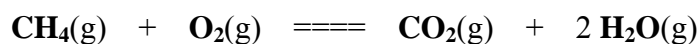


Everything You Always Wanted to Know (or better yet, need to know) About Chemical Kinetics, But Were Afraid to Ask...

Overall Reactions

An overall chemical reaction indicates reactants and products in the appropriate stoichiometric quantities. Overall chemical reactions can be used to predict quantities consumed or produced and write equilibrium expressions. Consequently, overall reactions are used in thermodynamic calculations, such as energy changes and equilibrium concentrations. However, the overall reaction provides no information about the molecular process involved in transforming reactants into products, the nature and number of individual steps involved, the presence of intermediates or the role of catalysis. Consequently, overall reactions provide no information about how fast a reaction proceeds or the various factors that influence reaction rates.

For example, the overall reaction for the combustion of methane is given by;

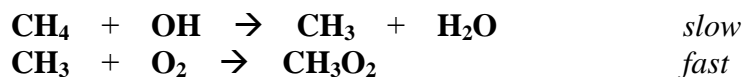


From which we can write an equilibrium expression, calculate free energy changes and so on, but which provide little insight into how long it may take for the reaction to occur or what species might act as catalysts.

Reaction Mechanisms

Mechanisms provide the individual steps that occur on the molecular level in transforming reactants into products. (Whereas the overall reaction indicates where we start and end up, the mechanism tells us how we got there). Reaction mechanisms are composed of a series of *elementary processes* (steps) which are indicative of the molecular encounters. Because of this, mechanisms are intimately related to chemical kinetics.

For example, the first two steps in the combustion of methane are given by;



Interestingly, mechanisms are never proven but rather postulated and checked for consistency with observed experimental kinetic data.

Elementary Processes or Steps

Each step in a proposed reaction mechanism is written as an elementary process which reflects an actual molecular event or encounter. In the first step in the example above, a **CH₄** molecule collides with a **OH** radical whereupon a **H** atom is transferred to form a **CH₃** radical and a **H₂O** molecule. Elementary processes can be used directly to write expressions for the rate of that particular step. Since the molecules written in an elementary process must actually meet in order to react, it stands to reason that the rate of this process will be proportional to the concentration of each reacting species. This is because the chance of the reacting molecules colliding will increase in proportion their concentration.

For example;

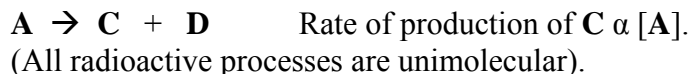


The rate of production of **C** \propto **[A]** and \propto **[B]**, so the rate of production of **C** \propto **[A] [B]**. Thus for an elementary step, the rate is given by the product of the concentrations of each reacting species and some proportionality constant (which we will call the *rate constant*). This rate constant converts chemical concentrations into reaction rates.

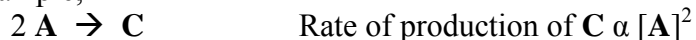
Thus, in the above example, the rate of production **C** = k **[A] [B]**, where k is the rate constant for the reaction.

Molecularity of Elementary Steps

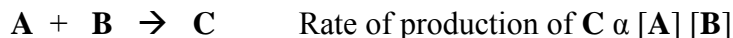
Elementary steps are described as uni-, bi- or termolecular depending on how many species are involved in the process. Unimolecular processes depend only on the concentration of a single species. For example,



Bimolecular processes involve two molecules and depend on the concentration of both. For example,



and



Rate Determining (Limiting) Step

In any multi-step mechanism, there will necessarily be one step that is slower than all the others. We call this the rate determining step, since the overall rate of reaction cannot occur any faster than the slowest step. In the analysis of the kinetic behaviour of a reaction, only the rate determining step and steps that precede it are relevant.

Rate Expressions (Differential Rate Laws)

Rate expressions relate reaction rates to species concentrations. As describe above, the rate of a reaction will increase in proportion to the concentration of reactants in an elementary process. Therefore, the rate expression can be written for any elementary step as the product of the rate constant for that particular step and the concentrations of the reacting species. The overall *order* of a reaction is equal to the number of molecules reacting in an elementary step. In the example below, the reaction is said to be first order in **A**, second order in **B** and third order overall.



$$\text{Rate of loss of } \mathbf{A} = -d[\mathbf{A}]/dt = k [\mathbf{A}] [\mathbf{B}]^2$$

Reaction rates are always expressed as a change in amount of a substance over a given change in time, e.g., $\Delta[\mathbf{A}]/\Delta t$. The units are typically (conc/time although could be expressed as mass/time or number/time). These expressions are referred to as differential rate expressions as the instantaneous rate at any given time can be written as $d[\mathbf{A}]/dt$. For a given reaction, the rate will typically slow down over time as the concentration of reactants decreases.

Reaction rates must be defined in terms of a particular reactant or product. If there are coefficients in the elementary steps, they are used in relating rates of appearance or disappearance of different species. In the above example, in can be seen that **A** and **B** will be disappearing at different rates since twice as many **B** molecules are consumed for every **A** molecule. In other words,

$$\text{rate of loss of } \mathbf{A} = \frac{1}{2} \text{ rate of loss of } \mathbf{B} = \frac{1}{3} \text{ rate of production of } \mathbf{C}$$

or

$$-d[\mathbf{A}]/dt = -d[\mathbf{B}]/2dt = d[\mathbf{C}]/3dt$$

where the minus signs are used to indicate a loss rate (i.e., a negative change in concentration).

