

# Chemical Kinetics

All rates written as  $\frac{\Delta \text{conc}}{\Delta \text{time}}$  or  $\frac{\Delta[A]}{\Delta t}$ . Instantaneous rate is the slope of a concentration vs time plot and is shown by the differential equation:  $\frac{d[A]}{dt}$ . Overall rates for forward reactions are shown as POSITIVE rates, therefore, all reactants (which have negative rate of change) must have their rates negated  $-\frac{d[A]}{dt}$ .

In general for the overall reaction:



Note that each individual rate is divided by its coefficient in the balanced chemical equation.

**Half-life ( $t_{1/2}$ ):** The time it takes for the concentration to drop to one half its current value during the course of the reaction. Note that the "current value" is typically the initial starting value - but not always.

**Rate Laws for:  $a A \rightarrow \text{products}$**  (all the following equations assume that  $k$  is for the overall reaction)

Zero Order	First Order	Second Order
rate = $ak$	rate = $ak[A]$	rate = $ak[A]^2$
$[A]_0 - [A]_t = akt$	$\ln[A]_0 - \ln[A]_t = akt$ $\ln\left(\frac{[A]_0}{[A]_t}\right) = akt$	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = akt$
$[A]_t = -akt + [A]_0$	$\ln[A]_t = -akt + \ln[A]_0$	$\frac{1}{[A]_t} = akt + \frac{1}{[A]_0}$
$t_{1/2} = \frac{[A]_0}{2ak}$	$t_{1/2} = \frac{\ln 2}{ak}$	$t_{1/2} = \frac{1}{ak[A]_0}$

**Watch out for this!** Make sure you know HOW  $k$  is defined for a reaction. It must be known WHICH component that the rate is being expressed. Is it A? B? C? D? Many times  $k$  is given for the *overall reaction*. If that is the case then you must remember to scale  $k$  by the coefficients ( $a$ ,  $b$ ,  $c$ , or  $d$ ) given in order to get the right rates for each component. That is:  $k = ak'$ , etc... (read page 709 from Zumdahl)

**Temperature dependence of rate (Arrhenius)**  $k = Ae^{-E_a/RT}$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{t_1}{t_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Note this is the typical Arrhenius Equation where you have 2 specific rate constants at 2 specific temperatures. Remember they come in pairs. Also note how the Arrhenius factor  $A$ , has factored OUT of the equation.

This is still the Arrhenius Equation, EXCEPT we now show TIME in place of rate constant. Time is inversely proportional to rate so the positions are switched. Any common timed event will work - half-life is the most common.

## Electrochemistry

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ}$$

$$\Delta G^{\circ} = -nFE^{\circ}$$

$$\frac{I \cdot t}{n \cdot F} = \text{moles}$$

$$E = E^{\circ} + \frac{RT}{nF} \ln Q$$

$$E = E^{\circ} - \frac{0.0257}{n} \ln Q$$

$$E = E^{\circ} - \frac{0.05916}{n} \log Q$$