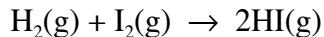


# CH 222 Chapter Twelve Concept Guide

## 1. Reaction Rate

### Problem

Express the rate of reaction for the following reaction:



### Approach

The rate of reaction is defined as the change in either reactant or product concentration divided by the change in time.

### Solution

In terms of reactants, the rate of reaction *could* be:

$$\text{Rate} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t}$$

One molecule of  $\text{H}_2$  and one molecule of  $\text{I}_2$  react with each other, thus the concentration of these two reactants changes at the same rate.

In terms of product, the rate of reaction *could* be:

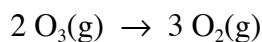
$$\text{Rate} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

Two molecules of HI are produced for every one molecule of  $\text{H}_2$  and one molecule of  $\text{I}_2$  that react. Thus, the change in concentration of HI will be twice as large as the rate of reaction defined in terms of  $\text{H}_2$  or  $\text{I}_2$ .

## 2. Reaction Rate

### Problem

Define the rate of reaction for the following equation:



### Approach

The rate of reaction is defined as the difference in either reactant or product concentration divided by the change in time.

### Solution

In terms of the reactant, the rate of reaction *could* be:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t}$$

In terms of product, the rate of reaction *could* be:

$$\text{Rate} = +\frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t}$$

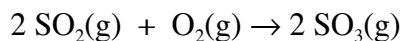
The relationship between the rate of O<sub>3</sub> consumption and O<sub>2</sub> production is:

$$\frac{\Delta[\text{O}_3]}{\Delta t} = -\frac{2}{3} \frac{\Delta[\text{O}_2]}{\Delta t}$$

### 3. Reaction Order

#### Question

The rate equation for the following reaction in the presence of platinum is as follows:



$$\text{Rate} = k[\text{SO}_2][\text{SO}_3]^{-1/2}$$

What is the order of the reaction with respect to each species in the rate equation? What is the reaction order?

#### Approach

The order of the reaction for each substance is given by the exponent on the concentration term in the rate equation.

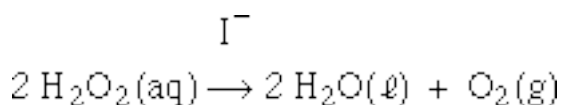
#### Solution

The reaction is first order with respect to SO<sub>2</sub> and one-half order with respect to SO<sub>3</sub>. The overall reaction order is -1/2.

### 4. Reaction Order

#### Question

The iodide-catalyzed decomposition of hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, is known to be first order with respect to H<sub>2</sub>O<sub>2</sub> and first order with respect to I<sup>-</sup>.



Write the rate equation for this reaction. What is the overall order of this reaction?

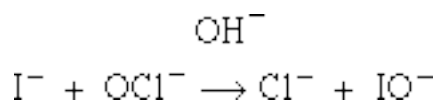
## Solution

The rate equation is:  $\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$ . The overall order of this reaction is the sum of the exponents of the concentration terms in the rate equation. This reaction is second order overall.

## 5. Method of Initial Rates

### Problem

The rate equation for the reaction of iodide ion with hypochlorite ion in an alkaline solution



was thought to be in the form of the following rate equation:

$$\text{Rate} = k[\text{I}^-]^x[\text{OCl}^-]^y[\text{OH}^-]^z$$

Using the method of initial rates, the following data were collected at 25 °C:

Experiment	$[\text{ClO}^-]_0$	$[\text{I}^-]_0$	$[\text{OH}^-]_0$	Initial Rate (mol/L s)
(a)	$2.00 \times 10^{-3}$	$2.00 \times 10^{-3}$	1.00	$2.42 \times 10^{-4}$
(b)	$4.00 \times 10^{-3}$	$2.00 \times 10^{-3}$	1.00	$4.82 \times 10^{-4}$
(c)	$2.00 \times 10^{-3}$	$4.00 \times 10^{-3}$	1.00	$5.02 \times 10^{-4}$
(d)	$2.00 \times 10^{-3}$	$2.00 \times 10^{-3}$	0.500	$4.64 \times 10^{-4}$

Determine the order of the reaction with respect to  $\text{OCl}^-$ ,  $\text{I}^-$ , and  $\text{OH}^-$ , then calculate the rate constant  $k$ .

