Dougherty Valley • AP Chemistry

AP Test Review

Name______________________________

Period ________ Date ____________

BIG IDEA 4: KINETICS

1 – Review the Content

Honors Chemistry:	Unit 7
AP Chemistry:	Unit 2
Textbook:	Chapter 15
D&S Review:	Ch 7
5 Steps to a 5:	Ch 14, Ch 19: #10-11
Princeton Review:	Ch 6
Crash Course:	Ch 14-17

2 – Review the Essential Knowledge and Learning Objectives

Read through and annotate the Essential Knowledge and Learning Objectives for this Big Idea. Then make a list of the ideas and topics here.

3 – Multiple Choice Review

List items that you missed. Make notes for why you missed them and what you learn from it.

Packet	Q#	Reason for Mistake	Takeaways

4 – Free Response Practice

Reflect on your responses for FR questions. Make notes about how to craft stronger responses.

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BIG IDEA 4: KINETICS

Essential Knowledge

4. Rates of chemical reactions are determined by details of the molecular collisions.

Chemical changes occur over a wide range of time scales. Practically, the manner in which the rate of change is observed is to measure changes in concentration of reactant or product species as a function of time. There are a number of possible factors that influence the observed speed of reaction at the macroscopic level, including the concentration of reactants, the temperature, and other environmental factors. Measured rates for reactions observed at the macroscopic level can generally be characterized mathematically in an expression referred to as the rate law. In addition to these macroscopic-level characterizations, the progress of reactions at the particulate level can be connected to the rate law. Factors that influence the rate of reaction, including speeding of the reaction by the use of a catalyst, can be delineated as well.

4.A. Reaction rates that depend on temperature and other environmental factors are determined by measuring changes in concentrations of reactants or products over time.

The rate of a reaction is the rate at which reactants are converted to products, and is given in terms of the change in concentrations with time. Rates of reactions span a wide range, and generally increase with reactant concentrations and with temperature. The rate may be measured by monitoring concentrations as a function of time, and the results of many experiments may be summarized with a mathematical expression known as the rate law. The rate law gives the dependence of the rate on reactant concentrations, and contains a proportionality constant called the rate constant.

4.A.1. The rate of a reaction is influenced by the concentration or pressure of reactants, the phase of the reactants and products, and environmental factors such as temperature and solvent.

a. The rate of a reaction is measured by the amount of reactants converted to products per unit of time.

b. A variety of means exist to experimentally measure the loss of reactants or increase of products as a function of time. One important method involves the spectroscopic determination of concentration through Beer's Law.

c. The rate of a reaction is influenced by reactant concentrations (except in zero-order processes), temperature, surface area, and other environmental factors.

4.A.2. The rate law shows how the rate depends on reactant concentrations.

a. The rate law expresses the rate of a reaction as proportional to the concentration of each reactant raised to a power. The power of each reactant in the rate law is the order of the reaction with respect to that reactant. The sum of the powers of the reactant concentrations in the rate law is the overall order of the reaction. When the rate is independent of the concentration of a reactant, the reaction is zeroth order in that reactant, since raising the reactant concentration to the power zero is equivalent to the reactant concentration being absent from the rate law.

b. In cases in which the concentration of any other reactants remain essentially constant during the course of the reaction, the order of a reaction with respect to a reactant concentration can be inferred from plots of the concentration of reactant versus time. An appropriate laboratory experience would be for students to use spectrophotometry to determine how concentration varies with time.

c. The method of initial rates is useful for developing conceptual understanding of what a rate law represents, but simple algorithmic application should not be considered mastery of the concept. Investigation of data for initial rates enables prediction of how concentration will vary as the reaction progresses.

4.A.3. The magnitude and temperature dependence of the rate of reaction is contained quantitatively in the rate constant.

- a. The proportionality constant in the rate law is called the rate constant.
- b. The rate constant is an important measurable quantity that characterizes a chemical reaction.
- c. Rate constants vary over many orders of magnitude because reaction rates vary widely.
- d. The temperature dependence of reaction rates is contained in the temperature dependence of the rate constant.
- e. For first-order reactions, half-life is often used as a representation for the rate constant because they are inversely proportional, and the half-life is independent of concentration. For example, radioactive decay processes provide real-world context.

4.B. Elementary reactions are mediated by collisions between molecules. Only collisions having sufficient energy and proper relative orientation of reactants lead to products.

Reactions proceed through elementary steps involving one or more reactants. In a uni-molecular reaction, collisions with other molecules activate the reactant such that it is converted into product. In bimolecular and higher-order reactions, collisions between reactants lead to formation of products, provided both the energy of the collision and the relative orientation of reactants are favorable for reaction. A successful collision can be viewed as proceeding along some single reaction coordinate. The energy profile along this reaction coordinate provides a useful construct for reasoning about the connection between the energetics of a reaction and the rate of the reaction. In particular, this profile includes the activation energy required to overcome the energy barrier between reactants and products.

