

**ALEXANDER MACKENZIE HIGH SCHOOL****SCH4U CHEMISTRY****CHAPTER 6 – CHEMICAL KINETICS****Rates of Reaction**

- Chemical kinetics is the study of speeding up or slowing down chemical reactions
- Rate of reaction (reaction rate) is the speed at which a chemical reaction occurs and is usually expressed as the change in concentration per unit of time
- Usually obtained by measuring the rate at which a product is formed or the consumption rate of a reactant being consumed over a series of time intervals
- Measurements can include mass, colour, conductivity, volume & pressure
- The rate of a reaction can be expressed with a number of units including mole/min or mL/s
- Reaction rates are can be expressed as “change in concentration per unit of time” or mathematically as;

$$\text{average reaction rate} = \frac{\text{change in concentration}}{\text{elapsed time}}$$

becomes  $r = \frac{\Delta c}{\Delta t}$

See sample problem on Page 360

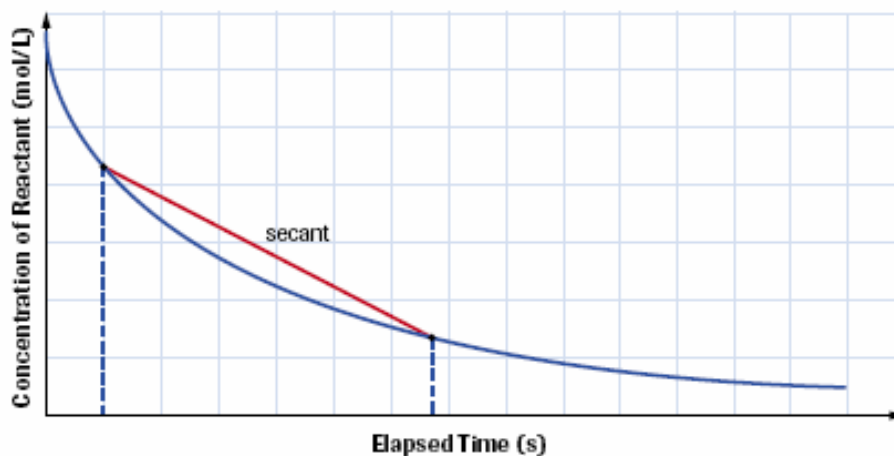
Homework: Nelson 12: Page 360, #'s 1 & 2

- Looking at a reaction like;  

$$\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$$

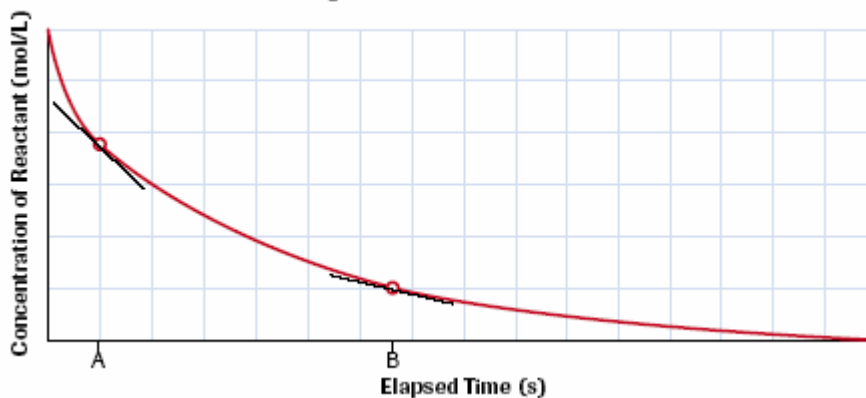
$\text{Cl}_2(\text{g})$  would fall as the reaction progresses

Finding Average Rate of Reaction

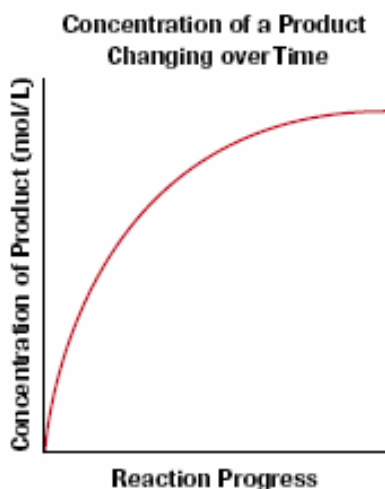


- The graph shows the *average rate of reaction* (or rate of consumption of  $\text{Cl}_2$ ) over a period of time and is the absolute value of the slope of the secant (a line between 2 points on a curve) drawn between 2 points
- Its also possible to determine the reaction rate at any point in time
- *Instantaneous rate of reaction* (or rate of consumption of  $\text{Cl}_2$ ) is the slope of the curve at that particular point

Finding Instantaneous Rate of Reaction



- From the graph (Fig. 4) at point B the slope is less steep – an indication that the reaction is slower
- If we plot the data for the concentration of product formed against time, the result is a rising curve with a steadily positive slope (see Fig. 5)



**Figure 5**

The concentration of a product, such as HCl, during the progress of a reaction increases continuously. The slope,  $\Delta[\text{HCl}]/\Delta t$ , is greatest in the early stages of the reaction.

