Quiz E

This quiz is open handout (w/any notes on them). Not open book.

Answer questions by selecting appropriate examples from the Standard Reduction Potentials handout and showing your work and/or explaining your reasoning.

1. Compare NADH to $FADH_2$ in terms of their ability to reduce an aldehyde to a primary alcohol under standard conditions. Which of these cofactors, if any, can carry out the reaction?

representative rxn

(1) acetaldehyde + $2H^+ + 2e^-$ ⟶ ethanol -0.197 V

(2) $FADH_2$ ⟶ FAD + $2H^+ + 2e^-$ 0.219 V

(3) NADH ⟶ $NAD^+ + H^+ + 2e^-$ 0.320 V

(2) + (1) and (3) + (1) both give a (+)ive $\Delta E'^o$ which means a (−)ive $\Delta G'^o$ so they both can carry out the reduction.

2. The conversion of acetate → acetaldehyde → ethanol represents a series of reductions. Is it harder to convert acetate → acetaldehyde or acetaldehyde → ethanol?

acetate → acetaldehyde has a more (−)ive E'^o so it is the harder step (a more (−)ive E'^o contributes to $\Delta E'^o$ in a way that makes it more (−)ive which means $\Delta G'^o$ is more (+)ive)

3. The reaction catalyzed by isocitrate dehydrogenase involves an oxidation followed by a decarboxylation (pg 213b). Show how one could compute $\Delta G'^o$ for the conversion of oxalosuccinate into α-ketoglutarate (in other words, what is $\Delta G'^o$ for the decarboxylation step, separate from the oxidation step?). In your answer, set up the calculation. Regardless of the outcome of the calculation (which you don't have to carry out), what would you *expect* for the sign of the result? Why?

losing CO_2 should be entropically strongly favored

Figure at $\Delta E'^o$ for the rxn on pg 213b:

(1) $Isocitrate^{3-}$ ⟶ α-ketoglutarate + $CO_2 + H^+ + 2e^-$ 0.38V

$2e^- + NAD^+ + H^+$ ⟶ NADH -0.320V

0.06V

This rxn (above) involves an oxidation of an α-hydroxy acid to an α-ketoacid and a decarboxylation. Find a representative (similar) oxidation-only step and compute $\Delta E'^o$ for it.

(2) $Malate^-$ ⟶ $oxaloacetate^- + 2H^+ + 2e^-$ 0.166V

$NAD^+ + 2e^- + H^+$ ⟶ NADH -0.320V

-0.154V

Now figure at a $\Delta\Delta E'^o$:

(oxidation + decarboxylation) − (oxidation only) = decarboxylation only

(1) − (2)

$0.06\text{V} - (-0.154\text{V}) = 0.214$ V

which is (+)ive so $\Delta G'^o$ will be (−)ive & rxn is spontaneous