☞ **Dear students: - Copy the note and do the given homework on your exercise book!**

Month _____**March**_____

Subject: ___chemistry _____

Grade & section _____11(**B – E**) ___

Unit: **4**

Main topic: **Integrated Rate Equation (concentration against time or the relation between concentration and time)**

Sub topic/s:

Page range from:

Monday, March 30, 2020

Dear my students this review questions and summary of main points in subtopics that helps you to do the question. The answer will be released after two days, so follow the page.

We will meet in person once this difficult season passes. Until then, Stay At Home! Take Care!

Integrated Rate Equation (concentration against time or the relation between concentration and time)

Rate law expressions enable us to calculate the rate of a reaction from the rate constant and reactant concentrations. The rate laws can also be used to determine the concentrations of reactants at any time during the course of a reaction. We will illustrate this application by first considering two of the most common rate laws those applying to reactions that are first order overall and those applying to reactions that are second order overall.

First-Order Reactions

A first-order reaction is a reaction whose rate depends on the reactant concentration raised to the first power. In a first-order reaction of the type

.   A ⟶   Products

Rate is   rate = $-\dfrac{d[A]}{dt}$ .... (1)

From the rate law in our first day of home lesson, we also know that

     rate = k[A] ....(2)

To obtain the units of k for this rate law, we write

$$K = \dfrac{rate}{[A]} = \dfrac{M/s}{M} = 1/s = s^{-1} \quad or \quad \dfrac{mol/L/s}{mol/L} = 1/s = s^{-1}$$

Combining the equation (1) and (2) for the rate we get

$$- \frac{d[A]}{dt} = k[A] \quad .... \ (3)$$

Rearranging equation (3), we get

$$\frac{-d[A]}{[A]} = kdt \ ....(4)$$

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

Integrating between, t = 0 and t = t gives

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

Where **ln** is the natural logarithm, and $[A]_0$ and $[A]_t$ are the concentrations of A at times t = 0 and t = t, respectively. It should be understood that t = 0 need not correspond to the beginning of the experiment; it can be any time when we choose to start monitoring the change in the concentration of A

$$\int_{Ao}^{At} \frac{[A]}{[A]} = -k \int_o^t dt \ ....(5)$$

$$\ln[A]_t - \ln[A]_o = kt ....(6)$$

$$\ln \frac{[A]_t}{[A]} = -kt \ ----------------------------------.................((8)$$

$$\ln[A]t = \ln[A]_o - kt ....(9)$$

Equation (9) has the form of the linear equation y = mx + b, in which m is the slope of the line that is the graph of the equation:

$$\ln [A]_t = (-k)(t) + \ln [A]_o$$

$$y = mx + b$$

. As we would expect during the course of a reaction, the concentration of the reactant A decreases with time for a first-order reaction, if we plot ln $[A]_t$ versus time (y versus x), we obtain a straight line with a slope equal to -k and a y intercept equal to ln $[A]_o$ Thus, we can calculate the rate constant from the slope of this plot.

Example 1

The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of 6.7 3 1024 s^{-1} at 500°C.

(a) If the initial concentration of cyclopropane was 0.25 M, what is the concentration after 8.8 min?

(b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from 0.25 M to 0.15 M?

(c) How long (in minutes) will it take to convert 74 percent of the starting material?

Strategy: The relationship between the concentrations of a reactant at different times in a first-order reaction is given in above equation. In (a) we are given $[A]_0 = 0.25$ M and asked for $[A]_t$ after 8.8 min. In (b) we are asked to calculate the time it takes for cyclopropane to decrease in concentration from 0.25 M to 0.15 M. No concentration values are given for (c). However, if initially we have 100 percent of the compound and 74 percent has reacted, then what is left must be (100% 2 74%), or 26%. Thus, the ratio of the percentages will be equal to the ratio of the actual concentrations; that is, $[A]_t / [A]_0 = 26\%/100\%$, or 0.26/1.00.

