Name Key

Chem 352 - Spring 2015 - Exam III

Use constants: Ideal gas law constant, R = 0.08206 (l•atm)/(mol•K) = 8.314 (J/(mol•K); Faraday's constant, $\mathscr{F}$= 9.659 x 10^4 J/(V•mol); Planck's constant, h = 6.626 x 10^{-34} J•s.

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1. Describe the metabolic purpose for each of the following pathways:
   a. Gluconeogenesis: This is the metabolic pathway that leads to the net synthesis of glucose from pyruvate, and other glycolytic intermediates.

   b. The citric acid cycle, when material enters the cycle as Acetyl-CoA: This is the catabolic route into the citric acid cycle. The two carbons that enter the cycle as acetylCoA, leave as CO_2.

   c. The alcohol fermentation pathway: The is the pathway used by yeast and other organisms to deoxidize the NADH + H^+ produced tin glycolysis, when the electron transport chain is not an option..

   d. Glycolysis: This is the pathway used to break the six-carbon glucose molecule down into two three-carbon pyruvate molecules, with the concomitant production of two ATP molecules.

   e. The citric acid cycle, when material enters the cycle as oxaloacetate: In this case, the end product of glucolysis, pyruvate is carboxylated to oxaloacetate. This increases the concentrations of all of the citric acid cycle intermediates, which can either speed up the citric acid cycle , or be used as starting material for various biosynthetic pathway.

   f. The oxidative phase of the pentose-phosphate pathway: The purpose of this pathway is two-fold; it converts the 6-carbon glucose 6-phosphate to the 5-carbon ribulose 5-phoshate; the 5-carbon sugars are need or nucleic acid synthesis. The pathway also produced NADPH + H^+ which is used as a reducing agent in biosynthetic retie.

2. The light reactions of photosynthesis and the electron transport chain in plants share many common features.

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   a. Identify the components of each that fit the following descriptions:

	Electron Transport Chain	Photosynthesis
The initial donor of electrons	NADH + H^+	H_2O
The final acceptor of electrons	O_2	$NADP^+$
The mobile 1-electron carrier involved in the Q cycle	Cytochrome *c* (*cyt c*)	Plastocyanin (PC)
The mobile 2-electron carrier involved in the Q cycle	Ubiquinone (QH_2)	Plastoquinone (PQH_2)
The name of the complex that is site of the Q-cycle	Complex III	Cytochrome *bf* (*cyt bf*)
Cellular location of each in eukaryotes	Mitochondrial inner membrane	Chloroplast the thylakoid membrane

Reduction half-reaction	$E°'$ (V)
Acetyl CoA + CO_2 + $H^{\oplus}$ + $2e^{\ominus}$ → Pyruvate + CoA	−0.48
Ferredoxin (spinach). Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	−0.43
2 $H^{\oplus}$ + $2e^{\ominus}$ → H_2 (at pH 7.0)	−0.42
α-Ketoglutarate + CO_2 + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Isocitrate	−0.38
Lipoyl dehydrogenase (FAD) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Lipoyl dehydrogenase ($FADH_2$)	−0.34
$NADP^{\oplus}$ + $H^{\oplus}$ + $2e^{\ominus}$ → NADPH	−0.32
$NAD^{\oplus}$ + $H^{\oplus}$ + $2e^{\ominus}$ → NADH	−0.32
Ubiquinone (Q) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → QH_2	0.04
Cytochrome *c*, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.23
Plastocyanin, Cu^{2+} + $e^{\ominus}$ → Cu^{+}	0.37
$NO_3^{\ominus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → $NO_2^{\ominus}$ + H_2O	0.42
Photosystem I (P700)	0.43
Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.77
$\frac{1}{2}O_2$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → H_2O	0.82
Photosystem II (P680)	1.1

3. Photosystem II (P680) in plants receives two electrons from a water molecule and uses light energy (photons) to use these electrons to reduce an oxidized plastoquinone molecule (PQ).

   a. Write the *net reaction equation* for the reduction of one PQ by one H_2O.

