AP Chemistry | Name ____________________________
Ms. Ye | Date ____________________Block ______

Kinetics = the study of the rate at which a chemical process occurs.

- also sheds light on the reaction mechanism (exactly *how* the reaction occurs).
- Thermodynamics (ΔG, ΔH, ΔS) determines whether a reaction will occur or not; kinetics will determine how fast reaction will occur

Collision Theory

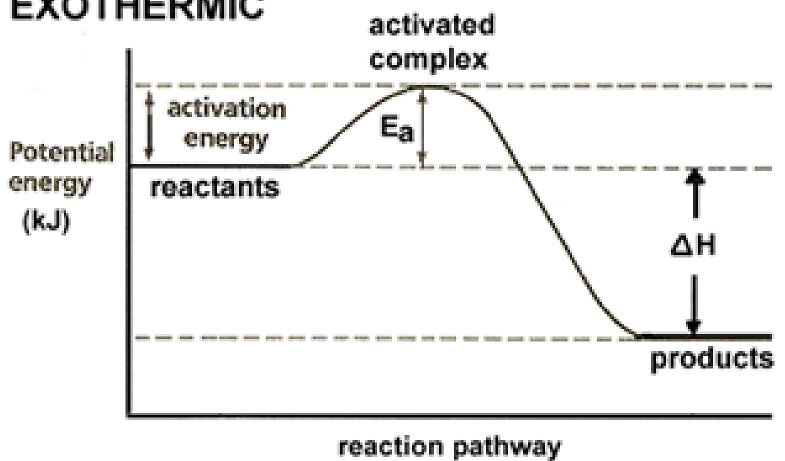
- Used to explain reaction rates.
- States that molecules must collide in order to react
- The ____________________ there are in a unit of time, ________________
- Collisions that result in a reaction are said to be "effective".
- For an effective collision:
  - The molecules must collide with ________________________________
  - The molecules must collide with ________________________________

Energy Diagram

- The ______________________

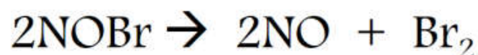
  ____

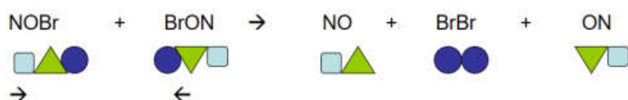
  is called the **activation energy.**
- On a potential energy diagram, this is the difference in energy between the reactants and the high point on the curve (Ea)
- The arrangement of atoms found at the top of the energy hill is called the activated complex.



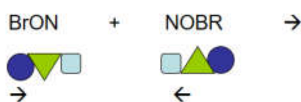
Orientation

$$2NOBr \rightarrow 2NO + Br_2$$





Reactants collide in proper orientation



No reaction;

Factors that Affect Reaction Rate

1. Temperature: As temperature increases, reaction rate increases.

- Explain why an alka-seltzer tablet will dissolve more quickly in water @ 80^oC than in water @ 20^oC.

2. Concentration: As concentration increases, reaction rate increases.

- Explain why a sample of magnesium metal will react more quickly in 10 *M* HCl than it will react in 1 *M* HCl.

3. Pressure: For a gaseous reaction, as pressure increases, reaction rate increases.

- Ex:

4. Surface Area: If the surface area of a solid is increased (the solid is ground up), the reaction rate will increase.

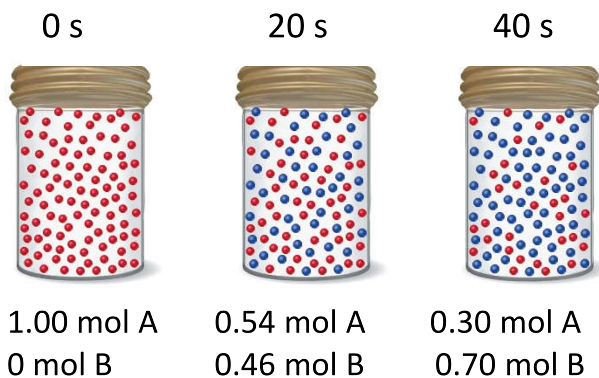
- Explain why 10 g of powdered zinc will react with hydrochloric acid more quickly than a solid zinc strip that weighs 10 g.

