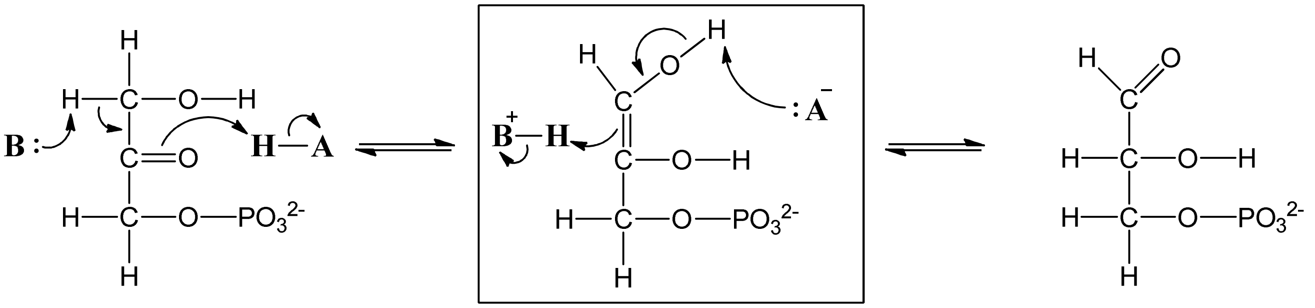
Chemistry and Biochemistry 153A, Spring 2011

Final Exam Answers

Note: For Page 2, points totaled 31 (instead of 33), so two points were added to the total blue sheet score

1. a. (5) C, E, I
   b. (3) B
2. (2) α-keto
3. a. (4) pyruvate DH complex, α-ketoglutarate DH complex
   b. (2) pyruvate decarboxylase
4. a. (1) incorrect – this statement would explain having one redox currency, but not multiple
   b. (1) correct
   c. (1) correct
   d. (1) incorrect – the different currencies tend to be used in one or the other (catabolic *or* anabolic)
   e. (1) correct
5. a. (2) F-1,6-BP → DHAP + GAP
   b. (5) To go in the forward direction, $\Delta G < 0$.
      Since $\Delta G = \Delta G'^{\circ} + RT\ln Q$,
      $\Delta G'^{\circ} + RT\ln Q < 0$, so $Q < e^{-\Delta G'^{\circ}/RT}$
      Also, $Q = \frac{[\text{DHAP}][\text{GAP}]}{[\text{F-1,6-BP}]} = \frac{x \cdot x}{x} = x$
      $x < e^{-(22.8\ \text{kJ/mol})/(0.00831\ \text{kJ/mol}\cdot\text{K})(310\ \text{K})}$
      $x < 1.4 \times 10^{-4}$ M
   c. (3) Coupling with the prior reaction, which is irreversible (highly exergonic). F-1,6-BP levels increase due to synthesis by PFK, and this pushes the aldolase reaction forward.
6. a. (2) catalyzes the rate-limiting step of glycogen breakdown
   b. (3) A, (B), D, E
   c. A. (1) decrease
      B. (1) decrease
      C. (1) decrease
      D. (1) increase
      E. (1) decrease
7. a. (1) False – the outer membrane has non-specific pores, so specific transporters are unnecessary
   b. (1) False – coenzyme A, not Q (also, it's the complex, not just pyruvate DH)
   c. (1) True
   d. (1) True
   e. (1) False – fermentation occurs in the cytosol
   f. (1) True
8. (7)



9. (5) Gluconeogenesis is not the reverse of glycolysis. Although both pathways share many enzymes, each has unique, highly exergonic (irreversible) steps that make the overall pathway favorable.
10. (3) b
11. (3) d
12. a. (3) 2 ATP eq, 2 NADH, 0 $FADH_2$
    b. (3) 6 ATP eq, 2 NADH, 0 $FADH_2$
    c. (3) 1 ATP eq, 3 NADH, 1 $FADH_2$
13. a. (2) False – each has a unique potential, due to unique positioning within the protein.
    b. (2) False – for example in fermentation, where NADH is oxidized by pyruvate or acetaldehyde (or another organic molecule), without the need for oxygen
    c. (2) False – Other FAD-containing proteins of the inner mitochondrial membrane transfer electrons to CoQ
    d. (2) False – only 1-electron transfers
    e. (2) False – although it produces citrate, it uses OAA, so there is no *net* synthesis of citric acid cycle intermediates
14. (1 point each) Possible answers:
    · Better resonance in products
    · Reduced charge repulsion in products
    · Ionization of product
    · More favored solvation of products
15. (3) FMN → [2Fe-2S] → [4Fe-4S] → CoQ → Cyt c_1 → Cyt a_3
16. (4) They link electron transfers from 2 electron donors (most biological molecules) to 1 electron acceptors (many metal-containing redox centers)
17. 3 drive a 120° rotation in ATP synthase, which releases 1 ATP; 1 brings P_i into the matrix

