CONCEPT: REACTION ORDERS

●*Reaction order*: a proportionality relationship between reaction rate (v) & each _____ [substrate].

□ Recall: *frequently* equals the _____ of the substrate but must be *experimentally* determined.

□ *Elementary* reactions (those with only _____ transition state): *Substrate Coefficients = reaction order.*

●*Overall Reaction Order*: always equal to the _____ of the individual *reaction orders* for all substrates.

EXAMPLE: Determine the overall reaction order for the following reactions.

Substrate Coefficients = Substrate Reaction Order

Elementary Reaction

$O_{3(g)} + O_{(g)} \longrightarrow 2O_{2(g)}$

$v = \kappa [O_3]^1[O]^1$

Overall Reaction Order = _____

Substrate Coefficients ≠ Substrate Reaction Order

Nonelementary Reaction

$NO_{2(g)} + CO_{(g)} \longrightarrow\longrightarrow NO_{(g)} + CO_{2(g)}$

$v = \kappa [NO_2]^2 [CO]^0$

Overall Reaction Order = _____

●There are ____ common *overall reaction orders*: □ _____ Order □ _____ Order □ _____ Order

PRACTICE: The rate law for an elementary and/or nonelementary reaction is _____:

a) always determined from the balanced chemical reaction.

b) the rate law for the fastest step in the reaction mechanism.

c) experimentally determined.

d) always 2nd order overall if there are 2 reactants.

Zero Order Reactions

●*Zero Order Reactions*: [substrate] has _____ effect on reaction rate (v).

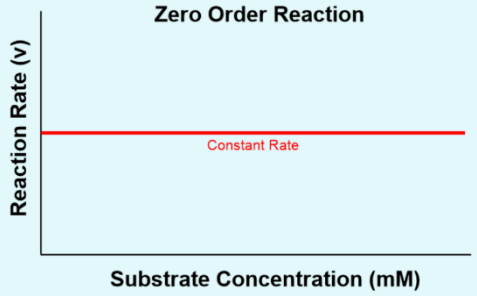
□ Zero-order kinetics are exhibited when an enzyme is _____ with substrate.

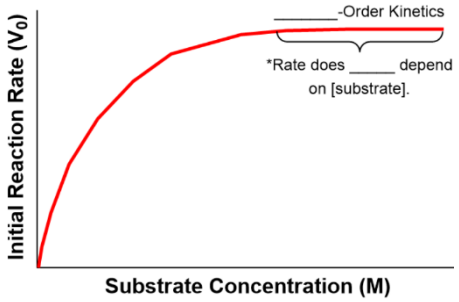
□ Zero Order r*ate constant* (*k*) _____ are Molarity x seconds^{-1} (M s^{-1}).

A ⟶ B

Zero Order Reaction:

Reaction Rate (v) = $\kappa [A]^0$ = ___





EXAMPLE: Zero Order Kinetics: Does increasing the # of cars also increase the rate that the cars cross the 1-lane bridge?

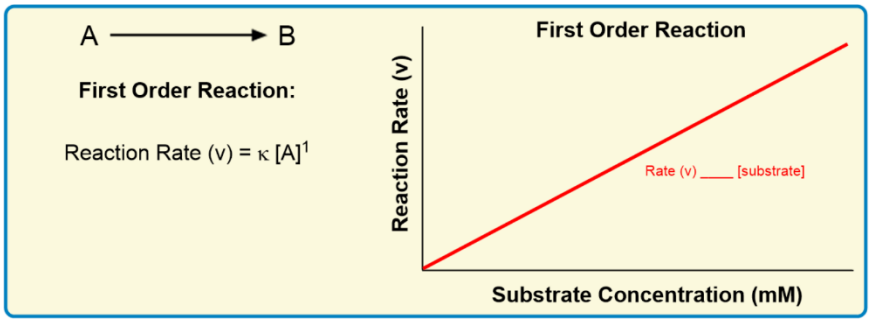
a) Yes b) No

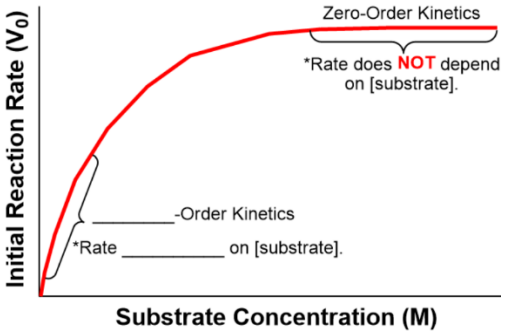
CONCEPT: REACTION ORDERS

1st Order Reactions

- _____ *Order Reactions*: reactions where the rates are *directly* proportional to only _____ [substrate].
  - □ Includes _____ reactions involving only a single substrate (ex. A → B).
  - □ First Order r*ate constant* (k) units are seconds^{-1} (s^{-1}).