5. Catalyst: speeds up a reaction, but is not used up during the reaction.

- A catalyst speeds up a reaction by ____________________________________
- If the activation energy is lowered, ___________________________________ ________________________________(allow for a chemical reaction to occur).
- One way a catalyst can work is by helping to hold the molecules in the correct orientation to react

Reaction Rates

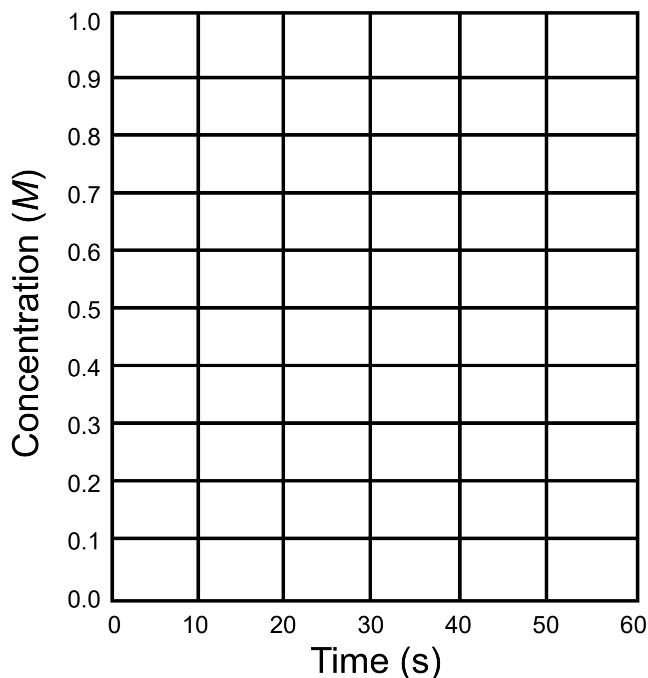
- Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time.



(a) The table below is based on the hypothetical chemical reaction **A → B**. Fill in the missing values for the amount of B produced.

Time (s)	0	10	20	30	40	50	60
Moles of A in the 1.0 L flask	1.00	0.73	0.54	0.40	0.30	0.21	0.16
Moles of B in the 1.0 L flask	0.00						

(b) Create a graph of the data from the table above. Use a **smooth line** to connect the data points for each substance. Use a solid line for A and a dashed line for B.



Concentration of A ▬▬▬

Concentration of B ▪▪▪▪▪▪

- **Average Reaction Rate** =

- Note: reaction rates are always expressed as a positive value!

(c) Based on the data table , calculate the average rate of disappearance of A for each of the following time intervals. Units of rate should be *M*/s.

