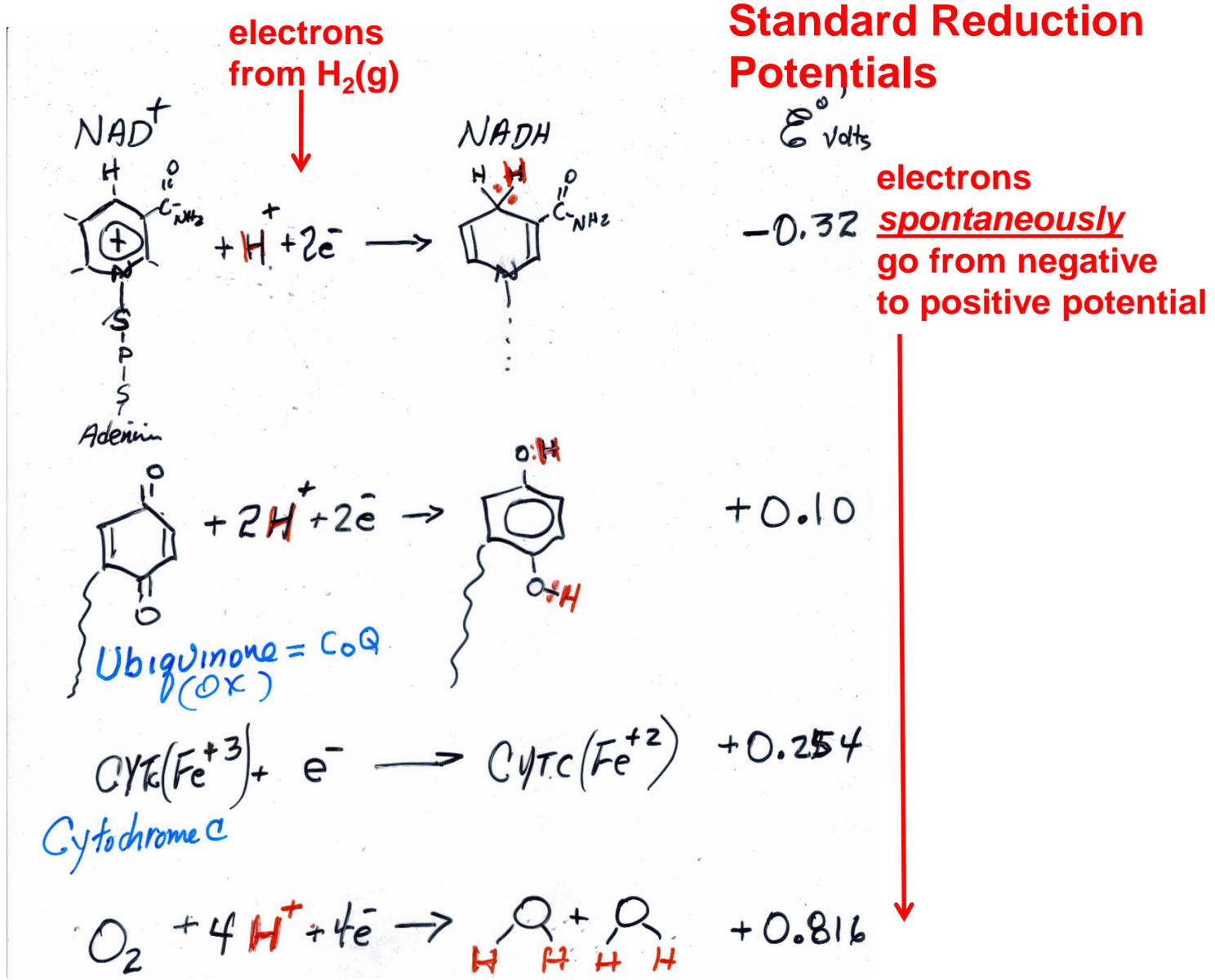


Chap. 5 pp 241-247  
Electrochemistry  
Will be on Exam 2  
(even though no homework)

