Unit \#4, Chapter 6 Outline
Rates of Chemical Reactions

| Lesson | Topics Covered | Reference | Homework Questions and Assignments |
| :---: | :---: | :---: | :---: |
| 1 | Introduction to Reaction Rates <br> - definitions: reaction rate, average rate, instantaneous rate, initial rate <br> - how rates can be measured <br> - stoichiometry and reaction rates <br> Reaction Rate Graphs | Pages 266-273 <br> Handout: Lab: <br> Factors <br> Affecting <br> Reaction Rate | 1. Page 272 Q $1-3$ <br> 2. Complete graph and questions at the end of the note <br> 3. Read through Lab \#6, ready for tomorrow. Complete calculations 1 and 2 (columns 1-4 in chart). You will need to be organized to get everything done. |
| 2 | Lab \#6: Factors Affecting Reaction Rate <br> - temperature <br> - surface area <br> - concentration of reactants <br> - nature of reactants | Page 276 <br> Handout: Lab: <br> Factors <br> Affecting <br> Reaction Rate | 1. Begin lab report for Lab 6 <br> 2. Page 276 Q $1-5,7$ <br> Lab 6 is due: |
| 3 | Collision Theory of Chemical Reactions <br> - effective and ineffective collisions <br> Reaction Pathway (Potential energy) diagrams <br> - activation energy <br> - activated complex (transition state) <br> - exo- and endothermic reactions <br> **Size of $\mathbf{E}_{\mathrm{a}}$ determines reaction rate | Pages 289-294 | 1. Work on Lab 6. <br> 2. Complete homework questions at end of note <br> 3. Be able to use collision theory to explain how concentration, temperature, surface area and the nature of the reactants affect the rate of chemical reactions. |
| 4 | Reaction Mechanisms <br> - reaction intermediates <br> - rate determining step <br> - potential energy diagrams | Handout: <br> Reaction <br> Mechanisms | 1. Complete homework on Handout: Reaction Mechanisms Homework |
| 5 | Reaction Mechanisms and the Rate Law <br> - order of reactions <br> - interpreting "k" <br> Rate Law Calculations <br> (don't worry about units for "k" yet) | Pages 278-284 | 1. On page 284: Q 5, 6, 7a, 8 . <br> 2. On page 288: 2, 3, 4a, b, 5a <br> 3. Answer questions on handout "Homework on Reaction Rate Laws" |
| 6 | The Rate Law Constant " $k$ " and its Units <br> Interpreting the Rate Law and Evaluating Reaction Mechanisms | Pages 298-301 <br> (begin at <br> Proposing and <br> Evaluating <br> Mechanisms). | 1. Go back and complete the summary chart on the units for " k " in Lesson 5 <br> 2. Go back and calculate the units for " $k$ " in all rate law questions from last night's homework <br> Questions on Evaluating Reaction <br> Mechanisms: Page 301: Q 17 - 20 |
| 7 | Catalysis: <br> - definitions <br> - homogeneous and heterogeneous catalysts <br> - how catalysts work <br> - inhibitors (negative catalysts) <br> The Half-life of First Order Reactions | Pages 302-303 <br> Pages 285-287 | 1. Re-read Unit 4, Lesson 03: Factors that Affect the Rate of a Chemical Reaction <br> 2. Questions on Catalysis: <br> Page 309: Q $6-8$ <br> 3. Questions on Half-life: <br> Page 287: Q 9 - 12 <br> Page 288: Q 7 <br> Begin review for the Unit Test on internet |

Reaction rate is a measure of how quickly or slowly reactants are consumed (used up), or products are formed, in a chemical reaction.

- a reaction that occurs in a short period of time has a $\qquad$ reaction rate, eg. $\qquad$
- a reaction that occurs over a long period of time has a $\qquad$ reaction rate, eg. $\qquad$
- by convention, reaction rates are always $\qquad$ values because they measure how fast the reaction is proceeding or moving forward. A $\qquad$ sign for a reaction rate is $\qquad$
- the study of reaction rates is called $\qquad$
- if a reaction is fast, the value for the rate will be $\qquad$
- if a reaction is slow, the value for the rate will be $\qquad$
To determine reaction rate, we need to measure how the amount of a reactant or product changes over time

$$
\text { Reaction Rate }=
$$

$\qquad$

There are many ways to measure reaction rate, depending on the properties of the reactants or products:

1. If a reaction produces a change in colour, rate can be measured visually or using a $\qquad$

$$
\mathrm{CH}_{2}=\mathrm{CH}_{2}(\mathrm{~g})+\mathrm{Br}_{2}(\mathrm{l}) \quad \rightarrow \quad \mathrm{CH}_{2} \mathrm{Br}-\mathrm{CH}_{2} \mathrm{Br}
$$

2. If a reaction produces a change in mass, rate can be measured by carrying out the reaction on a $\qquad$

$$
\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s}) \xrightarrow{\Delta} 2 \mathrm{Fe}(\mathrm{~s})+3 / 2 \mathrm{O}_{2}(\mathrm{~g})
$$

- the units will be mass/time eg. $\qquad$ or $\qquad$

3. If a reactant or product is a gas, rate can be measured using changes in $\qquad$ or $\qquad$

$$
\mathrm{Mg}(\mathrm{~s})+\mathrm{HCl}(\mathrm{aq}) \quad \rightarrow \quad \mathrm{MgCl}_{2}(\mathrm{aq})+\mathrm{H}_{2}(\mathrm{~g})
$$

