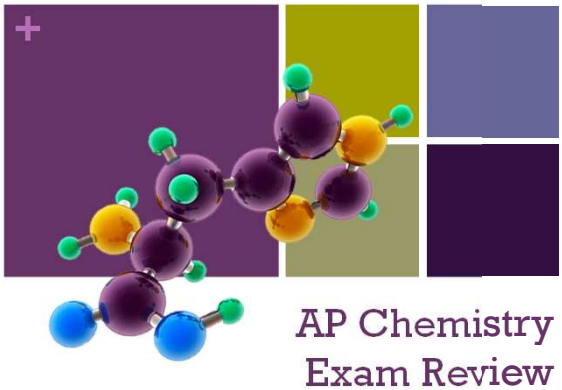
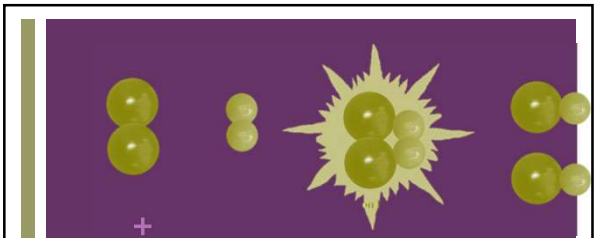


AP Chemistry Exam Review

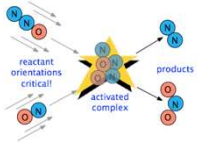


Big Idea #4

Kinetics

Factors Affecting Reaction Rate

Source



Collision theory states that reactants must collide in the correct orientation and with enough energy for the molecules to react; changing the number of collisions will affect the reaction rate

Rate is the change in concentration over time

$\Delta[A] / t$

- Factors that Affect Reaction Rate
  - **State of reactants**
    - Rate increases as state changes from solid → gas as increased molecular movement allows for more opportunity for collision
    - Greater surface area of solids will increase rate as more reactant is exposed and able participate in collisions
  - **Temperature** - more kinetic energy leads to more successful collisions between molecules
  - **Concentration** – more reactants → more collisions
  - **Use of a catalyst** – affect the mechanism of reaction leading to faster rate

Video

LO 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.

+ Determining Rate Order

Source

Video

- Rate law for a reaction has the form: rate = $k[A]^m[B]^n\ldots$ (only reactants are part of the rate law)
  - *Exponents (m, n, etc.) are determined from examining data, not coefficients:*

for ***A + B → C***

When [A] is doubled, the rate do not change, so the reaction is zero order with respect to A

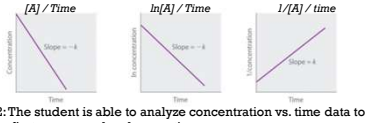
Trial	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial Rate (mol/(L•s)
1	0.100	0.100	0.002
2	0.200	0.100	0.002
3	0.200	0.200	0.004

When [B] is doubled, the rate doubles, so the reaction is first order with respect to B

- *The overall rate expression for the reaction is* ***rate = k [B]***
- *k* is the rate constant and is determined experimentally by plugging in data into the rate expression

Plot to create a straight line graph:

Zeroth Order	First Order	Second Order
[A] / Time	*ln[A] / Time*	*1/[A] / time*



The first and second order integrated rate laws can be found on the Kinetics section of the AP Equations Sheet

LO 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.

+ Half-life (First Order)

Source

Video

$$\ln[A] = -kt + \ln[A]_0$$

$$\ln\frac{[A]_0}{2} = -kt + \ln[A]_0$$

$$\ln[A]_0 - \ln 2 = -kt + \ln[A]_0$$

$$\ln[A]_0 - \ln[A]_0 - \ln 2 = -kt$$

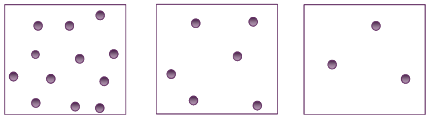
$$-\ln 2 = -kt$$

$$\ln 2 = kt$$

$$t_{1/2} = \frac{\ln 2}{k}$$

The first order half life equation is derived from the first order integrated rate law

- Time needed for the concentration of reactant to reach half its initial value
  - Time to reach half concentration is dependent on k, not initial concentration
  - Half life remains constant in a first order reaction
- **Example:** when $t_{1/2}$= 30 sec, the concentration is halved each 30 seconds



Initial Conditions *(12 molecules)*

After 30 seconds *(6 molecules)*

After 60 seconds *(3 molecules)*

LO 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.