- Plotting the concentration of reactant gives a falling curve with a steadily decreasing negative slope
- We can describe these rates using a notation that represents the negative slope of the reactant graph and the positive slope of the product graph and use the absolute value to represent the numerical value. i.e.

$$\begin{array}{l}
 -\frac{\Delta[\text{CH}_4]}{\Delta t} = x \text{ mol/(L}\cdot\text{s)} \quad \text{or} \quad -\frac{\Delta[\text{Cl}_2]}{\Delta t} = x \text{ mol/(L}\cdot\text{s)} \\
 \text{or} \quad +\frac{\Delta[\text{CH}_3\text{Cl}]}{\Delta t} = x \text{ mol/(L}\cdot\text{s)} \quad \text{or} \quad +\frac{\Delta[\text{HCl}]}{\Delta t} = x \text{ mol/(L}\cdot\text{s)}
 \end{array}$$

NOTE: A negative (-) sign indicates a rate of consumption of reactant & a positive (+) sign indicates a production of product.

The rate of reaction in terms of the reactants and products is the same for this chemical reaction because the mole ratios are all 1 to 1

See the sample problem on page 363 to determine the rate of reaction in the case where mole ratios for reactants and products are not 1 to 1

### Calculating Rates of Reaction

*Consider the reaction of iodate, iodide, and hydrogen ions to yield iodine and water.*



*What are the rates of reaction with respect to the various reactants and products?*

*The rate of reaction with respect to iodate ions (rate of consumption of  $\text{IO}_3^-$ ) is determined experimentally to be  $3.0 \times 10^{-5} \text{ mol}/(\text{L}\cdot\text{s})$ .*

As you can see in the equation, for every 1 mol of iodate ions ( $\text{IO}_3^-$ ) consumed, 5 mol of iodide ions ( $\text{I}^-$ ) and 6 mol of hydrogen ions are used up. As a result, the rates of consumption of the three reactant ions will be quite different.

We can express the rate of reaction of iodate ions as

$$-\frac{\Delta[\text{IO}_3^-]}{\Delta t} = 3.0 \times 10^{-5} \text{ mol}/(\text{L}\cdot\text{s})$$

We can therefore express the rate of the same reaction for the other reactants, taking into account that they are consumed or produced in different amounts, using the mole ratio as a conversion factor:

$$\begin{aligned} -\frac{\Delta[\text{I}^-]}{\Delta t} &= \frac{5 \text{ mol I}^-}{1 \text{ mol IO}_3^-} \times 3.0 \times 10^{-5} \text{ mol}/(\text{L}\cdot\text{s}) \\ &= 1.5 \times 10^{-4} \text{ mol}/(\text{L}\cdot\text{s}) \end{aligned}$$

You can check that you have the mole ratio correct, rather than inverted, by considering how much of the reactant is being consumed. In this case, because iodine ions are being consumed more rapidly than iodate ions, you would expect the change in concentration to be greater for the iodide ions than for the iodate ions.

Similarly,

$$\begin{aligned} -\frac{\Delta[\text{H}^+]}{\Delta t} &= \frac{6 \text{ mol H}^+}{1 \text{ mol IO}_3^-} \times 3.0 \times 10^{-5} \text{ mol}/(\text{L}\cdot\text{s}) \\ &= 1.8 \times 10^{-4} \text{ mol}/(\text{L}\cdot\text{s}) \end{aligned}$$

We can also express the rate of the reaction in terms of the products:

$$\begin{aligned} +\frac{\Delta[\text{I}_2]}{\Delta t} &= \frac{3 \text{ mol I}_2}{1 \text{ mol IO}_3^-} \times 3.0 \times 10^{-5} \text{ mol/(L}\cdot\text{s)} \\ &= 9.0 \times 10^{-5} \text{ mol/(L}\cdot\text{s)} \end{aligned}$$

and, since equal numbers of moles of each product are formed,

$$+\frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = 9.0 \times 10^{-5} \text{ mol/(L}\cdot\text{s)}$$

Note that all of these expressions describe the same system reacting at the same time. Chemists need to measure or calculate the rate of reaction for only one convenient reactant or product because we can use the balanced equation to deduce the other rates. However, we should state which substance we are considering.

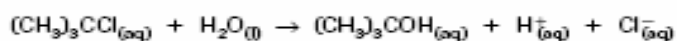
Homework: Nelson 12 Page 364 & 365, #'s 1-4

## Measuring Reaction Rates

- Different methods can be used to measure reaction rates depending on the types of reactions

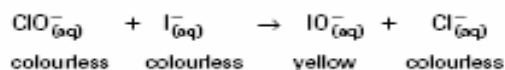
Reactions that produce a gas: can collect the gas and measure its volume and/or pressure

Reactions that involve ions: the conductivity of the solution changes as the reaction proceeds and can be measured and plotted as a function of time



e.g.

Reactions that change colour: the intensity (strength of colour) can be measured of a coloured reactant or product using a spectrophotometer. Can measure wavelengths of light that are invisible to the human eye



e.g.

