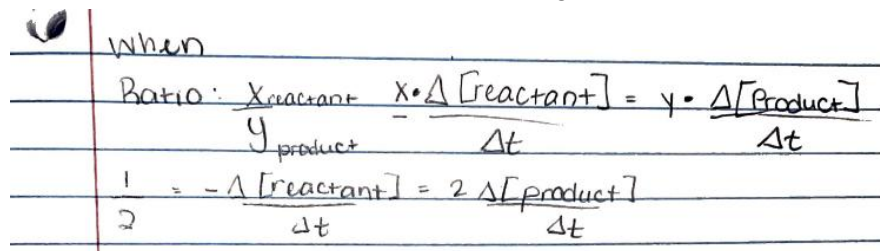


4.1 Introduction

Rate is measured in molarity per unit time.

4.2 Average and Instantaneous Reaction Rates of Change



X and y represent any values for ratio describing the reaction.

$$\text{Average rate of reaction} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Equation 4.1

The lowercase letters are stoichiometric values

Concentration curves: a graph measuring concentration over time

- Steep slope is proportional to speed of reaction; horizontal slope is a point of **chemical equilibrium**
- Slope of the tangent is the **instantaneous rate of change**

4.3 Kinetic experiments

4.3.1 methods of initial rates

Step 1: Pick any two datasets where only one reactant concentration changes. After identifying the dataset pairs, pick any pair to work with in Step 2. We'll select experiments 1 and 2 to start.

Datasets are the experiments.

Step 2: Write out the complete rate law for one experiment and set this as a ratio to the rate law expression for the other experiment. Use actual concentrations and initial rates from the data table for each experiment #. Your ratio will resemble:

$$\frac{\text{initial rate 1}}{\text{initial rate 2}} = \frac{k[A]^x [B]^y}{k[A]^x [B]^y}$$

Equation 4.7

Step 3: You now see why we keep one reactant concentration the same while varying the other! By doing so, we can cancel out the influence of one of the reactants and the rate constant, leaving one unknown value in our equation: the reaction order x .

If it does not cancel out to have a single variable, you may have to restart with different datasets.

Step 4: Solve for x , which gives us the reaction order with respect to $[A]$. You may need to refer to logarithm laws when dealing with method of initial rates:

$$\text{if } x = y^z, \text{ then } \log(x) = z \log(y)$$

Equation 4.9

Step 5: Steps 2–4 are repeated, this time using the other pair of datasets, which we determined to be experiments 2 and 3.

Step 6: Once all reaction orders are known, it's time to solve for the last missing parameter of the rate law: the rate constant k . This is the easiest part of the process. Simply choose any dataset and plug in all values into the dataset's expression for the rate law. Be sure to use the solved values for the reaction orders.

4.3.2 integrated rate laws

Integrated rate law: relationship between reactant concentration vs time

4.3.2A The Zeroth Order Integrated Rate Law

$$\int_{[A]_0}^{[A]} d[A] = - \int_0^t k dt$$

$$[A] = -kt + [A]_0$$

Equation 4.12

If the resultant line is linear, then this is the correct reaction order.

4.3.2B The First Order Integrated Rate Law

$$\int_{[A]_0}^{[A]} \frac{\partial[A]}{[A]} = - \int_0^t k \partial t$$

$$\ln[A] - \ln[A]_0 = -kt$$

$$\ln[A] = -kt + \ln[A]_0$$

If the resultant line is linear, then this is the correct reaction order.

4.3.2C The Second-Order Integrated Rate Law

$$\int_{[A]_0}^{[A]} \frac{\partial[A]}{[A]^2} = - \int_0^t k \partial t$$

$$-\frac{1}{[A]} - \left(\frac{-1}{[A]_0} \right) = -kt$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Equation 4.18

If the resultant line is linear, then this is the correct reaction order.