Solution (a). In applying Equation (8) we note that because k is given in units of s–1, we must first convert 8.8 min to seconds:

$$8.8 \text{ min} \times \frac{60s}{1min} = 528s$$

We write

$$\ln[A]_t = -kt + \ln [A]_0$$
$$= - (6.7 \times 10^{-4} \text{ s}^{-1}) (528 \text{ s}) + \ln (0.25)$$
$$= - 1.74$$
$$\text{Hence,} \quad [A]_t = e^{-1.74} = 0.15 \text{ M}$$

Note that in the $\ln[A]_0$ term, $[A]_0$ is expressed as a dimensionless quantity (0.25) because we cannot take the logarithm of units.
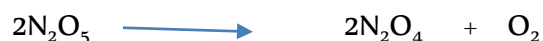
(b) Using Equation ( ),

$$\ln \frac{(0.15M)}{(0.25M)} = - (6.7 \times 10^{-4} \text{ s}^{-1})t$$

$$t = 7.6 \times 10^{2}s \times \frac{1min}{60s} = 13 \text{ min}$$

(c) From Equation (   )

$$\ln \frac{(0.26)}{1.00} = - (6.7 \times 10^{-4} \text{ s}^{-1})t$$

$$t = 33 \text{ min}$$

Example 2

Dinitrigen pentaoxide (N_2O_5) is not very stable. In the gas phase or dissolved in a nanoqueous solvent, like carbon tetrachloride, it decomposes by first order reaction into dinitrigen tetra oxide and molecular oxygen.

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

The rate law   is   rate $= k [N_2O_5]$

At 45°C, the rate constant for the reaction in carbon tetrachloride is 6.22 x 10^{-4} s^{-1} . If the initial concentration of N2O5 in at 45oC is 0.500 M, what will its concentration be after exactly one hour?

Solution:

- The reaction is first order

- $[N_2O_5]o$ = 0.50 M, $[N_2O_5]t$ = ?M

- K = 6.22 x 10^{-4} s^{-1} , t = 1hr = 3600s

Using equation ( )

$$[N_2O_5]_t = [N_2O_5]_o e^{-kt}$$

$$= (0.500m) \, e^{-(6.22 \times 10\text{-}4 \text{ M}) \, (3600s)}$$

$$= 0.055M$$

After one hour the concentration of N2O5 will have dropped to 0.055 M.

The calculation could also have been done using equation ( ). We would begin by solving for the concentration ratio, substituting values for k and t.

$$\ln \frac{([N_2O_5]_o)}{([N_2O_5]t)} = (6.22 \times 10^{-4} \text{ s}^{-1}) \, (3600s) = 2.24$$

To take the antilogarithm (antiln), we raise "e" to the 2.24 power

$$\text{antiln} \left\{ \ln \frac{([N2O5]o)}{([N_2O_5]t)} \right\} = \frac{[N_2O_5]_o}{[N_2O_5]_t}$$

$$\text{antiln} \, (2.24) = e^{2.24}$$

$$= 9.4$$

Now we can substitute the know concentration, $[N_2O_5]_o$ = 0.500M. This gives

$$\frac{0.500M}{[N_2O_5]_t} = 9.4$$

Hence, $[N_2O_5]_t$ = 0.053 M

Practice Exercise.