+ Reaction Mechanisms

Source

Video

$X_2 + Y_2 \rightarrow X_2Y_2$ **rate = k[X_2]**

A reaction and its experimentally determined rate law are represented above. A chemist proposes two different possible mechanisms for the reaction, which are given below.

Mechanism 1

$X_2 \rightarrow 2X$ (slow)
$X + Y_2 \rightarrow XY_2$ (fast)
$X + XY_2 \rightarrow X_2Y_2$ (fast)

Mechanism 2

$X_2 \rightarrow 2X$ (slow)
$X + Y_2 \rightarrow XY + Y$ (fast)
$X + XY \rightarrow X_2Y$ (fast)
$X_2Y + Y \rightarrow X_2Y_2$ (fast)

Based on the information above, which of the mechanisms is/are consistent with the rate law? List the intermediates in each mechanism:

Answer: Both are consistent. In both mechanisms, the molecularity of the slow, rate determining step is consistent with the rate law. Furthermore, the sum of the elementary steps for both mechanisms gives the overall balanced equation for the reaction.

Intermediates in mechanism 1: X, XY_2. Intermediates in mechanism 2: X, XY, Y, X_2Y

LO 4.7: 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.

Reaction Mechanisms

Source

Video

The rate law for a reaction is found to be Rate = $k[A]^2[B]$. What is the intermediate? Which of the following mechanisms gives this rate law?

I. A + B ⇄ E (fast)
E + B → C + D (slow)

II. A + B ⇄ E (fast)
E + A → C + D (slow)

III. A + A → E (slow)
E + B → C + D (fast)

A. I
B. II
C. III
D. Two of these

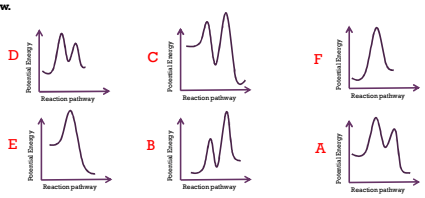
Answer: E is the intermediate. Only Mechanism II is consistent with the rate law. Whenever a fast equilibrium step producing an intermediate precedes the slow rate determining step and we want to remove the intermediate from the rate law, we can solve for the concentration of the intermediate by assuming that an equilibrium is established in the fast step. The concentration of the intermediate in the rate determining slow step can be replaced with an expression derived from the equilibrium constant $[E] = K_{eq}[A][B]$. This substitution gives us the desired rate law: rate = $k'[A]^2[B]$

LO 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.

Reaction Mechanisms and Energy Profiles – Practice Problem

Draw and label axes for the energy profiles below. Match the curves with the appropriate description.

A. exothermic reaction with a 2 step mechanism where the first step is slow.
B. endothermic reaction with a 2 step mechanism where the second step is slow
C. exothermic reaction with a 2 step mechanism where the second step is slow.
D. endothermic reaction with a 2 step mechanism where the first step is slow.
E. exothermic reaction with a 1 step mechanism.
F. endothermic reaction with a 1 step mechanism.

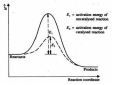


LO 4.7 Cont.

Catalysts

Source

Video

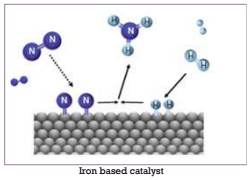


a. A catalyst can stabilize a transition state, lowering the activation energy.

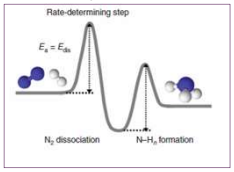
b. A catalyst can participate in the formation of a new reaction intermediate, providing a new reaction pathway.

The rate of the Haber process for the synthesis of ammonia is increased by the use of a heterogeneous catalyst which provides a lower energy pathway.

$N_2(g) + 2H_2(g) \rightarrow$ iron-based catalyst + $2NH_3(g)$



Iron based catalyst



LO 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.

+ Catalysts

catalysts provide alternative mechanisms with lower activation energy

Source

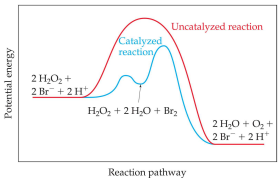
Video

a. In acid-base catalysis, a reactant either gains or loses a proton, changing the rate of the reaction.

b. In surface catalysis, either a new reaction intermediate is formed or the probability of successful collisions is increased.

c. In Enzyme catalysis enzymes bind to reactants in a way that lowers the activation energy. Other enzymes react to form new reaction intermediates.

Homogeneous catalysis of the decomposition of H_2O_2



LO 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.