Free energy from **spontaneous electron transfer** is used to make ATP by oxidative phosphorylation



max (reversible) Volts = J/coulomb is a measure of  $\Delta G$

$$\Delta G = -T \Delta S_{\text{univ}} + W_{\text{useful}} \quad \text{at const } T, P$$

for reversible process:  $-T \Delta S_{\text{univ}} = 0$  (as current  $\rightarrow 0$ )

$$\Delta G = W_{\text{useful, rev}} = -nF\xi = \text{coulombs} \times \text{volts} = \text{MAX useful work}$$

where  $n$  = moles of electrons and  $F = 96,485$  coulombs/mol

$$\xi = \text{equilibrium volts} = \text{J/coulomb}$$

$\xi = \Delta G/(-nF)$  *intensive variable ( does not depend on how much charge)*

$$\xi^0 = -\Delta G^0/(nF) = \text{STANDARD REDUCTION POTENTIAL}$$

$$\xi^0 = -\Delta G^0 / (nF) \text{ volts}$$

**Volt = J/coulomb, an intensive variable**

**(like temperature: does not depend on quantity)**

TABLE 7.1 Standard Reduction Electrode Potentials at 25°C (cont.)

Oxidant/Reductant	Electrode reaction	$\mathcal{E}^0(\text{V})$	$\mathcal{E}^0(\text{V})$ (pH 7)
$\text{Cu}^{2+}/\text{Cu}$	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.342	
$\text{I}_2/\text{I}^-$	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+0.535	
$\text{Ag}^+/\text{Ag}$	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+0.800	
$\text{O}_2/\text{H}_2\text{O}$	$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	+1.229	+0.815
$\text{NO}_3^-/\text{NO}_2^-$	$\text{NO}_3^- + 3\text{H}^+ + 2e^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O}$	+0.934	
$\text{Br}_2(\text{aq})/\text{Br}^-$	$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	+1.087	
$\text{Cl}_2(\text{g})/\text{Cl}^-$	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+1.358	
$\text{Mn}^{3+}/\text{Mn}^{2+}$	$\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$	+1.541	
$\text{F}_2(\text{g})/\text{F}^-$	$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	+2.866	

**TABLE 4.1 STANDARD REDUCTION POTENTIALS**

OXIDANT/REDUCTANT	ELECTRODE REACTION	$E^{\circ}$ Volts	$E^{\circ}'$
Na <sup>+</sup> /Na	Na <sup>+</sup> + e <sup>-</sup> → Na ↑ From 1/2 H <sub>2</sub> (g)	-2.7	-2.7
Zn <sup>2+</sup> /Zn	Zn <sup>2+</sup> + 2e <sup>-</sup> → Zn ↑ From H <sub>2</sub> (g)	-0.76	-0.76
H <sup>+</sup> /H <sub>2</sub> /Pt	2H <sup>+</sup> + 2e <sup>-</sup> → H <sub>2</sub> ↑ From H <sub>2</sub> (g)	0	-0.421
Cu <sup>2+</sup> /Cu	Cu <sup>2+</sup> + 2e <sup>-</sup> → Cu(s)	+0.34	+0.34
Ag <sup>+</sup> /Ag	Ag <sup>+</sup> + e <sup>-</sup> → Ag(s)	+0.8	+0.8
O <sub>2</sub> /H <sub>2</sub> O/Pt	O <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> → 2H <sub>2</sub> O	1.229	0.82
F <sub>2</sub> /F <sup>-</sup> /Pt	F <sub>2</sub> + 2e <sup>-</sup> → 2F <sup>-</sup> ↑ EASIEST TO REDUCE; BEST OXIDANT	2.87	2.87

Biological standard state (H<sup>+</sup> 1x10<sup>-7</sup>M)

Why is this 0?

All electrons from H<sub>2</sub>

Why are these more negative ??