0 s to 10 s ____________________

10 s to 20 s ____________________

20 s to 30 s ____________________

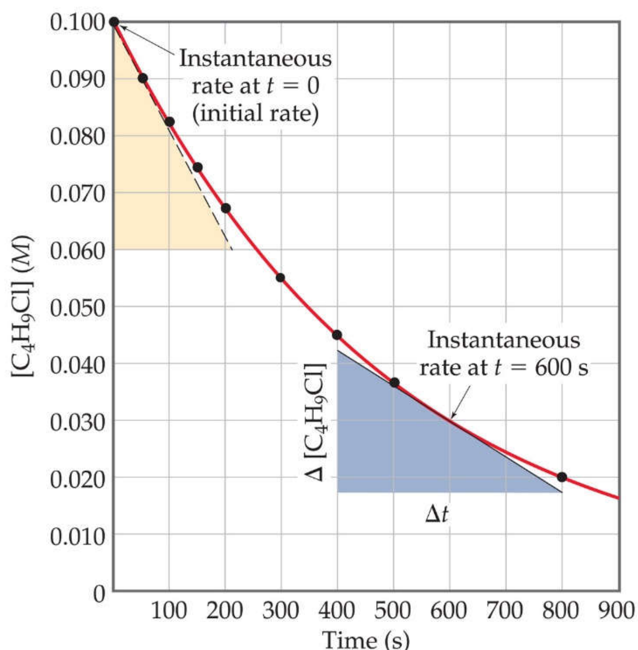
30 s to 40 s ____________________

40 s to 50 s ____________________

50 s to 60 s ____________________

(d) Examine the values for average rate that you calculated above. How is the reaction rate changing as the reaction proceeds over time (is it increasing, decreasing, or staying constant)? Why is it typical for this to occur?

Instantaneous Rate



• A plot of [C_4H_9Cl] vs. time for the reaction **C_4H_9Cl(*aq*) + H_2O(*l*) → C_4H_9OH(*aq*) + HCl(*aq*)** yields a curve like this.

• **instantaneous rate** of reaction= the **<u>slope of a line tangent to the curve at any point is the instantaneous rate at that time.</u>**

• The **instantaneous rate at t = 0** is called the ___________________________ of the reaction. All reactions slow down over time. Therefore, the best indicator of the rate of a reaction is the instantaneous rate near the *beginning* of the reaction.

<u>Reaction Rates and Stoichiometry</u>

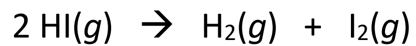
- In reactions we've looked at, the molar ratios are 1:1, therefore the rate of disappearance of the reactant is equal to the rate of formation of the product.
- Since the ratio is not always 1:1, here is a general formula that compares the rates of reaction based on stoichiometric coefficients

For the reaction: $aA + bB \longrightarrow cC + dD$

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

(a) Suppose that, in a certain reaction, $\frac{\Delta[A]}{\Delta t} = 2 \times \frac{\Delta[B]}{\Delta t}$

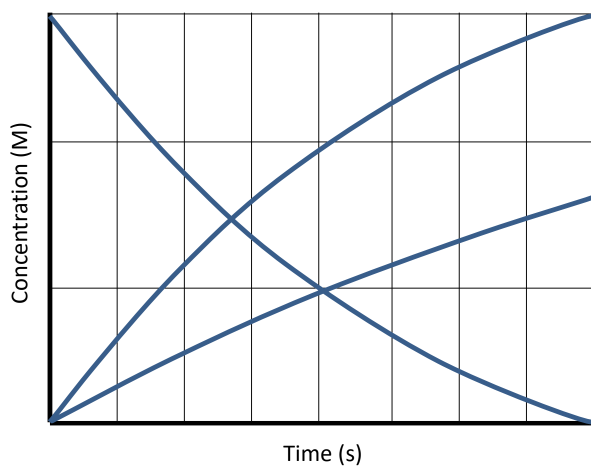
Which of the following reactions is consistent with this rate information? Explain.



$$2\ HI(g) \rightarrow H_2(g) + I_2(g)$$

(b) At a certain moment in time, the rate of formation of H_2 is equal to 1.8×10^{-6} *M*/s. Calculate the rate of disappearance of HI at this moment in time.

(c) The graph below displays the change in concentration for each species in the following reaction: 2 A → 2 B + C.
Label each curve on the graph below as A, B, or C.



Concentration and Rate Laws

One way of studying the effect of concentration on reaction rate is to determine the way in which the rate at the beginning of the reaction (the initial rate) depends on the starting concentrations. To illustrate this approach, consider the following reaction: **$NH_4^+ + NO_2^- \rightarrow N_2(g) + 2H_2O$**. The table below shows the initial reaction rate for various starting concentrations of the reactants.

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

(a) Compare experiments 1 & 2. What happens to the reaction rate when [NH_4^+] is doubled and [NO_2^-] is held constant? (is it doubled, cut in half, etc…)

(b) Compare experiments 1 & 3. What happens to the reaction rate when [NH_4^+] is quadrupled and [NO_2^-] is held constant?