In this example, the yellow colour of the aqueous hypiodite ions ( $\text{IO}^-_{(\text{aq})}$ ) appears initially, then becomes more intense as the reaction progresses and more ions form

Homework: Nelson 12 Pages 365 & 365, #'s 6, 8 & 9

## **Factors Affecting Reaction Rates**

- 5 basic factors affecting reaction rates
  - chemical nature of reactants
  - concentration of reactants
  - temperature
  - presence of a catalyst
  - surface area

### Chemical nature of reactants

- different elements react at different rates  
e.g Au and Ag react slowly in air while Na and K react so quickly in air that they are rarely found naturally in their elemental state
- similar elements in the same group tend to react similarly but at different rates e.g. Zn, Fe and Pb all react with HCl acid to produce H<sub>2</sub> gas, even when all the other conditions are the same, the rates of reaction are different  
e.g. activity series
- in homogeneous systems, such as reactions in aqueous solution, most reactions with monatomic ions (e.g. Ag<sup>+</sup> and Cl<sup>-</sup>) are extremely fast, while reactions of molecular substances are often slower (e.g. glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) and iron (II) ions (Fe<sup>2+</sup>) react with purple permanganate (MnO<sub>4</sub><sup>-</sup>) ions very visibly: glucose reacts slowly when compared to the reaction with Fe<sup>2+</sup>

### Concentration

- concentrated HCl vs. vinegar (acetic acid) or human stomach acid shows how different concentrations can cause different reaction rates
- experiments suggest that if the initial concentration of a reactant is increased, then the reaction rate generally increases e.g. when one adds a metal to acid, a higher initial concentration of acid increase the rate of gas production

- implies “concentrated is better & faster”

### Temperature

- mixing ingredients for a cake and nothing happens until the cake is placed in an oven
- cooking uses increased temperature to make changes in food happen more quickly
- paint dries faster when the temperature of the system increases, etc.
- rule of thumb is that around SATP a 10°C rise in temperature often doubles or triples the rate of a chemical reaction
- lowering the temperature can likewise lower the rate of a chemical reaction, useful for food storage
- humans apply cold substances to burned skin to slow unwanted physiological reactions (help minimize the effect of the burn)

### Presence of a catalyst

- catalysis is the effect of a catalyst
- a catalyst is a substance that alters the rate of a chemical reaction without becoming permanently changed itself
- palladium and platinum play an important role in the conversion of CO to CO<sub>2</sub> in catalytic converters
- enzymes in the human body are complex molecules (proteins) that act as catalysts e.g. amylase in saliva
- also people who cannot tolerate lactose when given lactase can tolerate lactose containing products
- enzymes are often very sensitive to temperature and pH and therefore conditions are critical for their use
- in industry, the use of catalysts can mean the difference between success and failure by making the reaction rate fast enough to be profitable but slow enough so that it is safe (see Table 1)

**Table 1** Examples of Industrial Catalysts

Industrial Product	Catalyst
sulfuric acid	vanadium(V) oxide
ammonia	magnetic iron oxide
acetaldehyde	vanadium(V) oxide
margarine	nickel
nitrogen dioxide	platinum
polyethylene	titanium(IV) oxide
polyester	nickel(II) oxide
methanol	chromium(VI) oxide

### Surface Area

- when a reaction system is heterogeneous (solid in liquid, etc), when a reaction occurs, it occurs where the two different phases make contact, so the amount of exposed surface area where contact can be made affects the reaction rate
- e.g. wood burns quite readily but sawdust can burn explosively
- when a metal reacts with an acid, the reaction only takes place where the metal makes contact with the acid solution
- in general, the reaction rate increases proportionally with the increase in surface area

Homework: Nelson 12 Page 371, #'s 1-5

## Rate Laws and Order of Reaction

- previous studies showed that the rate of a reaction can be linked to a variety of factors, with the concentration of the reactants being one key factor
- experimental evidence has shown that the rate of a reaction is exponentially proportional to the product of the initial concentration of the reactants (other factors held constant)
- Consider the reaction:  $aX + bY \rightarrow (\text{products})$

The Rate Law is:  $r \propto [X]^m [Y]^n$

Where:  $r$  is the rate of reaction  
 $m$  and  $n$  are some exponents determined from experimental data (any real number value) – NOT related to the coefficients  $a$  and  $b$  in the chemical equation  
 the concentrations refer to the initial concentrations of  $X$  and  $Y$

Using proportionality techniques, one can form the mathematical equation:

Rate Law Equation:  $r = k [X]^m [Y]^n$

Where:  $k$  is the rate constant or proportionality constant that is determined experimentally and valid only for the temperature specified

The exponents are also called the individual orders of reaction that show the dependence of the rate on the initial concentration of a particular reactant

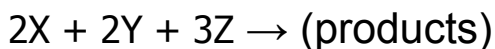
Eg. If  $m=1$  the order of reaction is 1 with respect to  $X$   
 If  $n=2$  the order of reaction is 2 with respect to  $Y$

The rate constant will assume units based on the orders of reaction to yield units for the rate in  $\text{mol}/(\text{L s})$

The overall order of reaction is the sum of the individual orders of reaction for each reactant

Eg. For the above example with  $m=1$  and  $n=2$ , the overall order of reaction is  $(1+2) = 3$

