Chemical Kinetics

Name: _____

AP Chemistry Lecture Outline

Video 1403 (9:31)

Introduction to Reaction Rates

collision model: addresses how/why particles react and how various factors affect reaction rate

Under applicable conditions, the reaction rate for a given system will ***increase*** when…

...temperature...

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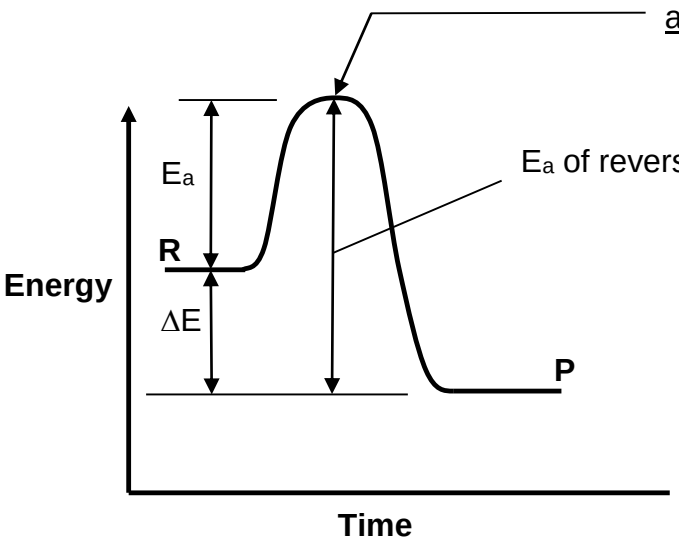
...reactant concentration...

...reactant surface area...

(i.e., as particle size…)

…extent of reactant mixing…



About ΔE...

-- it is ___ for endo.

and ___ for exo.

--

catalyst:

For a reaction to occur, collisions must take place with particles oriented in a certain way.

e.g., $Cl + NOCl \longrightarrow Cl_2 + NO$

Video 1406 (7:05)

Reaction rates are usually expressed in M/s.

Conc. of Substance x v. Time

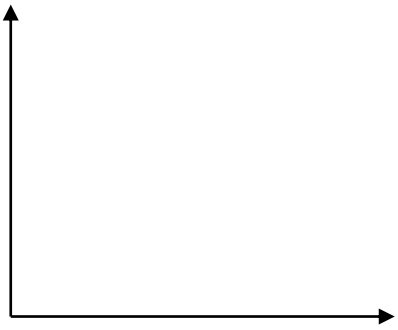
Δ[x] is (–) if x is a…

Δ[x] is (+) if x is a…

<u>instantaneous rate</u>: the reaction rate at any given time

-- it is equal to the slope of the [ ] – time curve at any point

Conc. of Substance x v. Time



For point P, one finds the instantaneous rate by:

-- constructing a tangent line

-- picking two points on the line

-- finding their coordinates

-- calculating the slope as…

Coefficients in the balanced equation are used when comparing rates for substances in a reaction.

EX. At a given time, the instantaneous rate of appearance of nitrogen dioxide is 3.2×10^{-6} M/s. Find the instantaneous rates of disappearance of nitrogen monoxide and oxygen at that time.

Video 1409 (9:39)

Finding Rate Laws from Experimental Data

Reaction rates are proportional to the [ ] of reactants.

<u>rate law</u>:

-- contains a <u>rate constant</u>, k:

k is independent of reactant ___, but increases

w/increasing _____ and w/presence of _____.

-- A rate law has the form… where m and n are...

-- Usually, reaction orders are 0, 1, or 2,

but some are fractions or are (–).

If a reaction is <u>zero order</u> in a particular reactant, changing its concentration...

<u>1st order</u>: <u>2nd order</u>: <u>3rd order</u>:

EX. $H_2(g) + Cl_2(g) \longrightarrow 2\ HCl(g)$

Find... (1) rxn order of each reactant
(2) overall reaction order
(3) units of rate constant

$[H_2]$ (M)	$[Cl_2]$ (M)	Init. rate of HCl formation ($M\ s^{-1}$)
0.100	0.100	0.340
0.100	0.200	0.680
0.200	0.200	2.720

Video 1412 (9:35)

Integrated Rate Law: 1st Order Reactions

Rate laws can be converted into equations that give the concentrations of substances at any time during the course of a reaction.