4.B.1. Elementary reactions can be uni-molecular or involve collisions between two or more molecules.

- a. The order of an elementary reaction can be inferred from the number of molecules participating in a collision: uni-molecular reactions are first order, reactions involving bimolecular collisions are second order, etc.
- b. Elementary reactions involving the simultaneous collision of three particles are rare.

4.B.2. Not all collisions are successful. To get over the activation energy barrier, the colliding species need sufficient energy. Also, the orientations of the reactant molecules during the collision must allow for the rearrangement of reactant bonds to form product bonds.

- a. Uni-molecular reactions occur because collisions with solvent or background molecules activate the molecule in a way that can be understood in terms of a Maxwell-Boltzmann thermal distribution of particle energies.
- b. Collision models provide a qualitative explanation for order of elementary reactions and the temperature dependence of the rate constant.
- c. In most reactions, only a small fraction of the collisions leads to a reaction. Successful collisions have both sufficient energy to overcome activation energy barriers and orientations that allow the bonds to rearrange in the required manner.
- d. The Maxwell-Boltzmann distribution describes the distribution of particle energies; this distribution can be used to gain a qualitative estimate of the fraction of collisions with sufficient energy to lead to a reaction, and also how that fraction depends on temperature.

4.B.3. A successful collision can be viewed as following a reaction path with an associated energy profile.

- a. Elementary reactions typically involve the breaking of some bonds and the forming of new ones. It is usually possible to view the complex set of motions involved in this rearrangement as occurring along a single reaction coordinate.
- b. The energy profile gives the energy along this path, which typically proceeds from reactants, through a transition state, to products.

c. The Arrhenius equation can be used to summarize experiments on the temperature dependence of the rate of an elementary reaction and to interpret this dependence in terms of the activation energy needed to reach the transition state.

4.C. Many reactions proceed via a series of elementary reactions.

Many reactions proceed through a series of elementary reactions or steps, and this series of steps is referred to as the reaction mechanism. The steps of the mechanism sum to give the overall reaction; the balanced chemical equation for the overall reaction specifies the stoichiometry. The overall rate of the reaction is an emergent property of the rates of the individual reaction steps. For many reactions, one step in the reaction mechanism is sufficiently slow so that it limits the rate of the overall reaction. For such reactions, this rate-limiting step sets the rate of the overall reaction. Reaction intermediates, which are formed by a step in the reaction mechanism and then consumed by a following step, play an important role in multistep reactions, and their experimental detection is an important means of investigating reaction mechanisms.

4.C.1. The mechanism of a multistep reaction consists of a series of elementary reactions that add up to the overall reaction.

a. The rate law of an elementary step is related to the number of reactants, as accounted for by collision theory.
b. The elementary steps add to give the overall reaction. The balanced chemical equation for the overall reaction specifies only the stoichiometry of the reaction, not the rate.
c. A number of mechanisms may be postulated for most reactions, and experimentally determining the dominant pathway of such reactions is a central activity of chemistry.

4.C.2. In many reactions, the rate is set by the slowest elementary reaction, or rate-limiting step.

a. For reactions in which each elementary step is irreversible, the rate of the reaction is set by the slowest elementary step (i.e., the rate-limiting step).

4.C.3. Reaction intermediates, which are formed during the reaction but not present in the overall reaction, play an important role in multistep reactions.

a. A reaction intermediate is produced by some elementary steps and consumed by others, such that it is present only while a reaction is occurring.
b. Experimental detection of a reaction intermediate is a common way to build evidence in support of one reaction mechanism over an alternative mechanism.

4.D. Reaction rates may be increased by the presence of a catalyst.

Catalysts, such as enzymes in biological systems and the surfaces in an automobile’s catalytic converter, increase the rate of a chemical reaction. Catalysts may function by lowering the activation energy of an elementary step in a reaction, thereby increasing the rate of that elementary step, but leaving the mechanism of the reaction otherwise unchanged. Other catalysts participate in the formation of a new reaction intermediate, thereby providing a new reaction mechanism that provides a faster pathway between reactants and products.

4.D.1. Catalysts function by lowering the activation energy of an elementary step in a reaction mechanism, and by providing a new and faster reaction mechanism.

a. A catalyst can stabilize a transition state, lowering the activation energy and thus increasing the rate of a reaction.
b. A catalyst can increase a reaction rate by participating in the formation of a new reaction intermediate, thereby providing a new reaction pathway or mechanism.