- for changes in volume of gas, units will be volume/time eg. $\qquad$ or $\qquad$
- for changes in pressure, units will be pressure/time eg. $\qquad$ or $\qquad$

4. If a reaction is endothermic or exothermic, rate can be measured using changes in $\qquad$
5. If a product or reactant is an ion, rate can be measured using changes in $\qquad$
6. If a product or reactant is an acid or base, rate can be measured using changes in $\qquad$
7. If a product or reactant is in solution, rate can be expressed as change in molar concentration:

- this is the most common method used to express rates in high school chemistry
- molar concentration (C) is defined as the number of $\qquad$ of solute per $\qquad$ of solution
- molar concentration is calculated using the equation:
where, $\qquad$ is the number of moles of solute, and
$\qquad$ is the volume of the solution in $\qquad$
- a $3.0 \mathrm{~mol} / \mathrm{L} \mathrm{HCl}$ solution can be expressed as: $\qquad$ or $\qquad$ or $\qquad$
- a $1.5 \mathrm{~mol} / \mathrm{L} \mathrm{OH}^{1-}$ solution can be expressed as: $\qquad$ or $\qquad$ or $\qquad$ $=1.5 \mathrm{M}$
- reaction rates are commonly expressed as the change in the concentration (in $\mathrm{mol} / \mathrm{L}$ ) of a reactant or product over time

If the molar concentration of a product is graphed over time, a typical graph has this shape:

At the beginning of the reaction:

- concentration of the product is $\qquad$
- product forms $\qquad$
- slope of line is $\qquad$
- reaction rate is $\qquad$
As the reaction proceeds:
- reactants are $\qquad$ (used up)
- the concentration of product increases
- slope of the line becomes $\qquad$
- reaction rate $\qquad$
Eventually, the maximum amount of product has formed, so the slope of the curve $\qquad$

If the molar concentration of a reactant for the same reaction is graphed over time, the graph has this shape:

At the beginning of the reaction:

- concentration of the reactants is $\qquad$
- reactant is consumed $\qquad$
- slope of line is $\qquad$
- reaction rate is $\qquad$
As the reaction procedes:
- reactants are $\qquad$
- the concentration of reactant $\qquad$
- slope of the line becomes $\qquad$
- reaction rate $\qquad$
Eventually, the concentration of the reactant is so low that the slope of the curve $\qquad$

Numerically, reaction rate will change depending on the period of time you study.
Change in Concentration of a Product Over Time


1. Initial rate: the rate at the very beginning of the reaction while the concentrations of the reactants are very close to their initial concentrations.
2. Instantaneous rate: the rate of the reaction at a single moment in time. It is calculated by finding the slope of the
$\qquad$ to the line at a certain point.
3. Average rate: the rate of the reaction over a specified period of time (eg. over the first 15 seconds).

Reaction rate depends on the period of time being studied. It also depends on which reactant or product is being measured.

For example, for the reaction: $\quad 2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \rightarrow 2 \mathrm{NO}_{2}(g)$
The molar coefficients in the balanced chemical reaction tell us that $\qquad$ moles of NO are used up for every
$\qquad$ mole of $\mathrm{O}_{2}$ that is used up. NO is used up $\qquad$ as fast as $\mathrm{O}_{2}$, so the reaction rate that is calculated using NO will be $\qquad$ the reaction rate calculated using $\mathrm{O}_{2}$.
eg. If the initial rate of disappearance of NO is $8.0 \mathrm{~mL} / \mathrm{s}$, then the initial rate of disappearance of $\mathrm{O}_{2}$ is
$\qquad$ —.

If the reaction rate for one of the reactants or products is known, the rate for other species in the equation can be determined using the molar coefficients in the balanced chemical reaction ( $\qquad$ ).
eg. If ammonia gas is produced at the rate of $1.60 \mathrm{~mL} / \mathrm{s}$ (a change in volume of gas produced with time), how fast is hydrogen gas being consumed?

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

The following rate data was collected for the reaction:

$$
\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})
$$

a) Use stoichiometry as shown in the example above, to complete the data table, starting from an initial pressure of $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})$ of $20.0 \mathrm{~atm} . \mathrm{NO}_{2}$ is produced at twice the rate that $\mathrm{N}_{2} \mathrm{O}_{4}$ is consumed, so the pressure of $\mathrm{N}_{2} \mathrm{O}_{4}$ is equal to $20.0 \mathrm{~atm}-1 / 2$ (pressure $\mathrm{NO}_{2}$ )
b) Following all graphing conventions, graph the pressures of both species.
c) Describe the reaction rate in the first 0.60 s of the reaction. Explain why it is like this.
d) Describe the reaction rate in the last 0.60 s of the reaction. Explain why it is like this.
e) From the graph, calculate the rate of the reaction for both species during the first 1.80 s (ie. between 0.0 and 1.80 s ). Is this an instantaneous, initial or average rate for the reaction?
f) From the graph, calculate the instantaneous rate of the reaction with regard to $\mathrm{NO}_{2}$ at 3.00 s . Show your work.