### Solution

Step 1. Find two experiments where different concentrations of  $\text{I}^-$  are used but  $[\text{OH}^-]$  and  $[\text{ClO}^-]$  are the same.

The data for experiments (a) and (c) show that the reaction rate doubles as the concentration of  $\text{I}^-$  doubles. Thus, the reaction is first order with respect to  $[\text{I}^-]$  and  $x = 1$ . Mathematically, this may be shown as:

$$\text{Rate} = \frac{5.02 \times 10^{-4}}{2.42 \times 10^{-4}} = \frac{k(2.00 \times 10^{-3})^x(4.00 \times 10^{-3})^y(1.00)^z}{k(2.00 \times 10^{-3})^x(2.00 \times 10^{-3})^y(1.00)^z}$$
$$\text{Rate} = 2.07 \approx 2.00$$

Thus, by inspection,  $y$  is 1. This may also be shown mathematically:  $\ln 2 = y \ln 2$ , thus  $y = 1$ .

Step 2. Find two experiments where different  $\text{ClO}^-$  concentrations are used but  $[\text{I}^-]$  and  $[\text{OH}^-]$  are the same.

The data for experiments (a) and (b) show that the reaction rate doubles as the concentration of  $\text{ClO}^-$  doubles. Thus, the reaction is first order with respect to  $[\text{OCl}^-]$  and  $y = 1$ .

Step 3. Find two experiments where different  $\text{OH}^-$  concentrations are used but  $[\text{OCl}^-]$  and  $[\text{I}^-]$  are the same.

The data for experiments (a) and (d) show that the reaction rate doubles as the concentration of  $\text{OH}^-$  is halved. Thus, the reaction is negative first order with respect to  $[\text{OH}^-]$  and  $z = -1$ . The reaction rate decreases with increasing  $[\text{OH}^-]$ .

The complete rate of reaction is:

$$\text{Rate} = k[\text{I}^-][\text{OCl}^-][\text{OH}^-]^{-1}$$

Step 4. The rate constant can be calculated by rearranging the rate equation and choosing data from one experiment.

Using the data from experiment (a):

$$\begin{aligned}k &= \frac{\text{rate}[\text{OH}^-]}{[\text{I}^-][\text{OCl}^-]} \\&= \frac{(2.42 \times 10^{-4} \text{ mol/Ls})(1.00 \text{ mol/L})}{(2.00 \times 10^{-3} \text{ mol/L})(2.00 \times 10^{-3} \text{ mol/L})} \\&= 60.5 \text{ s}^{-1}\end{aligned}$$

Using data from experiment (b),  $k = 60.3 \text{ s}^{-1}$ ; from (c),  $k = 62.8 \text{ s}^{-1}$ ; and from (d),  $k = 58.0 \text{ s}^{-1}$ . The average value of  $k = 60.4 \text{ s}^{-1}$ .

## 6. Half-life

### Question

Compound A decomposes to form B and C in a reaction that is first order with respect to A and first order overall. At  $25^\circ\text{C}$ ,  $k = 0.0470 \text{ s}^{-1}$ . What is the half-life for A at  $25^\circ\text{C}$ ?

### Approach

We will need to use the equation for  $t_{1/2}$ :

$$t_{1/2} = 0.693 / k$$

### Solution

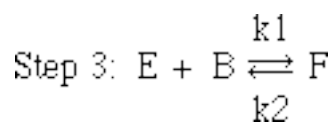
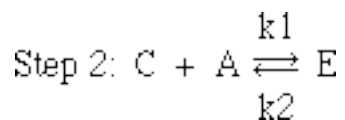
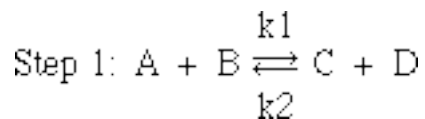
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0470 \text{ s}^{-1}} = 14.7 \text{ s}$$

Half of the original reactant remains after 14.7 s of reaction.