- To understand the effect of an order of reaction consider the following chemical equation:



experimental evidence will provide the rate law equation:

$$r = k [X]^1[Y]^2[Z]^0$$

the orders of reaction for each reactant can be interpreted by looking at the proportionality relationship between the rate and each reactant

- $r \propto [X]^1$  if  $[X]$  is doubled, than the rate is multiplied by 2 or  $2^1$   
If  $[X]$  is tripled, than the rate is multiplied by 3 or  $3^1$   
i.e. the multiplier relating R to  $[X]$  is 1
- $r \propto [Y]^2$  if  $[Y]$  is doubled, than the rate is multiplied by 4 or  $2^2$   
If  $[Y]$  is tripled, than the rate is multiplied by 9 or  $3^2$   
i.e. the multiplier relating R to  $[Y]$  is 2
- $r \propto [Z]^0$  if  $[Z]$  is doubled, than the rate is unchanged  
If  $[Z]$  is tripled, than the rate is unchanged  
i.e. the multiplier relating R to  $[Y]$  is 0

The overall order of the reaction is  $(1+2+0)= 3$

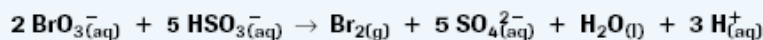
The rate law equation can be simplified to:

$$r = k [X]^1[Y]^2 \quad \text{as } [Z] \text{ has NO effect}$$

Review of the sample problem on p. 375 will provide an example of determining the orders of reaction from experimental data.

## Finding a Rate Equation

When aqueous bromate and bisulfite ions react to produce bromine, the overall equation is



Consider the series of experiments recorded in Table 2, in which initial reactant concentrations are varied and rates are compared. From the evidence provided, determine a rate equation.

**Table 2** Initial Concentrations of Reactants and Rate of Product Production

Trial	Initial $[\text{BrO}_3^-]$ (mmol/L)	Initial $[\text{HSO}_3^-]$ (mmol/L)	Initial rate of $\text{Br}_2$ production (mmol/(L·s))
1	4.0	6.0	1.60
2	2.0	6.0	0.80
3	2.0	3.0	0.20

The reaction rate,  $r$ , is proportional to the initial concentrations of bromate ions and of bisulfite ions.

$$r = k [\text{BrO}_3^-]^m [\text{HSO}_3^-]^n$$

where  $m$ ,  $n$ , and  $k$  are to be determined.

A key to solving problems of this type is to look for pairs of data in which the initial concentration of only one reactant changes.

To find  $m$ , look at the data from Trials 1 and 2, because the initial concentration of bromate changed while the initial concentration of bisulfite remained constant. Comparing these trials shows that when the initial concentration of  $\text{BrO}_3^-$  is doubled (from 2.0 to 4.0 mol/L), the rate changes by a factor of 1.60/0.80, or 2. This is in direct proportion to the change in initial concentration of  $\text{BrO}_3^-$ : As  $[\text{BrO}_3^-]$  doubles, the rate doubles. The exponent  $m$  in the rate equation is therefore 1; thus, the order of reaction with respect to  $\text{BrO}_3^-$  is 1.

To find  $n$ , look at the data from Trials 2 and 3, where the initial concentration of bisulfite changed while the initial concentration of bromate remained constant. Comparing these trials shows that when the concentration of  $\text{HSO}_3^-$  is doubled from 3.0 to 6.0 mol/L, the rate changes by a factor of 0.80/0.20, or 4. This is a direct square proportion to the change in concentration of bisulfite. Since  $2^2 = 4$ , the exponent  $n$  in the rate equation is 2, and the order of reaction with respect to bisulfite ions is 2.

To find the rate constant  $k$ , enter the values from Trial 1 (or any of the trials) into the rate equation, with the concentrations expressed in mol/L. For example, if we use the data from Trial 1 (converted to mol/L from mmol/L),

$$\begin{aligned} r &= k [\text{BrO}_3^-]^1 [\text{HSO}_3^-]^2 \\ 0.00160 \text{ mol/(L}\cdot\text{s)} &= k \times (0.0040 \text{ mol/L})^1 \times (0.0060 \text{ mol/L})^2 \end{aligned}$$

We can then solve for  $k$ :

$$k = \frac{0.00160 \text{ mol/(L}\cdot\text{s)}}{0.0040 \text{ mol/L} \times (0.0060 \text{ mol/L})^2}$$

$$k = 1.1 \times 10^4 \text{ L}^2/(\text{mol}^2\cdot\text{s})$$

The reaction is third order overall—first order with respect to bromate ion and second order with respect to bisulfite ion. The rate equation is

$$r = k[\text{BrO}_3^-]_{\text{(aq)}}[\text{HSO}_3^-]_{\text{(aq)}}^2$$

where

$$k = 1.1 \times 10^4 \text{ L}^2/(\text{mol}^2\cdot\text{s})$$

Homework: Nelson 12 Page 377, #'s 1-6

### Relating Reaction Rate to Time

- Earlier studies showed that the rate of reaction is inversely proportional to the elapsed time of a reaction