Pressures of Gases Measured for the Decomposition of $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})$

| Time <br> $(\mathbf{s})$ | Pressure $\mathbf{N}_{\mathbf{2}} \mathbf{O}_{\mathbf{4}}(\mathbf{a t m})$ | Pressure $\mathbf{N O}_{\mathbf{2}}$ <br> $(\mathbf{a t m})$ |
| :---: | :---: | :---: |
| 0.00 | 20.0 | 0.0 |
| 0.60 | $20.0-1 / 2(4.2)=$ | 4.2 |
| 1.20 | $20.0-1 / 2(7.2)=$ | 7.2 |
| 1.80 |  | 9.6 |
| 2.40 |  | 11.2 |
| 3.00 |  | 12.8 |
| 3.60 |  | 13.4 |
| 4.20 |  | 14.2 |
| 4.80 |  | 15.0 |
| 5.40 |  | 15.4 |
| 6.00 |  | 15.6 |

## Unit 4, Lesson 03: Collision Theory and the Rates of Chemical Reactions

The Kinetic Molecular Theory of Matter (KMT) states that matter is made up of $\qquad$
( $\qquad$ , $\qquad$ and $\qquad$ ) that are in constant $\qquad$ .

- temperature is a measure of the $\qquad$ kinetic energy ( $\qquad$ ) of the particles
- some particles are moving $\qquad$ than the average temperature, and some are moving $\qquad$
Collision theory states that in order for a chemical reaction to occur, the reactant atoms or molecules must
$\qquad$ with each other
- when molecules approach one another, the valence electrons from one molecule $\qquad$ the valence electrons in the other molecule and $\qquad$ the existing bonds
- if the reactant molecules collide with $\qquad$ and in the $\qquad$
$\qquad$ , the repulsion between valence electrons will break the $\qquad$ bonds, allowing new ( $\qquad$ ) bonds to form. This is an $\qquad$

- if the reactant molecules do not collide with $\qquad$ or collide in the
$\qquad$ , the existing bonds are not broken and $\qquad$
$\qquad$ . This is called an $\qquad$ .


The minimum amount of energy required for a successful collision is called $\qquad$ -.

This graph is called a

It shows the energy changes during the progress of a chemical reaction. .
$\qquad$


Reaction pathways show:

1. Activation Energy ( $\mathbf{E}_{\mathbf{a}}$ ): the minimum amount of energy that is required for a reaction to occur

- if the activation energy is low, the reaction will occur
- if the activation energy is high, it is $\qquad$ that the reaction will occur (the bonds in the reactants are too difficult to break for the reaction to proceed)
- in general, the lower the activation energy, the $\qquad$ the reaction rate

2. Activated complex: a theoretical high-energy particle that exists for a fraction of a second at the instant the particles collide

- if a collision is effective, the activated complex breaks down into the $\qquad$
- if a collision is ineffective, the activated complex breaks down into the $\qquad$

3. $\underline{\mathbf{H}}$ : the net change in $\qquad$ between the reactants and products if a reaction does occur

- if $\Delta \mathrm{H}$ is negative, the products are $\qquad$ energy than the reactants. The reaction is $\qquad$ and will occur if the activation energy can be reached
- if $\Delta \mathrm{H}$ is positive, the products of the reaction are $\qquad$ energy than the reactants. The reaction is $\qquad$ and energy must be put into the system in order for the reaction to occur
- the reaction tends to favour the $\qquad$ species (reactants or products)

A model may help you to visualize the energy changes during a reaction:
a) Activation energy $\left(\mathbf{E}_{a}\right)$ :

- the man must roll the rock to the top of the hill before the reaction will proceed
- the potential energy of the rock increases
- the bigger the hill, the greater the $\mathrm{E}_{\mathrm{a}}$
b) Activated complex:
- at the top of the hill, the rock is very high energy and can roll either way (it is unstable)
- if it gets to the very top, it will roll down the other side
c) $\Delta \mathbf{H}$ :

- after the "reaction", the rock has lower potential energy than before, so the reaction from $\mathrm{A} \rightarrow \mathrm{B}$ is exothermic
- if the rock rolled to position " $C$ ", it would have higher potential energy than before the reaction, so the reaction from $\mathrm{A} \rightarrow \mathrm{C}$ is endothermic

The model also shows that the reaction is $\qquad$ .

If the rock is in position $B$, it is entirely possible to push it back into position $A$, but it will take a great deal of energy to roll the rock back up the hill in the reverse direction.

- the activation energy for the reverse reaction is so high, it is very unlikely that the reaction can be made to occur without a huge input of energy
- the reverse reaction from $\mathrm{B} \rightarrow \mathrm{A}$ is also endothermic
- the fact that the $\mathrm{E}_{\mathrm{a}}$ for the reverse reaction is so large, and the reverse reaction is endothermic means that the reverse reaction, while possible, is unlikely


## Summary:

Many reactions are $\qquad$ and can occur in both directions. Which direction is favoured depends on two factors: the $\qquad$ and $\qquad$ -.

Activation energy $\left(\mathbf{E}_{\mathrm{a}}\right)$ determines the $\qquad$ of the forward and reverse reactions. The lower the
Ea, the $\qquad$ the rate.

Enthalpy change ( $\Delta \mathbf{H}$ ) determines whether the reaction will $\qquad$ once it gets going.
Exothermic reactions will proceed because they produce $\qquad$ products.
Endothermic reactions will only proceed if energy is continually $\qquad$ to the system.