Pseudo order reactions

A variation or simplification of the differential rate law expressions can be applied when the concentration of one or more of the reacting species remains constant over the course of the reaction. If this concentration term appears in the rate expression, but remains constant, it can be incorporated into the rate constant term. There are several reasons why the concentration of a species may remain constant. For example, if one or more reacting species is present in vast excess, its concentration is not change appreciably as the other reacting species are consumed. Other situations may arise, where a species is being produced as fast as its being consumed and therefore its concentration remains constant (*steady state*). For the bimolecular process;



The complete rate expression is given by,

$$\text{Rate of production of } \mathbf{C} = k [\mathbf{A}] [\mathbf{B}]$$

But if the $[\mathbf{B}]$ remains constant, this expression can be simplified to;

$$\text{Rate of production of } \mathbf{C} = k' [\mathbf{A}], \text{ where } k' = k [\mathbf{B}]$$

In atmospheric chemistry, this situation often arises when one of the reacting species is a *third body* species (M) required to remove excess energy. Termolecular reactions can be simplified to *pseudo* second order if one species remains constant or *pseudo* first order, if two species remain constant.

Rate Constants

Rate constants are specific for a particular reaction at a specified temperature. They are usually measured by following the concentration of species over time in a laboratory setting. The temperature dependence of k is often measured and can be used to calculate the activation energy. Consequently, rate constants are commonly given in a generalized form as a function of T (the absolute temperature). Therefore, if reactant concentrations and environmental temperatures are known, the rates of reactions under various conditions can be determined.

The units associated with a rate constant depend on the molecularity (order) of the reaction. This can be demonstrated by rearranging the differential rate equation to isolate k . For unimolecular or first order processes;

$$k = \frac{\text{rate}}{[\mathbf{A}]} \left[\frac{\text{conc time}^{-1}}{\text{conc}} = \text{time}^{-1} \right]$$

For bimolecular or second order processes;

$$k = \frac{\text{rate}}{[\mathbf{A}]^2} \left[\frac{\text{conc time}^{-1}}{\text{conc}^2} = \text{conc}^{-1} \text{ time}^{-1} \right]$$

And the rate constant for termolecular or third order processes will have units of $\text{conc}^{-2} \text{ time}^{-1}$. Since atmospheric concentrations are typically expressed as molecules/cm³, the units for rate constants often appear as;

$$\begin{array}{ll} 1^{\text{st}} \text{ order:} & \text{s}^{-1} \\ 2^{\text{nd}} \text{ order:} & \text{molec}^{-1} \text{ cm}^3 \text{ s}^{-1} \\ 3^{\text{rd}} \text{ order:} & \text{molec}^{-2} \text{ cm}^6 \text{ s}^{-1} \end{array}$$

The *Arrhenius Equation* is an empirically derived (based on experimental observation) expression that relates the magnitude of the rate constant to a temperature independent frequency factor (A), the activation energy (E_a) and the absolute temperature (T).

$$k = A e^{-\frac{E_a}{RT}}$$

A linearized form is obtained by taking the natural log of both sides to yield;

$$\ln k = \ln A - E_a/RT$$

Measuring rate constants at two or more temperatures allows for the determination of the activation energy.

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

Integrated Rate Laws

Integrated rate equations relate the concentrations of reactants to time. They are very useful in predicting how much of a species will remain at some time (t) or conversely, how long it will take for a species concentration to drop to some predetermined amount (e.g., one half). The integrated forms of the rate equations can be derived by rearranging the differential forms and integrating over concentration and time. The resulting integrated rate equation will depend on the order of the reaction.

First Order

Differential form; $\frac{-d[A]}{dt} = k [A]$

Integrating over conc and time; $\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$

Yields integrated form; $\ln \frac{[A]_t}{[A]_0} = -k t$

OR; $[A]_t = [A]_0 \exp^{-\{k t\}}$

Second Order

Differential form; $\frac{-d[A]}{dt} = k [A]^2$

Integrating over conc and time; $\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k \int_0^t dt$

Yields integrated form; $-\frac{1}{[A]_t} + \frac{1}{[A]_0} = -k t$

OR; $\frac{1}{[A]_t} = \frac{1}{[A]_0} + k t$

Both the half-life ($t_{1/2}$) and lifetime (τ) are commonly used to characterize how fast a reaction occurs or how long a species will last.

$$\text{At } t = t_{1/2}, [A]_t = \frac{1}{2} [A]_0$$

Substituting these into the integrated rate equations yields the following.

$$\text{First Order; } t_{1/2} = 0.693/k$$

(note that the half-life for first order process is independent of initial concentration and remains constant throughout the life of the species involved)

$$\text{Second Order; } t_{1/2} = 1/[A]_0 k$$

(note that the half life for a second order process depends on the concentration and as such, will vary over the course of the reaction)

The *lifetime* (τ , also referred to as the *residence time*) can be defined for first order processes as the time at which $t = 1/k$.

Substituting this into the integrated rate equation yields, $\ln [A]_t/[A]_0 = -k (1/k) = -1$.

$$\text{So at } t = \tau \text{ (i.e., } 1/k), \therefore [A]_t/[A]_0 = e^{-1} = 1/e = 0.37$$

(i.e., τ is the time required for the concentration to drop to 0.37 of its original value).

Recall, we saw earlier, that the lifetime (also known as the *residence time*) can be expressed as the ratio of amt/rate.

$$\tau = \frac{\text{amt}}{\text{rate}} = \frac{[A]}{k[A]} = \frac{1}{k}$$

If a chemical species reacts by a number of first order (or *pseudo* first order) processes the overall first order rate constant can be expressed as $k_{\text{overall}} = \sum k_i$, where k_i are individual first order rate constants. In such cases, the lifetime (residence time) is given by;

$$\tau = \frac{1}{\sum k_i}$$