In a reaction given by  $aX \rightarrow (\text{products})$

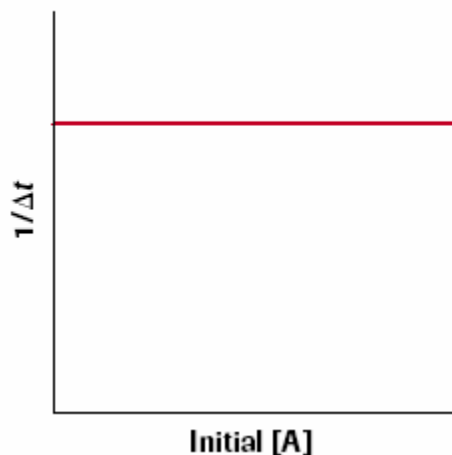
Remember:  $\text{ave rate} = \frac{-\Delta[X]}{\Delta t} = k[X]^n$ ,  $\Delta[X]$  is change in concentration over time

therefore we can say:  $\text{ave rate} \propto \frac{1}{\Delta t} \propto [X]^n$

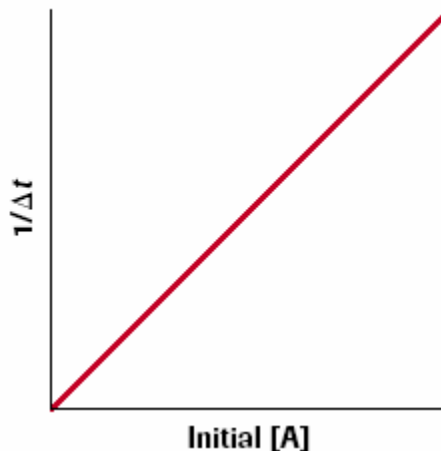
where  $[X]$  is the initial concentration of X

how will the graph of  $1/\Delta t$  vs  $[X]$  appear based on the order of reaction?

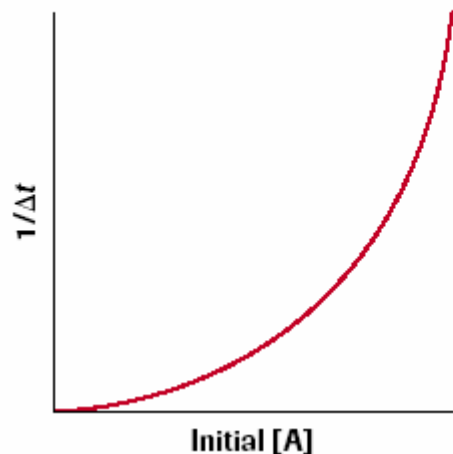
(a) Zeroth-Order Reaction



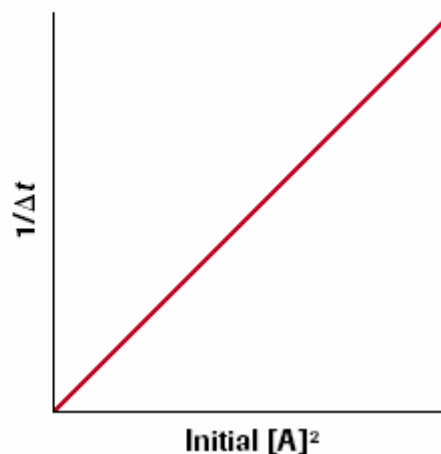
(b) First-Order Reaction



(c) Reaction with Order Greater than One



(d) Second-Order Reaction

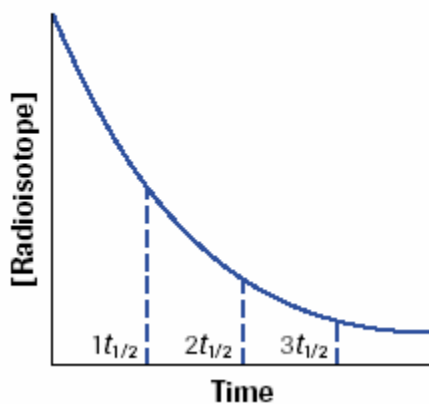


NOTE: the graph of d) is  $1/\Delta t$  vs.  $[A]^2$

### Chemical Kinetics and Half-Life

- The rate of reaction for many reactions is a first order reaction  
Eg. decomposition reactions or nuclear decay
- In a first order reaction the quantity of reactant remaining in a sample follows a predictable pattern
  - Many times we refer to the half-life of the reaction,  $t_{1/2}$ , which is the time required for half the sample to react

Concentration of Radioisotope  
Changing over Time



**Figure 4**

The decay or reaction of a reactant (such as carbon-14) shows first-order dependence in this plot of concentration vs. time. After each half-life, the concentration of the reactant is halved.

Consider the reaction:  $nA \rightarrow (\text{products})$

The rate law equation for a first order reaction will be:

$$\text{rate} = \frac{-\Delta[A]}{\Delta t} = k[A]^1$$

We can rewrite this equation as:

$$\frac{-\Delta[A]}{[A]} = k\Delta t$$

Using integral calculus, we get the following equation:

$$\ln \frac{[A]_t}{[A]_o} = -kt$$

Where:  $[A]_t$  = concentration of the reactant at any time t  
 $[A]_o$  = initial concentration of the reactant  
 $[A]_t/[A]_o$  = fraction of reactant remaining at time t  
 ln = natural logarithm (ln e = 1)

To calculate the half-life of the reactant A we set the ratio at  $1/2$

$$\ln 1/2 = -kt_{1/2} \quad \text{or} \quad \ln 2 = kt_{1/2}$$

Working with natural logarithms one would find:

$$kt_{1/2} = 0.693$$

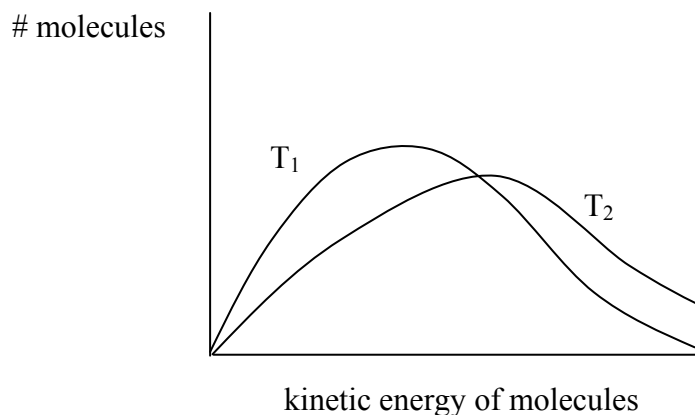
NOTE: This equation ONLY relates to first order reactions.

- Analysis of a second order reaction with one reactant can be carried out in a similar manner using the appropriate integral calculus and logarithmic algebra

Homework: Nelson 12 Page 381, #'s 7-8 and 2-5

## Collision Theory and Rates of Reaction

- Collision Theory was developed to understand why some reactions occur and others do not
- key elements
  - Particles are in constant random motion at various speeds: average kinetic energy is proportional to temperature



- A chemical reaction must involve collisions of particles with each other or the walls of the container
- An effective collision is one that has sufficient energy and correct orientation of the colliding particles so that bonds can be broken and new bonds formed
- Ineffective collisions involve particles that rebound from the collision, essentially unchanged
- The rate of a given reaction depends on the frequency of collisions and the fraction of those collisions that are effective

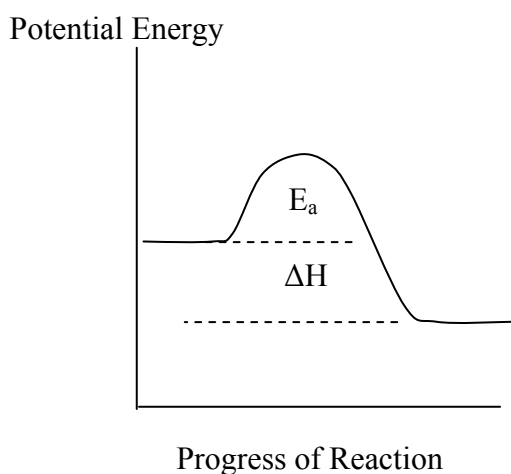
Rate = frequency of collisions x fraction of collisions that are effective

- increasing either factor will yield an increase in the rate

## Transition State Theory

### ➤ key elements

- looks at moment when molecules collide and break apart
  - at this point an activated complex is formed consisting of an unstable grouping of reactant molecules with bonds in the process of being broken and bonds in the process of being formed
- uses potential energy diagram to show energy change as reaction proceeds
  - reaction passes through a transition state where an activated complex is formed – intermediate product
  - difference between the initial energy of the reactants and the transition state is the activation energy ( $E_a$ )
    - activation energy is the minimum energy with which the molecules must collide before they can rearrange in structure, resulting in an effective collision



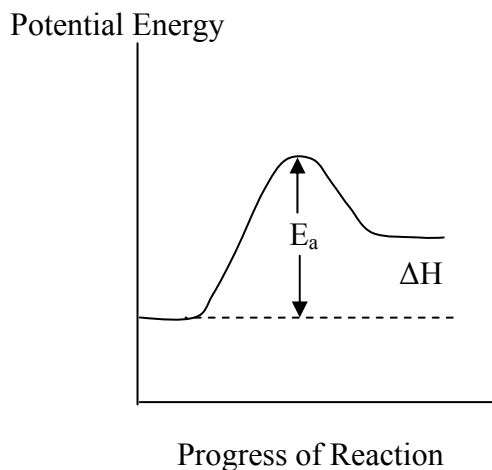
Exothermic Reaction

forward reaction



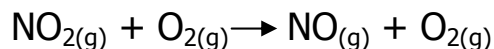
$$\Delta H^\circ = -200 \text{ kJ/mol}$$

$$E_a = +10 \text{ kJ/mol}$$



Endothermic Reaction

reverse reaction



$$\Delta H^\circ = +200 \text{ kJ/mol}$$

$$E_a = +210 \text{ kJ/mol}$$

- in an exothermic collision the molecules of the product will have a lower potential energy than the reactants and therefore a higher kinetic energy resulting in a rise in temperature – further collision will increase the speed of molecules
- in an endothermic reaction the molecules of the product will have a higher potential energy than the reactants and therefore a lower kinetic energy resulting in a drop in temperature – further collisions will tend to decrease the speed of molecules

