Molecules, Chemical Energy and Energy Conversion

Molecules

Molecules consist of atoms bonded together through the interaction of electrons and nuclei. Most of the electrons from each atom remain localized around the nucleus of that atom and do not participate in bonding. Chemical bonds are formed by a few electrons from each atom which can move to regions between atoms.

When isolated atoms are brought together, there are significant changes in the probability distributions of the electrons involved in bonding. When a molecule forms from isolated atoms, the total system of electrons and nuclei achieves a state of energy lower than the sum of the energies of the individual atoms. A molecule has many states characterized by discrete energy values and a set of different quantum numbers. More than one quantum number is necessary because the total energy of a molecule is the sum of the energies of the electrons, the energy of vibration of the molecule and the energy of rotation. The state of zero energy is taken to be the state of the system in which all the atoms are infinitely far apart, and the energies of the various bound states are all negative relative to this state of complete dissociation. The lowest energy state, known as the ground state, is the state in which a molecule is usually found to exist. The formation of a molecule in its ground state from a collection of isolated atoms requires that the energy of binding be released as photons or heat to the environment.

Chemical reactions

In a chemical reaction, one or more molecules known as reactants are brought into contact and a reorganization of electrons and nuclei takes place to produce a new set of molecules referred to as products. In a spontaneous reaction, the energy of the of the ground state of the products is less than that of the reactants. The difference in energy, $\Delta U = U_{products} - U_{reactants}$, is negative for a spontaneous reaction. Thus, the energy released upon reaction, $-\Delta U$, must be dissipated somehow.

In a thermal process, this energy is released as heat to the surroundings and perhaps some sort of work. Typically, a chemical reaction will occur under constant pressure conditions, and so pressure-volume work is done on the atmosphere. Suppose that $\Delta U < 0$ is the internal energy change that occurs with a particular reaction. Then under constant atmospheric pressure conditions the important energy quantity is the change in the enthalpy *enthalpy* $\Delta H = \Delta U + P\Delta V$. Note that if the volume increase upon reaction ($\Delta V > 0$), then the change in enthalpy is less negative than the change in internal energy because some of the energy release was converted into work on the atmosphere.

Beyond constant pressure condition, we normally consider the initial and final temperatures of the system to be the same, that is, T is room temperature before and after the reaction. So the even more important energy quantity is the change in the *Gibbs free energy* $\Delta G = \Delta H - T\Delta S$, where ΔS is the *entropy* change during the reaction. Since $-\Delta H$ is the energy available after PV work has been accounted for, $-\Delta G$ is the energy available for non-PV work after the flow of energy as heat due to the change in entropy has been accounted for. There are two important points to be remembered concerning ΔG. First, a reaction will occur spontaneously and irreversibly only

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if $\Delta G < 0$. Second, $-\Delta G$ is the energy available to be converted into non-pressure-volume work, such as electrical work. The ultimate efficiency of conversion of the chemical energy change in a reaction to non-PV work is simply the maximum non-PV work available divided by the energy available,

$$\eta = \frac{-\Delta G}{-\Delta H} = 1 - \frac{T\Delta S}{\Delta H}.$$

This is always less than 1.