There is between Ea and $\Delta \mathrm{H}$ !!

## Examples:



- the forward reaction is $\qquad$ so it is $\qquad$ to proceed
- the forward $E_{a}$ is $\qquad$ so the forward reaction will occur $\qquad$
- the reverse reaction is $\qquad$ so it is $\qquad$ to proceed
- the reverse $\mathrm{E}_{\mathrm{a}}$ is $\qquad$ so the reverse reaction will occur $\qquad$
- the rate of the forward reaction is $\qquad$ than the rate of the reverse reaction
- the forward reaction is $\qquad$ so it is $\qquad$ to proceed
- the forward $E_{a}$ is $\qquad$ so the forward reaction will occur $\qquad$
- the reverse reaction is $\qquad$ so it is $\qquad$ to proceed
- the reverse $\mathrm{E}_{\mathrm{a}}$ is $\qquad$ so the reverse reaction will occur $\qquad$
- the rate of the forward reaction is $\qquad$ than the rate of the reverse reaction


## Unit 4, Lesson 03: Factors that Affect the Rate of a Chemical Reaction

There are five factors that affect the rate of a chemical reaction. The effect of these factors can be explained using Collision Theory.

1. Temperature: a measure of the average kinetic energy (speed) of the particles in a substance

- increasing temperature causes the reaction rate to increase for TWO reasons:
a) the particles are moving faster (on average) so more particles have sufficient energy to achieve the activation energy and cause an effective collision
b) the particles are moving faster so they collide more often so there are more opportunities for reactions to occur
- on average, for every $10^{\circ} \mathrm{C}$ the temperature of a system increases, the reaction rate doubles

2. Concentration: the number of particles in a given volume of a gas or a solution ( $\mathrm{mol} / \mathrm{L}$ )

- as concentration increases, the particles are more "crowded" so they collide more frequently and the reaction rate will increase

3. Surface Area: the amount of exposed surface of a reactant that is available for collisions

- if the reactants are gases, the particles are free to move and collide, so there is a huge surface area that is exposed to react. As a rule, gas systems react very quickly.
- if one of the reactants is a solid or a liquid- the only particles that can react are the particles on the surface where the other reactants can collide with them
- if the solid or liquid reactant is spread out to increase the surface area, there will be more of the molecules exposed for collisions and reaction rate will increase
- for example, if we take a solid chunk of a chemical and grind it into a fine powder, there will be more surface area exposed and a faster reaction rate. Similarly, if we take a lump of metal and pound it out into a flat sheet, there will be more surface area and the reaction rate will increase.

4. Nature of the Reactants: refers to the size of the particles, their state and whether they are charged

- reactions in gas or aqueous system react more quickly than solids or liquids
- small, simple ions and molecules react more quickly than larger "clumsy" molecules
- charged particles such as ions in solution react very quickly because oppositely charged particles attract each other and the charges help to arrange the particles in the correct orientation
- precipitation and acid-base reactions are almost instantaneous because the reactants are small, charged particles that can move easily within the solution

5. The Presence of a Catalyst: a catalyst is a substance that increases or decreases the rate of a reaction without being consumed itself

- catalysts change the reaction rate by providing an alternative pathway for a reaction. A different activated complex is formed. Catalysts can be used to control the rate of a reaction:
- if $\mathrm{E}_{\mathrm{a}}$ is lowered, reaction rate will increase (a positive catalyst)
- if $\mathrm{E}_{\mathrm{a}}$ is raised, reaction rate will decrease (a negative catalyst or inhibitor)


Note: a catalyst lowers the activation energy for both the forward and reverse reactions so the rates of both increase. The overall enthalpy change $(\Delta \mathrm{H})$ for the reactions is not changed by the addition of a catalyst.

Reaction progress

## Unit 4, Lesson 03: Collision Theory and the Rates of Chemical Reactions

## Homework:

1. Read pages 289 to 294
2. On page 294, answer questions $13-16$
3. On page 296, answer questions $2,3,4,6,7$
4. Define: activation energy and activated complex (aka transition state).
5. Why, in general, does a reaction with a high activation energy have a low rate?
6. Why, in general, does a reaction with a low activation energy have a high rate?
7. A certain reaction has a very high activation energy and is slightly endothermic.
a) Sketch a possible potential energy diagram (reaction pathway) for the reaction.
b) On the diagram label the reactants, products, activated complex, heat of reaction $(\Delta \mathrm{H})$ and the activation energy $\left(\mathrm{E}_{\mathrm{a}}\right)$.
8. A certain reaction has a very low activation energy and is highly exothermic.
a) Sketch a possible potential energy diagram (reaction pathway) for the reaction.
b) On the diagram label the reactants, products, activated complex, heat of reaction $(\Delta \mathrm{H})$ and the activation energy $\left(\mathrm{E}_{\mathrm{a}}\right)$.
9. Many exothermic reactions (such as burning paper) require energy to get the reaction started, but they are able to sustain themselves one they start to burn. Explain why.
10. With regard to reaction rates, how might you:
a) slow food spoilage
b) slow the rusting of a car
c) increase the rate of combustion for a campfire?

