.7$ kcal mole⁻¹.



Step 3: The lone outer shell electron from the sodium is removed in an *endothermic* process. The enthalpy change here is the first ionization energy of atomic sodium: $\Delta H = +119$ kcal mole⁻¹.



Step 4: Next occurs the addition of the electrons from the ionization of sodium to the chlorine atoms. This is an *exothermic* process. The quantity of energy evolved is equal to the electron affinity of chlorine: $\Delta H = -83.5 \text{ kcal mole}^{-1}$.



Step 5: The final step involves the formation of solid NaCl occurs in a process, which like the preceding step, is *exothermic*. Remember that because energy would be required to separate positive and negative charges, so energy must be released when they are brought together. For a solid crystal, such as we produce here, we call the energy required to separate the ions, the **lattice energy**. The enthalpy change in forming the crystal lattice would be the opposite of this energy: $\Delta H = -188 \text{ kcal mole}^{-1}$.



We can now sum the enthalpies of the individual steps to attain the enthalpy of formation of NaCl:

$$\Delta H = (25.8 + 28.7 + 119 - 83.5 - 188) \text{ kcal mole}^{-1} = -98 \text{ kcal mole}^{-1}$$

Polar molecules and the dipole moment

Some substances in the liquid form, when placed between the charged plates of a capacitor, will partially neutralize the applied field. We would say that the substance has a **dielectric constant** greater than one. The molecules of such substances are called **polar** because within them there is separation between the centers of positive and negative charge. Between the plates of a capacitor, in liquid form, the molecules of a polar substance will partially orient themselves to oppose the applied field, as illustrated below:

A water molecule is polar, meaning that it possesses a **dipole moment**, a quantity expressing the separation of charge $+q$ from $-q$ over a distance d .

$$\text{dipole moment} = qd$$

We express the dipole moment graphically as a vector drawn from the region of positive charge to the region of negative charge:

