

CHAPTER 12: CHEMICAL KINETICS REVIEW

Chemical kinetics deals with the rate of chemical reactions.

DIFFERENTIAL RATE LAW (Commonly referred to as just the Rate Law)

A differential rate law is one in which the rate of the reaction is dependent upon the concentration of the reactants only. This means we study the rate of the reaction **INITIALLY** before any appreciable quantities of products are formed.



For the above reaction – the differential rate law would be $\text{RATE} = k[\text{A}]^x[\text{B}]^y$

Note the rate law is dependent upon reactant concentrations only. 'k' is the rate constant – the larger 'k' is the greater the rate. 'x' and 'y' are called the order for each reactant. The order of a reactant is **NOT** found by using the coefficient of the reactant. The order for each reactant can only be determined from experimental data.

For the above, let's say after looking at experimental data, we find the value of x to be 1 and the value of y to be 2. The rate law would be $\text{RATE} = k[\text{A}]^1[\text{B}]^2$. What would this mean? It would mean that if we doubled the concentration of A and kept B the same the RATE would also double. If we doubled the concentration of B and kept A the same the RATE would increase 4 times.

If we doubled both A and B, the RATE would increase 8 times.

FINDING THE VALUE AND UNITS FOR 'k'

The value of the rate constant can very easily be found by first finding the form of the rate law (find the value of the orders). You then take information from one of the experiments and plug it into the RATE law and solve for 'k'. This gives you the numeric value of 'k'. To obtain the units you apply the following. You find the total order (sum the individual orders). In the example in the preceding paragraph the total order is 3. You find the unit of 'k' by taking

$$\frac{\text{L}^{\text{---total order---}}}{\text{mol}^{\text{---total order---}} \times \text{sec (could be any time unit)}}$$

So for a total order of 3, the unit for 'k' would be $\text{L}^3 / \text{mol}^3 \times \text{sec}$

INTEGRATED RATE LAWS

An integrated rate law is one that will relate the concentration of a reactant to time. We limit our study of integrated rate laws to one reactant systems only. We do this to simplify the process. For a one reactant system such as the following

1ST ORDER INTEGRATED RATE LAW



If the order of the reactant A is 1 – then the differential rate law would be $\text{RATE} = k[\text{A}]^1$

The first order integrated rate law would be $\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$, or $\ln[\text{A}]_t - \ln[\text{A}]_0 = -kt$

The first equation is in the form of $y = mx + b$. This means that if given data for the $[\text{A}]$ and time plotting $\ln[\text{A}]_t$ would give a straight line of negative slope.

An important aspect of the first order integrated rate law is $t_{1/2}$ or $t_{1/2}$. This refers to the amount of time needed for 1/2 of the concentration of the reactant to be consumed. The formula for the first order $t_{1/2}$ equation is ---

$$t_{1/2} = \ln 2 / k$$

2nd ORDER INTEGRATED RATE LAW



If the order of the reactant A is 2 – then the differential rate law would be $\text{RATE} = k[\text{A}]^2$

The second order integrated rate law would be $1/[\text{A}]_t = kt + 1/[\text{A}]_0$, or $1/[\text{A}]_t - 1/[\text{A}]_0 = kt$

The first equation is in the form of $y = mx + b$. This means that if given data for the $[\text{A}]$ and time plotting $1/[\text{A}]_t$ would give a straight line of positive slope.

An important aspect of the second integrated rate law is $t_{1/2}$ or $t_{1/2}$. This refers to the amount of time needed for 1/2 of the concentration of the reactant to be consumed. The formula for the second order $t_{1/2}$ equation is ---

1 Review And Reinforcement Chemical Kinetics

Victor M. Corman



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