Notes: Chapter 16

Tuesday, January 09, 2007
11:38 AM

Chapter 16: Kinetics: Rates and Mechanisms of Chemical Reactions

Homework : 8,9,18,19,20,21,27,30,36,38,39,43,44,49,50,60,64,73,75,87,89,99

Rates of Reaction

The rate of a chemical reaction is dependent upon the **concentration** of reactants reacting, **temperature**, presence of a **catalyst**, and **surface area** of solid reactants. If one increases the quantity of any of these, the rate of reaction will usually increase. The rate of a reaction is expressed as:

rate = $-\Delta[A]/\Delta t$ for the change of concentration of a reactant and

rate = $\Delta[A]/\Delta t$ for the change of concentration of a product

where $\Delta[A]$ means the change in concentration of A in moles/liter and Δt is time. The negative sign is present because the sign of $\Delta[A]/\Delta t$ is negative and the rate must be positive. Remember that $\Delta[A] = [A]_f-[A]_i$, and for a reactant $\Delta[A]$ is negative and for a product $\Delta[A]$ is positive.

If we plot a graph of [A] vs time, the slope at any point would be would be the rate of the reaction at that time with respect to the [A].

Let us examine how the concentration of a reactant controls the rate of a reaction. If we did an experiment with several concentrations of reactants and examined the initial rate of reaction we could determine the reaction dependence or order of each reactant.

Consider the reaction:

$2NO + O_2 \text{--->} 2NO_2$

The rate expression will be in the form:

rate = $k[NO]^x[O_2]^y$

The experiment would consist of independently varying the concentration of each reactant and seeing how the initial rate varies.

Experiment	[NO]	$[O_2]$	Initial rate M/s
1	.0100	.0100	.00300
2	.0200	.0100	.01200
3	.0100	.0200	.00600
4	.0200	.0200	.02400

By comparing experiment 1 and 2 we see that doubling the NO concentration quadruples the rate which means the order with respect to NO is 2 or second order with respect to NO.

By comparing experiment 1 and 3 we see that doubling the concentration of O_2 doubles the rate of reaction; therefore, the rate dependence must be first order with respect to oxygen. The rate expression for this reaction is:

rate = $k[NO]^2[O_2]$

Whole number concentration dependences are not the rule. A reaction could have an order of 1/2 or 3/2 or any rational number. By careful observation of rate changes upon changes in concentration, it is possible to determine a whole numbered order; however, for fractional orders, it may be necessary to solve for the exponent (order).

Development of the 1st Order Rate Law

If we start with a simple reaction consisting of only one reactant, the general rate expression is:

$\text{rate} = \Delta[A]/\Delta t = -k[A]^x$

Taking this simple equation and expressing it in terms of differentials we get:

$d[A]/dt = -k[A]^x$

If we make the assumption that the reaction is first order (that means $x=1$), the equation becomes:

$d[A]/dt = -k[A]$ rearranging: $d[A]/[A] = -kdt$

Integrating between the initial and final conditions gives:

$\ln[A]_t - \ln[A]_o = -kt$

We can put this in the slope intercept form since $\ln[A]_o$ is a constant and get

$\mathbf{\ln[A]_t = -kt + \ln[A]_o}$ or for base 10 logs, $\mathbf{\log[A]_t = -kt/2.303 + \log[A]_o}$

Therefore if we plot $\ln[A]_t$ vs t for a real reaction the slope will be the -k (forward rate constant) and the y intercept will be $\ln[A]_o$ (initial concentration).

Following this same procedure, the second order rate law in the slope intercept format can be found by integrating $d[A]/dt = -k[A]^x$ for $x=2$;

$\mathbf{1/[A]_t = kt + 1/[A]_o}$

and for the zero order rate law in the slope intercept format can be found by integrating $d[A]/dt = -k[A]^x$ for $x=0$;

$\mathbf{[A]_t = -kt + [A]_o}$

Problem 1: An experiment was carried out and the following data were collected and the natural log concentrations and inverse concentrations were calculated. Determine the order of the reaction with respect to the $[N_2O_5]$.

