
Kinetics

The study of chemical reaction rates

Ron Robertson

Reaction Rate

We define reaction rate in terms of the rate of appearance of a product or the disappearance of a reactant

Although there are individual rates for each reactant or product, we do define one “rate” for the entire reaction. This rate is defined in terms of the stoichiometry of the reaction.



The rate of this reaction is
$$-\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

The brackets indicate concentrations, usually in moles/liter. The Δ means “change in” the following quantity and is “final” – “initial”. Thus reaction rates have units of moles/liter/s or moles/liter-s.

The rate of the reaction usually changes with time and can be obtained graphically by taking the slope of the concentration vs. time graph at any point in time.

Ways to monitor concentrations

1. **Pressure or volume of a gas reaction**
2. **Mass loss or gain (gas especially)**
3. **Spectra (IR, UV, GC, NMR, etc.)**
4. **pH**
5. **Titration**

Ways to take samples

1. **Real time analysis – withdraw a small sample or monitor the bulk**
2. **Quenching – stop RXN quickly**
3. **Flow – reactants are mixed, solutions flow through an outlet tube, different positions of the tube correspond to different times**

Collision Theory

We model reactions using our ideas of kinetic theory. The main idea is that molecules must collide in order to react; anything that affects these collisions affects the reaction rate.

Factors which affect the frequency and intensity of collisions

1. Nature of reactants

- **Reaction mechanism**

Most reactions proceed by many steps, not just one step. Each step is called an elementary step. If only one molecule is involved the reaction is called unimolecular; if two, bimolecular. The slowest step is the rate determining step and controls the rate of the summary reaction.

- **Activation energy**

Reactants must have a certain energy to become products. This is called the activation energy. A catalyst increases the rate of a reaction because it lowers the activation energy of a step or changes the reaction mechanism steps (providing an alternative pathway). A catalyst can be in the same phase as the reactants (homogeneous) or in a different phase (heterogeneous).

Enzymes are good examples of homogeneous catalysts; the catalytic converter in your car is a heterogeneous catalyst.

2. Concentration (includes surface area for solids)

3. Temperature

Temperature increases the number of collisions and the intensity (energy) of the collisions. Thus doubling temperature does more than just double reaction rate. A good “rule of thumb” is that an increase of 10C° doubles the reaction rate.

The Rate Law

The rate law combines these factors affecting reaction rate into a mathematical expression that allows us to predict (after the use of calculus) what the concentrations of products and reactants will be at any point in time. The original rate law shows how the rate depends on the concentrations of reactants and is sometimes called the “*differential*” rate law. After we integrate this expression mathematically we get the “*integrated*” rate law expression that shows how concentration changes over time.

In general for each step of a reaction mechanism there is a rate law. Some reactions are simple and only go through one step; most however have many steps.

For a sample step: $aA + bB \rightarrow xX$

The rate law would be:

$$\text{Reaction rate} = k [A]^a [B]^b$$

- “a” and “b” are called the order of the reaction for species A and B. The sum of “a+b” is the overall reaction order.
- “k” is the specific rate constant and includes the factors of nature of reactants and temperature.
- the concentrations of A and B show the concentration influence

The rate laws for the individual steps can be combined to get an overall rate law for the summary reaction. It is important to note that one cannot write a rate law expression from the equation for a reaction unless the mechanism is known. Since the exact mechanism steps are usually not known, the rate law for the summary equation is usually pieced together by experiment.

Determination of RXN Order and “k”

The reaction order and specific rate constant “k” must be verified by experiment. Two methods are outlined below.

- Look at the initial rates**

Compare the initial reaction rates for two experiments, keeping temperature constant and all concentrations of reactants the same except for one reactant (this is called an isolation technique). Deduce or mathematically solve for the reaction order. Once order is known for each species, a rate constant can be determined.

To mathematically solve use the expression

$$\text{Rate} = k [A]^x$$

Take the natural log of both sides and plot ln Rate vs ln [A]

The slope is equal to the order x

- **Fit to an Integrated Rate Law**

We assume a differential rate law (with an associated order) and integrate to get an equation which relates concentration and time. (It is possible for the products to be involved in the rate expression. This will depend on the reaction mechanism.) We then see if our actual numbers fit the assumed model. This might seem to be very difficult, but many reactions are either first or second order so we usually only have to see if our data fits a couple of models. Let's examine a couple of easy ones involving only one reactant.

The 1st Order Model

For a simple one step reaction $A \rightarrow P$ the following differential rate law holds

$$\text{Rate} = -D[A]/Dt = k [A]$$

This rate is a “slope” in mathematical language. What equation has this slope? This is what calculus can do for us that algebra cannot. If the D’s get very small we can replace them with d[A] and dt in calculus language and integrate to get the following expression.

$$[A] = [A]_0 e^{-kt}$$

Another form of this is

$$\ln[A] = -kt + \ln [A]_0$$

Thus if we graph $\ln[A]$ versus t and get a straight line our model is correct. The slope will be $-k$.

The amount of time that it takes for $\frac{1}{2}$ of A to become P is called the half-life ($t_{1/2}$). From the above equation

$$t_{1/2} = 0.693/k$$

The Second Order Model

For a simple one step reaction $2A \rightarrow P$ the following differential rate law holds

$$\text{Rate} = -(1/2)(d[A]/dt) = k [A]^2$$

The equation that has this slope is:

$$\frac{1}{[A]} = 2kt + \frac{1}{[A]_0}$$

Thus graphing $1/[A]$ versus t should give a straight line with a slope of $2k$ if our model is correct. The corresponding half-life

equation is
$$t_{\frac{1}{2}} = \frac{1}{2k[A]_0}$$

Notice that the half life of a first order reaction does not change. It does for a 2nd order reaction. *Note: For a 2nd order reaction where $A \rightarrow P$ (instead of $2A \rightarrow P$), remove the factor of 2 from the above equations.*

The Rate Constant k

The rate constant k can be represented by the following equation

$$k = Ae^{-\frac{E_a}{RT}}$$

The exponential factor represents the fraction of collisions that have the proper energy to react. The factor “A” takes into account that the geometry of the collision must also be right.

When we take the natural log of both sides of the equation we find the following form:

$$\ln(k) = \left(\frac{-E_a}{R}\right)\frac{1}{T} + \ln(A)$$

A graph of $\ln(k)$ versus $1/T$ should give a straight line with a slope of $-E_a/R$. This provides a good way to find the activation energy for a reaction.