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Chem 3511
Exam 4

The exam starts on the next page. It has 12 questions, worth a total of 100 points. Please write legibly and don't assume that long answers are required if there is a lot of space left for your response. No calculators are allowed.

A test-taking tip: go through the whole exam and do the easy questions first. Then tackle the ones you find to be more difficult. You may find the information on the table below useful. Good luck.

TABLE 14-4 Standard Reduction Potentials of Some Biochemically Important Half-Reactions

Half-Reaction	$\mathscr{E}^{\circ\prime}$ (V)
$\frac{1}{2}O_2 + 2H^+ + 2e^- \leftrightharpoons H_2O$	0.815
$NO_3^- + 2H^+ + 2e^- \leftrightharpoons NO_2^- + H_2O$	0.42
Cytochrome a_3 (Fe^{3+}) + e^- $\leftrightharpoons$ cytochrome a_3 (Fe^{2+})	0.385
$O_2 + 2H^+ + 2e^- \leftrightharpoons H_2O_2$	0.295
Cytochrome *a* (Fe^{3+}) + e^- $\leftrightharpoons$ cytochrome *a* (Fe^{2+})	0.29
Cytochrome *c* (Fe^{3+}) + e^- $\leftrightharpoons$ cytochrome *c* (Fe^{2+})	0.235
Cytochrome c_1 (Fe^{3+}) + e^- $\leftrightharpoons$ cytochrome c_1 (Fe^{2+})	0.22
Cytochrome *b* (Fe^{3+}) + e^- $\leftrightharpoons$ cytochrome *b* (Fe^{2+}) (*mitochondrial*)	0.077
Ubiquinone + $2H^+ + 2e^-$ $\leftrightharpoons$ ubiquinol	0.045
Fumarate$^-$ + $2H^+ + 2e^-$ $\leftrightharpoons$ succinate$^-$	0.031
FAD + $2H^+ + 2e^-$ $\leftrightharpoons$ $FADH_2$ (*in flavoproteins*)	−0.040
Oxaloacetate$^-$ + $2H^+ + 2e^-$ $\leftrightharpoons$ malate$^-$	−0.166
Pyruvate$^-$ + $2H^+ + 2e^-$ $\leftrightharpoons$ lactate$^-$	−0.185
Acetaldehyde + $2H^+ + 2e^-$ $\leftrightharpoons$ ethanol	−0.197
FAD + $2H^+ + 2e^-$ $\leftrightharpoons$ $FADH_2$ (*free coenzyme*)	−0.219
$S + 2H^+ + 2e^- \leftrightharpoons H_2S$	−0.23
Lipoic acid + $2H^+ + 2e^-$ $\leftrightharpoons$ dihydrolipoic acid	−0.29
$NAD^+ + H^+ + 2e^-$ $\leftrightharpoons$ NADH	−0.315
$NADP^+ + H^+ + 2e^-$ $\leftrightharpoons$ NADPH	−0.320
Cysteine disulfide + $2H^+ + 2e^-$ $\leftrightharpoons$ 2 cysteine	−0.340
Acetoacetate$^-$ + $2H^+ + 2e^-$ $\leftrightharpoons$ β-hydroxybutyrate$^-$	−0.346
$H^+ + e^- \leftrightharpoons \frac{1}{2}H_2$	−0.421
$SO_4^{2-} + 2H^+ + 2e^- \leftrightharpoons SO_3^{2-} + H_2O$	−0.515
Acetate$^-$ + $3H^+ + 2e^-$ $\leftrightharpoons$ acetaldehyde + H_2O	−0.581