(use LeChatelier)

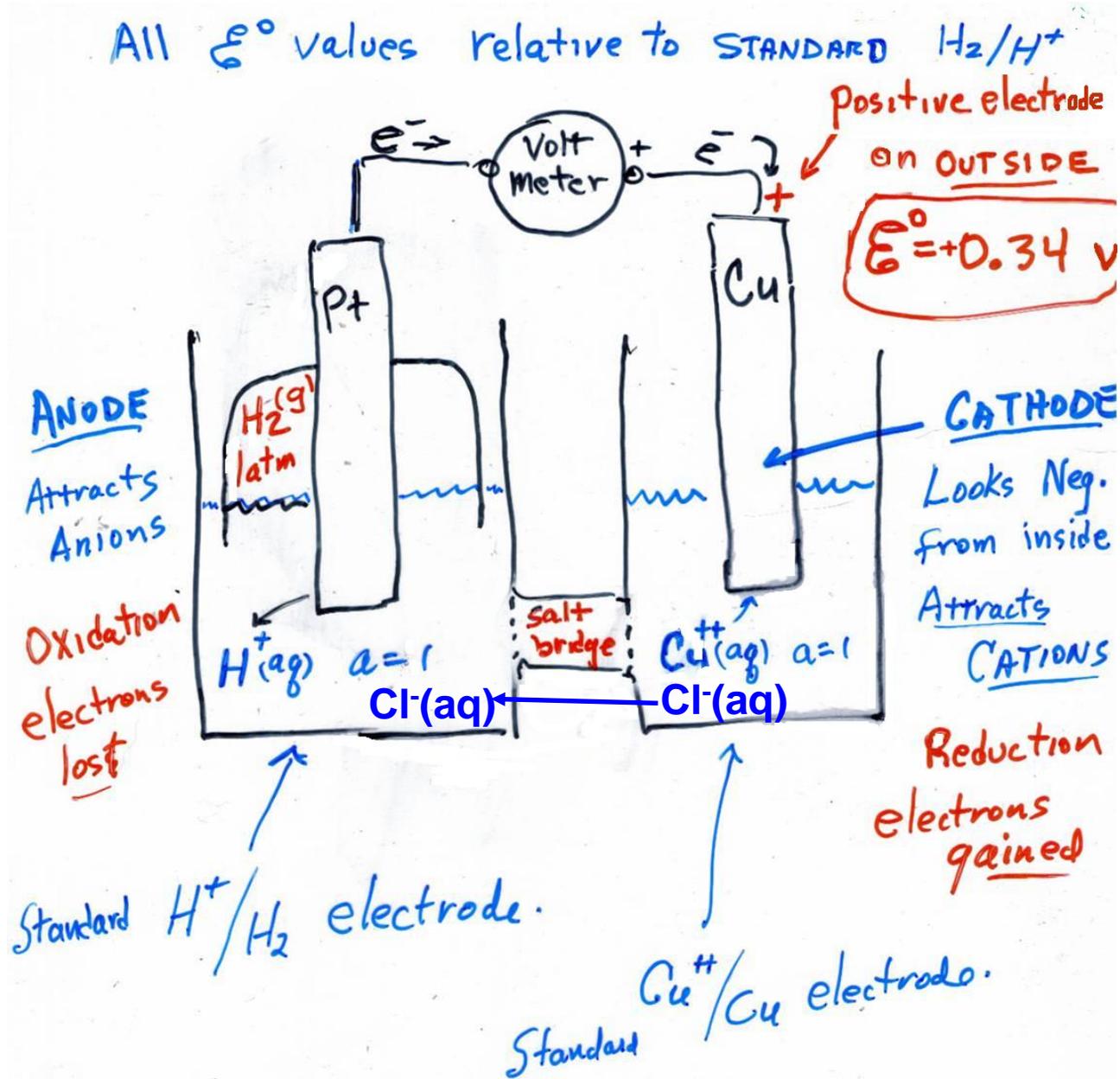
reactions less spontaneous at pH 7, if H<sup>+</sup> on left

