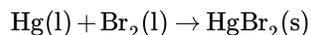


16.1: Prelude to Spontaneity



The experiences you have had in the chemical laboratory have probably already taught you that there is an uphill character to some reactions and a downhill character to others. A simple example is the combination of mercury with bromine which we considered in detail in the [section on macroscopic and microscopic views of a chemical reaction](#):



This reaction proceeds from $\text{Hg}(l)$ and $\text{Br}_2(l)$ to $\text{HgBr}_2(s)$, much as a ball rolls downhill. On the other hand, decomposition of HgBr_2 to the elements is an uphill process, and we must “push” this reaction to force it to occur. One way to do this is to dissolve HgBr_2 in water and pass an electrical current through the solution. Mercury will appear at one electrode and bromine at the other.

We want to understand why some chemical reactions are downhill while others are uphill. In particular we want to know what kinds of atomic and molecular processes proceed downhill, and which processes require a “push” to go uphill. We find that these questions of uphill and downhill nature of a reaction can be answered using concepts such as spontaneity, entropy, and free energy.

Chemical reactions which proceed downhill, are said to be [spontaneous](#). With spontaneity, we are considering *whether* a process will occur, but can say nothing about the [rate](#) at which it will occur. Spontaneous process may also require energy to overcome an activation barrier. This means that some processes may be spontaneous, but do not occur at a noticeable rate. An everyday example is burning a log of wood where the burning reaction is clearly “downhill” and thus defined spontaneous, but without a flame to supply heat to overcome the activation barrier, the reaction will not occur. A spontaneous process corresponds to a [rearrangement of atoms and molecules from a less probable to a more probable situation](#), as measured by the [thermodynamic probability \$W\$](#) of the reactants and products. W is defined as the number of alternative microscopic arrangements which correspond to the same macroscopic state. Because most macroscopic samples of matter contain 10^{15} particles or more, very large values of W are encountered. Therefore it is convenient to use the entropy S , which is proportional to the logarithm of W , as a measure of spontaneity. According to the second law of thermodynamics, when a spontaneous process occurs, there must be an increase in total entropy.

The entropy of a perfectly ordered crystal at absolute zero is zero according to the third law of thermodynamics. [Increasing the temperature, volume, or amount of substance increases the entropy](#). For a given amount of substance, [the heavier and more complex the molecules](#), the greater the entropy, while stronger forces between atoms, molecules, or ions result in lower entropy. In general the [greater the randomness or disorder of the atoms or molecules the greater the entropy](#) of a substance.

To determine whether a chemical reaction is spontaneous we must calculate the change in total entropy of the chemical system *and* its [surroundings](#). This can be done directly using $\Delta S^\circ_{\text{sys}}$ and $-\Delta H^\circ/T$ or indirectly using the change in [Gibbs free energy \$\Delta G^\circ\$](#) . For a spontaneous reaction occurring at constant temperature and pressure, ΔG° must be negative. Since $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$, a negative enthalpy change is the most important factor governing spontaneity of a reaction at low temperatures. At high values of T , $-T \Delta S^\circ$ becomes large and an increase in entropy of the system is essential for a spontaneous process.

The change in Gibbs free energy at standard pressure can be calculated from tables of ΔG_f° . Once obtained it can be used to determine two other useful values, the either the amount of [energy available to do work \$w_{\text{max}}\$](#) (or the amount of energy needed to drive a process in a non-spontaneous direction), and the [standard equilibrium constant \$K^\circ\$](#) . For a reaction in the gas phase K° is numerically the same as K_p , provided the latter is expressed in atmospheres. Knowledge of ΔG° thus allows calculation of the equilibrium partial pressures of reactants and products.

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