4.D.2. Important classes in catalysis include acid-base catalysis, surface catalysis, and enzyme catalysis.

  a. In acid-base catalysis, a reactant either gains or loses a proton; this changes the rate of the reaction.
  b. In surface catalysis, either a new reaction intermediate is formed, or the probability of successful collisions is modified.
  c. Some enzymes accelerate reactions by binding to the reactants in a way that lowers the activation energy. Other enzymes react with reactant species to form a new reaction intermediate.

Learning Objectives

4.1	The student is able to design and/or interpret the results of an experiment regarding the factors (i.e., temperature, concentration, surface area) that may influence the rate of a reaction.	EK 4.A.1
4.2	The student is able to analyze concentration vs. time data to determine the rate law for a zeroth-, first-, or second-order reaction.	EK 4.A.2
4.3	The student is able to connect the half-life of a reaction to the rate constant of a first-order reaction and justify the use of this relation in terms of the reaction being a first-order reaction.	EK 4.A.3
4.4	The student is able to connect the rate law for an elementary reaction to the frequency and success of molecular collisions, including connecting the frequency and success to the order and rate constant, respectively.	EK 4.B.1
4.5	The student is able to explain the difference between collisions that convert reactants to products and those that do not in terms of energy distributions and molecular orientation.	EK 4.B.2
4.6	The student is able to use representations of the energy profile for an elementary reaction (from the reactants, through the transition state, to the products) to make qualitative predictions regarding the relative temperature dependence of the reaction rate.	EK 4.B.3
4.7	The student is able to evaluate alternative explanations, as expressed by reaction mechanisms, to determine which are consistent with data regarding the overall rate of a reaction, and data that can be used to infer the presence of a reaction intermediate.	EU 4.C
4.8	The student can translate among reaction energy profile representations, particulate representations, and symbolic representations (chemical equations) of a chemical reaction occurring in the presence and absence of a catalyst.	EK 4.D.1
4.9	The student is able to explain changes in reaction rates arising from the use of acid-base catalysts, surface catalysts, or enzyme catalysts, including selecting appropriate mechanisms with or without the catalyst present.	EK 4.D.2

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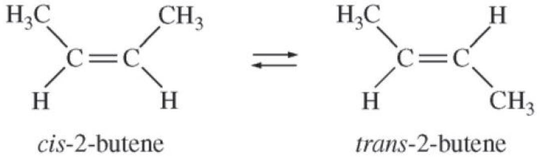
FREE RESPONSE PRACTICE

Abide by the time guidelines. Use only (1) a black or blue pen or No. 2 pencil, (2) a scientific or graphing calculator, and (3) the provided Periodic Table and list of Equations and Constants.

Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved at arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

Write clearly and legibly. Cross out any errors you make; erased or crossed-out work will not be scored.

2014 AP Chemistry #7 (9 minutes)



The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{cis\text{-}2\text{-butene}}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	600.	2.00	365	50.

(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

(b) Calculate the rate constant, k, for the reaction at 350. K. Include appropriate units with your answer.

(c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

GO ON TO THE NEXT PAGE.

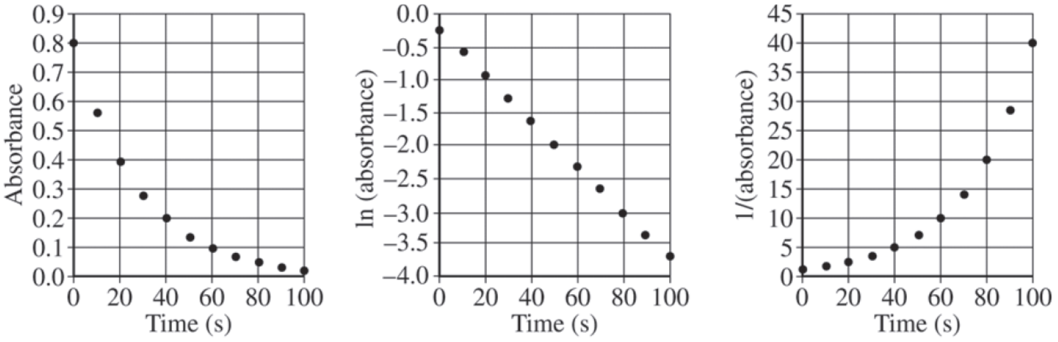
ADDITIONAL PAGE FOR ANSWERING QUESTION #7

GO ON TO THE NEXT PAGE.

2015 AP Chemistry #5 (9 minutes)

$$\underset{\textit{blue}}{Na_2C_{37}H_{34}N_2S_3O_9} + OCl^- \rightarrow \underset{\textit{colorless}}{\text{products}}$$

Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl^- is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.



Graph I Graph II Graph III

(a) Based on the graphs above, what is the order of the reaction with respect to the blue food coloring?

