12.13: Molecularity

Putting jigsaw puzzles together is an enjoyable hobby for some. Often these puzzles come in a box, so all the pieces must be spread out before starting the puzzle. Various internet sites sell jigsaw puzzles. Buyers can choose the level of difficulty, the shape of the pieces—and can time themselves to see how well they do compared to others that tried the puzzle. The puzzle often looks complicated, with the final product generally comprised of hundreds of pieces. However, in its assembly, there is a series of elementary steps, and the puzzle goes together one piece at a time.

Molecularity of a Reaction

The **molecularity** of a reaction is the number of molecules reacting in an elementary step. A unimolecular reaction is one in which only one reacting molecule participates in the reaction. Two reactant molecules collide with one another in a bimolecular reaction. A termolecular reaction involves three reacting molecules in one elementary step. Termolecular reactions are relatively rare because they involve the simultaneous collision of three molecules in the correct orientation, a rare event. When termolecular reactions do occur, they tend to be very slow.

Given the reaction:

$$2\text{NO}\,(g) + \text{O}_2\,(g) \rightarrow 2\text{NO}_2\,(g)$$

We might guess that the reaction was termolecular since it appears that three molecules of reactants are involved. However, our definition of molecularity states that we need to look at an elementary step, and not the overall reaction. Data on the reaction mechanism demonstrates that the reaction occurs in two steps:

Step 1: $2\text{NO}\,(g) \rightarrow \text{N}_2\text{O}_2\,(g)$

Step 2: $\text{N}_2\text{O}_2\,(g) + \text{O}_2\,(g) \rightarrow 2\text{NO}_2\,(g)$

So we see that each elementary step is bimolecular and not termolecular. Notice that the colliding molecules may be the same (as in step 1 above) or different (as in step 2 above).

Another reaction involves the conversion of ozone $\left(\text{O}_3\right)$ to oxygen $\left(\text{O}_2\right)$ with ultraviolet light. The two elementary steps are as follows:

$$\text{O}_3 + \text{ultraviolet light} \rightarrow \text{O}_2 + \text{O}\cdot\ \text{(free radical)}$$

$$\text{O}\cdot + \text{O}_3 \rightarrow 2\text{O}_2$$

The first step is unimolecular (one molecule of ozone reacts) and the second step is bimolecular (one ozone free radical and one ozone molecule react together).

Summary

- The **molecularity** of a reaction is the number of molecules reacting in an elementary step.
- Reactions can be unimolecular (one reacting molecule), bimolecular (two reacting molecules) or termolecular (three reacting molecules).