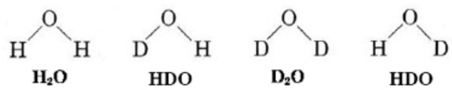
16.4: Rates of Spontaneous Processes

The phrase *as fast as possible* points up a major difficulty in dealing with spontaneous processes. Some of them occur quite rapidly, but others are so slow as to be imperceptible. A rapid spontaneous process occurs when 2 mol H_2O is mixed with 2 mol “heavy water,” D_2O, made from the isotope deuterium, ${}^{2}_{1}H$, or **D**. The two species start to transfer protons and deuterons (D^+ ions) as soon as they are stirred together, and we rapidly obtain a mixture consisting of 2 mol H—O—D and 1 mol each of H—O—H and D—O—D. Assuming that deuterium atoms behave the same chemically as ordinary hydrogen atoms, this is what the laws of probability would predict. There are four equally likely possibilities for a randomly selected water molecule:



Two of the four possibilities have the molecular formula HDO, and so the probability of finding an HDO molecule in our mixture is 1/2. Half the molecules (2 mol) will be HDO. Similarly 1/4 of the 4 mol water will be H_2O and 1/4 will be D_2O.

The shift from the improbable situation of 2 mol H_2O + 2 mol D_2O to the more probable 2 mol HDO + 1 mol H_2O + 1 mol D_2O occurs rapidly because of the ease with which protons and deuterons can transfer from one water molecule to another. When such a shuffling process is slow, however, the situation is quite different. For example, we would expect that mixing 2 mol H_2 with 2 mol D_2 would produce 2 mol HD and a mole each of H_2 and D_2. At room temperature, though, nothing happens, even over a period of days, because there is no easy way for H or D atoms to swap partners. Reshuffling requires breaking an H—H or a D—D bond, and this takes some 400 kJ mol^{-1}. The molecules are stuck in a situation of low probability because there is no pathway by which they can attain higher probability. If such a pathway is provided, by raising the temperature or adding a catalyst, the molecules start exchanging H and D and move toward the most probable situation.

The moral of this story is that saying a reaction is spontaneous is not the same as saying it *will* occur if the reactants are mixed. Rather, it means the reaction *can* occur but may be so slow that nothing seems to happen. In the case of a slow spontaneous reaction it is worthwhile to look for a catalyst, but if we know the reaction is nonspontaneous, there is no point in even mixing the reactants, let alone searching for a catalyst. A nonspontaneous reaction cannot occur of itself without outside intervention.