(c) Based on the results from experiments 1, 2 & 3, what can you conclude about how the initial NH_4^+ concentration and reaction rate are related (is it a direct relationship? Inverse? Inverse squared? Etc..)?

(d) Compare experiments 4-6, where the concentration of NO_2^- is varied and the concentration of NH_4^+ is held constant instead. what can you conclude about how the initial NO_2^- concentration and reaction rate are related?

(e) **Rate law** = an equation which shows how the rate depends on the concentration of reactants. For a general reaction,

$aA + bB \longrightarrow cC + dD$ the rate law generally has the form

$$\text{Rate} = k[A]^m[B]^n$$

- k = rate constant; temperature dependent
- m and n = typically small whole numbers; tell you about the reaction order

(f) Write the rate law for the reaction you analyzed in parts a-d:

(g) Use your rate law and the data to calculate the value of the rate constant *k* for the reaction **$NH_4^+ + NO_2^- \rightarrow N_2(g) + 2H_2O$**. Include units in your answer.

(h) Once we have both the rate law and the value of *k* for a reaction, we can calculate the rate of the reaction for any set of concentrations. Calculate the rate law at 25°C when the initial concentrations of NH_4^+ and NO_2^- are both 0.100 M.

Reaction Orders

- The exponents *m* and *n* are called reaction orders.
- If the exponent is 1, we say that the reaction is 1st order with respect to that reactant. If the exponent is 2, we say that the reaction is 2nd order with respect to that reactant.
- The overall reaction order is the sum of the orders with respect to each reactant. In most of the rate laws that you will encounter in chemistry, the order with respect to a reactant will either be 0, 1, or 2.
- For the reaction represented by the rate law: **Rate = $k[NH_4^+][NO_2^-]$**, the reaction is ____________ order in NH_4^+, ______________ order in NO_2^-, and the reaction is ______________________ overall

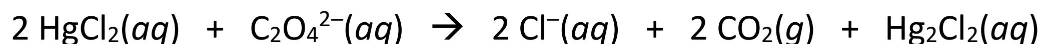
- The exponents for each substance in a rate law is NOT necessarily the same as the coefficient for that substance in the balanced chemical equation.
- The exponents in the rate law should always be determined from experimental data

(a) Suppose that the rate law for a reaction is as follows: rate = k
If you double the concentration of A, what effect would this have on the rate?

(b) Suppose that the rate law for a reaction is as follows: rate = k [A]
If you double the concentration of A, what effect would this have on the rate?

(c) Suppose that the rate law for a reaction is as follows: rate = k $[A]^2$
If you double the concentration of A, what effect would this have on the rate?

(d) The following problem requires you to determine the rate law from experimental data.



$$2\ HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2\ Cl^-(aq) + 2\ CO_2(g) + Hg_2Cl_2(aq)$$

The equation for the reaction between mercury(II) chloride and the oxalate ion in aqueous solution is shown above. The initial rate of formation of chloride ion was calculated for various initial concentrations of the reactants as shown in the following table.

Experiment	Initial $[HgCl_2]$ (M)	Initial $[C_2O_4^{2-}]$ (M)	Initial Rate of Formation of Cl^- (M/min)
1	0.0836	0.202	5.20×10^{-5}
2	0.0836	0.404	2.08×10^{-4}
3	0.0418	0.404	1.04×10^{-4}
4	0.0316	0.514	?

(i) What is the order of the reaction with respect to $HgCl_2$? Justify your answer.

(ii) What is the order of the reaction with respect to $C_2O_4^{2-}$? Justify your answer.