EXAMPLE: First Order Kinetics.

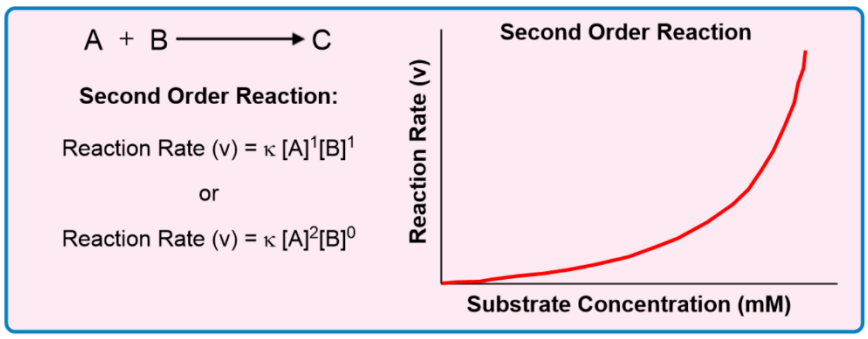


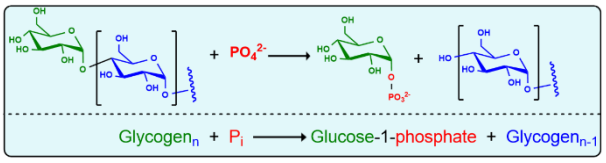


2nd Order Reactions

- _____ *Order Reactions*: reactions where the rates are directly proportional to _____ [substrates].
  - □ 2nd Order reaction rate could also be proportional to the _____ of only one [substrate].
  - □ Includes _____ reactions involving *two* substrates (ex. A + B → C).
  - □ Second Order r*ate constant* (k) units are Molar^{-1} x seconds^{-1} ($M^{-1}s^{-1}$).

EXAMPLE: Second Order Kinetics.





Rate Law = ___ = κ [_____]— [P_i]—

PRACTICE: What is the overall reaction order for the following rate law? $v = k\,[A]^1\,[B]^1\,[C]^0$

a) Zero order. b) 1st order. c) 2nd order. d) 3rd order.

Pseudo 1st Order Reactions

- _____-*First-Order Reactions*: those that are actually 2nd order reactions but _____ to be 1st order reactions.
  - □ Can occur when concentration of one substrate is much _____ than another (ex. [B] >>> [A]).
  - □ This makes substrate A the _____ reagent, so it *appears* that [A] alone dictates rate.

CONCEPT: REACTION ORDERS

PRACTICE: Which of the following options is true for a reaction with the provided rate law: $v = k\,[NO]^2\,[O_2]$

a) The reaction has an overall order of 3.
b) The reaction is first order with respect to the reactant O_2.
c) The reaction is endothermic.
d) The reaction has an overall order of 2.
e) a & b are true.
f) b & c are true.

PRACTICE: Consider the nonenzymatic elementary reaction from A → B. When the initial [A] = 20 mM, the reaction velocity is measured as 5 μM/min. Determine the reaction order and calculate the rate constant for the reaction.

a) 1st order reaction ; k = 100 min^{-1}.
b) 1st order reaction ; k = 0.25 min^{-1}.
c) 1st order reaction ; k = 2.5 x 10^{-4} min^{-1}.
d) 1st order reaction ; k = 4.0 x 10^{3} min^{-1}.
e) 2nd order reaction ; k = 100 min^{-1}.
f) 2nd order reaction ; k = 0.25 min^{-1}.
g) 2nd order reaction ; k = 2.5 x 10^{-4} min^{-1}.
h) 2nd order reaction ; k = 4.0 x 10^{3} min^{-1}.

PRACTICE: Consider the nonenzymatic elementary reaction A → B. When the [A] = 20 mM, the reaction velocity is measured as 5 μM of "B" produced per minute. Calculate the rate constant for the reaction. Hint: Consider the rate law.

a) 6.0 x 10^{2} min^{-1}.
b) 2.5 x 10^{-4} min^{-1}.
c) 3.7 x 10^{-5} min^{-1}.
d) 9.1 x 10^{-2} min^{-1}.

PRACTICE: The hypothetical elementary reaction 2A → B + C has a rate constant of 10^{-6} $M^{-1}s^{-1}$. What is the reaction velocity when the concentration of A is 10 mM?

a) 8 x 10^{-3} Ms^{-1}.
b) 2 x 10^{-7} Ms^{-1}.
c) 4 x 10^{-5} Ms^{-1}.
d) 1 x 10^{-10} Ms^{-1}.