Time (min)	[N2O5]	ln[N2O5]	1/[N2O5]
0	0.0165	-4.10439	60.60606
10	0.0124	-4.39006	80.64516
20	0.0093	-4.67774	107.5269
30	0.0071	-4.94766	140.8451
40	0.0053	-5.24005	188.6792
50	0.0039	-5.54678	256.4103
60	0.0029	-5.843	344.82

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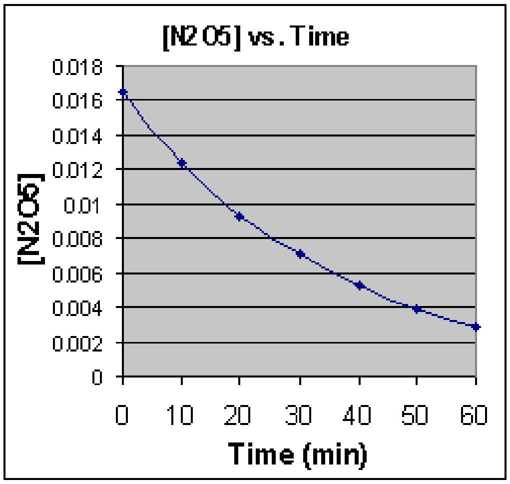
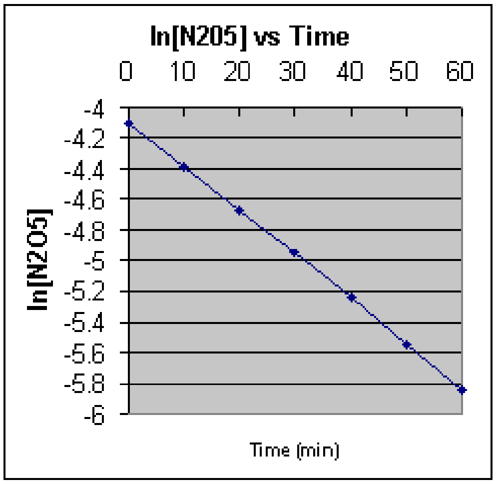
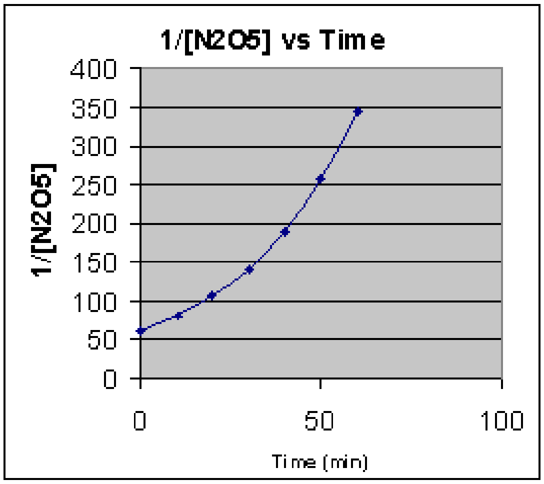
By graphing data the zero, first, and second order rate laws, the order can be determined.







After graphing, what is the order of the reaction? Why?

Half-Life

Half-life is the length of time required for half of the reactants to be consumed. Using the equations above we can derive half-life equations for zero, first and second order reactions.

Example: For a first order reaction:

$\ln[A]_t - \ln[A]_o = -kt = \ln([A]_t/[A]_o)$

$-kt = \ln(.5[A]_o/[A]_o)$

$t_{1/2} = \ln(.5[A]_o/[A]_o)/k = \ln(1/2)/k = .693/k$

$t_{1/2} = .693/k$

Problem 2: How long will it take for the reaction depicted above to reach 1/8 the original concentration? a) Determine directly from the $[N_2O_5]$ vs time graph, b) determine by finding the initial rate (initial slope) from the $[N_2O_5]$ vs time graph to find k, and c) determine by finding k from the $\ln[N_2O_5]$ vs time.

Solution: a) From the graph of $[N_2O_5]$ vs time the initial concentration is .0165 M and half that would be .00825 M. The half-life from the graph is approximately 24 minutes. Since 1/8 the initial concentration is 3 half-lives (1/2 x 1/2 x 1/2 = 1/8) the length of time will be 3 x 24 min or 72 minutes.

b) From the graph of $[N_2O_5]$ vs time the initial slope of the line is the initial rate. $\Delta[A]/\Delta t = (0-.0165\text{ M})/(35-0\text{ min}) = -4.71\times10^{-4}\text{M/min} = -k[.0165]^1$

sloving for k

$k=(-4.71\times10^{-4}\text{M/min})/(-.0165\text{M}) = 0.0286\text{ min}^{-1}$

$t_{1/2} = .693/k = .693/0.0286\text{ min}^{-1} = 24.3\text{ min}$

3 half-lives x 24.3 min/half-life = 72.8min

c) From the linear graph of $\ln[N_2O_5]$ vs time, the slope is -k:

$(-5.85-(-4.1))/(60-0)=-k$

$k=0.0292$

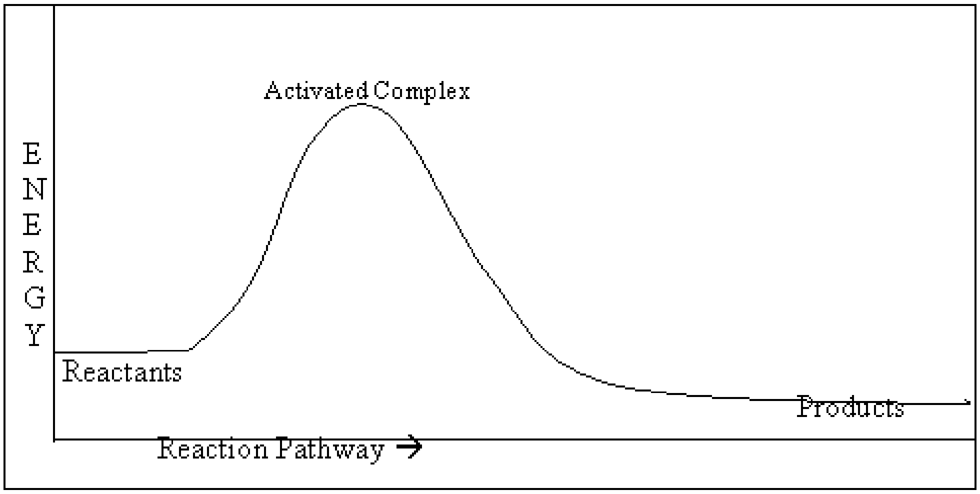
$t_{1/2} = .693/.0292\text{min}^{-1} = 23.76\text{ min}$

Total time is 3x23.76 min = 71.3 min

Which is most accurate?

ACTIVATION ENERGY

Reactions also depend upon the temperature. Generally the rate of a reaction will increase at higher temperature. The reaction rate is also dependent upon the energy barrier separating the reactants from products.



The higher the reaction barrier, the slower a reaction will be. The amount of energy needed to reach the top of the energy barrier is called the activation energy, E_a.

The Arrhenius equation relates the forward rate constant to the temperature and the activation energy:

$$k = Ae^{Ea/RT}$$

where A is the frequency factor and is related to the number of collisions per unit time, E_a is the activation energy, R is the gas constant (8.314joules/(Kxmol)) and T is the absolute temperature.

By carrying out two experiments one at a low temperature and the other at a higher temperature, we can derive an expression to find the activation energy for a set of reactants.

$$\text{Log}(k_1/k_2) = E_a(1/T_2-1/T_1)/(2.303R)$$

Problem 3:Using the table of data below find the activation energy for the reaction by estimating the slope and using the above equation.

Time (min)	25°C [N2O5]	25°C ln[N2O5]	45°C [N2O5]	45°C ln[N2O5]
0	0.0165	-4.10439	0.0165	-4.1043949
10	0.0124	-4.39006	0.010939	-4.5153949
20	0.0093	-4.67774	0.007253	-4.9263949
30	0.0071	-4.94766	0.004808	-5.3373949
40	0.0053	-5.24005	0.003188	-5.7483949
50	0.0039	-5.54678	0.002114	-6.1593949
60	0.0029	-5.84304	0.001401	-6.5703949

An approximation for the slope of the graph of ln[N_2O_5] vs time at each temperature gives:

At 25°C

$-k = \text{slope} = (-5.84304+4.10439)/(60-0)$

$k_1=0.0290$

At 45°C

$-k = \text{slope} = (-6.5703949+4.10439)/(60-0)$

$k_2=0.0411$

$\log(k_1/k_2) = E_a(1/T_2-1/T_1)/(2.303R)$

$E_a=\log(.0290/.0411)\text{x}2.303\text{x}8.314\text{J/Kxmol}/(1/318\text{K}-1/298\text{K})$

$E_a=13700$ J/mole or 13.7kJ/mol

REACTION MECHANISM

A reaction mechanism is a step-by-step description of how molecules interact and re-associate to form products. A reaction mechanism can be concocted from kinetic data; however, the reaction mechanism may not be real.

The rate law for simple reactions, or elementary reactions, occuring in one step such as:

$aA + bB + cC ... \dashrightarrow$ products

is:

rate = $k_f[A]^a[B]^b[C]^c$...

and requires all reactants to come together simultaneously and in the right orientation. If a reaction occurs in a series of steps, then the rate is determined by the slow step in the reaction sequence. Consider the analogy:

A man needs to make a series of errands. First, he needs to pick up some bread at the market, second, he needs to pick up some cash at the bank, third he needs to drive to Los Angeles to see a friend and fourth he will eat some bread with the friend. It is clear that the item on this list that will take the greatest amount of time is the trip to Los Angeles. We can therefore state that the time it takes to complete the first two items is negligible in relation to the third; therefore the third item is the rate-determining step...