## Unit 4, Lesson 04: Reaction Mechanisms

We have considered chemical reactions as happening in one collision or one step. While some reactions do occur this simply, imagine the reaction between heptane and oxygen:


One molecule of heptane and 11 molecules of oxygen are involved in this reaction- a total of 12 molecules. What are the chances that all 12 molecules will collide at the same time, in the correct orientation and with enough energy to make this reaction proceed? Not very good! But we know that all alkanes burn readily and rapidly in air, once a spark is added to provide sufficient $\qquad$ —.

Rather than occurring as one massive collision, most reactions proceed as a series of steps, called
$\qquad$
The series of elementary steps that take place as a reaction proceeds from reactants to products is called the
$\qquad$ _.

The number of particles ( $\qquad$ , $\qquad$ or $\qquad$ ) that collide in an elementary reaction is called the $\qquad$ of that step.

- if a single molecule breaks down, then the molecularity of that step is $\qquad$ . It is $\qquad$
- if two particles collide, molecularity of that step is $\qquad$ . It is $\qquad$
- if three particles collide, molecularity of that step is $\qquad$ . It is $\qquad$
(" $\qquad$ " from $\qquad$ ). Termolecular reactions are very rare.

The molecules that form during the elementary steps are called the $\qquad$ .
Reaction intermediates are $\qquad$ in one elementary step and $\qquad$ in a subsequent elementary step, so they do NOT appear in the overall chemical equation.

Every elementary step in the reaction mechanism has its own activation energy, the $\qquad$ amount of energy that must be present in order for the elementary step to proceed, so each elementary step will occur at a $\qquad$ . The elementary step that has the $\qquad$ activation energy will have the $\qquad$ rate, and it will determine the rate of the overall chemical reaction. The slowest elementary step is called the $\qquad$
$\qquad$ ( $\qquad$ ).

For the overall reaction:

- the Ea for the reaction depends on the Ea for the $\qquad$ . It is the difference between the enthalpy of the $\qquad$ and the $\qquad$ reached.
- the $\Delta \mathrm{H}$ for the reaction is the $\Delta \mathrm{H}$ between the $\qquad$ reactants and $\qquad$ products. It doesn't matter what happens in between because $\Delta \mathrm{H}$ is a $\qquad$ function.

Reaction mechanisms are determined $\qquad$ ( $\qquad$ ).
Once the mechanism is determined, the rate determining step and energy change for each step can be found. This allows chemists to find ways to control or speed up reactions.

Let's look at an example for a chemical reaction: $\mathrm{NO}_{2}+\mathrm{CO} \rightarrow \mathrm{NO}+\mathrm{CO}_{2}$
The reaction mechanism could occur as a single, bimolecular collision:
Step 1: $\quad \mathrm{NO}_{2}+\mathrm{CO} \rightarrow \mathrm{NO}+\mathrm{CO}_{2}$
The reaction mechanism could occur as a bimolecular collision followed by a unimolecular step:
Step 1: $\quad \mathrm{NO}_{2}+\mathrm{CO} \rightarrow \mathrm{CNO}_{3}$
Step 2: $\quad \mathrm{CNO}_{3} \rightarrow \mathrm{NO}+\mathrm{CO}_{2}$
The reaction mechanism could occur as two bimolecular collisions:
Step 1: $\quad 2 \mathrm{NO}_{2} \rightarrow \mathrm{NO}+\mathrm{NO}_{3}$
Step 2: $\quad \mathrm{NO}_{3}+\mathrm{CO} \rightarrow \mathrm{NO}_{2}+\mathrm{CO}_{2}$
The reaction mechanism could be a very complex series of elementary reactions:
Step 1: $\quad \mathrm{CO}+\mathrm{CO} \rightarrow \mathrm{C}_{2} \mathrm{O}_{2}$
Step 2: $\quad \mathrm{C}_{2} \mathrm{O}_{2}+\mathrm{NO}_{2} \rightarrow \mathrm{C}_{2} \mathrm{NO}_{4}$
Step 3: $\quad \mathrm{C}_{2} \mathrm{NO}_{4} \rightarrow \mathrm{NO}+\mathrm{C}_{2} \mathrm{O}_{3}$
Step 4: $\quad \mathrm{C}_{2} \mathrm{O}_{3} \rightarrow \mathrm{CO}+\mathrm{CO}_{2}$
Or, it could be any other series of elementary steps that give the final overall equation.
The actual mechanism was determined empirically (by experiment) to be:

Step 1: $\quad 2 \mathrm{NO}_{2} \rightarrow \mathrm{NO}+\mathrm{NO}_{3}$
Step 2: $\quad \mathrm{NO}_{3}+\mathrm{CO} \rightarrow \mathrm{NO}_{2}+\mathrm{CO}_{2}$
The potential energy diagram for this reaction mechanism is shown to the left, below.
i) How many elementary steps are in the reaction mechanism?

ii) Which step is the ratedetermining step?
iii) Is the overall reaction exothermic or endothermic?
iv) What is the $\Delta \mathrm{H}$ for the overall reaction?

v) What is the activation energy for the reverse reaction?
vi) What is the $\mathrm{E}_{\mathrm{a}}$ for the rate-determining step for the forward reaction?
vii) What is the $\mathrm{E}_{\mathrm{a}}$ for the overall forward reaction?