### Effect of Chemical Nature of Reactant

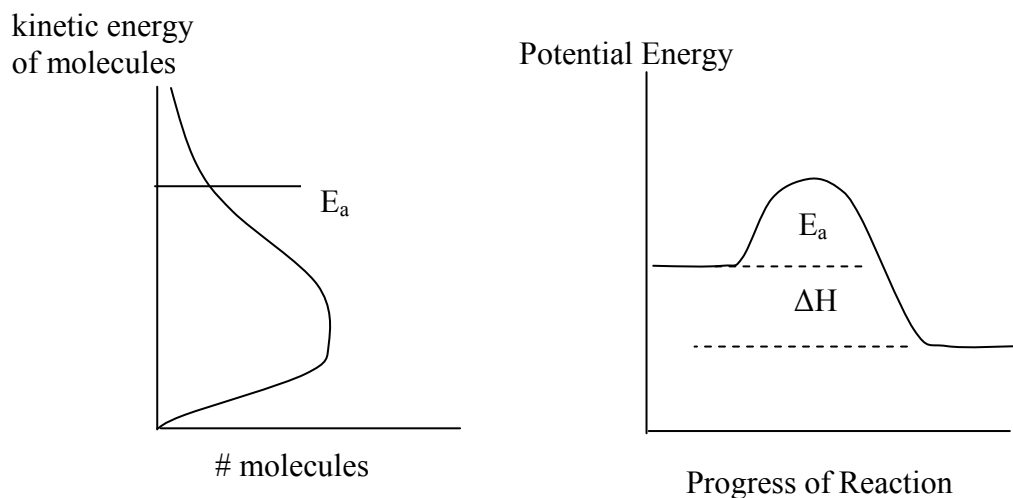
- The chemical nature of reactants affects the activation energy in two ways:
  - Some molecules have bonds that are relatively weak and have small activation energy barriers, so the threshold energy (activation energy) is relatively low and a large fraction of molecules is capable of colliding effectively, while other molecules have strong bonds and high activation energy barriers resulting in ineffective collisions
  - Collision geometry – some reactions involve complicated molecular substances or complex ions that are often less reactive because more bonds have to be broken and the collision must occur in the correct orientation

### Effect of Concentration and Surface Area

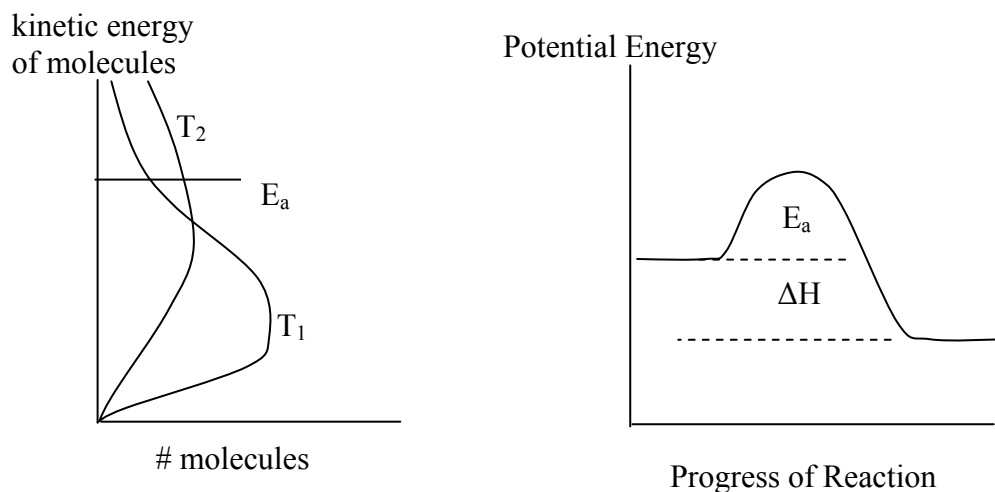
- Concentration
  - a higher concentration means a larger number of particles per unit volume, which are more likely to collide – if there are twice as many particles, then there is twice the probability of an effective collision
- Surface Area
  - Only applies to heterogeneous reactions – gas with a solid or a solid with a liquid
  - Surface affects collision frequency because reactants can collide only at the surface where the reactants are in contact

## Effect of Temperature on the Rate of Reaction

- higher molecule speed increases the # of collisions - as the average kinetic energy of molecules increases more collisions will have enough energy to overcome the activation energy
- consider the distribution of molecular energy (Maxwell-Boltzmann Distribution)



the activation energy for a given reaction and set of conditions is constant

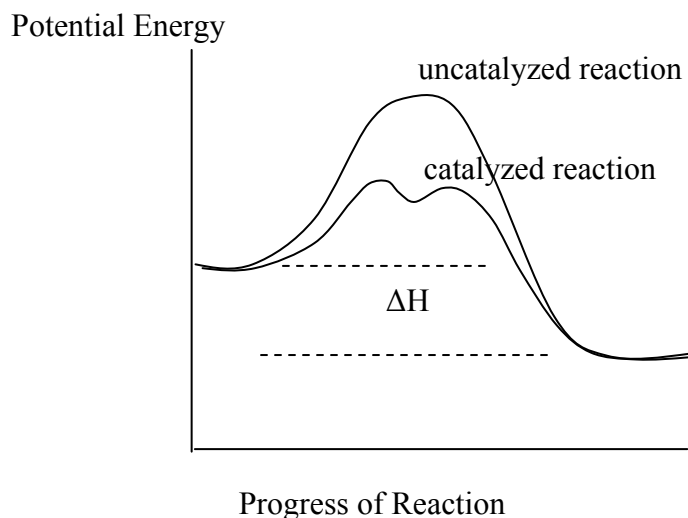


- If temperature  $T_2$  is greater than temperature  $T_1$ , then the distribution of molecules with kinetic energy greater than the activation energy,  $E_a$ , increases – the number of collisions with

sufficient energy will increase, resulting in an increase in the rate of reaction

