

University of Canterbury

End of Year Examination 2006

Prescription Number(s):	CHEM 325 BCHM 302
Paper Title:	Biological Chemistry

Time Allowed: 130 MINUTES

Number of pages: SIX

Answer **TWO** questions from Part A
and **TWO** questions from Part B.

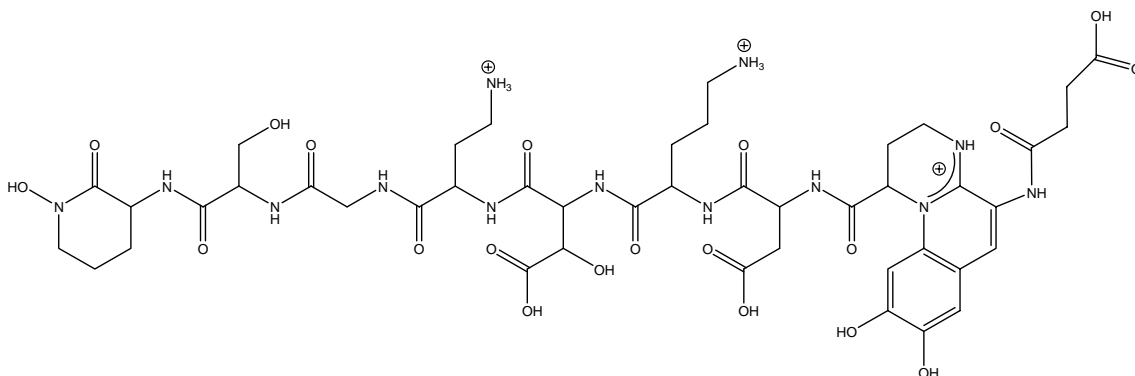
All questions are of equal value.

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SECTION A

(Answer **TWO** questions from this section)

1. (a) Examine the structure below and discuss possible roles for this molecule in biological systems.



- (b) Discuss, in detail, whether you would expect electron-transfer reactions involving the iron enterobactin complex to be fast or slow. Your answer should refer explicitly to the factors that contribute to the rates of electron transfer reactions.
2. (a) Describe briefly the operation of the Na^+/K^+ pump. What is its purpose?
- (b) What can be learned about the Na^+/K^+ pump through a study of the chemistry of crown ethers and cryptands.
- (c) Comment on the similarities and differences between Ca^{2+} , K^+ , Mg^{2+} , and Na^+ ions, and then discuss the implications that these may have for the structure of Ca^{2+} channels that span cell membranes.
3. (a) Outline the factors that lead to the Zn^{2+} ion being widely used in metalloenzymes.
- (b) Compare and contrast the zinc-carbonyl and zinc-hydroxide mechanisms for amide hydrolysis.
- (c) Discuss the merits of employing a second metal ion in the active site of a hydrolytic metalloenzyme. Give examples of such systems.

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SECTION B(Answer **TWO** questions from this section)

4. (a) The Michaelis-Menten equation for the rate of an enzyme-catalyzed reaction is:

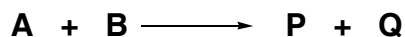
$$v = \frac{k_{\text{cat}}[E]_0[S]}{K_M + [S]}$$

- (i) Define the five variables, v , k_{cat} , $[E]_0$, $[S]$ and K_M , in this equation and define V_{max} in terms of these variables.
- (ii) On the basis of the Michaelis-Menten equation, qualitatively sketch the way in which v is predicted to vary with $[S]$. On your sketch, indicate the values of V_{max} and K_M .
- (iii) Using the Briggs-Haldane method, derive the Michaelis-Menten equation.
- (iv) Use your derivation of the Michaelis-Menten equation in part (iii), above, to explain why K_M is usually considered to be greater than K_S (where K_S is the dissociation constant for the enzyme-substrate complex).
- (b) An inhibitor is a substance that changes the rate of an enzyme-catalyzed reaction. Types of inhibiting action include ‘competitive inhibition’ and ‘noncompetitive inhibition’.
- (i) **Briefly outline** these two mechanisms of inhibitor action.
- (ii) If the mechanism of inhibitor action is purely **competitive**, then the following rate expression holds, where V_{max} , K_M and K_I are kinetic constants:

$$v = \frac{V_{\text{max}}[S]}{K_M \left(1 + \frac{[I]}{K_I} \right) + [S]}$$

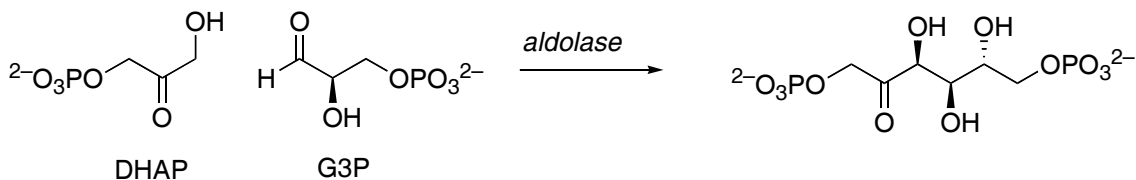
Use this rate expression to **show** what the Lineweaver-Burk plot of the outlined experimental data would look like if the mechanism of inhibitor action were purely **competitive**.

