AT Chemistry 2012

# **Kinetics** The Study of Reaction Rates and Mechanisms

**Kinetics** - deal with how and how fast a reaction occurs; it has nothing to do with the extent to which a reaction will occur; the extent is governed by thermodynamics.

Let's first considerb reaction rates. How can we define a rate of a reaction?

**Rate** =  $\Delta$ concentration/ $\Delta$ time =  $\Delta$ [product]/ $\Delta$ t = - $\Delta$ [reactant]/ $\Delta$ t

Given:  $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ 

rate =



For the reaction of hydrogen and oxygen to give water,

 $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ 

The rate of disappearance of  $H_2$  must be twice the rate for  $O_2$ , and equal to the rate of appearance of  $H_2O$ . This is because the coefficients of the chemical equation tell you the <u>relative</u> rates. That is,

where "[]" means concentration in moles/liter. This says that for every mole of  $O_2$  that reacts, per unit time, 2 moles of  $H_2$  react and 2 moles of  $H_2O$  are produced. Note that the rate of disappearance of the reactants is given a negative ("") sign. This implies that we are losing reactants, while gaining the product ("+" rate). Note also that your textbook uses the standard that all reaction rates should be positive.

#### **Rate Laws**

Reaction rate depends only on the concentration of the reactants (the reverse reaction will be neglected). A rate law shows how the rate depends on the concentrations of reactants.

rate  $=k[A]^n$  k = rate constantn = order

The [products] do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate. The value of the exponent n must be determined by experiment; it cannot be written from the balanced equation.

Types of Rate Laws - two types:

1. Differential rate law shows how the rate of a reaction depends on concentration.

2. Integrated rate law shows how the concentration of species in the reaction depend on time.

Experimental convenience usually dictates which type of rate law is determined experimentally; if you know one you also know the other. The importance of the rate law arises mainly from the fact that we can usually infer the individual steps involved in the reaction (i.e. reaction mechanism) from the specific form of the rate law.

#### Determining the Form of the Rate Law

Use the <u>method of initial rates</u> to determine rate laws and rate constants. Let's consider the following example:

$$A + B \rightarrow products$$

We want to determine a rate law for the decomposition of "A" that takes into account both [A] and [B]. We can hypothesize that the rate of the reaction is proportional to the concentrations of A and B. The more of each, the faster the reaction.

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

Gathering experimental data will allow us to determine the rate law. Our goal is to determine x, y, and k. The sum of the exponents, x + y, is called the overall reaction order.

Zero order:	r = k	rate won't change with concentration changes
First order in A:	$r\Delta = k[A]$	rate will change linearly with the concentration of A (i.e. you double [A] the rate should double)
Second Order in A: $r = k[A]^2$		rate will change as the square of a change in [A] (i.e. if you double [A] the rate will increase by a factor of 4)

#### **Problem:**

Reaction #	[A] <u>o</u>	[B] <sub>0</sub>	Initial Rate of Reaction (M/s)
1	0.100	0.100	1.53 X 10 <sup>-4</sup>
2	0.100	0.300	4.59 X 10 <sup>-4</sup>
3	0.200	0.100	6.12 X 10 <sup>-4</sup>
4	0.100	0.200	3.06 X 10 <sup>-4</sup>
5	0.300	0.600	8.26 X 10 <sup>-3</sup>

**KEY IDEA:** Determining how the rate varies with varying concentration of one component while the concentration of the other is held constant.

What happens to the rate when you vary [A]<sub>o</sub> while holding [B]<sub>o</sub> constant?

 $\Delta \operatorname{ration}[A]_0^{X} = \operatorname{ratio rate}, \quad \operatorname{solve for } x$ 

What happens to the rate when you vary [B]<sub>o</sub> while holding [A]<sub>o</sub> constant?