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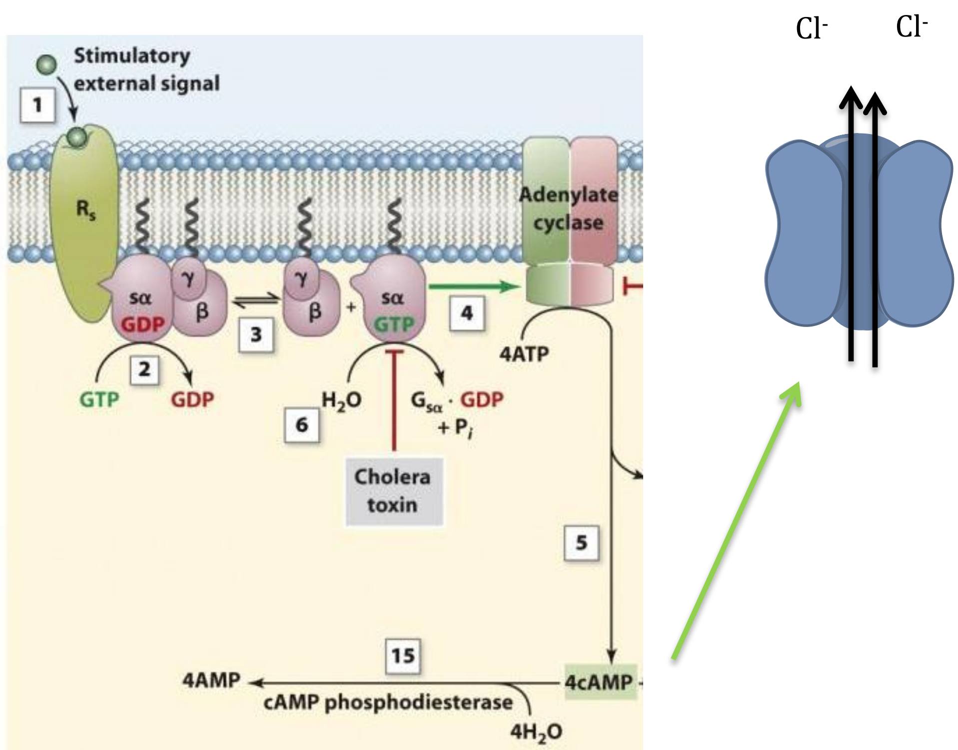
1. (**10 pts**) You go backpacking through South America. The guidebook says you should only drink boiled water. However, one day, you are so thirsty (and impatient) that you take a sip of water straight from the faucet. The next day you have severe diarrhea and the doctor tells you it is cholera.

You pull up your phone and find out that

- Cholera modifies the Gα subunit so that it is unable to hydrolyze GTP into GDP.
- The ultimate cellular response is chlorine secretion into the intestine that, via osmotic pressure, results in water also being secreted to the intestine.

Map out the biochemical signaling cascade triggered by cholera. Make sure to draw and label all the key steps involved in this signaling cascade and state the effect of the Gα subunit not being able to hydrolyze GTP into GDP.

The Gα subunit is continuously in an "on" state. The Gα subunit continuously activates adenylate cyclase, which results in an increase of cAMP. Increase in cAMP results in the activation of a chloride pump.



2 points: identification that the biochemical cascade affected is the GPCR signaling cascade

2 points: stating that the Gα subunit is continuously in an "on" state

2 points: G alpha activation of adenylate cyclase

2 points: Adenylate cyclase dependent conversion of ATP to cAMP

(if only cAMP is written and the ATP->cAMP reaction is not clearly stated, 1pt)

2 points: showing that cAMp elevation leads to activation of a chlorine pump

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2. (**14 pts**) Your T.A. inoculates two test tubes containing the same growth medium with the same number of yeast cells. He incubates one test tube in the presence of oxygen and another one in the absence of oxygen

a. Which culture will have a greater cell density (number of cells) after 24 hrs of incubation (doubling time 3 hours)? (**2 pts**)

The culture incubated in the presence of oxygen.

b. Explain why the culture that you chose above can make more cells with the same amount of glucose than the other culture. (**3 pts**)

The cells are undergoing cellular respiration resulting in more ATP production per Glucose unit (net 36 ATP/glucose) compared to the one in anaerobic conditions (net 2 ATP/glucose).

c. Are the cells in both cultures able to obtain the same amount of ATP from the glycolysis of one glucose? Explain. (**3 pts**)

Yes. Glycolysis is the same under aerobic and anaerobic conditions.
The difference is what happens after glycolysis. In the case of anaerobic conditions pyruvate will go to ethanol producing no more ATPs. However, in the case of aerobic conditions, pyruvate will be converted to acetyl-CoA and enter citric acid cycle. The reduicing equivalents generated during the citric acid cycle (NADH, FADH2) will then be converted to ATP via oxidative phosphorylation.

d. What is the fate of pyruvate when yeast is grown under anaerobic conditions? (**3 pt**)