Notice where Na metal silver, O<sub>2</sub> and F<sub>2</sub> are in table

Most positive potential means most spontaneous

# Actual chemical reactions for Standard Reduction Potentials:

electrons come from  $\text{H}_2(\text{g})$ :  $\text{Cu}^{++}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{Cu}(\text{s}) + 2\text{H}^+(\text{aq})$



## A previous Edition

### EXAMPLE 7.2

should be  $\text{NADP}^+/\text{NADPH}$

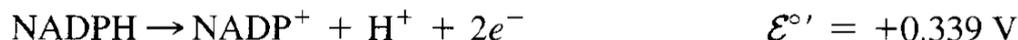
The enzyme glutathione reductase replenishes the cell's supply of glutathione (GSH), regenerating two molecules of GSH from a single molecule of oxidized glutathione (GSSG), using NADPH as a source of two reducing equivalents. Using the data in table 7.1 and a typical cellular  $\text{NADP}^+/\text{NADPH}$  ratio of 0.005, calculate the equilibrium cellular concentration of GSSG at pH 7 and 25°C, if the GSH concentration is 4 mM.

#### SOLUTION

The two half-reactions are:



(1) Reverse the second reaction and multiply the electrochemical potential by  $-1$ :



(2) The number of electrons is balanced.

(3) Add the reactions and the electrochemical potentials:



$$K = \frac{[\text{GSH}]_{\text{eq}}^2 [\text{NADPH}]_{\text{eq}}}{[\text{GSSG}]_{\text{eq}} [\text{NADP}^+]_{\text{eq}}} = \frac{(4 \times 10^{-3})^2}{0.005 [\text{GSSG}]_{\text{eq}}}$$

We do not include the  $\text{H}^+$  concentration, since the activity of  $\text{H}^+$  is defined as 1 at pH 7 in the biochemists' standard state.

Solving Eq. 7.13 gives us  $K = 2223$ , which in turn gives  $[\text{GSSG}] = 1.44 \times 10^{-7} \text{ M} = 0.144 \text{ } \mu\text{M}$ . Healthy cells keep GSSG concentrations very low!

## More recent printing (Corrected)

### EXAMPLE 7.2

The enzyme glutathione reductase replenishes the cell's supply of glutathione (GSH), regenerating two molecules of GSH from a single molecule of oxidized glutathione (GSSG), using NADPH as a source of two reducing equivalents. Using the data in table 7.1 and a typical cellular  $\text{NADP}^+/\text{NADPH}$  ratio of 0.005, calculate the equilibrium cellular concentration of GSSG at pH 7 and  $25^\circ\text{C}$ , if the GSH concentration is 4 mM.

#### SOLUTION

The two half-reactions are:



(1) Reverse the second reaction and multiply the electrochemical potential by  $-1$ :



(2) The number of electrons is balanced. ← True but irrelevant at this stage!

(3) Add the reactions and the electrochemical potentials:



$$K = \frac{[\text{GSH}]_{\text{eq}}^2 [\text{NADP}^+]_{\text{eq}}}{[\text{GSSG}]_{\text{eq}} [\text{NADPH}]_{\text{eq}}} = \frac{0.005(4 \times 10^{-3})^2}{[\text{GSSG}]_{\text{eq}}}$$

$$\begin{aligned} \Delta G^{\circ'} &= -nF \xi^{\circ'} \\ &= -2 * 96485.33 * 0.099 \\ &= -19104.1 \text{ J/mol} \end{aligned}$$

We do not include the  $\text{H}^+$  concentration, since the activity of  $\text{H}^+$  is defined as 1 at pH 7 in the biochemists' standard state.

only true at pH7; Do NOT do this!

Solving Eq. 7.13 gives us  $K = 2223$ , which in turn gives  $[\text{GSSG}] = 3.6 \times 10^{-11}$  M = 36 pM. Healthy cells keep GSSG concentrations very low!