5. (a) For the following two-substrate, two-product reaction:



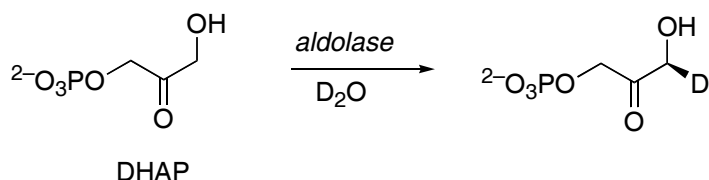
- (i) Outline the following two kinetic mechanisms:
 ordered sequential;
 and ping-pong.
- (ii) Qualitatively sketch the appearance of the Lineweaver-Burk plot when the rate of reaction is measured as a function of [A] at variable concentrations of [B] for *each mechanism*. Briefly explain why this type of plot distinguishes between these two mechanisms.

- (b) Aldolase catalyses the aldol reaction between dihydroxyacetone phosphate (DHAP) and glyceraldehyde 3-phosphate (G3P).



Outline the mechanism of this transformation, and use this mechanism to explain the following observations:

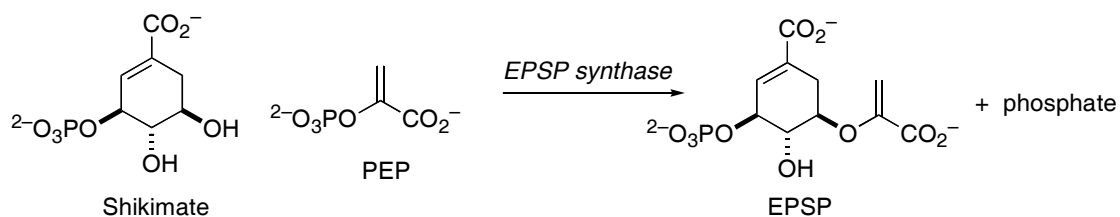
- (i) Incubation of the enzyme with DHAP and D_2O results in the stereospecific incorporation of one deuterium.



- (ii) Incubation of aldolase with the DHAP in the presence of sodium borohydride results in inactivation of the enzyme.

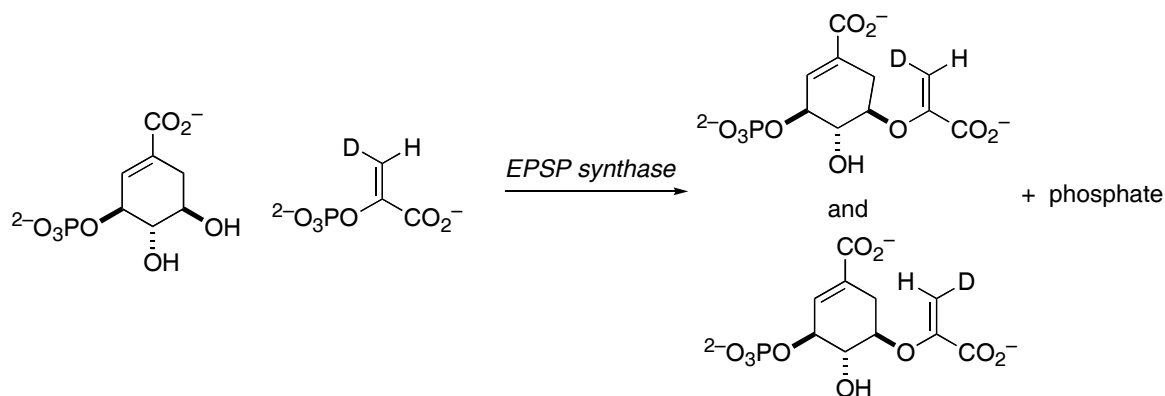
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6. (a) EPSP synthase catalyses the formation of EPSP from shikimate and phosphoenol pyruvate (PEP).

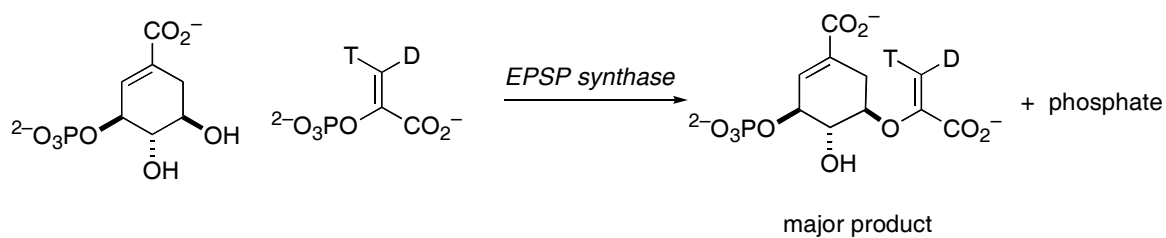


Describe the mechanism of this transformation and use it to account for the following experimental observations:

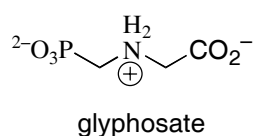
- (i) When the reaction is carried out with deuterium-labelled PEP, the deuterium label becomes scrambled in the product.



- (ii) When the reaction is carried out with deuterium- and tritium-labelled PEP, predominantly one product is formed.



- (iii) The enzyme is inhibited by glyphosate, the active ingredient of Roundup[®].



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