Sim Pack 3:

Rate of Reaction & Arrhenius Behaviour

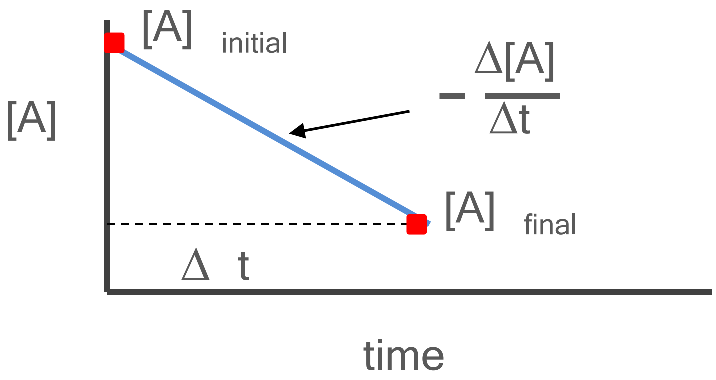
Version 1.1

Learning Outcomes:

After reading these notes you will learn about the following terms

- **Instantaneous Rate of Reaction**
- **Rate Laws and Reaction Order**
- **Rate constant**
- **Arrhenius Behaviour**

The Instantaneous Rate of Reaction

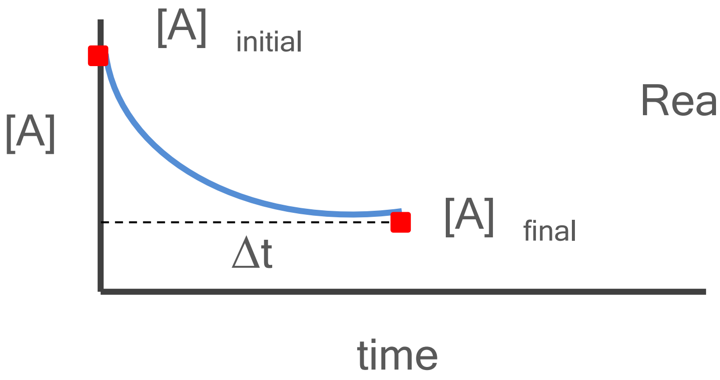


Average rate (constant)

Figure 1: Concentration vs time profile

In general, most reactions will display a much more complicated concentration *vs* time profile since reactions generally slow down as reactants are used up (see Figure 2). As a result, the average reaction rate may change from one time interval to the next as the reaction proceeds. In addition, the reaction rate may also change in the time interval in which the change in concentration is measured.

More common:



Reaction rate not constant

Figure 2: Concentration vs time profile

This is known as a zero order reaction since the rate is independent of concentration

A general expression for a rate law can therefore be defined

$$\boxed{\text{Rate} = \frac{-\,d\,[A]}{d\,t} = k\,[\,A\,]^{a}} \qquad \textit{Eq 10}$$

where a is the order of reaction

Concentration and Time

The rate equation (which gives the instantaneous rate of reaction) is known as the differential rate equation.

Differentiation is a mathematical procedure which allows examination of very small changes in variables (e.g., concentration and time).

Second Order Integrated Rate Law

To obtain the integrated rate law for a second order reaction we need to use the differential rate law:

$$-\frac{d[A]}{dt} = k[A]^2 \qquad \textit{Eq 28}$$

Which can be rearranged to give

$$-d[A] = k[A]^2\,dt \qquad \textit{Eq 29}$$

➡ $$-\frac{d[A]}{[A]^2} = k\,d\,t \equiv \frac{d[A]}{[A]^2} = -k\,d\,t \qquad \textit{Eq 30}$$

To solve, we need to integrate between the same limits as in the first order case

i.e., $[A]_o$ at $t = 0$ and $[A]_t$ at $t = t$

Arrhenius Behaviour

A relationship between reaction rate and temperature was developed by a Swedish chemist, Svante Arrhenius.

He noted that a straight line resulted from a plot of natural logarithim (ln) of the rate constant (k_R) against the inverse of absolute temperature (in degrees kelvin).

The Arrhenius equation can be formally written in its linear form as:

$$\boxed{\ln k_R = \ln A - \frac{E_A}{R\,T}} \qquad \textit{Eq 37}$$

where R is the gas constant

The two constants, A and E_A are known as the Arrhenius parameters for the reaction (and are determined by experiment).

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