 $\Delta[B]_0^y = \Delta rate solve, for y$ 

Rate Law:

Solve for  $\mathbf{k}$  and use other data to verify our solution (to check that our rate law reflects the data):

**Problem:** Determine the rate law and solve for the order and value of the rate constant for the reaction

 $C + D + E \rightarrow Products$ 

given the following data:

Reaction #	[ <u>C]</u> <sub>o</sub>	[D] <sub>0</sub>	[E] <sub>o</sub>	Initial Rate (M s1)
1	0.400	0.300	0.560	7.14 X 10 <sup>-4</sup>
2	0.100	0.500	0.200	4.55 X 10 <sup>-5</sup>
3	0.100	0.200	0.200	4.55 X 10 <sup>-5</sup>
4	0.400	0.300	0.750	1.28 X 10 <sup>-3</sup>
5	0.100	0.300	0.560	3.57 X 10 <sup>-4</sup>

With respect to C:

With respect to D:

With respect to E:

Rate law:

Value of k:

## Units of k

given rate = -  $\Delta[A]/\Delta t = k[A]^n$  for nth order  $k = M^{1-n}s^{-1}$ 

**Integrated Rate Law** - relates concentration to time. The integrated rate law problems are a little tougher than differential rate law problems because you have to look at the entire data set to determine the rate relationship. We won't need to use calculus to solve these problems but if you know some basic integral calculus it's easy to see where the relationships come from. What you will need to determine is what form of [A] vs time (t) will get a linear relationship. Using your TI calculators makes this POC (piece of cake).



As an example of how to use the TI-89 in solving integrated rate law problems, let's try graphing data from problem 29 in the text. First we will see if its first order by graphing  $ln[H_2O_2]$  vs time

Steps:

- 1. turn on the calculator. DUH!
- 2. press the APPS button
- 3. scroll down to Data/Matrix editor
- 4. hit the right arrow button
- 5. scroll down to new

- 6. hit down twice until you reach Variables box and type in a proper name do not use one letter names
- 7. type in the time results under c1 column
- 8. type in [H<sub>2</sub>O<sub>2</sub>] values under c2 column
- highlight the c3 header and hit 2<sup>nd</sup>x, this will give you the ln function. Then hit "alpha" key to type the letter c. Then hit 2. The c3 header, when highlighted, should look like:

c3 = ln(c2)

- 10. next aroow right and up to highlight the c4 header. Then type in (1/(c2))
- 11. now hit F2 followed by F1
- 12. type in c1 next to the x and c3 next to the y
- 13. hit enter twice
- 14. then hit "diamond" and F3
- 15. once the calculator stops graphing, hit F2 and scroll down to the zoom data
- 16. if you see a straight line with a negative slope then you know its first order; if not then repeat steps 11-15 but type in c1 for x and c4 for y (2<sup>nd</sup> order – straight line with positive slope) or type in c1 for x and c2 for y (zero order – straight line with negative slope)

to determine the slope:

- 1. press APPS button
- 2. scroll down to Data/Matrix editor
- 3. hit enter for current
- 4. then hit F5 button
- 5. scroll down to x type in c1 and then c3 for y
- 6. scroll back up to Calculation Type, hit right arrow and select LinReg (5)
- 7. hit enter; the slope is the a value

## SUMMARY TABLE

Order	Zero	First	Second
Rate Law	rate = k	rate = $k[A]$	rate = $k[A]^2$
Integrated Rate Law	$[\mathbf{A}] = -\mathbf{k}\mathbf{t} + [\mathbf{A}]_{0}$	$\ln[A] = -kt + \ln[A]_{o}$	$1/[\mathbf{A}] = \mathbf{k}\mathbf{t} + 1/[\mathbf{A}]_{0}$
Plot needed to give a straight line	[A] vs t	ln[A] vs t	1/[A] vs t
Relationship of k to slope	slope = -k	slope = -k	slope = k
Half-life	$t_{1/2} = [A]_0/2k$	$t_{1/2} = 0.693/k$	$t_{1/2} = 1/k[A]_o$

Summary of the Kinetics for Reactions of the Type aA  $\rightarrow$  Products that are Zero, First, or Second Order in [A]

# Half-Life

All radioactive elements have nuclei which follow a first-order rate law when decaying.

Problem: Given

 $^{222}$ Rn  $\rightarrow$   $^{218}$ Pb +  $^{4}$ He

 $k = 0.181 \text{ d}^{-1}$ . If  $[A_0] = 5.28 \text{ g}$ , what is [A] after 1.96 days? after 3.82 days?

Problem: Given  $2I(g) \rightarrow I_2(g)$ 

rate = k[I]<sup>2</sup> 
$$k = 7.0 \times 10^9$$

a) What are the units of k?

b) If  $[I_0] = 0.40$  M, what is [I] at  $t = 2.5 \times 10^{-7}$  sec?

c) If  $[I_0] = 0.40$  M, calculate  $t_{1/2}$ .

d) If  $[I_0] = 0.80$  M, how much time would it take for 75% of iodine atoms to react?