(iii) Write the rate law for this reaction. ______________________________

(iv) What is the overall order of this reaction? ____________________

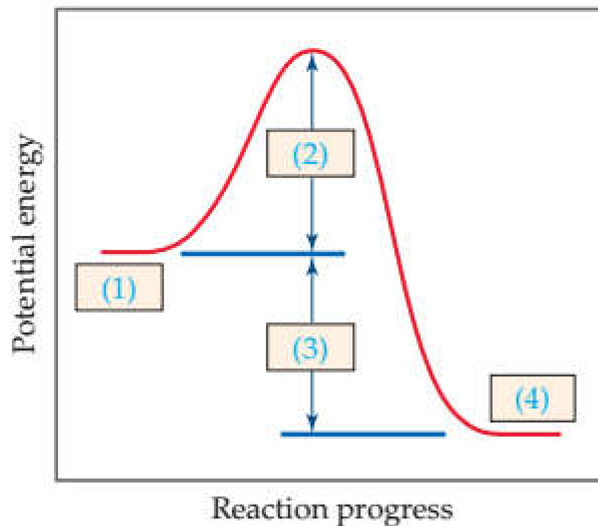
(v) Calculate the value of the rate constant *k*. Specify the units in your answer.

(vi) What is the value for the initial rate of disappearance of $C_2O_4^{2-}$ for Exp 1?

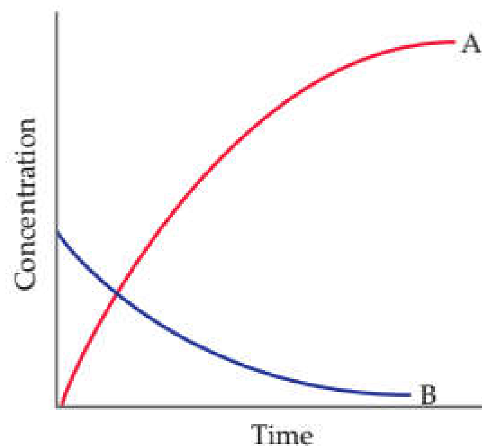
(vii) Calculate the initial rate of formation of Cl^- for Experiment 4.

Kinetics Problems

1. The following diagram shows the reaction profile of a reaction. Label the components indicated by the boxes



2. You study the rate of a reaction, measuring both the concentration of the reactant and the concentration of the product as a function of time, and obtain the following results:
   Which chemical equation is consistent with these data:
   (a) A → B (b) B → A
   (c) A → 2 B (d) B → 2 A?
   Explain your choice.



3. Consider the reaction: $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

The following data were obtained from three experiments using the method of initial rates:

	Initial [NO] mol L^{-1}	Initial $[O_2]$ mol L^{-1}	Initial rate NO mol $L^{-1}s^{-1}$
Experiment 1	0.010	0.010	2.5×10^{-5}
Experiment 2	0.020	0.010	1.0×10^{-4}
Experiment 3	0.010	0.020	5.0×10^{-5}

a. Determine the order of the reaction for each reactant.

b. Write the rate law equation for the reaction.

c. Calculate the rate constant.

d. Calculate the rate (in mol $L^{-1}s^{-1}$) at the instant when [NO] = 0.015 mol L^{-1} and $[O_2]$ = 0.0050 mol L^{-1}

e. At the instant when NO is reacting at the rate 1.0 x 10^{-4} mol $L^{-1}s^{-1}$, what is the rate at which O_2 is reacting and NO_2 is forming?

4. The reaction of ^{t}butyl-bromide $(CH_3)_3CBr$ with water is represented by the equation: $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$

The following data were obtained from three experiments using the method of initial rates:

	Initial $[(CH_3)_3CBr]$ mol L^{-1}	Initial $[H_2O]$ mol L^{-1}	Initial rate mol $L^{-1}min^{-1}$
Experiment 1	5.0 x 10^{-2}	2.0 x 10^{-2}	2.0 x 10^{-6}
Experiment 2	5.0 x 10^{-2}	4.0 x 10^{-2}	2.0 x 10^{-6}
Experiment 3	1.0 x 10^{-1}	4.0 x 10^{-2}	4.0 x 10^{-6}

a. What is the order with respect to $(CH_3)_3CBr$?

b. What is the order with respect to H_2O?

c. What is the overall order of the reaction?

d. Write the rate equation.

e. Calculate the rate constant, k, for the reaction.