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$$H_2O + PQ \longrightarrow 1/2\ O_2 + PQH_2$$

   b. Using the appropriate reduction potentials provided in the table above, calculate the minimum light energy required to drive this reaction under standard condition? You may assume that plastoquinone has the same reduction potential as ubiquinone

   $\Delta G°'$ = $\Delta G° = 151$ kJ/mol

$$PQ + 2e^- + H^+ \longrightarrow PQH_2 \qquad E^o = 0.04\ V$$
$$H_2O \longrightarrow 1/2\ O_2 + 2e^- + \qquad E^o = -0.82\ V$$
$$H_2O + PQ \longrightarrow 1/2\ O_2 + PQH_2 \qquad \Delta E^o = -0.78\ V$$

$$\Delta G^o = -n\mathscr{F}\,\Delta E^o$$
$$= -(2)\left(9.659\ x\ 10^4\ \frac{J}{mol \cdot V}\right)(-0.78\,V)$$
$$\Delta G^o = 151{,}000\ \frac{J}{mol} = 151\frac{kJ}{mol}$$

   c. The reduced plastoquinone (PQH_2) produced by PSII is subsequently used to reduce two plastocyanin molecules. Write the *net reaction equation* for this reaction.

$$PQH_2 + 2\ PC_{ox} \longrightarrow PQ + 2\ PC_{red}$$

   d. Using the appropriate reduction potentials provided in the table above, calculate the standard free energy change for this reaction?

   $\Delta G°'$ = $\Delta G° = -64$ kJ/mol

$$2\ PC_{ox} + 2e^- \longrightarrow 2\ PC_{red} \qquad E^o = 0.37\ V$$
$$PQH_2 \longrightarrow PQ + 2e^- + 2H^+ \qquad E^o = -0.04\ V$$
$$PQH_2 + 2\ PC_{ox} \longrightarrow PQ + 2\ PC_{red} \qquad \Delta E^o = 0.33\ V$$

$$\Delta G^o = -n\mathscr{F}\,\Delta E^o$$
$$= -(2)\left(9.659\ x\ 10^4\ \frac{J}{mol \cdot V}\right)(0.33\,V)$$
$$\Delta G^o = -64{,}00\ \frac{J}{mol} = -64\frac{kJ}{mol}$$

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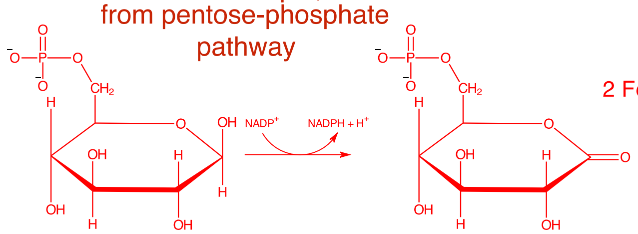
4. Describe the biochemical role played by NADPH + H^+?

NADPH + H^+ is a reducing agent used in biological oxidation/reduction reactions. Structurally, it is a dinucleotide containing the nicotinamide and adenine nucleotide bases. Compared with the closely related NADH + H^+ molecule, it has an additional phosphate group, which tags it to be used in anabolic, but not catabolic pathways.

a. Write a *balanced chemical reaction equation* for one example of a reaction in which NADPH + H^+ is produced. *Use structural formulas* for the intermediates involved.

For example, from pentose-phosphate pathway



D-glucose 6-phosphate → D-6-phosphoglucolactone

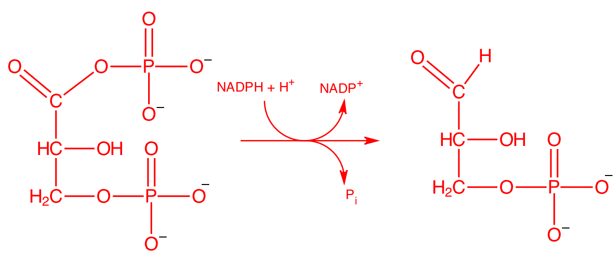
or from photosynthesis

$$2\ Fd_{red} + 2\ H^+ + NADP^+ \longrightarrow 2\ Fd_{ox} + NADPH + H^+$$

b. What metabolic pathway does your chosen reaction belong to?