Example 2: For the reaction mechanism:

| Step 1: | $\mathrm{A}+\mathrm{B}_{2}$ | $\rightarrow$ | $\mathrm{AB}_{2}$ | $\mathrm{Ea}=5 \mathrm{~kJ}$ | $\Delta \mathrm{H}=-10 \mathrm{~kJ}$ |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Step 2: | $\mathrm{AB}_{2}+2 \mathrm{C}$ | $\rightarrow$ | $\mathrm{ABC}+\mathrm{BC}$ | $\mathrm{Ea}=25 \mathrm{~kJ}$ | $\Delta \mathrm{H}=+5 \mathrm{~kJ}$ |  |
| Step 3: | ABC | $+\quad \mathrm{B}_{2}$ | $\rightarrow$ | $\mathrm{AB}_{2}+\mathrm{BC}$ | $\mathrm{Ea}=40 \mathrm{~kJ}$ | $\Delta \mathrm{H}=-15 \mathrm{~kJ}$ |

## Question Types:

1. Determine the overall equation for this reaction. What is the overall $\Delta \mathrm{H}$ ?
2. Assuming that the enthalpy of the reactants is 5.0 kJ , draw the energy profile for the reaction.
3. On the graph, label two activated complexes (transition states) and two reaction intermediates.
4. What is the overall $\mathrm{E}_{\mathrm{a}}$ for the reaction?
5. What is the rate-determining step for the reaction?
6. Which would produce a greater increase in the overall rate of the reaction: increasing the concentration of C or increasing the concentration of $\mathrm{B}_{2}$ ? Explain.


Example 3: The reaction mechanism for a reaction has been determined to be:
step \#1: $\quad 2 \mathrm{NO}+\mathrm{H}_{2} \rightarrow \mathrm{~N}_{2}+\mathrm{H}_{2} \mathrm{O}_{2} \quad$ slow, $\Delta \mathrm{H}=+30 \mathrm{~kJ}$
step \#2: $\mathrm{H}_{2}+\mathrm{H}_{2} \mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O} \quad$ fast, $\Delta \mathrm{H}=-50 \mathrm{~kJ}$
a) Determine the equation for the overall reaction.
b) Identify any "reaction intermediates" in the reaction:
c) What is the rate-determining step for this reaction? $\qquad$
d) If the initial enthalpy of the reactants is 10 kJ , sketch an approximate potential energy diagram (energy profile) for the reaction.


1. Read pages 297-299 (do not read "The Rate Determining Step and the Rate Law", yet)
2. Define: reaction mechanism, elementary reaction, reaction intermediates, molecularity, unimolecular, bimolecular, termolecular
3. The following equations represent the elementary steps in a reaction mechanism. The overall reaction is exothermic.
Step 1: $\mathrm{P}+\mathrm{T} \rightarrow \mathrm{PT}$
Step 2: $\mathrm{PT}+\mathrm{Q}_{2} \rightarrow \mathrm{PQ}+\mathrm{TQ}$
Step 3: $\quad \mathrm{TQ}+\mathrm{P} \quad \rightarrow \mathrm{PQ}+\mathrm{T}$
fast, exothermic
slow, endothermic
fast, exothermic
a) Write the equation for the overall reaction.
b) Identify any "reaction intermediates" in the reaction.
c) What is the rate-determining step for this reaction?
d) Which would produce a greater increase in the overall rate of the reaction: increasing the concentration of P or increasing the concentration of $\mathrm{Q}_{2}$ ? Explain.
e) Sketch an approximate potential energy diagram (energy profile) for the reaction.
4. Consider these three reactions as the elementary steps in the mechanism for a chemical reaction.

$$
\begin{equation*}
\mathrm{H}_{2(\mathrm{~g})}+\mathrm{NO}_{(\mathrm{g})} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}+\mathrm{N}_{(\mathrm{g})} \tag{i}
\end{equation*}
$$

$$
\mathrm{E}_{\mathrm{a}}=1690 \mathrm{~kJ}
$$

$$
\Delta \mathrm{H}=+131 \mathrm{~kJ}
$$

(ii)

$$
\mathrm{N}_{(\mathrm{g})}+\mathrm{NO}_{(\mathrm{g})} \rightarrow \mathrm{N}_{2(\mathrm{~g})}+\mathrm{O}_{(\mathrm{g})}
$$

$$
\mathrm{E}_{\mathrm{a}}=625 \mathrm{~kJ}
$$

$$
\Delta \mathrm{H}=-312 \mathrm{~kJ}
$$

$$
\begin{equation*}
\Delta \mathrm{H}=-491 \mathrm{~kJ} \tag{iii}
\end{equation*}
$$

a) What is the equation for the overall reaction?
b) Calculate $\Delta \mathrm{H}$ for the overall reaction.
c) Draw, with an appropriate scale, the potential energy diagram (energy profile) for the reaction. Assume that the potential energy of the reactants is 800 kJ (ie. start with the reactants at 800 kJ ).
d) Which is the rate-determining step?
e) What is $\mathrm{E}_{\mathrm{a}}$ for the overall reaction?
f) Suggest why the activation energy for the first step is larger than for the other two steps.
5. The following are steps in a reaction mechanism:

$$
\begin{align*}
& \mathrm{X}_{2} \rightarrow \mathrm{X}+\mathrm{X}  \tag{i}\\
& \mathrm{X}+\mathrm{YH}_{4} \rightarrow \mathrm{YH}_{3}+\mathrm{HX}
\end{align*}
$$

