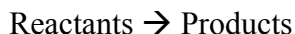


## The Rate of a Reaction

The area of chemistry that deals with the rate or speed of chemical reactions is known as *chemical kinetics*. The word “kinetic” is derived from the Greek name *kinitikos* that means movement or motion. In the present context, the kinetic means the reaction rate or rate of a reaction that is defined as the change in concentration of a reactant or a product with time (M/s).

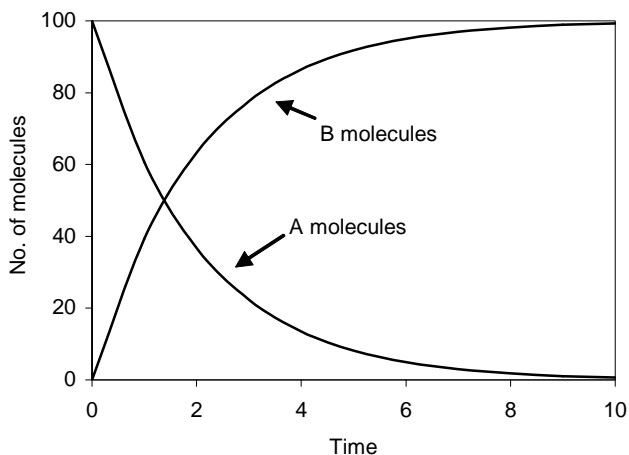
Chemical reaction can be represented by the following general equation.



It is very important for you to understand the meaning of the above equation, which tells us that, during the course of a reaction, the reactant molecules are used up and product molecules are formed. The arrow between the reactants and products indicates the direction of the reaction. Let us represent reactant molecules by A and product molecules by B. Then we can re-write the above equation in the following form:



This is a very simple reaction where A molecules are converted into B molecules or one mole of A disappears for each mole of B forms. As the time progresses, the number A molecules decrease and B molecules increase that is shown in the following figure.



When we say “rate”, it usually means the change in some property with change in time.

$$\text{rate} = \frac{\text{change in property}}{\text{change in time}} = \frac{\Delta \text{property}}{\Delta \text{time}}$$

where the Greek symbol  $\Delta$  (pronounced as *delta*) is used to mean “change”. Let us say that you have a plant in your house that grew from 10 cm to 25 cm in two weeks (14 days). Then the rate of growth of a plant per day is,

$$\text{rate of growth} = (25 \text{ cm} - 10 \text{ cm}) / 14 \text{ day} = 15 \text{ cm} / 14 \text{ day} = 1.07 \text{ cm/day}$$

Keep in mind that here the day is used for time. In addition, the calculated rate is the **overall rate** for the entire time period (14 day); it does not give you the growth by day.

As far as chemical reactions are concerned, some property is the concentration and time is in seconds. Hence, the rate in chemical reactions is defined as the change in concentration of either the reactant or the product with change in time, which is expressed as

$$\text{rate of reaction} = -\frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate of reaction} = \frac{\Delta[B]}{\Delta t}$$

The square bracket [ ] is used to mean molar concentration (mol / l = M). And also, there is a negative sign (-) in front of  $\Delta[A]$  because concentration of A decreases during the time interval. The rate is a positive quantity and therefore the negative sign is required in the expression of rate of disappearance of A to make it positive. On the other hand, the minus sign does not require in the expression of rate formation of products as the concentration of B increases with time.

The reaction given in Equation (1) is very simple and writing the rate expression is not difficult. However, if the reaction is more complex care must be taken in writing the rate expression. Consider the following reaction.



Here two moles of A convert into 3 moles of B. It means that for every 3 moles of B formed, 2 moles of A must disappear. **Remember that rate of chemical reaction is the same whether it is expressed in terms of reactant concentration or product concentration**; the rate of disappearance of A must be equal to rate of formation of B. To equalize them, we must divide the rate expressions by their corresponding moles. The expression for the above reaction is

$$\text{rate of reaction} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate of reaction} = \frac{1}{3} \frac{\Delta[B]}{\Delta t}$$

We can generalize the rate expression by considering the general chemical reaction, which is usually written as



Here  $a$  moles of A combine with  $b$  moles of B and produce  $c$  moles C and  $d$  moles of D. The rate expression for this general reaction is

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

### Example

Write the rate expressions for the following chemical reactions in terms of the rate of disappearance of reactants and the rate of formation of products:

- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2 \text{HI}(\text{g})$
- $5\text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6 \text{H}^+ \rightarrow 3 \text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
- $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
- $2 \text{C}_2\text{H}_6(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$

### Answer

$$\text{a. } \text{rate of reaction} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

$$\text{b. } \text{rate of reaction} = -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

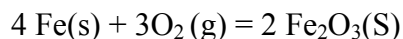
$$\text{c. } \text{rate of reaction} = -\frac{\Delta[\text{NO}]}{\Delta t} = -\frac{\Delta[\text{O}_3]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

$$\text{d. } \text{rate of reaction} = -\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$$

$$\text{e. } \text{rate of reaction} = -\frac{1}{2} \frac{\Delta[\text{C}_2\text{H}_6]}{\Delta t} = -\frac{1}{7} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

### Example

Consider the following chemical reaction of rusting of iron nail.



If the rate of consumption (disappearance) of  $\text{O}_2(\text{g})$  is  $0.065 \text{ /s}$ , what is the (a) rate of disappearance of  $\text{Fe}(\text{s})$ ? And (b) rate of formation of  $\text{Fe}_2\text{O}_3(\text{s})$

### Answer

$$\text{Rate of consumption of } O_2 = -\frac{\Delta[O_2]}{\Delta t} = 0.065 /s$$

$$\text{Or } \frac{\Delta[O_2]}{\Delta t} = -0.065 /s$$

(a) rate of disappearance of Fe(s)

$$-\frac{1}{4} \frac{\Delta Fe(s)}{\Delta t} = -\frac{1}{3} \frac{\Delta [O_2]}{\Delta t} = -\frac{1}{3} \times 0.065 /s$$

$$\text{Therefore } \frac{\Delta Fe(s)}{\Delta t} = 4/3 \times 0.065 /s = 0.0867 /s$$

(b) rate of formation of Fe<sub>2</sub>O<sub>3</sub>(S)

$$-\frac{1}{3} \frac{\Delta[O_2]}{\Delta t} = -\frac{1}{3} \times (-0.065 /s) = \frac{1}{2} \frac{\Delta[Fe_2O_3]}{\Delta t}$$

$$\text{Therefore } \frac{\Delta Fe(s)}{\Delta t} = 2/3 \times (0.065 /s) = 0.0433 /s$$

**Check:** Remember the rate should be the same no matter hoe it is defined either with reactants of products. Let us verify this.

$$\frac{1}{3} \frac{\Delta[O_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[Fe]}{\Delta t} = \frac{1}{2} \frac{\Delta[Fe_2O_3]}{\Delta t}$$

$$\begin{array}{ccc} 1/3 \times 0.065 /s & = & 1/4 \times 0.0867 /s & = & 1/2 \times 0.0433 /s \\ \downarrow & & \downarrow & & \downarrow \\ 0.0217 /s & = & 0.0217 /s & = & 0.0217 /s \end{array}$$