Pentose-phosphate pathway or photosynthesis

c. Write a *balanced chemical reaction equation* for one example of a reaction which uses NADPH + H^+. *Use structural formulas* for the intermediates involved.



1,3 *bisphosphoglycerate* → *glyceraldehyde* 3*-phosphate*

d. What metabolic pathway does your chosen example belong to?

Light reactions of the Calvin Cycle

5. The citric acid cycle, along with the pyruvate dehydrogenase reaction, play a big role in the oxidation of the glucose to CO_2 and H_2O ($C_6H_{12}O_6 + 6\ O_2 \rightarrow 6CO_2 + 6\ H_2O$). In this net reaction the carbon atoms from the glucose are oxidized to CO_2 while the hydrogen atoms are oxidized to H_2O.

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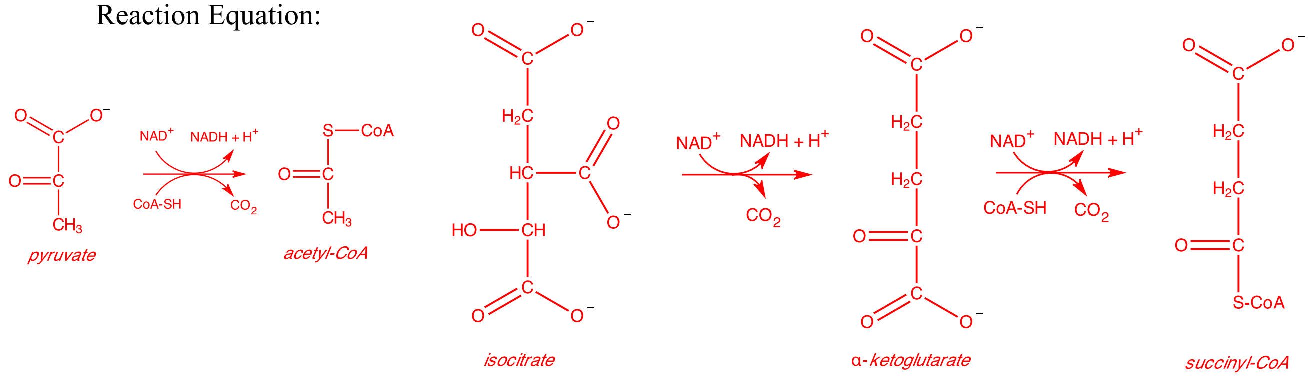
a. While the CO_2 molecules produced in the overall oxidation of glucose are released in the pyruvate dehydrogenase reaction, along with reactions in the citric acid cycle, molecular oxygen (O_2) is not used as the oxidizing agent in these reactions. What oxidizing agents are used instead in these reactions? NAD+ and Ubiquinone (Q)

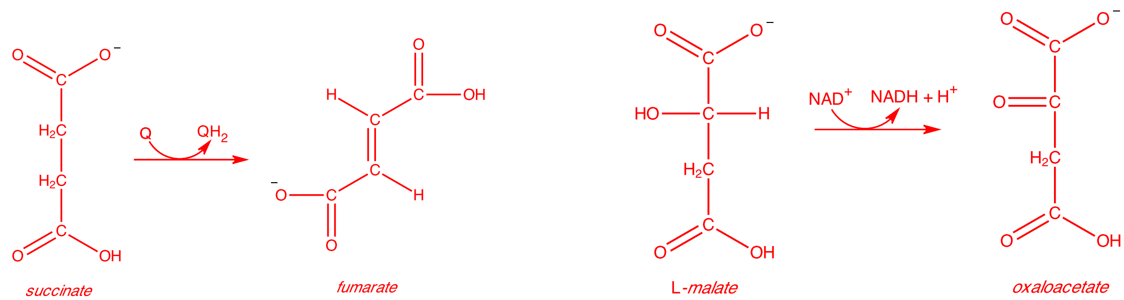
b. After theses oxidizing agents are reduced in the pyruvate dehydrogenase and citric acid cycle reactions, where are they reoxidized, and what oxidizing agent is used to reoxidize them?