First-Order Reactions

-- Rate laws for 1st order rxns have the form:

-- To find rxn [ ]s over time, use…

Plotting ln $[A]_t$ v. t gives a straight line w/slope…

EX. $(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$

If this is a first-order process, with $k = 6.8 \times 10^{-4}\ s^{-1}$ and w/the initial pressure of $(CH_3)_2O$ being 256 torr, find the partial pressure of $(CH_3)_2O$ after 36.5 min.

Half-life of a reaction, $t_{1/2}$: the time required for a reactant's [ ] to drop to ½ of its orig. value

For 1st order rxns:

For 1st order reactions:

-- $t_{1/2}$ is independent of initial concentration

-- the [ ] of reactants is cut in half...every half-life

EX. Find the half-life for the decomposition of dimethyl ether $(CH_3)_2O$, based on data from the previous problem.

Video 1415 (10:00)

Second-Order Reactions (that are 2nd order in just one reactant)

i.e.,

and

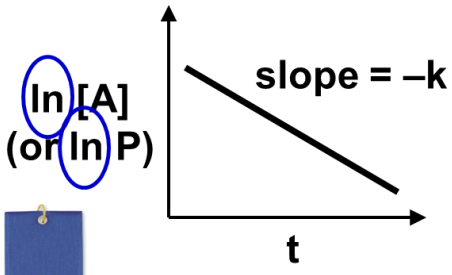
Plotting $1/[A]_t$ v. t gives a straight line w/slope…

EX. Data were taken on the decomposition of an initial 2.45 M solution of reactant X. Several graphs were made. The [X] vs. time graph was curved, with a generally (–) slope; the ln [X] vs. time graph, too, was curved with a generally (–) slope; the 1/[X] vs. time graph was linear, with a (+) slope of $4.33 \times 10^{-3}\ M^{-1}s^{-1}$. Determine the rxn's initial half-life and the [X] at 105 s.

1st order rxns

$$k\,t_{1/2} = 0.693 = \ln 2$$

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

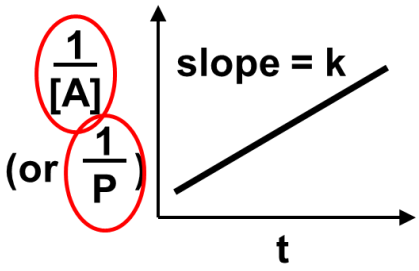


"It's natural to want to finish 1st."

2nd-order-in-only-one-R rxns

$$k\,t_{1/2} = \frac{1}{[A]_o}$$

$$kt = \frac{1}{[A]_t} - \frac{1}{[A]_o}$$

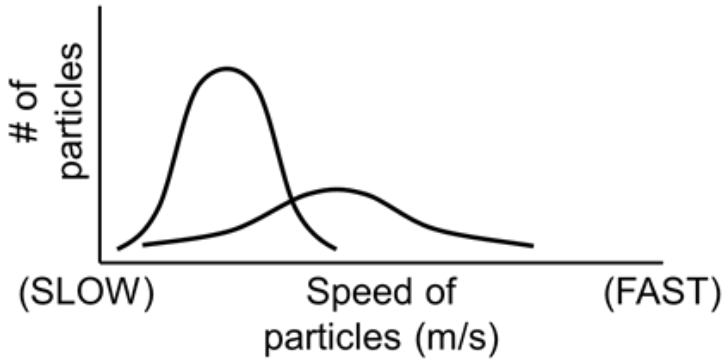


"To **want** to finish 2nd? That's upside-down thinking."

Video 1418 (5:23)

The Maxwell-Boltzmann Distribution and Rates

On a Maxwell-Boltzmann distribution of reactant particle velocities, all particles above a certain threshold of energy have enough energy to potentially initiate a rxn.



Video 1421 (6:35)

The Arrhenius Equation

For a given reaction, the E_a relates rate constants at two different temps WITH those temps.

E_a in J/mol

R = 8.314 J/mol-K

T = absolute temp.

EX. Using the following information, find... (1) ...E_a

(2) ...k at 430.0 K

T (^oC)	k (s^{-1})
189.7	2.52×10^{-5}
251.2	3.16×10^{-3}

Video 1424 (4:52)

Reaction Mechanisms -- the processes by which reactions occur

--

-- sometimes, mechanisms are dependent on temp.

elementary steps (or elementary reactions):

A reaction's molecularity is defined by the number of particles that participate as reactants in an elementary step.

unimolecular
bimolecular
termolecular

Rate laws for the elementary steps are found as follows...