Pyruvate is converted to acetaldehyde and then ethanol

e. What is the fate of pyruvate when yeast is grown under aerobic conditions? (**3 pt**)

Pyruvate is converted to acetyl-CoA which is then fed into citric acid cycle. (1.5 pts)

Eventually all glucose is converted to carbon dioxide. (1.5pt)

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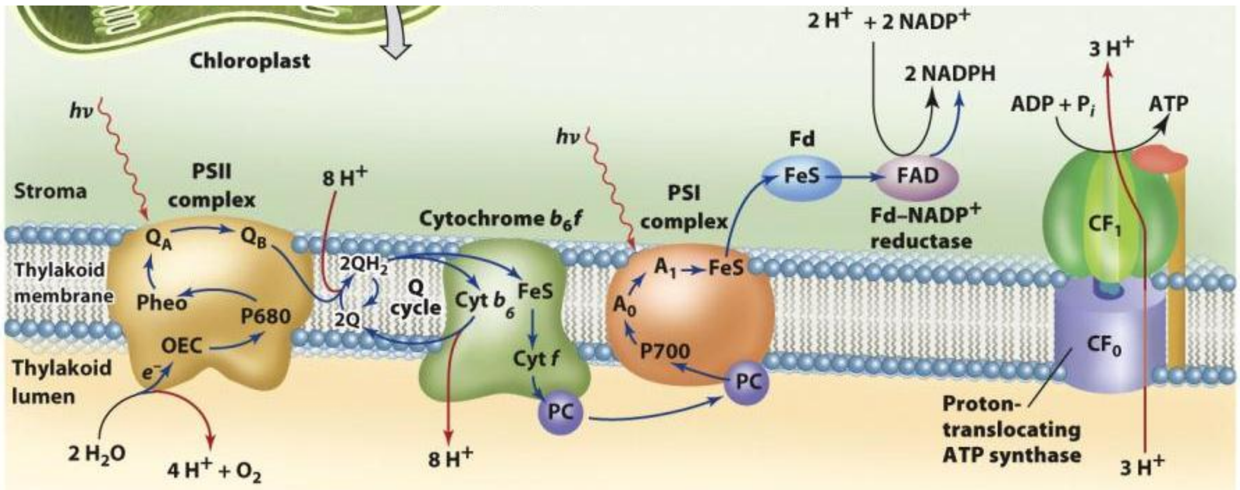
3. (**11 pts**) You friend has heard that plants consume carbon dioxide and release oxygen. So, before he goes to sleep, he moves his plant from the living room to his bedroom to increase the concentration of oxygen in the bedroom while he is sleeping.

a. Is your friend's plan sound? (**1pt**) Using a diagram, explain the process plants use to release oxygen and what the ultimate goal of this process is from the plant's perspective. (**7 pts**)

No, because in the dark the plant would be evolving oxygen from glycolysis and the TCA cycle rather than producing oxygen. Oxygen release only takes place in photosynthesis in the presence of light. Diagram of photosynthesis



2 pts: H_2O->$4H^+$ + O_2 donating electrons to the transmembrane complex

2pts: electron transport chain eventually transfers the electrons to NADP+ to make NADPH

2pts: electron transport chain results in a proton gradient

1pt: the proton gradient is used to produce ATPs via ATP synthase

b. What cycle is more likely to occur at night? (**1pt**). What compound is consumed in this cycle? (**1pt**).

Calvin cycle (1pt)

CO_2 (1pt)

c. Eventually, what compound will be released from the reactions that take place at night? (**1pt**)

Eventually the calvin cycle is going to feed into glycolysis.

- The sugar in glycolysis can be used to biosynthesize other compounds and produce ATP eventually being converted into carbon dioxide.
- The sugar can also be converted to starch
  1 pt for either answer.

