

AP Chemistry

Kinetics Notes

Plotting the concentration of a chemical in a reaction as a function of time is called a Kinetic Curve or Concentration vs. Time Curve

Calculate the slope at a given time by drawing a tangent at that point and calculating the slope of the line. This is the derivative of the function at that point

Always use a positive value for rate

$$\text{Rate} = \Delta C_{\text{products}}/\Delta t \quad \text{Rate} = -\Delta C_{\text{reactants}}/\Delta t$$

Once the rate of one component is determined, others can be determined using stoichiometric ratios.

Units: mol/Ls or mol L⁻¹s⁻¹

Reaction Rate Factors

1. Concentration of reactants
2. Temperature (Increasing temperature increases the reaction rates)
3. Catalyst (Substance that participates but is not changed by the reaction. It is not included in the balanced equation)

The general rate of reaction is obtained by dividing the rate of disappearance of a reactant or the rate of formation of a product by the stoichiometric coefficient of that reactant or product in the balanced chemical equation.

For equation $aA + bB \rightarrow cC + dD$

The **general rate of reaction** is:

$$\text{Rate} = -(1/a) \Delta[A]/\Delta t = -(1/b) \Delta[B]/\Delta t = (1/c) \Delta[C]/\Delta t = (1/d) \Delta[D]/\Delta t$$

This represents the average rate of a reaction over a time interval, as the rate is generally greater when the concentration of reactant(s) is greater.

Details

1. Concentration

Expressed in the rate law

$$\text{Rate} = k[A]^x[B]^y[C]^z \quad k = \text{rate constant}$$

-Exponents are usually small whole numbers but may be negative or rational fractions

-They are **NOT** stoichiometric coefficients.

-The rate law must be determined experimentally. There is no theoretical way to predict exponents.

The rate law is determined by taking the ratios of experimental results on a reaction such that one or more of the concentrations cancel out leaving one to be determined

Ex:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[.1]^x[.2]^y}{k[.05]^x[.2]^y}$$

This is sort of a process of elimination

After the exponents are determined, k may be determined from any of the reactions (see section in text for examples)

Order of the rate law

Either: 1. refers to the individual exponents of each component
Or 2. refers to the sum of all of them for the overall reaction

The units of the rate constant k vary with the order of the rate law, however they must be such that the overall rate is given in units of concentration per unit time.

If the concentration of a component has no effect on the reaction rate (i.e. zeroth order) it is not included in the rate law

2. Temperature

Arrhenius equation relates the rate constant and temperature

$$k = Ae^{-E_a/RT}$$

E_a = activation energy
 $R = 8.314 \text{ J/molK}$
 T = temperature in K
 A = proportionality constant

Taking the natural log of both sides gives

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

we can plot $\ln k$ vs. $1/T$ after determining the rate constant (k) at different temperatures

Slope = $-E_a/R$, from this you can determine the activation and also the rate constant at other temperatures (from the plot)

Also, determining the rate constant at two different temperatures and then subtracting one Arrhenius equation from another gives

$$\ln(k_1/k_2) = -E_a/R (1/T_1 - 1/T_2) \text{ or}$$

$$\ln(\text{rate}_1/\text{rate}_2) = -E_a/R (1/T_1 - 1/T_2)$$

Note: Larger rate constants at higher temperatures
Activation energy is ALWAYS positive.

Note: Near room temperature, rates of reactions roughly double for every 10°C rise in temperature

Points of Interest

1. **Zeroth order** reactions are ones in which the rate of the reaction is not dependent upon the initial concentration of the reactants (i.e. **rate = k**). They have kinetic curves that are straight lines. If the equation is integrated with respect to time you get $[A]_t = -kt + [A]_0$

2. **1st order** equations of the form **rate = k[A]** can be integrated to

$$\ln([A]_0/[A]_t) = kt \quad \text{or} \quad \ln[A]_0 - \ln[A]_t = kt$$

Plotting $\ln[A]$ vs. T is a straight line with slope $-k$

Nuclear decay processes are also 1st order and are solved using a similar equation.

3. **2nd order** reactions, those of the form;

$$\text{Rate} = k[A]^2 \text{ or Rate} = k[A][B] \text{ where } [A] = [B]$$

may be similarly integrated to

$$1/[A]_t - 1/[A]_0 = kt$$

from which the half-life equation $t_{1/2} = 1/(k[A]_0)$ is derived

Note that for this 2nd order reaction the half-life depends upon the initial concentrations

A plot of $1/[A]$ vs. t gives a straight line with slope $-k$

Summary of reaction types of the form $A \rightarrow \text{Products}$

Order	Rate Law	Integrated Rate Law	Straight-Line Plot	$k =$	Units of k	Half-life
0	Rate = k	$[A]_t = -kt + [A]_o$	$[A]$ vs. t	-slope	$M s^{-1}$	$[A]_o/2k$
1	Rate = $k[A]$	$\ln[A]_t = -kt + \ln[A]_o$	$\ln[A]$ vs. t	-slope	s^{-1}	$0.693/k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_o$	$1/[A]$ vs. t	slope	$M^{-1} s^{-1}$	$1/(k[A]_o)$

Theory of Reaction Rates

Collision Theory

Envisions interactions between atoms and molecules as elastic

Reaction rate depends upon:

Sufficient energy of the interacting particles

Proper orientation

-Kinetic energy of collision is turned into potential energy of the reaction

-The increase in potential energy must be at least = E_a

Fraction of molecules or atoms with sufficient reaction energy is related to the Kinetic Molecular Theory (Chapter 7)

Reaction Rate = $N f_e f_o$

N = number of collisions per second (temperature and concentration dependent).

f_e = fraction of collisions with minimum required energy (increases with increasing temperature)

f_o = fraction of collisions with correct orientation (constant for a given reaction)