They used  
6 sig. figures!

$$K = 10^{(-19104.1 / (2.30259 * 298.15 * 8.31446))} = 2222.73 = 2223$$

# Read the following critique of this example CAREFULLY

## EXAMPLE 7.2

The enzyme glutathione reductase replenishes the cell's supply of glutathione (GSH), regenerating two molecules of GSH from a single molecule of oxidized glutathione (GSSG), using NADPH as a source of two reducing equivalents. Using the data in table 7.1 and a typical cellular  $\text{NADP}^+/\text{NADPH}$  ratio of 0.005, calculate the equilibrium cellular concentration of GSSG at pH 7 and  $25^\circ\text{C}$ , if the GSH concentration is 4 mM.

### SOLUTION

The two half-reactions are:



(1) Reverse the second reaction and multiply the electrochemical potential by  $-1$ :



(2) The number of electrons is balanced. **non sequitur**

(3) Add the reactions and the electrochemical potentials:



$$K = \frac{[\text{GSH}]_{\text{eq}}^2 [\text{NADP}^+]_{\text{eq}}}{[\text{GSSG}]_{\text{eq}} [\text{NADPH}]_{\text{eq}}} = \frac{0.005(4 \times 10^{-3})^2}{[\text{GSSG}]_{\text{eq}}}$$

We do not include the  $\text{H}^+$  concentration, since the activity of  $\text{H}^+$  is defined as 1 at pH 7 in the biochemists' standard state.

Solving Eq. 7.13 gives us  $K = 2223$ , which in turn gives  $[\text{GSSG}] = 3.6 \times 10^{-11}\text{ M} = 36\text{ pM}$ . Healthy cells keep GSSG concentrations very low!

## Critique:

The *problem with this example* is that it gives the *impression* that to find  $\xi^{\circ'}$  requires balancing the equation (which includes balancing the electrons).

You do NOT need to have balanced electrons to find  $\xi^{\circ'}$  for the reaction. (That's the beauty of using  $\xi^{\circ'}$  !

Here is a better way to say it:

To make the two half reactions *eventually* add to the desired equation, one of them must be reversed.

(1) Reverse the sign on  $\xi^{\circ'}$  for the reaction that is reversed and **add** the two  $\xi^{\circ'}$  values. In other words, the reaction  $\xi^{\circ'}$  is given by:  $\xi^{\circ'} = \xi^{\circ'}_{\text{NOTreversed}} - \xi^{\circ'}_{\text{reversed}}$  i.e., **subtract** the reversed one from the NOT-reversed one.

No balancing needed because  $\xi^{\circ'}$  is **INTENSIVE**.

However, I recommend this: (which is **EXACTLY** the **SAME**)

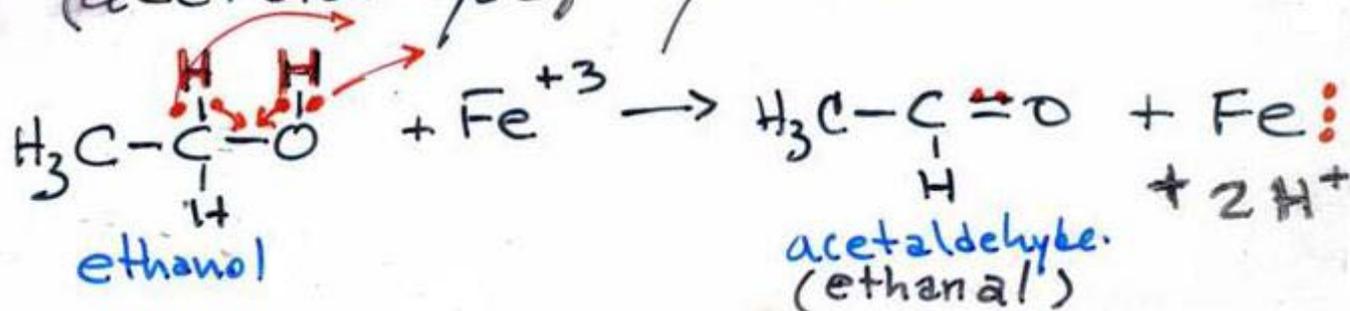
Identify where the electrons are initially (NADPH) and finally (GSH). The reaction  $\xi^{\circ'}$  is given by:

$$\begin{aligned} \xi^{\circ'} &= \xi^{\circ'}_{\text{Final}} - \xi^{\circ'}_{\text{Initial}} \\ &= -0.240 - (-0.339) = +0.099 \end{aligned}$$

