15.1: Prelude to Thermodynamics

In the sections on Using Chemical Equations in Calculations we indicate that heat is a form of energy and show how the quantity of heat energy absorbed or released by a chemical change can be related to the corresponding chemical equation. We also state the law of conservation of energy, and arguments in other sections have often been based on the idea that energy can neither be created nor destroyed. The law of conservation of energy is the first of three important laws involving energy and matter, which were discovered over a century ago. These laws were originally based on the movement or transfer (dynamics) of heat (thermo), and the law of conservation of energy is therefore referred to as the **first law of thermodynamics**.

We assign the symbol ΔH and the name enthalpy change to the quantity of heat absorbed by a chemical or physical change under conditions of constant pressure. You may wonder just how heat energy could be absorbed or given off when atoms and molecules change position and structure during a chemical reaction, but we have not yet developed theories of chemical bonding, molecular structure, intermolecular forces, and molecular motion to the point where a satisfactory explanation can be given. We are in a position to investigate what can happen to molecules when matter absorbs or releases heat. One result of this study will be a clearer understanding of enthalpy. At the same time we will begin to appreciate what molecular factors contribute to making a reaction exothermic or endothermic. This gives us a solid basis for discussing several aspects of what is probably the most important problem facing our technological society today—the energy crisis.

The first law of thermodynamics (the law of conservation of energy) states that when heat energy is supplied to a substance, that energy cannot disappear-it must still be present in the atoms or molecules of the substance. Some of the added energy makes the atoms or molecules move faster. This is called translational energy. In the case of molecules, which can rotate and vibrate, some of the added energy increases the rotational and vibrational energies of the molecules. You can investigate vibrations of the ethane molecule above in the Jmol. Finally, any atom or molecule will have a certain electronic energy which depends on how close its electron clouds are to positively charged nuclei.

The total of translational, rotational, vibrational, and electronic energies is the internal energy of an atom or molecule. When chemical reactions occur, the internal energy of the products is usually different from that of the reactants, and the difference appears as heat energy in the surroundings. If the reaction is carried out in a closed container (bomb calorimeter, for example), the increase in internal energy of the atoms and molecules is exactly equal to the heat energy absorbed from the surroundings. If the internal energy decreases, the energy of the surroundings must increase; i.e., heat energy is given off.

When a chemical reaction occurs at constant pressure, as in a coffee-cup calorimeter, there is a change in potential energy of the atmosphere (given by $P\ \Delta V$) as well as a change in heat energy of the surroundings. Because the heat energy absorbed can be measured more easily than $P\ \Delta V$, it is convenient to define the enthalpy as the internal energy plus the increased potential energy of the atmosphere. Thus the enthalpy increase equals the heat absorbed at constant pressure.

Enthalpy changes for a variety of reactions may be calculated from standard enthalpies of formation. They may also be estimated by summing the bond enthalpies of all bonds broken and subtracting the bond enthalpies of all bonds formed. Because the dissociation enthalpy for the same type of bond varies from one molecule to another, the second method is not as accurate as the first. However, it has the advantage that enthalpy changes for reactions of a particular compound can be estimated even if the compound has not yet been synthesized.

The enthalpy change for a reaction depends on the relative strengths of the bonds broken and formed and on the relative number of bonds broken and formed. A good fuel is a substance which can combine with oxygen from the air, forming more bonds and/or stronger bonds than were originally present. The fossil fuels, coal, petroleum, and natural gas consist mainly of carbon and hydrogen. When they burn in air, strong O—H and C=O bonds are formed in the resulting H_2O and CO_2 molecules. The supply of fossil fuels is limited, and they constitute a nonrenewable resource. Coal supplies ought to last another century or two, but petroleum and natural-gas supplies will be essentially depleted in half a century or less. During the next few decades it will be possible to gasify or liquefy coal to extend our supply of gaseous and liquid fuels. Conservation of these fuels can also make a major contribution toward continuing their use. Eventually, however, it will be necessary to develop nuclear or solar energy or some unknown source of energy if we are to continue our current energy-intensive way of life.