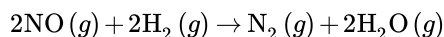


12.10: Determining the Rate Law from Experimental Data

Determining the amount of time a process requires calls for a timer. These devices can be simple kitchen timers (not very precise) or complex systems that can measure to a fraction of a second. Accurate time measurement is essential in kinetics studies for assessing rates of chemical reactions.

Determining the Rate Law from Experimental Data

In order to experimentally determine a rate law, a series of experiments must be performed with various starting concentrations of reactants. The initial rate law is then measured for each of the reactions. Consider the reaction between nitrogen monoxide gas and hydrogen gas to form nitrogen gas and water vapor:



The following data were collected for this reaction at 1280°C (see table below).

Reaction between nitrogen monoxide gas and hydrogen gas to form nitrogen gas and water vapor

Table 12.10.1			
Experiment	[NO]	[H ₂]	Initial Rate (M/s)
1	0.0050	0.0020	1.25×10^{-5}
2	0.010	0.0020	5.00×10^{-5}
3	0.010	0.0040	1.00×10^{-4}

Notice that the starting concentrations of NO and H₂ were varied in a specific way. In order to compare the rates of reaction and determine the order with respect to each reactant, the initial concentration of each reactant must be changed while the other is held constant.

Comparing experiments 1 and 2: The concentration of NO was doubled, while the concentration of H₂ was held constant. The initial rate of the reaction quadrupled, since $\frac{5.00 \times 10^{-5}}{1.25 \times 10^{-5}} = 4$. Therefore, the order of the reaction with respect to NO is 2. In other words, $\text{rate} \propto [\text{NO}]^2$. Because $2^2 = 4$, the doubling of [NO] results in a rate that is four times greater.

Comparing experiments 2 and 3: The concentration of H₂ was doubled while the concentration of NO was held constant. The initial rate of the reaction doubled, since $\frac{1.00 \times 10^{-4}}{5.00 \times 10^{-5}} = 2$. Therefore, the order of the reaction with respect to H₂ is 1, or $\text{rate} \propto [\text{H}_2]^1$. Because $2^1 = 2$, the doubling of H₂ results in a rate that is twice as great. The overall rate law then includes both of these results.

$$\text{rate} = k[\text{NO}]^2 [\text{H}_2]$$

The sum of the exponents is $2 + 1 = 3$, making the reaction third-order overall. Once the rate law for a reaction is determined, the specific rate constant can be found by substituting the data for any of the experiments into the rate law and solving for k .

$$k = \frac{\text{rate}}{[\text{NO}]^2 [\text{H}_2]} = \frac{1.25 \times 10^{-5} \text{ M/s}}{(0.0050 \text{ M})^2 (0.0020 \text{ M})} = 250 \text{ M}^{-2} \text{ s}^{-1}$$

Notice that the rate law for the reaction does not relate to the balanced equation for the overall reaction. The coefficients of NO and H₂ are both 2, while the order of the reaction with respect to the H₂ is only one. The units for the specific rate constant vary with the order of the reaction. So far, we have seen reactions that are first or second order with respect to a given reactant. Occasionally, the rate of a reaction may not depend on the concentration of one of the reactants at all. In this case, the reaction is said to be zero-order with respect to that reactant.

Summary

- The process of using experimental data to determine a rate law is described.
- Once the rate law for a reaction is determined, the specific rate constant can be found by substituting the data for any of the experiments.

- Occasionally, the rate of a reaction may not depend on the concentration of one of the reactants at all; the reaction is said to be zero-order with respect to that reactant.

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