(2) Balancing is a separate issue: If the two half reactions have different numbers of electrons, multiply the two reactions by different numbers so that the electrons cancel **and** so that the moles of one of the reactants is **what you want**, and **then** add the reactions. **Make sure the electrons cancel.**

EXAMPLE: Oxidation of ethanol to ethanal (acetaldehyde) by  $Fe^{+3}$

NOT →  
BALANCED



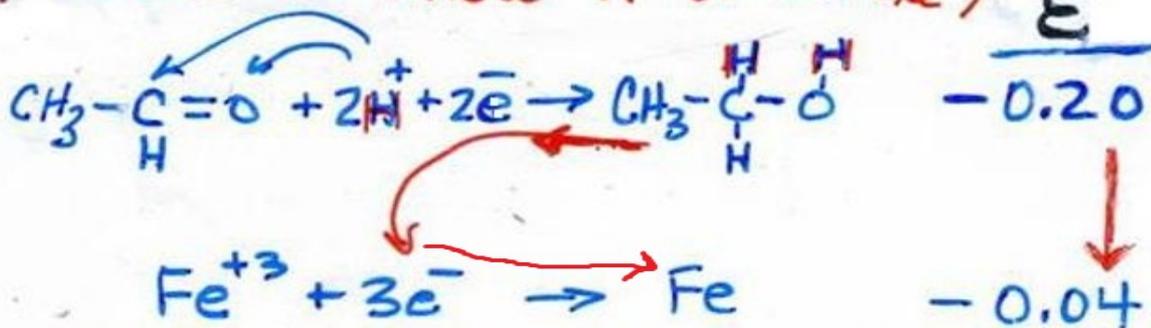
(a) What is  $\epsilon^{\circ}$  for this reaction as written?

Because intensive (Don't need to know n or balance)

From Table: 4.1

ethanal / ethanol

$Fe^{+3}/Fe$



**Remember: Watch the electrons as the reaction is written**

Note that the electrons are on the **R**educed species  
ALWAYS on the **RIGHT** in **R**eduction tables

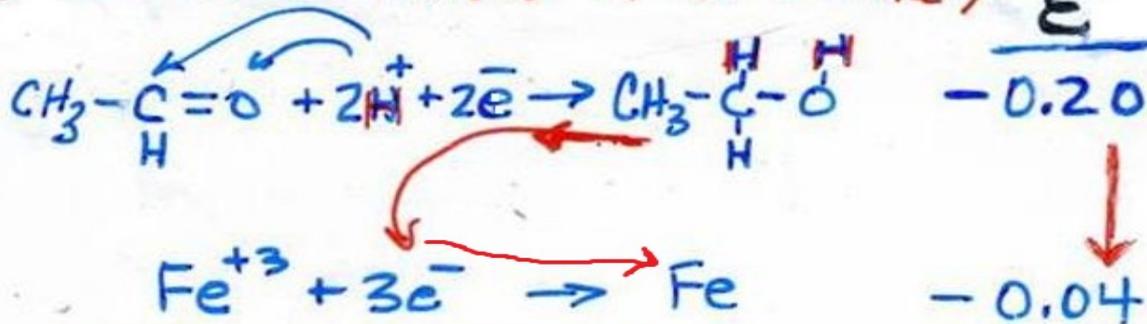
(a) What is  $\epsilon^{o'}$  for this reaction as written?