The electron transport chain, where O_2 is the ultimate oxidizing agent

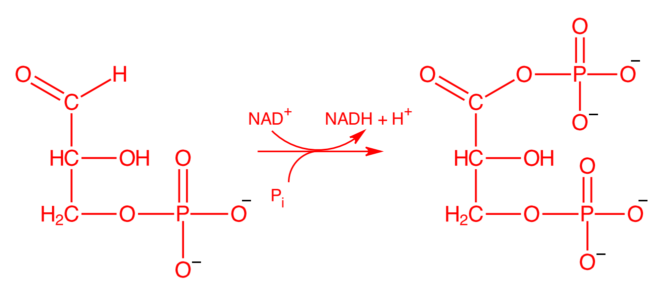
c. Pick one of the three reactions among pyruvate dehydrogenation and the reactions in the citric acid cycle in which both CO_2 is produced and an oxidation occurs, and *using structural formulas* for the intermediates, write a balanced chemical reaction equation for the reaction you have chosen. Also, label the intermediates and give the name of the enzyme involved.
Enzyme Name Pyruvate Dehydrogenase/Isocitrate Dehydrogenase/α-Ketoglutarte Dehydrogenase
Reaction Equation:



d. The citric acid cycle also contains two addition oxidation reactions, which are *not coupled* to the release of CO_2. *Using structural formulas* for the intermediates, write a balanced chemical reaction equation for one of these. Also, label the intermediates and give the name of the enzyme involved.
Enzyme Name succinate dehydrogenase or malate dehydrogenase
Reaction Equation:



e. While glycolysis contains more reaction steps than the pyruvate dehydrogenase reaction and citric acid cycle combined, only one of these is an oxidation reaction. *Using structural formulas* for the intermediates, write a balanced chemical reaction equation for this one reaction. Also, label the intermediates and give the name of the enzyme involved.
Enzyme Name glyceraldehyde 3-phosphate dehydrogenase
Reaction Equation:



f. In the absence of, or ability to use molecular oxygen, describe the two options that organisms have for reoxidizing the oxidizing agent that is used in glycolysis.

The two options are the fermenation pathways. Lactic acid fermentation is used by bacteria and mammals and uses the reduced NADH + H^+ to reduce the pyruvate to lactic acid. The second option is used by yeast, and first decarboxylates the the pyruvate to acetaldehyde and CO_2, then the reduced NADH + H^+ is used to reduce the acetaldehyde to ethanol.

6. Describe what the Cori cycle is

When human muscles are under strenuous activity and unable to receive adequate O_2 they use lactic acid fermentation to reoxidize the NADH + H^+ from glycolysis to NAD^+. The lactic acid is then transported through the blood to the liver, where it is reoxidized to pyruvate and used, *via* gluconeogenesis to synthesized glucose. The glucose is then shipped through the blood to the muscles where it can be used in glycolysis to produce ATP.

7. There are three reactions in glycolysis that are under allosteric regulation. Name two of these using their enzyme names and indicate at least one metabolite that regulates each allosterically. Also indicate the cellular condition that the regulation is responding to.

Enzyme Name	Allosteric Regulator	Activator or Inhibitor	Cellular Condition
Hexokinase	Glucose 6-phosphate	Inhibitor	Glucose 6-phosphate is not being used for glycolysis or the pentose-phosphate pathways and so is building up in the cell.
Phosphofructokinase I	ATP or Citrate	Inhibitor	This is the first committed step in glycolysis. Glycolysis is not needed for the regeneration of ATP or to generate biosynthetic precursors.