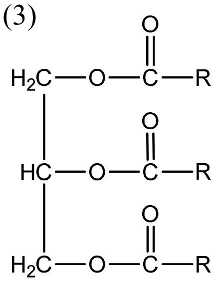
18. a. (3 points:)
    1 acetyl-CoA
    2 citrate
    3 isocitrate
    4 succinate
    5 malate
    6 oxaloacetate
  b. (5 points:)
    A lyase (or transferase)
    B lyase (isomerase also accepted)
    C lyase
    D lyase (or transferase)
    E oxidoreductase
  c. (3) A, B, E
  d. (4) A, D; they catalyze irreversible reactions

19. a. (2) 2 acetyl-CoA + 2 H_2O + NAD^+ → 2 CoA + succinate + NADH + 3 H^+
  b. (3) succinate → OAA via TCA cycle; 2 oxaloacetate → glucose + 2 CO_2 via gluconeogenesis
  c. (5) Methyl of AcCoA → C2 or C3 of succinate (either, b/c of symmetry) → C2 or C3 of OAA → C2 or C3 of PEP → C2 or C3 of GAP → C2 or phosphorylated carbon of DHAP → C1, 2, 5, or 6 of glucose

20. a. (3) Glyoxylate cycle: 4 AcCoA → 2 sucinate: 2 NADH
    TCA cycle: 2 succinate → 2 OAA: 2 $FADH_2$ + 2 NADH
    Gluconeogenesis: 2OAA → glucose: -2 ATP, -2 GTP, -2 NADH
    Total: -4 ATP (or eq), 2 NADH, 2 $FADH_2$
  b. (3) AcCoA → 2 CO2 via TCA cycle: 1 GTP, 3 NADH, 1 $FADH_2$
    Since 4 AcCoA are needed to make 1 glucose, multiply by 4:
    Total: 4 ATP (or eq), 12 NADH, 4 $FADH_2$
  c. (3) subtract b total from a total: -8 ATP, -10 NADH, -2 $FADH_2$
    NADH → 2.5 ATP; $FADH_2$ → 1.5 ATP
    Loss of 8 + (2.5)(10) + (1.5)(2) = 8 + 25 + 3 = 36 ATP
    Cell gives up 36 ATP to make 1 glucose

21. (2) True

22. a. (1) triacylglycerols (or triglycerides)
  b. (3)



  c. (3) B

23. (4) a, d, h

24. a. (2) L
  b. (2) L
  c. (2) P
  d. (4) L → higher affinity = higher K_a

$$K_a = \frac{k_a}{k_d} = \frac{k_{-3}}{k_3}$$

$$K_a(\mathrm{P}) = \frac{986{,}000\ \mathrm{M^{-1}s^{-1}}}{197\ \mathrm{s^{-1}}} = 5005\ \mathrm{M^{-1}}$$

$$K_a(\mathrm{L}) = \frac{145{,}000\ \mathrm{M^{-1}s^{-1}}}{12\ \mathrm{s^{-1}}} = 12{,}083\ \mathrm{M^{-1}}$$

  e. (2) P
  f. (4) P → catalytic efficiency measured by specificity constant, kcat/Km

$$\frac{k_{cat}}{K_m}(\mathrm{P}) = \frac{46\ \mathrm{s^{-1}}}{0.08\ \mathrm{mM}} = 575\ \mathrm{mM^{-1}s^{-1}}$$

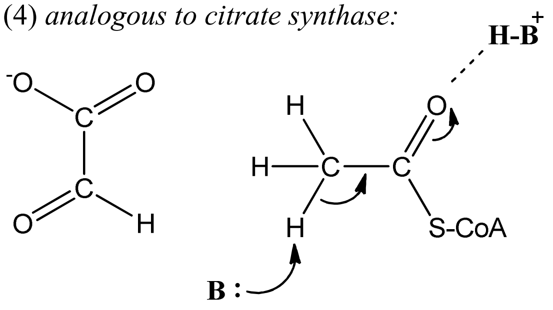
$$\frac{k_{cat}}{K_m}(\mathrm{L}) = \frac{10\ \mathrm{s^{-1}}}{0.03\ \mathrm{mM}} = 333\ \mathrm{mM^{-1}s^{-1}}$$

  g. (4) L. Since L has greater affinity for glyoxylate (from part d), it will be more affected; glyoxylate will spend more time bound, preventing substrate from binding (competitive inhibition).

25. (4) a, b, d, f

26. a. (4) A, B, E
  b. (4) They are flexible, adopting different conformations (in each unit of the crystal)
  c. (2) *possible answers included:* substrate analog, TS analog, product analog

27. a. (4) B, C, D, F, G
  b. (4) *analogous to citrate synthase:*



  c. (3) thioester hydrolysis (to remove CoA)

28. a. (4) HEPES. HEPES and glycylglycine have the closest pKa's to the desired pH. Since the pathway produces H^+, we want a buffer that is more deprotonated (pKa < pH) to absorb excess protons.
  b. (4) $pH = pK_a + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right)$

$$\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = 10^{pH-pK_a} = 10^{7.9-7.6} = 10^{0.3} = 2 = \frac{2}{1}$$

$$\frac{[\mathrm{HA}]}{[\mathrm{A^-}] + [\mathrm{HA}]} = \frac{1}{2+1} = \mathbf{\frac{1}{3}}$$