CONCEPT: RATE CONSTANTS & RATE LAW

●*Rate Constant* (k): a ___________ positive value indicating reaction rate efficiency/probability under set conditions.

□ The *higher* the k, the ________ likely the reaction is ________; No reaction occurs if k = 0, & k is never negative.

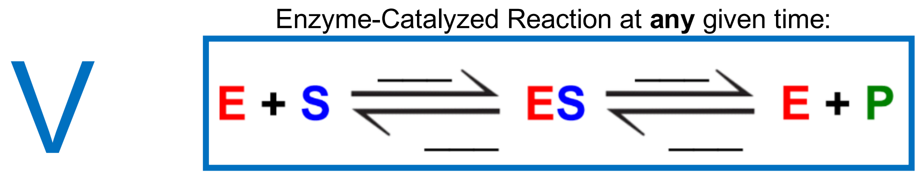
●There are _____ rate constants for a standard enzyme-catalyzed reaction.

1) k_1: E + S association rate constant to form ES.

2) k_{-1}: ES dissociation rate constant back to E + S.

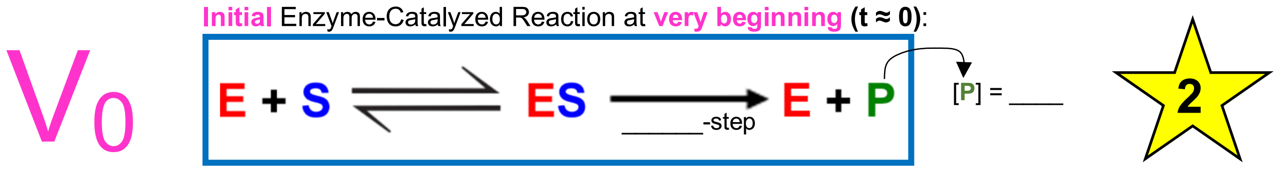
3) k_2: ES dissociation rate constant to form P.

4) k_{-2}: E + P association rate constant to reform ES.



●At initial stages of an enzyme-catalyzed reaction, there are only _____ rate constants (no product means ____ is *ignored*).

□ _________ velocity (V_0): velocity at the *very beginning* of a reaction where k_{-2} is *negligible*.



PRACTICE: Which of the following rate constants is negligible for the initial velocity (V_0) of an enzyme-catalyzed reaction?

a) k_1.   b) k_{-1}.   c) k_2.   d) k_{-2}.

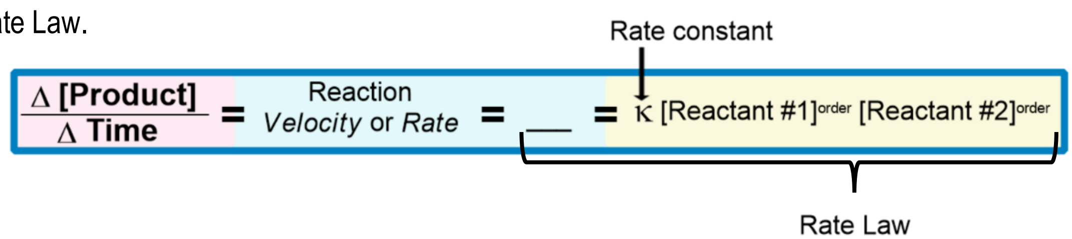
Rate Law: Calculating Reaction Rate (v) with Rate Constant (k)

●If final concentrations of reactants/products are unknown, reaction rate (v) can be determined by the ________ law.

□ *Rate Law*: mathematical relationship between reaction rate (v), rate constant (k), & each __________ [reactant].

□ Multiply rate constant (k) by all *initial* [reactant]$^{\_\_\_\_\_}$.

EXAMPLE: Rate Law.



●*Reaction order* must be *experimentally* determined but *frequently* equals the ______________ of the reactant.

EXAMPLE: Determine the rate law for each *simple* reaction.

A ⟶ B

v =

A + B ⟶ C + D

v =

CONCEPT: RATE CONSTANTS & RATE LAW

PRACTICE: Calculate the reaction rate for the following simple reaction if k = 1.3 x 10^{-1} $M^{-1}s^{-1}$, initial [A] = 4.0 x 10^{-3} M, and the initial [B] = 6.0 x 10^{-3} M (for simple reactions, assume coefficients are reaction orders): **A + B → 2C**

a) 2.13 x 10^{-6} M.

b) 3.12 x 10^{-6} M/s.

c) 1.32 x 10^{-6} s.

d) 3.12 x 10^{-6} $M^{-1}s^{-1}$.

Rate Laws for Enzyme-Catalyzed Reactions

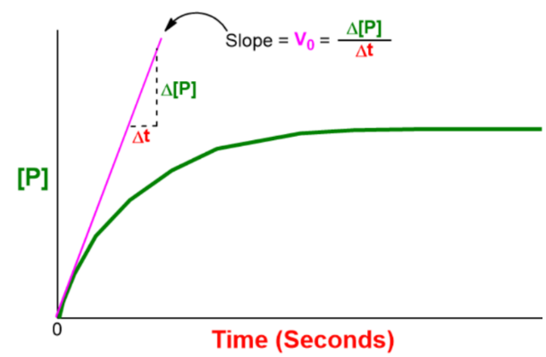
●Recall: Reaction *Velocity or Rate* = ___ = $\frac{\Delta\ [\text{Product}]}{\Delta\ \text{Time}}$, but v can be rewritten with the *rate law*.

●For an enzyme-catalyzed reaction, *formation* of the **product** depends only on _____ (k_1 and k_{-1} alone do *not* affect [P]).

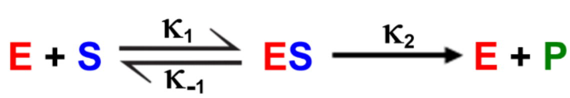
□ Biochemists measure/plot the initial velocity (___) of this **product**-formation step.

EXAMPLE: Write the rate-law for the product-formation step.

P Formation Rate Law: V_0 = ____ (____)



PRACTICE: Write out the rate law equations for each association/dissociation indicated below.



a) Rate law for ES dissociation into E + P: V = ______________

b) Rate law for E + S association: V = ______________

c) Rate law for ES dissociation back into E + S: V = ______________

PRACTICE: In a typical enzyme-catalyzed reaction, when & why is the rate constant k_{-2} negligible?

a) At the very beginning of a reaction because the [S] & [P] are at equilibrium and not yet disturbed by the enzyme.

b) Initially towards the beginning of a reaction because enzymes are getting off to a slow start.

c) At the start of a reaction when [S] are at their highest, [P] are at their lowest, & the reverse reaction is unlikely.

d) At the end of a reaction when the substrate and product are at equilibrium with each other.

e) As soon as the reaction begins when the reaction rate is at its lowest.