7.1: Collisions and Chemical Reactions

First we will state the obvious: chemical reactions are linked to change but not all change involves a chemical reaction. When liquid water boils or freezes, it undergoes a change of state (a phase change) but the water molecules are still discrete H_2O molecules. In ice, they remain more or less anchored to one another through H-bonding interactions, whereas in liquid and water vapor they are constantly moving with respect to one another and the interactions that occur between the molecules are transient. We can write out this transition in symbolic form as:

$$H_2O\text{ (solid) } \rightleftarrows H_2O\text{ (liquid) } \rightleftarrows H_2O\text{ (vapor)} \tag{7.1.1}$$

The double arrows mean that the changes are reversible. In this case, reversibility is a function of temperature, which controls whether the interactions between molecules are stable (as in ice), transient (as in liquid water), or basically non-existent (as in water vapor). What you notice immediately is that there are water molecules present in each phase. This helps shed light on the common misconception that bubbles found in boiling water are composed of oxygen and hydrogen. Boiling does not break the bonds in a water molecule, so the bubbles are actually composed of water vapor. That said, within liquid water there is actually a chemical reaction going on: the disassociation of water into ^{-}OH and H^{+} (which we will discuss in more detail shortly). However a naked proton (that is, H^{+} as discrete entity) does not exist in water. Therefore, this reaction is more accurately written as:

$$H_2O + H_2O \rightleftarrows H_3O^{+} + {}^{-}OH \tag{7.1.2}$$

Here we see the signature of a chemical reaction. The molecules on the two sides of the equation are different; covalent bonds are broken (an $O—H$ bond in one water molecule) and formed (a $H—O$ bond in the other.) All chemical reactions can be recognized in this way. The water dissociation reaction also illustrates how reactions can vary in terms of the extent to which they occur. In liquid water, which has a concentration of about $\sim 55\text{ M}$, very few molecules undergo this reaction. In fact, in pure water the concentration of H_3O^{+} is only 10^{-7} M, which is eight orders of magnitude less than the concentration of water molecules. Another interesting feature of this reaction is that it is going in both directions, as indicated by the double arrows $\rightleftarrows$.

Water reacts with itself to form $H_3O^{+} + {}^{-}OH$, and at the same time $H_3O^{+} + {}^{-}OH$ are reacting to generate water molecules. The reaction is at equilibrium, and in this case the position of the equilibrium indicates that the majority of the species in water are actually water molecules.

In contrast, other reactions essentially go to completion (proceed until essentially all the reactants are used up and the reaction is a equilibrium).[1] For example, pure ethanol (CH_3CH_2OH), is $\sim 17.1\text{ M}$ and it will burn in air (which contains O_2). We can write the reaction going to completion as:

$$CH_3CH_2OH + 3O_2 \rightleftarrows 2CO_2 + 3H_2O \tag{7.1.3}$$

There is very little ethanol left if this reaction occurs in the presence of sufficient O_2.[2] In the real world, the reaction is irreversible because the system is open and both CO_2 and H_2O escape and are therefore not able to collide with each other – which would be a prerequisite for the reverse reaction to occur. Another interesting feature of the ethanol burning reaction is that pure ethanol can be quite stable in contact with the atmosphere, which typically contains $\sim 20\% O_2$. It takes a spark or a little heat to initiate the reaction. For example, vodka, which is about 50% ethanol, will not burst into flames without a little help! Most reactions need a spark of energy to get them started, but once started, many of them release enough energy to keep them going. As we saw in our discussion of solutions, some reactions release energy (are exothermic) and some require energy (are endothermic). It is important to note that this overall energy change is not related to the spark or energy that is required to get some reactions started. We will return to these ideas in chapter 8.

Another feature of reactions is that some are faster than others. For example, if we add hydrogen chloride gas to water, a reaction occurs almost instantaneously:

$$HCl(g) + H_2O(l) \rightleftarrows H_3O^{+}(aq) + Cl^{-}(aq) \tag{7.1.4}$$

Very little time elapses between dissolving the HCl and the reaction occurring. We say the rate of the reaction is fast or instantaneous (in Chapter 8, we will look more closely at reaction rate and what affects it.) In contrast, when iron nails are left out in the weather, they form rust, a complex mixture of iron oxides and hydroxides. This reaction is slow and can take many years, although in hot climates the reaction goes faster. Similarly, when we cook food, the reactions that take place occur at a faster rate than they would at room temperature.

As we have seen previously, bonded atoms are typically more stable than unbonded atoms. For a reaction to occur, some bonds have to break and new ones have to form. What leads to a bond breaking? Why are new bonds formed? What are the factors that affect whether reactions occur, how much energy is released or absorbed, where they come to equilibrium, and how fast they occur? All these questions and more will be addressed in Chapter 8.

