

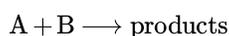
## 2.1.5.1: Pseudo-1st-order reactions

Under certain conditions, the 2nd order kinetics can be approximated as first-order kinetics. These **pseudo-1<sup>st</sup>-order reactions** greatly simplify quantifying the reaction dynamics.

### Introduction

A 2nd-order reaction can be challenging to follow mostly because the two reactants involved must be measured simultaneously. There can be additional complications because certain amounts of each reactant are required to determine the reaction rate, for example, which can make the cost of one's experiment high if one or both of the needed reactants are expensive. To avoid more complicated, expensive experiments and calculations, we can use the pseudo-1<sup>st</sup>-order reaction, which involves treating a 2<sup>nd</sup> order reaction like a 1<sup>st</sup> order reaction.

In **second-order reactions** with two reactant species,



the rate of disappearance of  $A$  is

$$\frac{d[A]}{dt} = -k[A][B]$$

as discussed previously (**Case 2a**), the integrated rate equation under the condition that  $[A]$  and  $[B]$  are not equal is

$$\frac{1}{[B]_0 - [A]_0} \ln \frac{[B][A]_0}{[A][B]_0} = kt \quad (2.1.5.1.1)$$

However, when  $[B]_0 \gg [A]_0$ , then  $[B]_0 \approx [B]$  and Equation 2.1.5.1.1 becomes

$$\frac{1}{[B]_0 - [A]_0} \ln \frac{[B][A]_0}{[B]_0[A]} \approx \frac{1}{[B]} \ln \frac{[A]_0}{[A]} = kt$$

or

$$[A] = [A]_0 e^{-[B]kt}$$

This functional form of the decay kinetics is similar to the first order kinetics and the system is said to operate under pseudo-first order kinetics. To reach a pseudo-1<sup>st</sup>-order reaction, we can manipulate the initial concentrations of the reactants. One of the reactants,  $B$ , for example, would have a significantly higher concentration, while the other reactant,  $A$ , would have a significantly lower concentration. We can then assume that the concentration of reactant  $B$  effectively remains constant during the reaction because its consumption is so small that the change in concentration becomes negligible. Because of this assumption, we can multiply the reaction rate,  $k$ , with the reactant with assumed constant concentration,  $B$ , to create a new rate constant ( $k' = k[B]$ ) that will be used in the new rate equation,

$$\text{Rate} = k'[A]$$

as the new rate constant so we can treat the 2<sup>nd</sup> order reaction as a 1<sup>st</sup> order reaction.

#### Overloading

One can also do the same by overloading the initial concentration of  $A$  so that it effectively remains constant during the course of the reaction. For example, if one were to dump a liter of 5 M HCl into a 55 M ocean, the concentration of the mixture would be closer or equal to that of the ocean because there is so much water physically compared to the HCl. Even if the amount of water was one liter this would still be the case because 55 M is relatively large compared to 5 M.

If we have an instance where there are more than two reactants involved in a reaction, all we would have to do to make the reaction pseudo-1<sup>st</sup>-order is to make the concentrations of all but one of the reactants very large. If there were three reactants, for example, we would make two of the three reactants be in excess (whether in amount or in concentration) and then monitor the dependency of the third reactant.

We can write the pseudo<sup>st</sup>-order reaction equation as:

$$[A] = [A]_0 e^{-[B]_0 k t} \quad (2.1.5.1.2)$$

or

$$[A] = [A]_0 e^{-k' t}$$

where

- $[A]_0$  is the initial concentration of  $A$ ,
- $[B]_0$  is the initial concentration of  $B$ ,
- $k'$  is the pseudo-1<sup>st</sup>-order reaction rate constant,
- $k$  is the 2<sup>nd</sup> order reaction rate constant, and
- $[A]$  is the concentration of  $A$  at time  $t$ .

By using natural log to both sides of the pseudo-1<sup>st</sup>-order equation we get:

$$\ln\left(\frac{A}{A_0}\right) = -k[B]_0 t$$

or

$$\ln\left(\frac{A}{A_0}\right) = -k' t$$

#### ✓ Example 2.1.5.1.1

If a 2<sup>nd</sup> order reaction has the rate equation  $\text{Rate} = k[A][B]$ , and the rate constant,  $k$ , is  $3.67 \text{ M}^{-1} \text{ s}^{-1}$ ,  $[A]$  is  $4.5 \text{ M}$  and  $[B]$  is  $99 \text{ M}$ , what is the rate constant of its pseudo-1<sup>st</sup>-order reaction?