(b) The reaction is known to be first order with respect to bleach. In a second experiment, the student prepares solutions of food coloring and bleach with concentrations that differ from those used in the first experiment. When the solutions are combined, the student observes that the reaction mixture reaches an absorbance near zero too rapidly. In order to correct the problem, the student proposes the following three possible modifications to the experiment.

- Increasing the temperature
- Increasing the concentration of the food coloring
- Increasing the concentration of the bleach

Circle the one proposed modification above that could correct the problem, and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

(c) In another experiment, a student wishes to study the oxidation of red food coloring with bleach. How would the student need to modify the original experimental procedure to determine the order of the reaction with respect to the red food coloring?

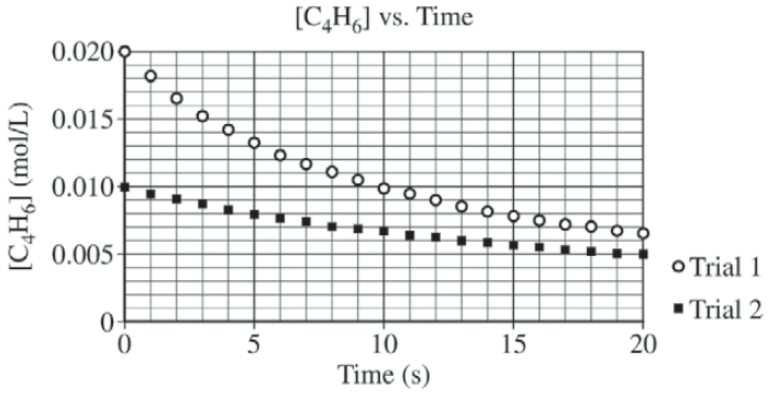
ADDITIONAL PAGE FOR ANSWERING QUESTION #5

GO ON TO THE NEXT PAGE.

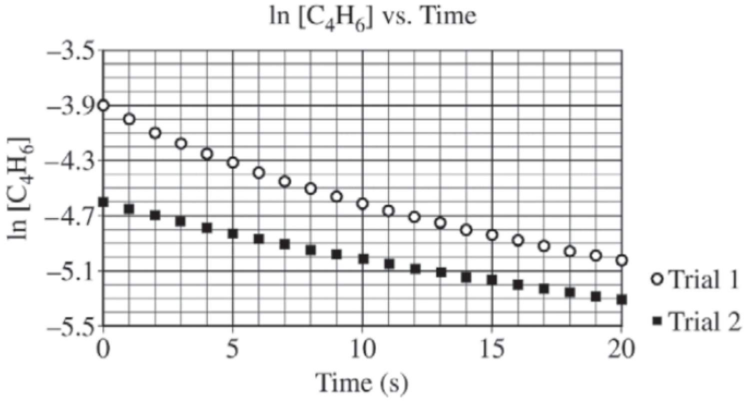
2016 AP Chemistry #5 (9 minutes)

$$2\ C_4H_6(g) \rightarrow C_8H_{12}(g)$$

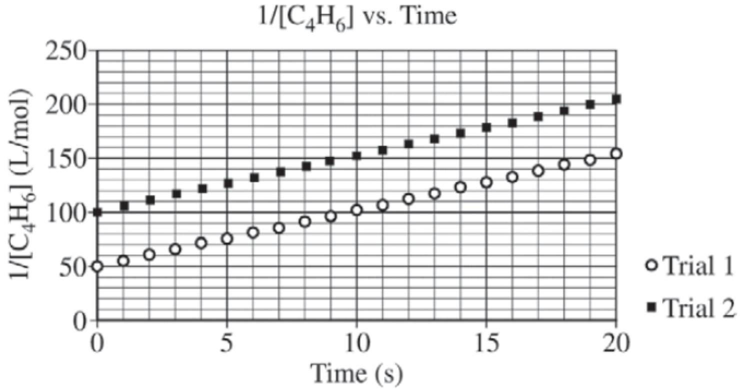
At high temperatures the compound C4H6 (1,3-butadiene) reacts according to the equation above. The rate of the reaction was studied at 625 K in a rigid reaction vessel. Two different trials, each with a different starting concentration, were carried out. The data were plotted in three different ways, as shown below.



$[C_4H_6]$ vs. Time



$\ln [C_4H_6]$ vs. Time



$1/[C_4H_6]$ vs. Time

(a) For trial 1, calculate the initial pressure, in atm, in the vessel at 625 K. Assume that initially all the gas present in the vessel is C_4H_6.

(b) Use the data plotted in the graphs to determine the order of the reaction with respect to C_4H_6.

(c) The initial rate of the reaction in trial 1 is 0.0010 mol/(L·s). Calculate the rate constant, *k*, for the reaction at 625 K.

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION #5

GO ON TO THE NEXT PAGE.