Similarly, the slowest reaction in a sequence of reactions controls the overall rate of the reaction and gives enough time for the prior faster steps to come to equilibrium so that their forward and reverse rates are equal. Any step prior to the rate-determining step can be assumed to be in equilibrium and relatively fast. All steps that follow the rate-determining step are considered fast and lead quickly to the products.

Before we tackle a problem with reaction mechanisms, we need to understand the idea of equilibrium. At equilibrium, the forward rate and reverse rate of a reaction are equal.

Consider a reaction in equilibrium:

$$aA + bB \overset{k_f}{\underset{k_r}{<===>}} cC + d\,D$$

The forward rate is:

$Rate_f = k_f[A]^a[B]^b$

and the reverse rate is:

$Rate_r = k_r[C]^c[D]^d$

Since:

$Rate_f = Rate_r$ at equilibrium,

$k_f[A]^a[B]^b = k_r[C]^c[D]^d$

Solving for the constants we get:

$k_f/k_r = [C]^c[D]d/[A]^a[B]^b$

We will call the ratio k_f/k_r the equilibrium constant (K_{eq}) since the ration is simply a constant.

$K_{eq} = [C]^c[D]^d/[A]^a[B]^b$ that is $K_{eq} = [\text{Products}]^x/[\text{Reactants}]^y$

We can now attack the problem of reaction mechanisms.

Consider the reaction:

$Cl_2 + CHCl_3 \text{--->} HCl + CCl_4$

The experimentally observed rate law is:

$\text{Rate} = k[CHCl_3][Cl_2]^{1/2}$

We can consider this reaction to occur in any number of steps so long as the observed rate is deducible from our proposed mechanism.

Problem 4: Determine the rate expression for the proposed mechanism:

$Cl_2 \underset{k_{1r}}{\overset{k_{1f}}{\Longleftrightarrow}} 2Cl$ FAST

$Cl + CHCl_3 \xrightarrow{k_{2f}} HCl + CCl_3$ SLOW Rate Determining Step

$Cl + CCl_3 \rightarrow CCl_4$ FAST

The rate determining step is the second step and has a rate expression:

$\text{rate} = k[Cl][CHCl_3]$

which does not match the experimental rate expression; however, the [Cl] comes from the previous step which is in equilibrium. The equilibrium expression for the first step is:

$K_{eq} = [Cl]^2/[Cl_2]$

Solving for [Cl] we get: $[Cl] = K_{eq}^{1/2}[Cl_2]^{1/2}$

Plugging this into the rate expression above we get:

$\text{rate} = kK_{eq}^{1/2}[Cl_2]^{1/2}[CHCl_3]$ or $\text{rate} = k'[Cl_2]^{1/2}[CHCl_3]$

This is precisely the experimentally observed rate expression. Other mechanisms are possible which will give the same rate expression and other experiments would need to be carried out to determine the truth.

Catalysts

A catalyst is a substance that can **aid a reaction's** reactants to become products. The catalyst reacts with one or more of the reactants to provide an **alternate path** for the formation of products. During the course of the reaction, the catalyst is regenerated and is **not consumed**. The net effect of a catalyst is to **lower the activation energy** for the overall reaction by providing an alternate way for the reactants to become products. Consider the uncatalyzed reaction:

$2H_2O_2 \rightarrow 2H_2O + O_2$ Extremely slow!!

Hydrogen peroxide can exist in bottles for months with very little decomposition.

Consider the catalyzed reaction:

$H_2O_2 + I^- \rightarrow H_2O + IO^-$ Iodide catalyst forms the hypoiodite ion.

$H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$ Iodide ion is reformed.

$2H_2O_2 \rightarrow 2H_2O + O_2$

Overall reaction is the same as the uncatalyzed reaction but the reaction occurs much more rapidly.
Problem 5: Sketch the energy barrier for both the uncatalyzed and the catalyzed reaction above. Label all parts of the energy diagram.

Surfaces can also act as catalysts by changing the electron density of the adsorbing species. When a substance adsorbs onto the surface of a catalyst, it forms a weak bond to the surface atoms of the catalyst. This bond changes the charge of the adsorbed atom and makes the substance susceptible to reaction with other substance. Consider carbon monoxide :C:::O: which normally has a triple bond might respond to adsorption onto the surface of a catalyst.

C+ ← Positive charge imparted to carbon due to adsorption of oxygen
| | ← Electrons are donated to metal surface and bond order reduced to 2.
O
| ← Platinum Metal surface

CO can be removed from automobile exhaust by reaction with oxygen in the car's catalytic converter. $2CO + O_2 \rightarrow 2CO_2$

Pasted from <http://fp.academic.venturacollege.edu/doliver/chem1b/notes/Chap16new.htm>