1. The reaction 2A ⟶ B is first order in A with a rate constant of 2.8 x 10^{-2} s^{-1} at 80°C. How long (in seconds) will it take for A to decrease from 0.88 M to 0.14 M?
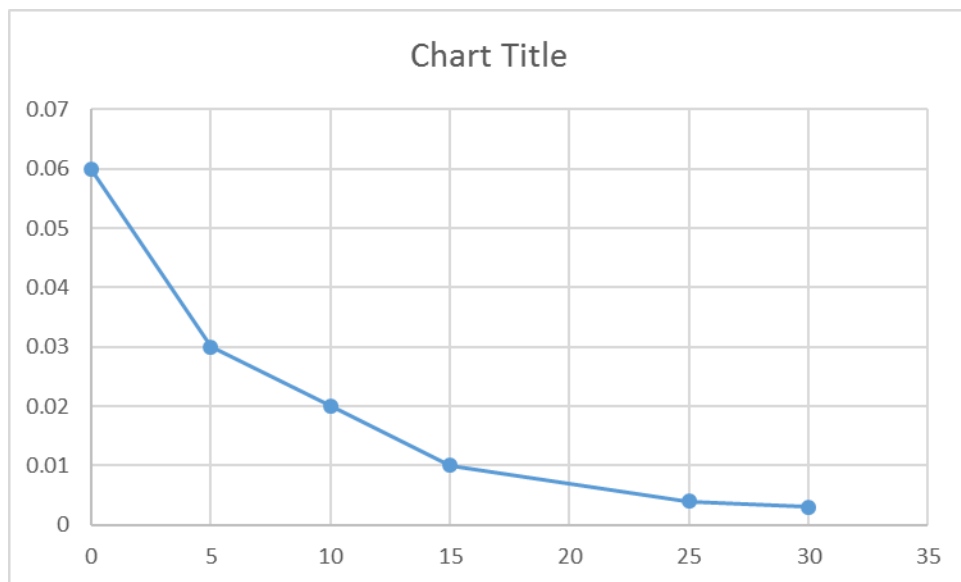
Tuesday, March 31, 2020

From Monday's lesson, we can take the antilongarithm of both sides of equation (9) and rearrange it to obtain the concentration at time "t" directly as a function of time

$$[A]_t = [A]_o\, e^{-kt} \quad\text{..(10)}$$

Graphical Determination of rate constant for First order reaction

a) Concentration against time

Chart Title

K is the slope of the graph

Unit of k for first order reaction is s^{-1} or min^{-1} or general it is inverse $(time^{-1})$

Practice Exercise

Draw the graph of rate against concentration by using the table in our previous lesson and compare with (a).

Half –life of a reactant is a measure of its speed of reaction for first order

The half-life of a reactant is a convenient way to describe how fast it reacts, particularly for a first order process. A reactant's half-life, $t_{1/2}$ is the amount of time required for half of the reactant to disappear. A rapid reaction has a short half-life because half of the reactant disappears quickly. The equations for half-lives depend on the order of the reaction.

When a reaction, overall, is first order, the half-life of the reactant can obtained from Equation (9) by setting $[A]_t$, equal to one-half-life of $[A]_o$.

$$[A]_t = 1/2[A]_o$$

Substituting $_{1/2}[A]_t$ for $[A]_o$ and $t_{1/2}$ for t in equation (9), we have

$$\frac{\ln[A]_o}{_{1/2}[A]_o} = kt1/2$$

Noting that the left-hand side of the equation simplifies to ln2, and solving for $t_{1/2}$, we have

$$t_{1/2} = \ln2/k\ldots\ldots\ldots(11).$$

Since $\ln2 = 0.693$, the equation (11) can be written as

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

- ✓ Because k is constant for a given reaction, the half- life is also a constant for any particular first-order reaction (at any given temperature).
- ✓ Half-life of a first order is not affected by the initial concentration of the reactant

Wednesday, April 1, 2020

SECOND-ORDER REACTIONS

A second-order reaction is a reaction whose rate depends on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power. The simpler type involves only one kind of reactant molecule:

$$A \longrightarrow product$$

Where, rate $= \dfrac{-d[A]}{dt}$
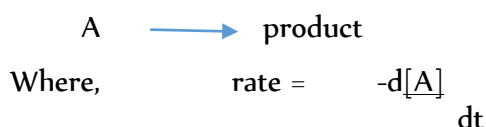
From the rate law, rate $= k[A]^2$ .... (9)

As before, we can determine the units of k by writing

$$K = \dfrac{rate}{[A]^2} = \dfrac{M/s}{M^2} = 1/ M.s \text{ or } 1/ mol/L.s \text{ or } L.s.mol^{-1}$$

