## 9.3: Molecularity of a Reaction

In general, it is necessary to experimentally measure the concentrations of species over time in order to determine the apparent rate law governing the reaction. If the reactions are elementary reactions, (i.e. they cannot be expressed as a series of simpler reactions), then we can directly define the rate law based on the chemical equation. For example, an elementary reaction in which a single reactant transforms into a single product, is unimolecular reaction. These reactions follow $1^{st}$ order rate kinetics. An example of this type of reaction would be the isomerization of butane:

$$nC_4H_{10} \longrightarrow iC_4H_{10} \tag{9.3.1}$$

From the chemical reaction equation, we can directly write the rate law as

$$\frac{d\left[nC_4H_{10}\right]}{dt} = -k\left[nC_4H_{10}\right] \tag{9.3.2}$$

without the need to carry out experiments.

Elementary bimolecular reactions that involve two molecules interacting to form one or more products follow second order rate kinetics. An example would be the following reaction between a nitrate molecule and carbon monoxide to form nitrogen dioxide and carbon dioxide:

$$NO_3 + CO \longrightarrow NO_2 + CO_2 \tag{9.3.3}$$

For the above elementary reaction, we can directly write the rate law as:

$$\frac{d\left[NO_3\right]}{dt} = -k\left[NO_3\right]\left[CO\right] \tag{9.3.4}$$

Trimolecular elementary reactions involving three reactant molecules to form one or more products are rare due to the low probability of three molecules simultaneously colliding with one another.