The energetics of a generic chemical reaction is shown in Figure 1. Products will form spontaneously only if the total energy of the products is less than that of the reactants. There can be an energy barrier to the reaction, that is, an energy required to allow the transformation to take place. An example is $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. Energy is required to separate the two H atoms. The time for the reaction to occur is inversely proportional to the height of this barrier. For $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ the barrier is so large that the reaction never occurs at room temperature. To increase the rate of reaction the molecules can be heated, as in a flame. Alternatively, the barrier can be lowered by allowing the molecules to interact with a catalyst. Platinum is the catalyst of choice for this reaction since H_2 molecules dissociate into H atoms which wander over the surface of the metal.
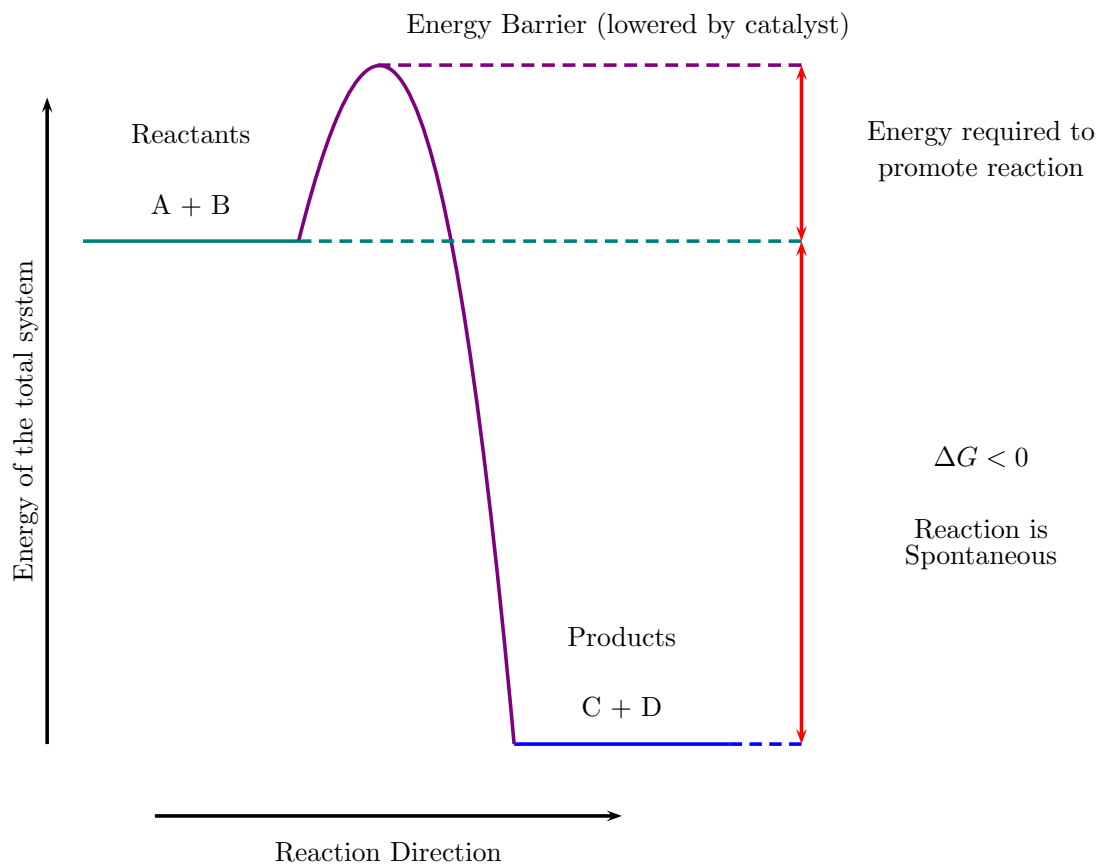

Figure 1: Thermodynamics of a chemical reaction. The value of ΔG determines the direction of the reaction and the amount of energy available as non-PV work. The height of the barrier determines the rate of the reaction, the time for the reaction to occur to some extent.

Conversion of chemical energy to another form

For the generation of electrical energy from fuels, the goal is to most efficiently convert $-\Delta G$. If a fuel is simply burned, this energy $-\Delta G$ is converted into the disordered form of energy we know as heat, that is, energy distributed among the many types of molecular motions. The thermodynamic limit on the efficiency of a heat engine makes this approach undesirable.

To devise a more efficient energy conversion scheme, consider the fact that during a chemical reaction electrons and atoms are rearranged. If one could insert wires into the molecules involved, the electrons could, in principle, be directed through an electrical device and thereby could dissipate this energy $-\Delta G$ as electrical work. This concept is the basis for fuel cells and batteries.

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