## 7. Reaction Mechanisms

### Question

The proposed mechanism for a reaction is:



What is the overall reaction?

### Approach

We need to add the reactants on the left side of each arrow and add the products on the right side of each arrow, canceling out like terms to determine the overall reaction.

### Solution

The overall reaction is:  $2A + 2B = D + F$ .

## 8. Determining Rate Laws

### Question

Refer to question 7. What is the experimental rate law if the first step is the slow step?

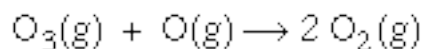
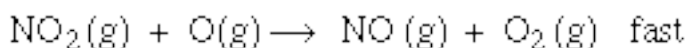
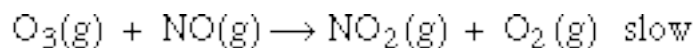
### Solution

The experimental rate law, contingent upon the first step being the slow step, is:  $R = k[A][B]$ .

## 9. Catalysts

### Question

One pathway for the destruction of ozone in the upper atmosphere is:



Which species is the catalyst and which species is the intermediate?

### Solution

The catalyst is a species that increases the rate of a chemical reaction without itself undergoing any permanent change. It is involved in one step of the mechanism and regenerated at a later step. It is not a reactant or product in the overall reaction. In this example, the catalyst is NO. The intermediate is a species that is produced during the course of a reaction but always reacts further and is not among the final products. Here, the intermediate is NO<sub>2</sub>.

## 10. Determining Activation Energy

### Question

A plot of  $\ln k$  vs.  $\frac{1}{T}$  gives a slope of  $-1.50 \times 10^4 \text{ K}$ . What is the activation energy for this particular reaction?

### Approach

We will need to use the following equation:

$$\ln k = \ln A - \left( \frac{E_a}{R} \right) \left( \frac{1}{T} \right)$$

When plotting  $\ln k$  vs.  $(1/T)$ , the slope of the line is equal to  $-\frac{E_a}{R}$

### Solution

$$\ln k = \ln A - \left( \frac{E_a}{R} \right) \left( \frac{1}{T} \right)$$

$$E_a = -(-1.50 \times 10^4 \text{ K})(8.314 \text{ J/K}) = 125000 \text{ J} = 125 \text{ kJ}$$

## 11. Activation Energy

### Question

Do reactions with larger activation energies have smaller or larger values of  $k$ , and as a result, are these reactions slow or fast?

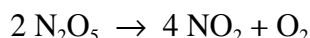
### Solution

Large values of activation energy lead to small values of  $k$ . These reactions are slower, as we would expect from our understanding of effective collisions and energy relationships. With a large activation energy, only a small fraction of the collisions between molecules lead to products.

## 12. Activation Energy and Temperature

### Question

The rate constant for the following reaction



was measured at two different temperatures: at  $T_1 = 25.0 \text{ }^\circ\text{C}$ ,  $k_1 = 5.60 \times 10^{-5} \text{ s}^{-1}$ , and at  $T_2 = 67.0 \text{ }^\circ\text{C}$ ,  $k_2 = 9.32 \times 10^{-3} \text{ s}^{-1}$ . What is the activation energy for this reaction?

### Approach

The solution to this problem requires solving for  $E_a$  using the following equation and substituting in  $k_1$ ,  $k_2$ ,  $T_1$ , and  $T_2$ :

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

### Solution

$$\left( \frac{-E_a}{8.314 \text{ J/K} \cdot \text{mol}} \right) \left( \frac{1}{340.0} - \frac{1}{298.0} \right) = \ln \frac{9.32 \times 10^{-3}}{5.60 \times 10^{-5}}$$

$$E_a = 1.0 \times 10^5 \text{ J/mol}$$