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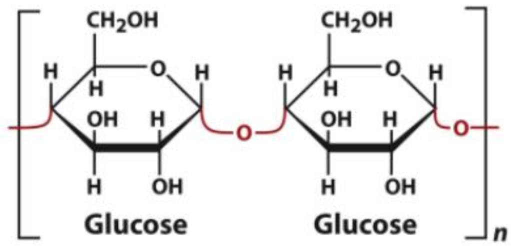
4. (**13pt**) Your friend has heard that increasing the consumption of fruits and vegetables will result in weight loss. When presented with a plate of celery sticks and roasted potatoes, your friend, thinking they are both equivalent vegetables, proceeds to eat the potatoes and not the celery sticks. A month later your friend has not lost, but gained weight.

a. Draw the main polysaccharide found in potatoes (**4pts**). What is the major carbohydrate monomer? (**1pt**)



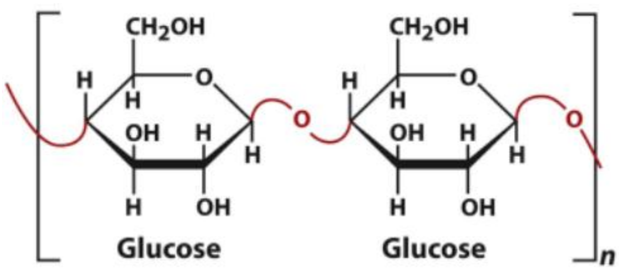
α-amylose
α-(1,4)-linked D-glucose

α-amylose is also called starched
2 points for drawing the glucose units in a chair conformation

2 point for the correct linkage (1pt: 1,4, 1pt: alpha)

1 point for stating that the monomer is glucose

b. Draw the main polysaccharide found in celery (**4 pts**). What is the major carbohydrate monomer? (**1pt**)



cellulose

β (1→4)-Linked D-glucose

2 points for drawing the glucose units in a chair conformation

2 point for the correct linkage(1pt: 1,4, 1pt: beta)

1point for stating that the monomer is glucose

c. Why is it not metabolically equivalent for humans to eat potatoes and celery? (**3pts**)

Potatoes contain starch which have α-1,4 glucose linkages recognized by enzymes human have, amylases. Humans cannot break down α-1,4 glucose linkages because they lack the enzymes to break this linkage (celulases). Therefore, humans cannot digest cellulose.

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5. (**3 pts**) You are trying to engineer a cell to produce more ATPs per glucose unit. Which of the following approaches (under aerobic conditions) would result in the highest increase in ATP? **(Apologies: B and D were the same. Stephen made an announcement in class to replace cytosol with mitochondria in B.)**

a. Introduce a metabolic reaction in the cytosol that produces one more ATP per glucose unit.

b. Introduce a metabolic reaction in the ~~cytosol~~ (mitochondria) that produces one more NADH per glucose unit.

c. Introduce a metabolic reaction in the mitochondria that produces one more ATP per glucose unit.

d. Introduce a metabolic reaction in the cytosol that produces one more NADH per glucose unit.

e. Introduce a metabolic reaction in the cytosol that produces one more $FADH_2$ per glucose unit.

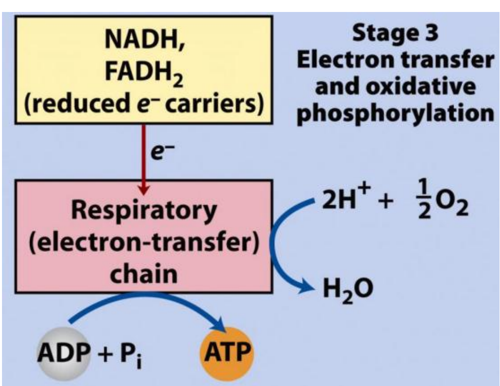
6. (**7 pts**) Explain the logic behind your answer choice in question 5. Make sure to use a diagram to explain the process that results in ATP formation.

NADH in the mitochondria can enter oxidative phosphorylation unlike NADH in the cytosol (3 points)

NADH donates electrons to the electron transport chain to generate a proton gradient (3 points)

The electrons are eventually donated to hydrogen and oxygen to produce water (1pt)

The proton gradient drives the production of ATP via ATP-synthase in the membrane (3 points).