Molecularity	Elementary Step	Rate Law for that Elementary Step
uni-	A → P	
bi-	A + A → P	
bi-	A + B → P	
ter-	A + A + A → P	
ter-	A + A + B → P	
ter-	A + B + C → P	

In other words, IF we know that "HERE is an equation for an elementary reaction", THEN (and ONLY then) we can write the rate law for that step based solely on the balanced equation.

Video 1427 (9:05)

Multistep Mechanisms

For multistep mechanisms, sequences of elementary steps are needed to go from R to P.

e.g., For the reaction $NO_2 + CO \longrightarrow NO + CO_2$

Elem. Step 1:

Elem. Step 2:

Above, NO_3 is an intermediate. All multistep mechanisms have them.

Most reactions have multiple elementary steps. The slowest of these is the...

The correct rate law for a reaction must: 1) be based on…

2) have ONLY…

EX. $CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g)$ has the following elementary steps:

E. S. 1: $Cl_2 \rightleftharpoons 2\ Cl$ (fast, eq)

E. S. 2: $CHCl_3 + Cl \rightarrow CCl_3 + HCl$ (slow)

E. S. 3: $CCl_3 + Cl \rightarrow CCl_4$ (fast)

State the rate law and the units on the rate constant.

Video 1430 (7:57)

Catalysis the process by which a catalyst changes the rate and mechanism of a chemical reaction

-- a catalyst is…

-- Catalyzed and uncatalyzed reactions have…

Homogeneous catalysts are present in the same phase as the reacting molecules.

Heterogeneous catalysts exist in a different phase than the reacting molecules.

--

The first step in catalysis is _____ of the reactant molecules onto the _____ (i.e., the "docking points") on the catalyst molecules.

--

-- then, the products detach from the catalyst

enzymes:

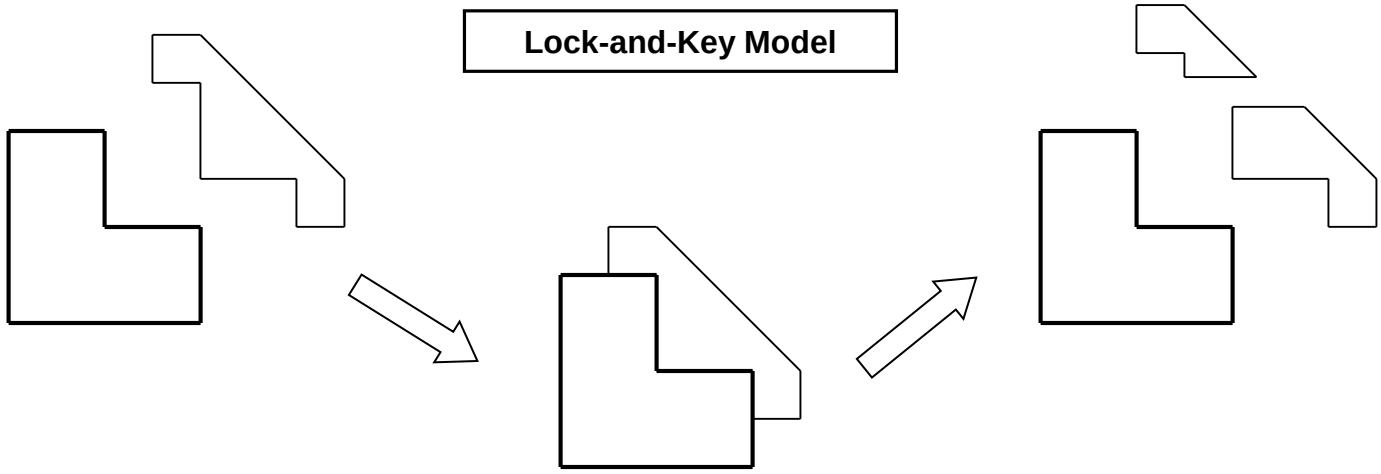
-- large protein molecules

-- usually very specific

-- names end in... "____"

-- substrates: substances (i.e., reactants) that react at the active sites of enzymes

-- The lock-and-key model explains how an enzyme affects a substrate molecule and changes it into a new substance.



turnover number:

Enzyme inhibitors bind to the active site or alter the unique shape of an enzyme molecule, destroying the enzyme's activity. e.g.,