4.3.2D Reaction Half-Lives

Half-life ($t_{1/2}$): is the time required for the concentration of reactants to be reduced to $\frac{1}{2}$ of its initial amount

$$[A] = -kt + [A]_0$$

$$\frac{1}{2}[A]_0 = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = \frac{1}{2}[A]_0$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

Equation 4.13

- - This is only for the **Zeroth order half life**
 - You may need the initial equation to plug into the derived equation
-

$$\ln[A] = -kt + \ln[A]_0$$

$$\ln(\frac{1}{2}[A]_0) = -kt_{1/2} + \ln[A]_0$$

$$kt_{1/2} = \ln[A]_0 - \ln(\frac{1}{2}[A]_0) = \ln\left(\frac{[A]_0}{\frac{1}{2}[A]_0}\right) = \ln 2$$

$$t_{1/2} = \frac{\ln 2}{k}$$

Equation 4.16

- - For first order half life
-

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{\frac{1}{2}[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$kt_{1/2} = \frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

Equation 4.19

- - For second order half life

4.3.2E Integrated Rate Law Summary

	Zero Order	First Order	Second Order
Rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
Units for k	$M s^{-1}$	s^{-1}	$M^{-1} s^{-1}$
Half-life	$\frac{[A]_0}{2k}$	$\frac{\ln 2}{k}$	$\frac{1}{k[A]_0}$
Integrated rate law in straight-line form	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
Plot for straight line	$[A]_t$ vs. t	$\ln[A]_t$ vs. t	$\frac{1}{[A]_t}$ vs. t
Slope, y intercept	$-k, [A]_0$	$-k, \ln[A]_0$	$k, \frac{1}{[A]_0}$

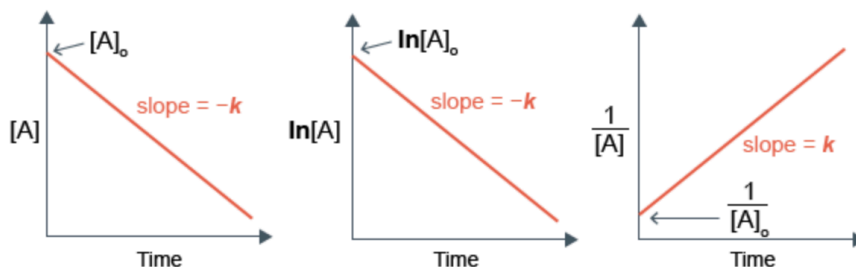


Table 4.2. Integrated rate laws for 0th–2nd order reactions with reactant “A”

4.4 Additional Factors Influencing Reaction Rate

4.4.1 Reaction Rates and Temperature

Total area under the curve at higher kinetic energies also increases; thus, a larger percentage of molecules achieves energies $> E_a$. The net effect is an increase in the rate of a reaction.

Essentially, an increase in temperature increases not only the frequency of collisions but also the frequency of higher energy collisions.

$$k = Ae^{-\frac{E_a}{RT}}$$

Equation 4.21

where k is the rate constant, A is the product of the collision frequency with the fraction of collisions with correct spatial orientation, R is the universal gas constant $8.314 \text{ J/K}\cdot\text{mol}$, T is the Kelvin temperature, and E_a is the activation energy in J/mol .

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$

Equation 4.22

$$\ln k_1 - \ln k_2 = -\frac{E_a}{RT_1} + \frac{E_a}{RT_2}$$

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Equation 4.25

4.4.2 Reaction Rate and Surface Area

- Greater surface area of reactants is proportional to frequency of collisions

4.4.3 Reaction Rate and Catalysts

- A catalyst is usually a compound that increases the rate of a reaction by lowering the activation energy E_a .
- **Homogeneous catalysts:** catalysts that are in the same phase as the reactants
- Enzymes have an active site which the reactants (substrate) are able to bind.
- **Heterogeneous catalysts:** catalysts in different phase as reactants

4.5 Connection Between Kinetics and Equilibrium

- Standard conditions
- Equilibrium conditions
 - Dynamic equilibrium: though there is no overall change, the reactants and products still undergo reactions at eqm
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