Transition-state Theory

Envisions interactions between atoms and molecules as due to a distortion of the electron cloud that breaks and reforms bonds (molecular configurations and energies)

At the moment of impact, we may think of one bond as partially broken and the new bond as partially formed. This state is known as the **activated complex** (and occurs at the peak of the energy in the reaction profile)

This is the critical point at which the reaction may continue to products or fall back on the energy curve to reactants

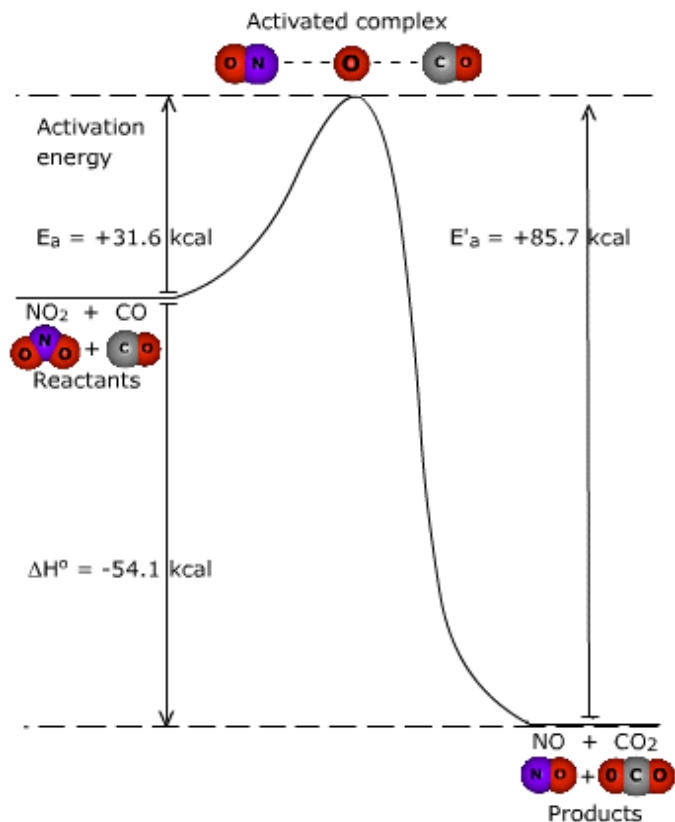
A **reaction profile** plots the changes in potential energy as a reaction progresses from reactants, through the activated complex, then to products.

A reaction profile may be used to determine:

1. that the rate of a reaction is inversely proportional to the height of the energy barrier
2. whether a reaction is endothermic or exothermic (ΔH)
3. the activation energy for the reaction in the reverse direction

4. the action of catalysts

- A catalyst increases the rate of a reaction by providing an alternative pathway for reactant to get to products by way of a lower activation energy
- A catalyst is not consumed or altered in the overall reaction
- A catalyst will bring a reaction to equilibrium more quickly



Enzymes in the body are natural catalysts

Most have optimal temperatures of around 36°C

The enzyme is designed to fit a very specific set of reactant(s) known as the substrate

This is known as the lock and key model (see text for more detail)

Reaction Mechanisms

- Most chemical reactions actually occur in a series of intermediate steps called **elementary reactions**
- All elementary reactions must add up to the overall balanced equation for the reaction
- The sequence of steps is called the **reaction mechanism**

Elementary Reactions

- Most are collisions between two molecules. (Rarely between three and virtually never between four or more). The number of molecules involved in the collision is known as the *molecularity*.
- Coefficients **ARE** the exponents used in the rate law
- The slowest reaction (**rate-determining step**) determines the overall rate of the reaction.

Application

1. Scientists determine the rate law for an overall reaction
2. Next they propose a series of elementary steps
3. Finally the check to see if the rate-determining step agrees with the overall rate law

Any chemical that is part of a mechanism but is not in the overall equation for the reaction is called an **intermediate**.

- Sometimes you can react intermediates to determine the rate limiting step
- This is not always possible though as some intermediates are unstable and short lived

Rate Laws of Elementary Reactions

- Coefficients in the balanced equations are the exponents of the reaction concentrations
- If the expression involves intermediates, substitution of the combination of other elementary steps must be used so that only reactants appear in the equation.*
- This substitution is made possible by the “**steady-state assumption**” that non-limiting steps are fast and reversible.
- Sometimes two different mechanisms will have the same rate-determining step. If this is true, further tests must be done.

Chemical Equilibrium

As product concentration increases, the reverse reaction rate law becomes more significant (Rate overall = Rate_f - Rate_r), therefore scientists use initial reaction rates to determine rate laws

At equilibrium, Rate_f = Rate_r

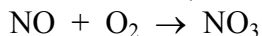
if Rate₁ = k_f[A]^x[B]^y and Rate₂ = k_r[C]^z[D]^w then rearranging gives

$$\frac{k_f}{k_r} = \frac{[C]^z[D]^w}{[A]^x[B]^y} \text{ which is the equilibrium law.}$$

*Example of substitution

Reaction: $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

Possible mechanism (elementary reactions):



Rate laws

Step 1: $k[\text{NO}][\text{O}_2]$

Step 2: $k[\text{NO}_3][\text{NO}]$ (contains NO₃)

Steady-state assumption NO₃ rate of formation equals rate of disappearance, so

$$k_f[\text{NO}][\text{O}_2] = k_r[\text{NO}_3]$$

solving for [NO₃] gives:

$$[\text{NO}_3] = k_f/k_r [\text{NO}][\text{O}_2]$$

substituting into the rate law give:

$$\text{Rate} = k(k_f/k_r)[\text{NO}][\text{O}_2][\text{NO}]$$

or combining rate constants:

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2], \text{ the rate law for the second step.}$$