$$
\mathrm{E}_{\mathrm{a}}=20 \mathrm{~kJ}
$$

$$
\Delta \mathrm{H}=+15 \mathrm{~kJ}
$$

(ii)
$\mathrm{E}_{\mathrm{a}}=25 \mathrm{~kJ}$
$\Delta \mathrm{H}=-10 \mathrm{~kJ}$
(iii)
$\mathrm{YH}_{3}+\mathrm{X}_{2} \rightarrow \mathrm{YH}_{3} \mathrm{X}+\mathrm{X}$
$\mathrm{E}_{\mathrm{a}}=15 \mathrm{~kJ}$
$\Delta \mathrm{H}=-35 \mathrm{~kJ}$
(iv)
$\mathrm{X}+\mathrm{X} \rightarrow \mathrm{X}_{2}$
$\mathrm{E}_{\mathrm{a}}=10 \mathrm{~kJ}$
$\Delta \mathrm{H}=-15 \mathrm{~kJ}$
a) What is the equation for the overall reaction?
b) Calculate $\Delta \mathrm{H}$ for the overall reaction.
c) Draw, with an appropriate scale, the potential energy diagram (energy profile) for the reaction. Assume that the potential energy of the reactants is 50 kJ .
d) Which is the rate-determining step?
e) What is $E_{a}$ for the overall reaction?

## Unit 4, Lesson 05: The Rate Law

Chemical reactions occur as a series of elementary steps called the $\qquad$ .

The overall rate of a reaction is determined by the $\qquad$ step in the reaction mechanism (the
$\qquad$ RDS).

- if we increase the concentration [ ] of the reactants in the RDS, the reaction rate will $\qquad$
- if we increase the concentration [ ] of reactants in the other steps, the reaction rate will $\qquad$
By experimentally changing the concentration of $\qquad$ at a time while all other variables are $\qquad$ (especially $\qquad$ ):
- the effect of the concentration of each reactant on the reaction rate can be observed
- the reactants and kinetics of the RDS can be determined
eg. Find the relationship between the concentration [ ] of the reactants and the reaction rate at SATP for:

$$
2 \mathrm{NO}(\mathrm{~g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

| Trial \# | $[\mathbf{N O}]$ | $\left[\mathbf{H}_{\mathbf{2}}\right]$ | Initial Rate (mol/L $\cdot \mathbf{s})$ |
| :---: | :---: | :---: | :---: |
| 1 | 0.0040 | 0.0010 | 0.80 |
| 2 | 0.0040 | 0.0020 | 1.60 |
| 3 | 0.0080 | 0.0020 | 6.40 |

Look for trials in which the concentration of one reactant is held constant while the concentration of the other reactant(s) changes:

Trials 1 and 2: $\qquad$ is held constant

- as $\left[\mathrm{H}_{2}\right]$ $\qquad$ , the reaction rate $\qquad$

Trials 2 and 3: $\qquad$ is held constant

- as [NO] $\qquad$ , the reaction rate $\qquad$


## Overall:

To find the value of " $k$ " (the $\qquad$ constant), substitute in values from any single trial rate $=\mathrm{k}\left[\mathrm{H}_{2}\right]^{1}[\mathrm{NO}]^{2}$ or $\mathrm{k}=$

So, the overall Rate Law for the reaction: $2 \mathrm{NO}(\mathrm{g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ is:

- the reaction is $\qquad$ order with respect to $\left[\mathrm{H}_{2}\right]$
- the reaction is $\qquad$ order with respect to [NO]
- the reaction is $\qquad$ order overall
- the value of the rate constant " $k$ " is $\qquad$ , so the reaction rate is $\qquad$

In general, for any reaction: $\mathrm{A}+\mathrm{B}+\mathrm{C} \rightarrow$

- the Rate Law is:
- $\qquad$ are exponents that must be determined $\qquad$ and can have
the values $\qquad$ . The sum of $\qquad$ gives the overall reaction order
- " $k$ " is the $\qquad$ . The value of $k$ changes with $\qquad$

The units for " k " depend on the overall reaction order:

| Reaction Order | Example Rate Law | Units for " $k$ "' |
| :--- | :--- | :--- |
| First |  |  |
| Second |  |  |
| Third |  |  |
|  |  |  |
| In General, order <br> "m" |  |  |

eg. Determine the rate law for the hypothetical reaction: $\mathrm{A}+2 \mathrm{~B}+\rightarrow \mathrm{AB}_{2}$ Calculate the reaction rate when $[\mathrm{A}]=0.052 \mathrm{~mol} / \mathrm{L}$ and $[\mathrm{B}]=0.045 \mathrm{~mol} / \mathrm{L}$

| Trial \# | $[\mathbf{A}]$ | $[B]$ | Initial Rate (mol/L•s) |
| :---: | :---: | :---: | :---: |
| 1 | 0.10 | 0.10 | $1.2 \times 10^{-2}$ |
| 2 | 0.20 | 0.10 | $9.6 \times 10^{-2}$ |
| 3 | 0.10 | 0.20 | $1.2 \times 10^{-2}$ |