It is important to note the difference between the half-life for first order vs second order reactions. First order depends only on k and not the initial concentration  $[A]_0$ ; a constant time is required to reduce the concentration of the reactant by half, and then again by half and so forth. For second order reaction  $t_{1/2}$  depends on k and  $[A]_0$  and each successive half-life is double the proceeding one.

## **Factors Affecting Reaction Rate**

The key idea here is that anything that **increases the frequency of collisions** will increase the reaction rate.

- **Surface Area** the more reactant molecules are exposed to each other, the faster they will react
- **Temperature** generally increasing the temperature will increase the rate because of two reasons:
  - 1. at higher temperatures, bonds within the reacting molecules are vibrating with more energy and are closer to the breaking point than at lower temperatures. So molecules themselves are less stable.
  - 2. At higher temperatures the average velocity of molecules increases and therefore collide with a greater frequency. The number molecules with the required  $E_a$  are greater at a higher temperature compared to a lower one.

- **Catalyst** increases rate by providing an alternate mechanism one with a lower E<sub>a</sub>.
- **Concentration** more molecules available to react, the faster the rate

Now let's consider Reaction Mechanism and Collision Theory

We know that in order for two molecules to react, they must collide. To be an *effective collision*, that is, one that results in a chemical reaction, two important criteria must be met:

- The two reacting molecules must have *sufficient kinetic energy* to overcome their electron cloud repulsions so they can hit
- The reactant molecules must hit at the *correct angle* one that allows their "active sites" (i.e. valence orbitals) to interact to transfer or share electrons

When we see a balanced molecular equation such as

 $2NO + 2H_2 \rightarrow 2H_2O + N_2$ 

We might think that two molecules of NO collide with two molecules of  $H_2$  to form products. The probability of four reactant molecules all having sufficient kinetic energy to overcome electron cloud repulsions and also all four hitting at the correct angle is statistically impossible. This is not how the reaction occurs. Instead, chemists beieve reactions occur in a series of bimolecular (or unimolecular) collisions that add up to produce the net reaction we observe. Two molecules having sufficient kinetic energy and hitting at the right angle is statistically the most likely to occur.

**Reaction Mechanism** - the sequence of *elementary steps* (generally **unimolecular** - one molecule splits apart) or mostly **bimolecular** - two molecules interact) which add up to the net reaction.

**Intermediate** - substance produced in one elementary step and used in a subsequent elementary step; intermediates cancel out in addition of steps.

**Molecularity** - the number of species that collide to produce the reaction indicated by the elementary step. Unimolecular and bimolecular are the two most important molecularities. Why not ternary?

**Rate-determining step** - the slowest step in the mechanism; the reaction can go only as fast as the slowest step.

**KEY IDEA:** The differential rate law is determined by the rate-determining step. This step may be in one direction or reversible. For any elementary step in a mechanism you can use its stoichiometric coefficients as its rate order. Our goal is to be able to determine whether mechanisms are consistent with experimentally determined rate laws. For the proposed mechanism to be consistent, the rate law of the slow step must match the

observed rate law of the reaction. In writing the rate law of the slow step in the mechanism, it may be necessary to substitute for intermediates.

Problem: The balanced equation for the reaction of nitric oxide with hydrogen is:

$$2NO + 2H_2 \rightarrow 2H_2O + N_2$$

The experimentally determined rate law is

rate = 
$$k[NO]^2[H_2]$$

The following mechanism has been proposed,

$$NO + H_2 \rightarrow N + H_2O$$
 (slow)  

$$k_1$$

$$N + NO \rightarrow N_2O$$
 (fast)  

$$k_2$$

$$N_2O + H_2 \rightarrow N_2 + H_2O$$
 (fast)  

$$k_3$$

Is this mechanism consistent with the observed rate law?

Your textbook says there are two criteria that must be met if a mechanism is to be considered acceptable.

1. The sum of the elementary steps must give the balanced equation. If you add up the three steps, you will find that this is in fact true here.

2. The mechanism must agree with the observed rate law. According to the proposed mechanism, the first step is ratedetermining. This means that the overall mechanism must be given by the first step.

#### rate = $k_1[NO][H_2]$

This does not agree with the experimentally determined rate law, therefore our observed mechanism is incorrect.

Consider the same balanced equation as in the previous example. Is the following mechanism consistent with the experimentally determined rate law?