### Effect of Catalysts on the Rate of Reaction

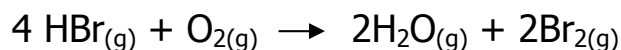
- A catalyst is a substance that increases the rate of reaction without being consumed
- a catalyst decreases the activation energy of a reaction and also provides additional reaction steps



- types of catalysts
  - homogeneous catalyst - catalyst is the same phase as the reactants
 
$$2\text{SO}_{2(g)} + \text{O}_2 \xrightarrow{\text{NO}_2} \text{SO}_{3(g)}$$
  - heterogeneous catalyst – catalysis occurs at a point between the two phases
 
$$2\text{H}_2\text{O}_{2(aq)} \xrightarrow{\text{MnO}_2} 2\text{H}_2\text{O}_{(l)} + \text{O}_{2(g)}$$
- also available are inhibitors to slow down the rate of reaction

## Reaction Mechanisms

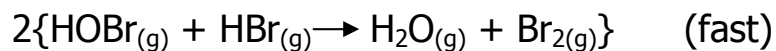
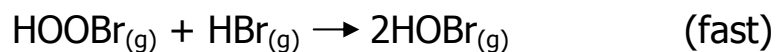
- Collision theory suggests that collisions of three particles at the same time must be less frequent than two particle collisions – four particle collisions would even more rare
- What about reactions with one reactant?
  - a single molecule can hit a container wall or other molecule such that enough energy is converted from kinetic to potential energy for the molecule to decompose
- it is believed that most chemical reactions occur as a sequence of elementary steps called a reaction mechanism
  - take the example of the oxidation of hydrogen bromide (at 400 to 600 °C)



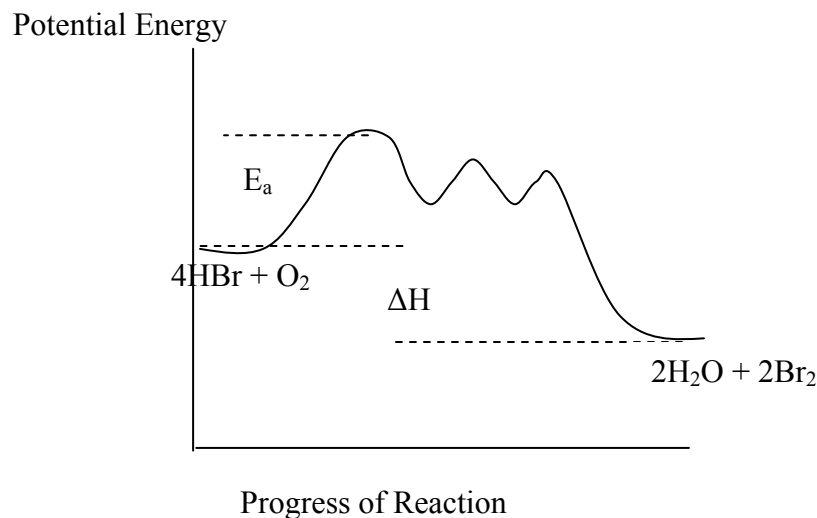
- the rate law equation has been proven experimentally as:

$$r = k [\text{HBr}][\text{O}_2]$$

- although the number of molecules of HBr involved in the reaction is four times that of O<sub>2</sub>, it has an equal influence on the rate of reaction as O<sub>2</sub>; this has been explained by theorizing that the reaction occurs in the following elementary steps:



- the potential energy diagram appears as:



- the slowest step (first step) is considered the **rate-determining step**, i.e. as shown in the potential energy diagram it has the largest activation energy of the three steps
- the second reaction cannot proceed any faster than the production of HOObR in the first step
- the chemicals HOObR and HOBR are not present when the reaction is complete and are called **reaction intermediates**
- unstable activated complexes occur at the peaks of the potential energy diagram, while slightly more stable reaction intermediates occur in the valleys
- experimental determination of the rate law equation is closely linked to the slowest step in the reaction mechanism

the rate law equation was:  $r = k [\text{HBr}][\text{O}_2]$

- both reactants are found in the slowest step – they are not found together in any other reaction step
- the exponents of the reactants in the rate law equation are also related to the coefficients of the reactants in the slowest step of the reaction mechanism, i.e. the exponents are both one (1) because of the coefficients are one (1) for each of the reactants in the slowest step

In the general case:

If the rate law equation is found to be:

$$r = [\text{molecule X}]^n[\text{molecule Y}]^m$$

then the rate-determining step can be identified as:

