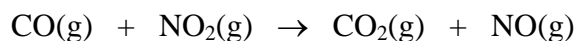


Chemical Kinetics, Reaction Rates, and the Rate Law

1. Consider the following reaction



The kinetic data of initial reaction rate were collected for the initial concentration conditions. The rates are average initial rates, obtained graphically from the original kinetic data. Use the method of initial rates to determine the rate law and rate constant.

	[CO] ₀ (M)	[NO ₂] ₀ (M)	Initial Rate (M/h)
1	5.1×10^{-4}	0.35×10^{-4}	3.4×10^{-8}
2	5.1×10^{-4}	0.70×10^{-4}	6.8×10^{-8}
3	5.1×10^{-4}	0.18×10^{-4}	1.7×10^{-8}
4	1.0×10^{-3}	0.35×10^{-4}	6.8×10^{-8}
5	1.5×10^{-3}	0.35×10^{-4}	10.2×10^{-8}

Rate Law:

$$\text{Rate} = k[\text{CO}]^x[\text{NO}_2]^y$$

To get x , pick 2 reactions where $[\text{NO}_2]$ is held constant...

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{CO}]_1^x[\text{NO}_2]^y}{k[\text{CO}]_2^x[\text{NO}_2]^y}$$
$$\frac{3.4 \times 10^{-8} \text{M/h}}{6.8 \times 10^{-8} \text{M/h}} = \left(\frac{5.1 \times 10^{-4} \text{M}}{1.0 \times 10^{-3} \text{M}} \right)^x$$

$$0.50 = 0.51^x \quad x = 1$$

now repeat the analysis, holding $[\text{CO}]$ constant:

$$\frac{6.8 \times 10^{-8} \text{M/h}}{1.7 \times 10^{-8} \text{M/h}} = \frac{0.70 \times 10^{-4} \text{M}}{0.18 \times 10^{-4} \text{M}}$$

$$4.0 = 3.9^y$$

$$y = 1$$

finally, get the rate constant using any experiment:

$$\text{Rate} = k[\text{CO}][\text{NO}_2]^1$$

$$k = \frac{3.4 \times 10^{-8} \text{M/h}}{(5.1 \times 10^{-4} \text{M})(0.35 \times 10^{-4} \text{M})} = 1.90 \text{ M}^{-1}\text{h}^{-1}$$

2. A first-order reaction proceeds with a rate constant of 0.020/s. If the initial concentration of the reactant is 0.012 M, what will be the concentration after 30 s?

$$k = 0.020 \text{ s}^{-1}$$

$$C = C_0 e^{-kt} = (0.012 \text{ M})e^{-(0.020 \text{ s}^{-1})(30 \text{ s})} = 0.0066 \text{ M}$$

3. Referring to the previous question, what fraction of starting material remains after 15 s?

$$\text{fraction} = \frac{C_t}{C_0} = e^{-kt} = e^{-(0.020 \text{ s}^{-1})(15 \text{ s})} = 0.74$$

That is, 74% of the reactant remains after 15 s.

4. What is the half-life of this reaction?

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{0.020 \text{ s}^{-1}} = 34.7 \text{ s}$$

5. Radioactive isotopes decay obeying a first-order kinetic rate law. Tritium, a radioactive isotope of hydrogen, has a half-life of 12.3 y. It has a natural abundance of 10^{-18} percent (by mol). What mass of tritium (atomic weight 3.016 u) is present in 1000 kg of water? After 100 years, what mass of tritium will remain?

$$t_{\frac{1}{2}} = \frac{0.693}{12.3 \text{ y}} = 5.63 \times 10^{-2} \text{ y}^{-1}$$

$$\text{abundance} = \frac{10^{-18} \text{ atoms } ^3\text{H}}{100 \text{ atoms H}}$$

$$m_{^3\text{H}} = 1000 \times 10^3 \text{ g} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{\text{mol H}_2\text{O}} \times \frac{10^{-18} \text{ atoms } ^3\text{H}}{100 \text{ atoms H}} \times 3.016 \frac{\text{g } ^3\text{H}}{\text{mol } ^3\text{H}}$$

$$m_{^3\text{H}} = 3.35 \times 10^{-15} \text{ g } ^3\text{H}$$

$$m_{100} = 3.35 \times 10^{-15} \text{ g} \times e^{-(5.63 \times 10^{-2} \text{ y}^{-1})(100 \text{ y})} = 1.2 \times 10^{-17} \text{ g}$$