$\mathbf{k}_1$	
$NO + H_2 \rightarrow N + H_2O$	(fast, with
$\leftarrow$	equal rates)

Same problem as before, same data. Test this mechasnism:

$$NO + H_{2} \rightarrow N + H_{2}O \qquad (fast)$$

$$N + NO \rightarrow N_{2}O \qquad (fast)$$

$$k_{2}$$

$$N_{2}O + H_{2} \rightarrow N_{2} + H_{2}O \qquad (slow)$$

$$k_{3}$$

To review, in the Collision Model for Chemical Kinetics - molecules must collide to react:

- 1. Molecules must move toward each other.
- 2. Molecules must hit with proper orientation.
- 3. Molecules must hit with sufficiently high energy.
- 4. Molecules must separate after reaction occurs.

Numbers 2 and 3 make reaction unlikely. The odds of a collision are increased with higher concentration. The odds of collisions with sufficiently high energy are increased with increasing temperature.

Activation Energy  $(E_a)$  = minimum of threshold energy needed to produce a reaction.

**Potential Energy Diagram:** for Reactants  $\rightarrow$  Products + Energy



Time (min)

As two molecules approach each other they slow down due to electron cloud repulsions. Thus, their kinetic energies decrease. Since the total energy is conserved, this means their potential energy increases. At the moment the molecule hit and interact to form an activated complex (and are motionless for a billionth (?) of a second), all kinetic energy has been converted to potential energy. The product molecules then fly off, increasing the kinetic energy while decreasing the potential energy. The energy needed for the reactants to reach the activated complex is the activation energy ( $E_a$ ). The net difference between the potential energies of the reactants and products is the heat of the reaction ( $\Delta$ H, or  $\Delta$ E). Note that for an exothermic reaction the PE of the products is less than that of the reactants (and vice versa). Note also that adding a catalyst lowers the activation energy (by providing an alternate path – one requiring less energy) but has no effect on  $\Delta$ H.



Below is another way to look at the effect of adding a catalyst:



Note that the result is a greter number of molecules having the required E<sub>a</sub> to react.

The diagram below shows how increasing temperature effects the activation energy. The y axis refers to the total number of reacting molecules.



Explain the above diagram:

Draw a rough potential energy diagram for a reaction having  $\Delta H = -105$  kJ with an  $E_a = 75$  kJ/mol. On your diagram label the following:

- a) PE of reactants
- b) PE of products
- c)  $\Delta H$
- d) PE of activated complex
- e) Ea of forward reaction
- f) Ea of reverse reaction

Use a dashed line to show how the diagram would be changed by the addition of a catalyst.

The rate constant, k, is a measure of the fraction of collisions with sufficient energy to produce a reaction. Svante Arrhenius showed that

$$\begin{split} k &= Ae^{\text{-}Ea/RT} \\ k &= \text{rate constant} \\ A &= \text{frequency factor} \\ E_a &= \text{activation energy}(J/\text{mol}) \\ R &= 8.31 \text{ J/mol K} \\ T &= \text{temperature (K)} \end{split}$$

Taking the ln of both sides:

$$ln(k) = -E_a/R[1/T] + ln[A]$$
  
y = m x + b

ln(k) can be plotted graphically vs 1/T for a series of data to determine the slope and intercept, or for quick work, two sets of data can be used mathematically, yielding:

$$\frac{k_1}{\ln k_2} = \frac{E_a}{R} \frac{1}{[T_2 - \frac{1}{T_1}]}$$

Does this look familiar? Ahh the Clausius Calperyon equation relating vapor pressures, temperatures and heats of vaporizations! The above is known as the Arhennius equation and it relates rate constants, temperatures and activation energies.

*Problem*:  $H_2(g) + I_2(g) \rightarrow 2HI(g)$ 

 $E_a = 167 \text{ kJ/mol}$   $k = 2.45 \text{ X } 10^{-4} \text{ M}^{-1} \text{ at } 320^{\circ}\text{C}$ 

What is the rate constant at 205°C?

Problem:

A second-order reaction has rate constants of 8.9 X  $10^{-3}$  M<sup>-1</sup> and 7.1 X  $10^{-2}$ M<sup>-1</sup> at 3.0°C and 35.0°C respectively. Calculate E<sub>a</sub>.

## Given: $2ClO_2(g) + F_2(g) \rightarrow 2ClO_2F(g)$

The following data were obtained when the reaction represented above was studied at 25°C.