Another type of second-order reaction is

$$A + B \longrightarrow product$$

$$Rate = k[A][B]$$

The reaction is first order in A and first order in B, so it has an overall reaction order of 2.
Using calculus, we can obtain the following expressions for "A $\longrightarrow$ product" second-order reactions:

$$\dfrac{-d[A]}{dt} = k [A]^2 \quad ....(11)$$

Integrating between t = 0, t = t and $[A]_0$, $[A]_t$, as we did in our Monday's lesson it gives

$$1/[A]_t = 1/[A]_o + kt \quad .... (12)$$

Equation (12) has the form of a linear equation. As below Figure shows, a plot of $1/[A]_t$ versus t gives a straight line with slope 5 k and y intercept 5 $1/[A]0$. (The corresponding equation for "A + B product" reactions is too complex for our discussion.)
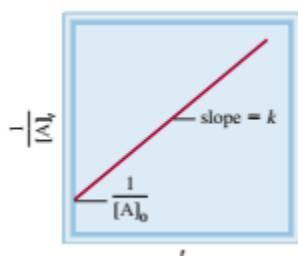
A plot of $1/[A]_t$ versus t for a second-order reaction. The slope of the line is equal to k.

We can obtain an equation for the half-life of a second-order reaction by setting

$$[A]_t = [A]_0/_2 \text{ in Equation (12)}$$

$$1/[A]0/_2 = kt_{1/2} + 1/[A]_o$$

Solving for $t_{1/2}$ we obtain

$$t_{1/2} = 1/ k[A]0 ....(13)$$

Example

Iodine atoms combine to form molecular iodine in the gas phase

$$I(g) + I(g) \longrightarrow I_2(g)$$

This reaction follows second-order kinetics and has the high rate constant 7.0 3 109/M . s at 23°C. (a) If the initial concentration of I was 0.086 M, calculate the concentration after 2.0 min.

(b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 M and if it is 0.42M.

Strategy (a) the relationship between the concentrations of a reactant at different times is given by the integrated rate law. Because this is a second-order reaction, we use Equation (12).

(b) We are asked to calculate the half-life. The half-life for a second-order reaction is given by Equation (13).

Solution (a) to calculate the concentration of a species at a later time of a second order reaction, we need the initial concentration and the rate constant. Applying Equation (12)

$$1/[A]_t = kt + 1/[A]_o$$

$$= (7.0 \ 3 \ 10^9/M. \ s) \ (2.0 \ min \ x \ 60s/1 \ min) + 1/0.086 \ M$$

Where $[A]_t$ is the concentration at t = 2.0 min. Solving the equation, we get

$[A]_t = 1.2 \times 10^{-12} \ M$

This is such a low concentration that it is virtually undetectable. The very large rate constant for the reaction means that practically all the I atoms combine after only 2.0 min of reaction time.

(b) We need Equation (13) for this part. For $[I]_o = 0.60 \ M$

$$t_{1/2} = 1/k[A]_o$$

$$= 1/ \ (7.0 \times 10^9/M. \ s) \ (0.42 \ M)$$

$$= 3.4 \times 10^{-10} \ s$$

Check

These results confirm that the half-life of a second-order reaction, unlike that of a first-order reaction, is not a constant but depends on the initial concentration of the reactant(s).

Review of Concepts

Consider the reaction A $\longrightarrow$ products.

✓ The half-life of the reaction depends on **the initial concentration of A.**

✓ Which of the following statements is inconsistent with the given information?

✓ The half-life of the reaction decreases as the initial concentration increases.

✓ A plot of ln $[A]_t$ versus t yields a straight line.

✓ Doubling the concentration of A quadruples the rate.

Practice Exercise

The reaction 2A $\longrightarrow$ B is second order with a rate constant of 5 1/M . min at 24°C. (a) Starting with $[A]_o$ = 0.0092 M, how long will it take for $[A]_t$ = 3.7 x 10-3 M? (b) Calculate the half-life of the reaction.