##### Solution

Because  $[B]$  is in excess we multiply  $99 \text{ M}$  with  $3.67 \text{ M}^{-1} \text{ s}^{-1}$

$$(99 \text{ M})(3.67 \text{ M}^{-1} \text{ s}^{-1}) = 363.33 \text{ s}^{-1}$$

#### ✓ Example 2.1.5.1.2

If  $[A] = 55 \text{ M}$  at  $39 \text{ s}$ ,  $[A]_0 = 99 \text{ M}$ , and  $[B]_0 = 1000 \text{ M}$ , what is the 2<sup>nd</sup> order reaction rate constant?

##### Solution

Use the Equation 2.1.5.1.2

$$(55 \text{ M}) = (99 \text{ M})e^{-k(1000\text{M})(39\text{s})}$$

$$k' = 1.507 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$$

#### ✓ Example 2.1.5.1.3

What is the concentration of  $A$  at time  $45 \text{ s}$  if  $[A]_0 = 1 \text{ M}$ ,  $[B]_0 = 45 \text{ M}$ , and 2<sup>nd</sup> order rate constant is  $0.6 \text{ M}^{-1} \text{ s}^{-1}$ ?

##### Solution

Use the Equation 2.1.5.1.2

$$[A] = (1)e^{-(0.6 \text{ M}^{-1} \text{ s}^{-1})(45)}$$

$$[A] = 1.88 \times 10^{-12} \text{ M}$$

#### ✓ Example 2.1.5.1.4

What is the rate of a reaction if  $[A]_0 = 560 \text{ M}$ ,  $[B]_0 = 0.2 \text{ M}$ , and 2<sup>nd</sup> order rate constant is  $0.1 \text{ M}^{-1} \text{ s}^{-1}$ ?

##### Solution

Use the equation  $R = k'[A][B]$

$$R = (0.1\text{M}^{-1}\text{s}^{-1})(560\text{M})(0.2\text{M})$$

$$\text{Rate} = 11.2\text{Ms}^{-1}$$

### Half-Life in a Pseudo-1st Order reaction

Half-life refers to the time required to decrease the concentration of a reactant by half, so we must solve for  $t$ . Here,  $[B]$  will be the reactant in excess, and its concentration will stay constant.  $[A]_o$  is the initial concentration of  $A$ ; thus the half-life concentration of  $A$  is  $0.5[A]_o$ .

The pseudo-1<sup>st</sup>-order reaction equation can be written as:

$$[A] = [A]_o e^{-[B]kt} \quad \text{or} \quad \frac{[A]}{[A]_o} = e^{-k't}$$

By taking natural logs on both sides of the pseudo-1<sup>st</sup>-order equation, we get:

$$\ln\left(\frac{[A]}{[A]_o}\right) = -k't$$

Because the concentration of  $A$  for a half-life  $t_{1/2}$  is  $1/2[A]_o$ :

$$\ln\left(\frac{1/2[A]_o}{[A]_o}\right) = \ln\left(\frac{1}{2}\right) = -k't_{1/2}$$

Recalling that  $k' = k[B]$ ,  $[B] \approx [B]_o$  and that  $-\ln(1/2) = \ln 2$ :

$$\ln(2) = k[B]_o t_{1/2}$$

or

$$t_{1/2} = \frac{\ln 2}{k[B]_o}$$

#### ✓ Example 2.1.5.1.5

What is the half-life of a reaction with  $[A]_o = 109\text{ M}$ ,  $[B]_o = 1\text{ M}$ ,  $k' = 45\text{ M}^{-1}\text{s}^{-1}$ ?

#### Solution

Because  $[A]$  is in excess we can multiply the  $k'$  with  $[A]_o$  to find  $k$

$$(109\text{M})(45\text{M}^{-1}\text{s}^{-1}) = 4905\text{s}^{-1}$$

$$t_{1/2} = (\ln 0.5 / -k)$$

$$t_{1/2} = 1.41 \times 10^{-4}\text{s}$$

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