## Unit 4, Lesson 05: Homework on Reaction Rate Laws

1. Read pages $278-283$. Do problems $5-8$ on page 284.
2. Do problems $2-5$ on page 288.
3. The following table shows the variation in rate with the concentrations of the reactants for the process:

$$
2 \mathrm{~A}+\mathrm{B} \rightarrow \mathrm{C}+\mathrm{D}
$$

| Initial Concentration |  | Initial Rate <br> $(\mathrm{mol} / \mathrm{L} \cdot \mathrm{s})$ |
| :---: | :---: | :---: |
| $[\mathrm{A}]$ | $[\mathrm{B}]$ |  |
| 1.0 | 1.0 | 1.6 |
| 2.0 | 1.0 | 5.4 |
| 3.0 | 1.0 | 3.2 |
| 2.0 | 2.0 | 0.60 |
| 1.0 | 3.0 |  |

a) Find the relationship between rate and the concentration of A .
b) What is the relationship between rate and [B] ?
c) Calculate " $k$ " and write the rate law expression for this process.
d) What change would be observed in the rate if the concentrations of both A and B were doubled?
e) Calculate the relative reaction rate when $[\mathrm{A}]$ is 4 and $[\mathrm{B}]$ is 5 .
4. The following rate information is for the reaction: $\mathrm{NO}_{2}+\mathrm{CO} \rightarrow \mathrm{NO}+\mathrm{CO}_{2}$

| Initial Concentration |  | Initial Rate <br> $(\mathrm{mol} / \mathrm{L} \cdot \mathrm{s})$ |
| :---: | :---: | :---: |
| $\mathrm{NO}_{2}$ | CO |  |
| 0.010 | 0.010 | 8.0 |
| 0.010 | 0.020 | 27.0 |
| 0.010 | 0.030 | 2.0 |
| 0.020 | 0.010 | 48.0 |
| 0.060 | 0.020 |  |

a) Write the rate law expression for this system.
b) What change would there be in the rate if:
i) $\left[\mathrm{NO}_{2}\right]$ is doubled
ii) $[\mathrm{CO}]$ is tripled
iii) both $\left[\mathrm{NO}_{2}\right]$ and $[\mathrm{CO}]$ are doubled
iv) both $\left[\mathrm{NO}_{2}\right]$ and $[\mathrm{CO}]$ are halved
v) $\quad\left[\mathrm{NO}_{2}\right]$ is doubled and $[\mathrm{CO}]$ is halved
c) What is the relative reaction rate when $\left[\mathrm{NO}_{2}\right]$ is 0.040 and $[\mathrm{CO}]$ is 0.060 ?

## Unit 4, Lesson 06: Evaluating Reaction Mechanisms

The Rate Law for a reaction is determined $\qquad$ by changing the concentration of
$\qquad$ at a time, while all other variables are held $\qquad$ .

If changing the concentration of a reactant causes a change the reaction rate, then that reactant is involved in the $\qquad$ (__).

If changing the concentration of a reactant does not cause a change in the reaction rate, then that reactant is
$\qquad$ in the rate-determining step (RDS).

The Rate Law for a reaction is very useful in proposing and evaluating possible reaction mechanisms.
A proposed reaction mechanism is $\qquad$ (possible) if:

1. the $\qquad$ of the steps of the reaction mechanism adds up to give the overall reaction equation \&
2. the $\qquad$ of the reactants in the $\qquad$ agree with the
$\qquad$ for these reactants in the Rate Law.

It is the $\qquad$ and $\qquad$ of the RDS that determines the rate and molecularity of the overall reaction.
eg. For the reaction: $2 \mathrm{NO}(\mathrm{g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{v})$
The following reaction mechanism has been proposed:

$$
\begin{equation*}
\mathrm{H}_{2(\mathrm{~g})}+\mathrm{NO}_{(\mathrm{g})} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}+\mathrm{N}_{(\mathrm{g})} \quad \text { (slow) } \tag{i}
\end{equation*}
$$

$$
\begin{equation*}
\mathrm{N}_{(\mathrm{g})}+\mathrm{NO}_{(\mathrm{g})} \rightarrow \mathrm{N}_{2(\mathrm{~g})}+\mathrm{O}_{(\mathrm{g})} \tag{ii}
\end{equation*}
$$

(iii) $\quad \mathrm{O}_{(\mathrm{g})}+\mathrm{H}_{2(\mathrm{~g})} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}$

The Rate Law for this reaction was determined experimentally to be: rate $=\mathrm{k}\left[\mathrm{H}_{2}\right]^{1}[\mathrm{NO}]^{1}$. Is the proposed reaction mechanism plausible?
eg. For the reaction: $\quad \mathrm{N}_{2} \mathrm{O}_{5}(\mathrm{~g})+\mathrm{NO}(\mathrm{g}) \rightarrow 3 \mathrm{NO}_{2}(\mathrm{~g})$
The following reaction mechanism has been proposed:
(i) $\quad \mathrm{N}_{2} \mathrm{O}_{5}(\mathrm{~g}) \rightarrow \mathrm{NO}_{2}(\mathrm{~g})+\mathrm{NO}_{3}(\mathrm{~g})$ (fast)
(ii) $\quad \mathrm{NO}(\mathrm{g})+\mathrm{NO}_{3}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})$

The Rate Law for this reaction was determined experimentally to be: rate $=\mathrm{k}\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$. Is the proposed reaction mechanism plausible?

Homework: Read pages 298 to 300 (begin at "Proposing and Evaluating Mechanisms). Answer questions 17 to 20 on page 301.