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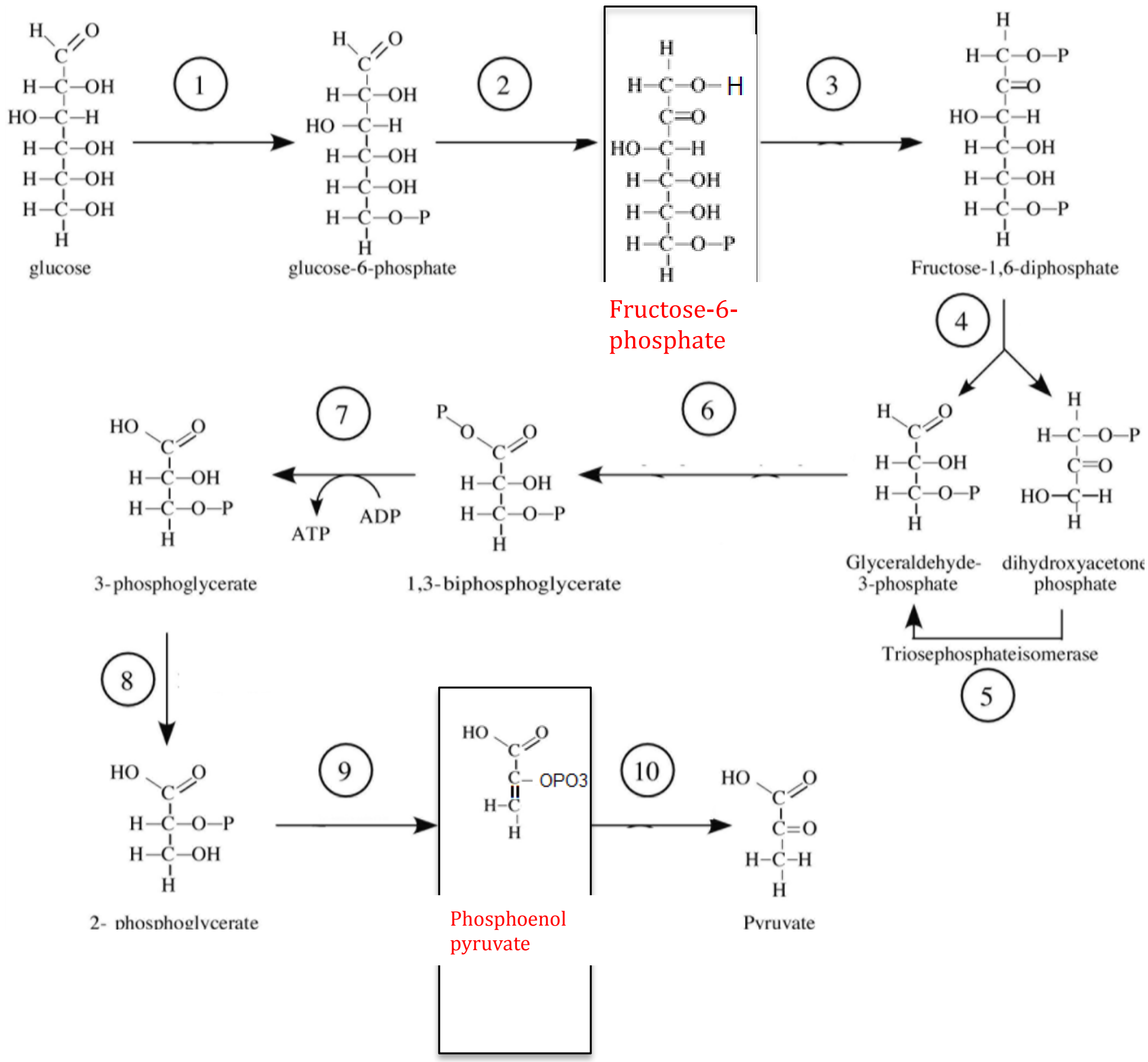
7. (**21 pts**) All questions refer to the diagram below



a. Draw the missing glycolysis intermediates in the boxes provided **(4 pts total: 2 pts per structure**)

b. Each of the enzymatic steps has been numbered 1-10.

i. Which step number/s produce ATP? (**2 pts**) 7, 10

ii. Which step number/s produce NAD^+? (**2 pts**) None

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iii. Which step number/s is/are an isomerization reaction/s? (**2pts**)

2, 5

iv. There are three metabolic flux control points in glycolysis. Name one of the steps that serves as a metabolic flux control. (**2pts**)

3, phosphofructokinase step

v. Explain how the metabolic control step that you have chosen works. (**3 sentence max. 5pts**)