Because intensive (Don't need to know n or balance)  $\epsilon^{o'}$

From Table: 4.1

ethanal / ethanol

$Fe^{+3}/Fe$



Note that the electrons are on the **R**educed species ALWAYS on the **R**IGHT in **R**eduction tables, so take the **final – initial** (as always)

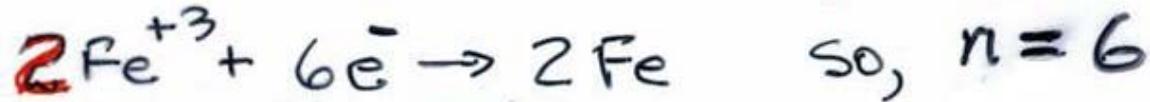
$$\boxed{\epsilon^{o'} = -0.04 - (-0.20) = +0.16}$$

Take the DIFFERENCE between where electrons end up and where they start.

$$\begin{aligned}
 \epsilon^{o'}_{\text{final}} - \epsilon^{o'}_{\text{start}} &= \epsilon^{o'}_{Fe} - \epsilon^{o'}_{\text{ethanol}} \\
 &= -0.04 - (-0.20)
 \end{aligned}$$

Because EXTENSIVE

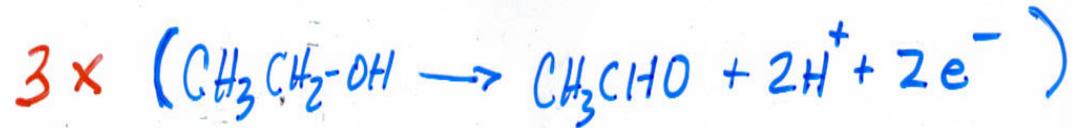
(b) Find  $\Delta G^{\circ}$  Do NEED TO BALANCE (FIND  $n$ )  
For 2 moles Fe produced. (arbitrary choice)



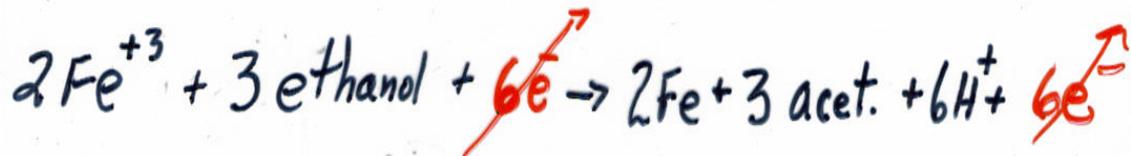
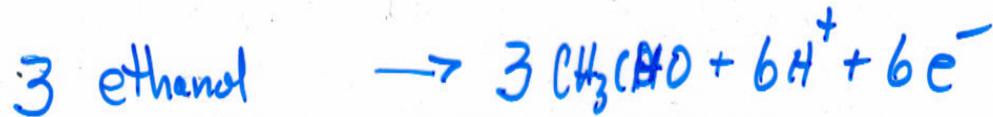
$$\begin{aligned}\Delta G^{\circ} &= -nFE^{\circ} = -6 \times 96,500 \times (+0.16) \\ &= -93,200 \frac{\text{J}}{\text{mol}} = -93.2 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

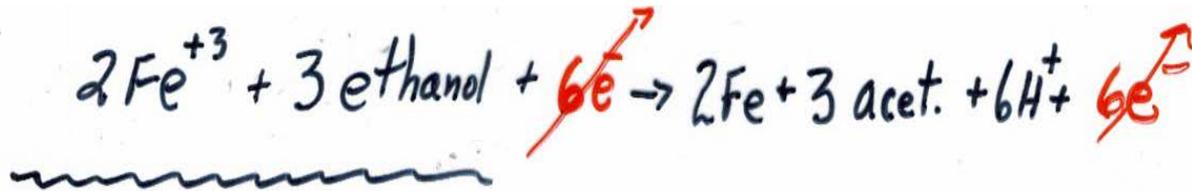
(C) BALANCED EQUATION

How MANY MOLES ETHANOL?

