Half-Life and First Order Reactions

The rate constant, ***k***, is a good indicator of the speed of a chemical reaction. Another useful measure of reaction speed is the ***Reaction Half Life*** ($t_{1/2}$). The half-life of a reaction is the time required for the concentration of a reactant to decrease to one half of its initial concentration. All first-order reactions have constant half-lives. (A second order curve will have half-lives which get successively larger.)

Half-life has numerous uses such as:

- It can be used to determine the order of a reaction.
- Half-life indicates the stability of a reactant, the longer the half-life, the greater the stability of the reactant(s).
- It can also be used to determine the rate constant of a first order reaction.

Half-life can also be associated with drug use as it is the time required for ½ the drug to be eliminated from the body. For example, the half-life of cocaine is only a few minutes whereas the half-life of marijuana is higher – marijuana can be detected up to 28 days after use because it is absorbed by fatty tissues thus making diffusion into the blood stream an extremely slow process.

For a reactant ***A***, in a reaction that is first order in ***A***, $t_{1/2}$ is the time when:

$$[A]_t = \frac{1}{2}[A]_0 \qquad \text{or} \qquad \frac{[A]_t}{[A]_0} = \frac{1}{2}$$

By taking the natural log of both sides the result is:

$$\ln\frac{[A]_t}{[A]_0} = -kt$$

Now substituting the fact that $\frac{[A]_t}{[A]_0} = \frac{1}{2}$ when $t = t_{1/2}$, we have:

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

$$0.693 = kt_{1/2}$$

$$t_{1/2} = \frac{0.693}{k} \rightarrow \text{Equation 1}$$

Equation (1) shows that the half-life of a first order reaction is a constant and independent of the initial concentration of the reactant. Thus, it would take the same time for the concentration of the reactant to decrease from 1.0 M to 0.5 M as it would to decrease from 0.10 M to 0.05 M. It also shows that the half-life indicates the magnitude of the rate constant. The shorter the half-life the larger the value of ***k,*** thus the faster the reaction will occur. This means that less time is required to reach the half-way point.

Two examples of half-life are:

^{125}Iodine has a half-life of 63 days where $k = 0.011$/day

^{241}Americium has a half-life of 430 years where $k = 0.0016$/year

Example 1

Given the reaction $2H_2O_2 \rightarrow H_2O + O_2$ where the rate is $k[H_2O_2]^1$ and the rate constant is $1.06 * 10^{-3}$/min, find the half-life.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.06*10^{-3}/\text{min}} = 654\,\text{min}$$

This implies the following that if the concentration of H_2O_2 is 0.02 M then after 654 min the concentration will now be 0.01 M. After another 654 min the concentration will now be 0.005 M.

In summary:

a) After one half-life → 50% remains → 0.01M → 50% of the reactant has been consumed
b) After two half-lives → 25% remains → 0.005M → 75% of the reactant has been consumed
c) After three half-lives → 12.5% remains → 0.0025M → 87.5% of the reactant has been consumed

Question 1

Sucrose $C_{12}H_{22}O_{11}$ decomposes to fructose and glucose in acid solution with the rate law: Rate = k[sucrose]^1; where k = 0.208/hour at 25°C.

a) **Find the half-life of sucrose under these conditions.**
b) **Calculate the time required for 87.5% of the initial concentration of sucrose to disappear.**

Question 2

The rate constant for the transformation of cyclopropane to propene is $5.40 * 10^{-2}$/hour.

a) **What is the half-life of the reaction?**
b) **What fraction of cyclopropane remains after 51.2 hours?**
c) **What fraction remains after 18.0 hours?**

Question 3

The decomposition of ethane, C_2H_6, to methyl radicals is a first order reaction with a rate constant of 5.36 * 10^{-4}/second at 700°C. Calculate the half-life of the reaction ($C_2H_6 \rightarrow 2CH_3^{\bullet}{}_{(g)}$) in minutes.

Question 4

Calculate the half-life of the decomposition of $2N_2O_5 \rightarrow 4NO_2 + O_2$ where the rate constant is 5.7 * 10^{-4}/second. Also, calculate E_A using the Arrhenius equation given that A = 25/second at 834°C.

Question 5

A certain first order reaction has a half-life of 20.0 minutes.

a) **Calculate the rate constant for this reaction.**
b) **How much time is required for this reaction to be 75% complete?**

Answers

1a) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.208} = 3.33\ hours$

b) After three half-lives 12.5% of the reactant will remain i.e. 87.5% will have been used up. Therefore the time required is three times the half-life, which is approximately 9.99 hours.

2a) $t_{1/2} = \frac{0.693}{5.40*10^{-2}\ /\ hour} = 12.8\ hours$

b) 51.2 hours is equal to four half-lives meaning that 1/16 of the original amount will remain because ½ * ½ * ½ * ½ = 1/16.

c) $\ln(\frac{[A]_t}{[A]_0}) = -kt = -(5.40*10^{-2}\ /\ hour)(18\ hours) = -0.97$

Therefore, the fraction remaining = $\frac{[A]_t}{[A]_0} = e^{-0.97} = 0.38$

3) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.36*10^{-4}\ /\sec} = 1.29*10^3\ \sec = 21.5\ \min$

4) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.7*10^{-4}\ /\sec} = 1.21*10^3\ \sec = 20.3\ \min$

For Arrhenius Equation:

$$k = Ae^{-E_A/RT}$$

$$\ln(\frac{k}{A}) = -\frac{E_A}{RT}$$

$$E_A = -\frac{\ln(\frac{k}{A})}{RT}$$

$$E_A = -\frac{\ln(\frac{5.7*10^{-4}/\sec}{25/\sec})}{(8.314)(1107K)}$$

$$E_A = 1.16 * 10^{-3}$$

5a) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20 \text{ min}} = 3.47*10^{-2}/\text{min}$

b) If 75% is consumed than 25% remains (0.25) so:

$$\ln(\frac{[A]_t}{[A]_0}) = -kt$$

$$\ln(\frac{0.25}{1}) = -(3.47*10^{-2}/\text{min}) * t$$

$$t = 40 \text{ minutes}$$

Half-life for a Second Order Reaction

The rate of a second order reaction is defined by: $k[A]^2$

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

Since one half-life has elapsed when $[A]_t = \frac{[A]_0}{2}$:

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

Solving for the initial $t_{1/2}$ gives:

$$t_{1/2} = \frac{1}{k[A]_0} \rightarrow \text{Equation (2)}$$

Equation (2) tells us that half-life depends upon the initial concentration of the reactant so one can shorten the half-life by increasing the initial concentration. For example, if the initial concentration is doubled the half-life is halved.

IB Questions

8a) The rate of a decomposition is studied by measuring the reactant concentration at certain times.

Time/min	0	20	40	60	80	100	120
Conc/10^{-2} mol dm^{-3}	1	0.69	0.48	0.34	0.24	0.16	0.11

i) Plot a graph of concentration versus time.

ii) How could the rate be determined from the graph at any selected time? Explain the shape of the graph in terms of the rate.

iii) What is meant by half-life? Measure three half-life values from the graph. Deduce the order of this reaction.

iv) Calculate a value of the rate constant from the half-life and one from the initial rate of reaction.