The phosphofructokinase step (3) is allosterically controlled. When ATP levels are high, an ATP molecule binds to an allosteric site (away from active site) and induces a conformational change that inhibits the enzyme's activity and hinders glycolysis as a result.

vi. If you drink milk, you are consuming the sugar lactose, which is composed of one glucose unit and a galactose unit. At what step does galactose enter glycolysis? (**2 pts**)

Converted to Glucose-6-P

vii. Soda's main ingredients are: carbonated water, high fructose corn syrup, caramel color and phosphoric acid. Name one of the steps where the carbohydrate present in soda enters glycolysis. (**2pts**)

Converted to Fructose-6-P

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8. (**4 pts**) Consider the following metabolic reaction:

Succinyl-CoA + Acetoacetate → Acetoacetyl-CoA + Succinate $\Delta G°' = -1.25$ kJ/mol

The $\Delta G°'$ for the hydrolysis of Succinyl-CoA is –33.9 kJ/mol. What is the $\Delta G°'$ for the hydrolysis of Acetoacetyl-CoA: Acetoacetyl-CoA → Acetoacetate + CoA

a. –35.2 kJ/mol
b. –32.7 kJ/mol
c. +32.7 kJ/mol
d. +35.2 kJ/mol
e. none of the above

9. (**4pts**) What is the $\Delta \mathcal{E}°'$ for the oxidation of malate by NAD^+:

Malate + NAD^+ → Oxaloacetate + NADH + H^+

a. –4.81 V
b. + 4.81 V
c. –0.149 V
d. +0.149 V
e. +0.052 V

Malate -> oxaloacetate = 0.166

NAD+ -> NADH = -0.315

$\Delta \mathcal{E}° = 0.166 + (-0.315) = -0.149$

10. (**4 pts**) Creatine is compound naturally produced in humans and is metabolically important in muscle cells. Creatine participates in the following reaction in muscle cells:

ATP + creatine → phosphocreatine + ADP $\Delta G°' = +12.6$ kJ/mol

Under intracellular conditions, the ΔG for the reaction, which is catalyzed by the enzyme creatine kinase, is ~0 kJ/mol. From this information we can conclude that:

a. creatine kinase catalysis would not be necessary under intracellular conditions.
b. ATP has a greater phosphoryl group transfer potential compared to phosphocreatine.
c. at equilibrium, most intracellular creatine is phosphorylated.
d. the reaction operates close to equilibrium in cells.
e. None of the above is a correct conclusion.

11. (**5pts**) Some athletes take creatine supplements hoping to improve their physical endurance. Can you speculate why athletes believe that creatine supplementation may help improve physical endurance?

Given that the reaction works close to equilibrium under intracellular conditions, creatine

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would be rapidly phosphorylated to phosphocreatine. Given that

phosphocreatine + ADP → creatine + ATP $\Delta G°' = -12.6$ kJ/mol

Transfering the phosphoryl group from phosphocreatine to ADP is energetically favored based on $\Delta G°'$, so the assumption is that if you consume creatine, you will store phosphocreatine that rapidly transfer the phosphoryl group to ADP making ATP whenever needed.

The problem is that the intracellular ΔG *of the reaction is close to zero so you may not change the* ΔG *that much by increasing the concentration of creatine.*

12. (**4pts**) Compound "K" is the ultimate product of a linear metabolic pathway consisting of ten enzymatically catalyzed reactions as shown below.

$$A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D \xrightarrow{4} E \xrightarrow{5} F \xrightarrow{6} G \xrightarrow{7} H \xrightarrow{8} I \xrightarrow{9} J \xrightarrow{10} K$$

Complete the following description.

If "K" inhibits activity of enzyme "5", then enzyme "5" is under __allosteric_ control.
If enzyme "3" becomes activated in response to activity of protein kinase A only when compound "A" is present, then enzyme "3" is under _covalent modification__ control.
If enzyme "2" is only expressed in the presence of high concentrations of "A," then enzyme "2" is under _genetic __ control.
If all of these are true, high concentrations of "_K_" will decrease the flux through the pathway.

a. covalent modification; allosteric; genetic; A
b. allosteric; covalent modification; genetic; K
c. genetic; allosteric; genetic; K
d. allosteric; genetic; genetic; K
e. allosteric; genetic; genetic; A