Need to accept  $6\text{e}^-$  ( $n=6$ )

So Multiply by 3

(d) What is  $\xi^0$ ? $\xi^0$  NOT  $\xi^0$



(d) What is  $\xi^0$ ? we already have  $\xi^{0'}$

First, *qualitatively* by Lechatelier,  
will  $\xi^0$  be **more positive** or more **negative** than  $\xi^{0'}$ ?

Will shift **LEFT**;  $\xi^0$  is 1 molar  $\text{H}^+$ ; less spontaneous  
so **more negative** than  $\xi^{0'}$ ; About how much?

about  $0.0592 \times 7 \times 6 = \text{about } -0.06 \times 42 = -0.24$  more neg

**Where did that come from???**

What equation tells us the concentration dependence of  $\xi$ ?

The Nernst equation tells us the concentration dependence of  $\xi$

# NERNST EQUATION

Begin with the familiar  $\Delta G = \Delta G^\circ + RT \ln Q$

Divide by Coulombs:  $-nF$

Nernst: 
$$\frac{\Delta G}{-nF} = \frac{\Delta G^\circ}{-nF} + \frac{RT \ln Q}{-nF}$$

$$E = E^\circ - \frac{RT \ln Q}{nF}$$

Use log<sub>10</sub> and 298K

This is 5700/96485

$$E = E^\circ - \frac{0.05916}{n} \log Q$$

For every power of 10 that Q increases  
E DECREASES 0.0592 Volts

i.e. Reaction gets less spontaneous

## EXAMPLE PROBLEM part (d)

$$E^{\circ} = E^{\circ'} + \frac{0.0592}{n} \log \frac{Q^{\circ}}{Q^{\circ'}}$$

← [H<sup>+</sup>] = 1 M  
← [H<sup>+</sup>] = 10<sup>-7</sup> M

$$E^{\circ} = E^{\circ'} + \frac{0.0592}{6} \log \left[ \frac{X_{Fe}^2 [acet]^3 [H^+]^6}{[Fe^{3+}]^2 [eth]^3} \right]$$
$$\left[ \frac{(1)^2 (1)^3 (10^{-7})^6}{(1)^2 (1)^3} \right]$$

$$E^{\circ} = 0.161 - \frac{0.0592}{6} \log \frac{1^2 1^3 1^6}{1^2 1^3}$$
$$\frac{1^2 1^3 10^{-42}}{1^2 1^3}$$

$$E^{\circ} = 0.161 - \frac{0.0592}{6} \cdot 42$$

$$E^{\circ} = 0.161 - 0.41 = \boxed{-0.25 \text{ volts}}$$

MUCH LESS SPONTANEOUS!

## EXAMPLE PROBLEM part (d)

$$\xi = \xi^{\circ'} + \frac{0.0592}{n} \log \frac{Q}{Q^{\circ'}} \quad \begin{array}{l} \leftarrow [H^+] = 10^{-5} \text{ M} \\ \leftarrow [H^+] = 10^{-7} \text{ M} \end{array}$$

$$\xi = \xi^{\circ'} + \frac{0.0592}{6} \log \left[ \frac{X_{\text{Fe}}^2 [\text{acet}]^3 10^{-5}}{[\text{Fe}^{3+}]^2 [\text{eth}]^3} \right]$$
$$\left[ \frac{(1)^2 (1)^3 (10^{-7})^6}{(1)^2 (1)^3} \right]$$

$$\xi^{\circ} = 0.161 - \frac{0.0592}{6} \log \frac{1^2 1^3 10^{-30}}{1^2 1^3}$$
$$\frac{1^2 1^3 10^{-42}}{1^2 1^3}$$

$$\begin{aligned} \xi &= 0.161 - \frac{0.0592}{6} 12 \\ &= 0.161 - 0.1084 = 0.0526 \end{aligned}$$

Only a little less spontaneous