But first things first, in order for a reaction to occur, the reacting molecules have to collide. They have to bump into each other to have a chance of reacting at all. An important point to remember is that molecules are not sitting still. They may be moving from one place to another (if they are in liquid or gaseous phase) and/or they are vibrating and rotating. Remember that the temperature of a system of molecules is a function of the average kinetic energy of those molecules. Normally, it is enough to define the kinetic energy of a molecule as $\frac{1}{2}mv^2$, but if we are being completely rigorous this equation applies only to monatomic gases. Molecules are more complex because they can flex, bend, rotate around bonds, and vibrate. Many reactions occur in solution where molecules are constantly in contact with each other—bumping and transferring energy, which may appear as either kinetic or vibrational energy. Nevertheless, we can keep things simple for now as long as we remember what simplifications we are assuming. Recall that although temperature is proportional to the average kinetic energy of the molecules, this does not mean that all the molecules in the system are moving with the same velocity. There is typically a broad range of molecular velocities, even if all the molecules are of the same type. There is an even broader range in reaction mixtures, which have more than one type of molecule in them. Since the system has only a single temperature, all types of molecules must have the same average kinetic energy, which means that the more massive molecules are moving more slowly, on average, than the less massive molecules. At the same time, all the molecules are (of course) moving so they inevitably collide with one another and, if the system has a rigid boundary, with the boundary. We have previously described the distribution of velocities found in the system in terms of a distribution of velocity (or speed) and the percent or even absolute number of molecules with that speed, the Boltzmann distribution. At any particular temperature, there are molecules that move much faster (have higher kinetic energy) and other molecules that move much slower (have less kinetic energy) than the average kinetic energy of the population. This means that when any two molecules collide with one another, the energetics of that interaction can vary dramatically. Some collisions involve relatively little energy, whereas others involve a lot!

These collisions may or may not lead to a chemical reaction, so let's consider what happens during a chemical reaction. To focus our attention, we will consider the specific reaction of hydrogen and oxygen gases to form water:

$$\mathrm{2H_2 + O_2 \rightleftarrows 2H_2O} \tag{7.1.5}$$

This is, in fact, a very complex reaction, so let's simplify it in a way that may seem cartoonish but which is, nevertheless, accurate. If we have a closed flask of pure oxygen, and we add some hydrogen (H_2) to the flask, the two types of gas molecules quickly mix, because – as you will recall – the mixed system is more probable (that is the entropy of the mixed gases is higher than the unmixed.) Some of the molecules collide with each other, but the overwhelming majority of these collisions are unproductive. Neither the hydrogen molecule (H_2) nor the oxygen molecule (O_2) are altered, although there are changes in their respective kinetic energies. However, when we add kinetic energy (say, from a burning match, which is itself a chemical reaction), the average kinetic energy of the molecules in the heated region increases, thus increasing the energy that can be transferred upon collision, which increases the probability that a particular collision will lead to a bond breaking, which therefore increases the probability of the $H_2 + O_2$ reaction. In addition, because the stability of the bonds in H_2O is greater than those of H_2 and O_2, the reaction releases energy to the surroundings. This energy can take the form of kinetic energy (which leads to a further increase in the temperature) and electromagnetic energy (which results in the emission of photons of light.) In this way, the system becomes self-sustaining. It no longer needs the burning match because the energy released as the reaction continues is enough to keep new molecules reacting. The reaction of H_2 and O_2 is explosive (it rapidly releases thermal energy and light), but only after that initial spark has been supplied.

We can plot out the behavior of the reaction, as a function of time, beginning with the addition of the burning match. It is worth keeping in mind that the reaction converts H_2 and O_2 into water. Therefore, the concentrations of H_2 and O_2 in the system decrease as the reaction proceeds while the concentration of H_2O increases. As the reaction proceeds, the probability of productive collisions between H_2 and O_2 molecules decreases simply because there are fewer H_2 and O_2 molecules present. We can think of it this way: the rate at which the reaction occurs in the forward (to the right) direction is based on the probability of productive collisions between molecules of H_2 and O_2. This in turn depends upon their relative concentration (this is why hydrogen will not burn in the absence of O_2). As the concentrations of the two molecules decrease, the reaction rate slows down. Normally, the water molecules produced by burning disperse and the concentration (molecules per unit volume) of H_2O never grows very large. But if the molecules are in a container, then their concentrations increase, and eventually the backward reaction could begin to occur. The reaction will reach equilibrium, at which point the rate of forward and backward reactions would be equal. Because the forward reaction is so favorable, some (but very little) H_2 and O_2 would remain at equilibrium. The point is to recognize that reactions are dynamic and, depending on the conditions, the exact nature of the equilibrium state will be determined by concentrations, temperatures, and the nature of the reaction.

? Questions

Questions to Answer

- In your own words, define the term chemical reaction. How can you tell when a chemical reaction has occurred?
- Give some examples of reactions that you already know about or have learned about in previous courses.
- What do we mean by rate of reaction? How might you determine a reaction rate?
- What conditions must exist in order for something to react?
- How does the concentration of reactants and products influence the rate of a reaction?
- Are chemical reactions possible in the solid phase?
- What factors are required for a reaction to reach a stable (albeit dynamic) equilibrium?
- Why is a burning building unlikely to reach equilibrium?
- Assuming you have encountered them before, define the terms acidic and basic in your own words.

Questions to Ponder

- What reactions are going on around you right now?
- What is required in order for a reaction to go backwards?