Experiment	[ClO <sub>2</sub> ] <sub>0</sub> (M)	[F2] <u>o</u> (M)	Initial Rate increase [ClO <sub>2</sub> F] (M/sec)
1	0.010	0.10	2.4 X 10 <sup>-3</sup>
2	0.010	0.40	9.6 X 10 <sup>-</sup> 3
3	0.020	0.20	9.6 X 10 <sup>-3</sup>

(a) Write the rate law expression for the reaction above. This is an interesting problem because one the reactants is not held constant! What do we do now?

(b) Calculate the numerical value of the rate constant and specify the units.

(c) In experiment 2, what is the initial rate of decrease of  $F_2$ ?

(d) Which of the following mechanisms is consistent with the rate law developed in part (a)? Justify your choice.

$ClO_2 + F_2 = ClO_2F_2$	(fast)
$ClO_2F_2 \rightarrow ClO_2F + F$	(slow)
$ClO_2 + F \rightarrow ClO_2F$	(fast)
$F_2 \rightarrow 2F$ 2(ClO <sub>2</sub> + F $\rightarrow$ ClO <sub>2</sub> F)	(slow) (fast)
	$ClO_{2} + F_{2} = ClO_{2}F_{2}$ $ClO_{2}F_{2} \rightarrow ClO_{2}F + F$ $ClO_{2} + F \rightarrow ClO_{2}F$ $F_{2} \rightarrow 2F$ $2(ClO_{2} + F \rightarrow ClO_{2}F)$

# Demonstrations

## Catalytic Decomposition of Hydrogen Peroxide (Foam Production or Elephant Toothpaste)

The rate of decomposition of hydrogen peroxide to water and oxygen gas can be greatly increased by the addition of potassium iodide as a catalyst. The net reaction is:

$$2 H_2O_2(aq) \rightarrow 2 H_2O(l) + O_2(g)$$
  
KI

It is believed the reaction involves a two-step mechanism:

1) 
$$H_2O_2(aq) + I(aq) \rightarrow H_2O(l) + OI(aq)$$
 (slow)

2) 
$$H_2O_2(aq) + OI^-(aq) \rightarrow H_2O(1) + O_2(g) + I^-(aq)$$

## Questions

- 1. What is the net reaction?
- 2. What is the molecularity of each step?
- 3. How doees a catalyst work?
- 4. Which substance is the catalyst in this reaction? How do you know?
- 5. Was the catalyst used homogeneous or heterogeneous?
- 6. Identify the intermediate(s):
- 7. What happens to the KI?
- 8. How can you verify that oxygen gas was produced?

Hydrogen peroxide can be decomposed by absorbing light energy. Draw the Lewis structure for hydrogen peroxide. Based on bond energies, determine the wavelength of light needed to decompose hydrogen peroxide.

Note: O - O bond energy = 146 kJ/mol  $h = 6.626 \times 10^{-34} \text{ J-s}$   $c = 3.00 \times 10^8 \text{ m/s}$ 

Demo 2

## The Oxidation of Tartaric Acid

The oxidation of tartaric acid by hydrogen peroxide yields carbon dioxide and water. The rate can be increased by the addition of cobalt chloride. This demonstration is one of the few that allows one to actually observe the formation of an activated complex. The effect of temperature on the rate can also be easily demonstrated. The reaction is:

 $\begin{array}{rl} HC_4H_4O_6(aq) + H_2O_2(aq) & -----> & ----> CO_2(g) + H_2O(l) \\ & Co^{2+} & Co\text{-complex} \\ & pink & green \end{array}$ 

Demo 3

#### **Oxidation of Baby Powder**

The efffect of surface area on the reaction is dramatically shown here!

Demo 4

#### **Catalytic Decomposition of Acetone**

In this reaction acetone, (CH<sub>3</sub>COCH<sub>3</sub>), catalytically decomposes on a hot copper surface to give a variety of products, the principle ones being ketene CH<sub>2</sub>CO and methane,

CH<sub>4</sub>. Hot copper metal acts as a catalyst. Note in this reaction the copper is an example of a heterogeneous catalyst.

The copper is heated in a flame of a bunsen burner until it is glowing hot. The copper is suspended above a layer of acetone in a beaker. The copper continues to glow red hot due to the exothermic decopmposition of acetone. The reaction is:

 $\begin{array}{cc} CH_3COCH_3 & \twoheadrightarrow & CH_2CO + CH_4 \\ Cu & \end{array}$