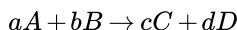


9.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

9.1.1: The Reaction Rate

The rate of a chemical reaction (or the **reaction rate**) can be defined by the time needed for a change in concentration to occur. But there is a problem in that this allows for the definition to be made based on concentration changes for either the reactants or the products. Plus, due to stoichiometric concerns, the rates at which the concentrations are generally different! Toward this end, the following convention is used.

For a general reaction



the reaction rate can be defined by any of the ratios

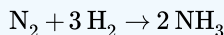
$$\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{dt} = -\frac{1}{b} \frac{\Delta[B]}{dt} = +\frac{1}{c} \frac{\Delta[C]}{dt} = +\frac{1}{d} \frac{\Delta[D]}{dt}$$

Or for infinitesimal time intervals

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$

✓ Example 9.1.1:

Under a certain set of conditions, the rate of the reaction



the reaction rate is $6.0 \times 10^{-4} \text{ M/s}$. Calculate the time-rate of change for the concentrations of N_2 , H_2 , and NH_3 .

Solution:

Due to the stoichiometry of the reaction,

$$\text{rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

so

$$\frac{d[\text{N}_2]}{dt} = -6.0 \times 10^{-4} \text{ M/s}$$

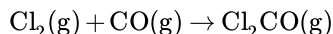
$$\frac{d[\text{H}_2]}{dt} = -2.0 \times 10^{-4} \text{ M/s}$$

$$\frac{d[\text{NH}_3]}{dt} = 3.0 \times 10^{-4} \text{ M/s}$$

Note: The time derivatives for the reactants are negative because the reactant concentrations are decreasing, and those of products are positive since the concentrations of products increase as the reaction progresses.

9.1.2: The Rate Law

As shown above, the rate of the reaction can be followed experimentally by measuring the rate of the loss of a reactant or the rate of the production of a product. The rate of the reaction is often related to the concentration of some or all of the chemical species present at a given time. An equation called the *rate law* is used to show this relationship. The rate law **cannot** be predicted by looking at the balanced chemical reaction but must be determined by experiment. For example, the rate law for the reaction



was experimentally determined to be

$$\text{rate} = k[\text{Cl}_2]^{3/2}[\text{CO}]$$

In this equation, k is the rate constant, and $[\text{Cl}_2]$ and $[\text{CO}]$ are the molar concentrations of Cl_2 and of CO . Each exponent is called the *order* of the given species. Thus, the rate law is second order in Cl_2 and first order in CO . The sum of the individual reactant orders is called the **reaction order**. This reaction has a reaction order of two and a half.

In the next section, we will discuss methods to experimentally determine the rate law.

9.1.3: Contributors and Attributions

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