TABLE 4.1 STANDARD REDUCTION POTENTIALS

OXIDANT/REDUCTANT	ELECTRODE REACTION	$\mathcal{E}^\circ$ Volts	$\mathcal{E}^{\circ\prime}$
Na^+/Na	$Na^+ + e^- \rightarrow Na$ ↑ From $\frac{1}{2}H_{2(g)}$	−2.7	−2.7
Zn^{+2}/Zn	$Zn^{+2} + 2e^- \rightarrow Zn$ ↑ From $H_{2(g)}$	−0.76	−0.76
$H^+/H_2/Pt$	$2H^+ + 2e^- \rightarrow H_2$ ↑ From $H_{2(g)}$	0 ↑	−0.421
Cu^{++}/Cu	$Cu^{++} + 2e^- \rightarrow Cu_{(s)}$	+0.34	+0.34
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag_{(s)}$	+0.8	+0.8
$O_2/H_2O/Pt$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229	0.82
$F_2/F^-/Pt$	$F_2 + 2e^- \rightarrow 2F^-$	2.87	2.87

↑EASIEST TO REDUCE ; BEST OXIDANT

Biological standard state (H^+ 1×10^{-7}M)

Why is this 0?

All electrons from H_2

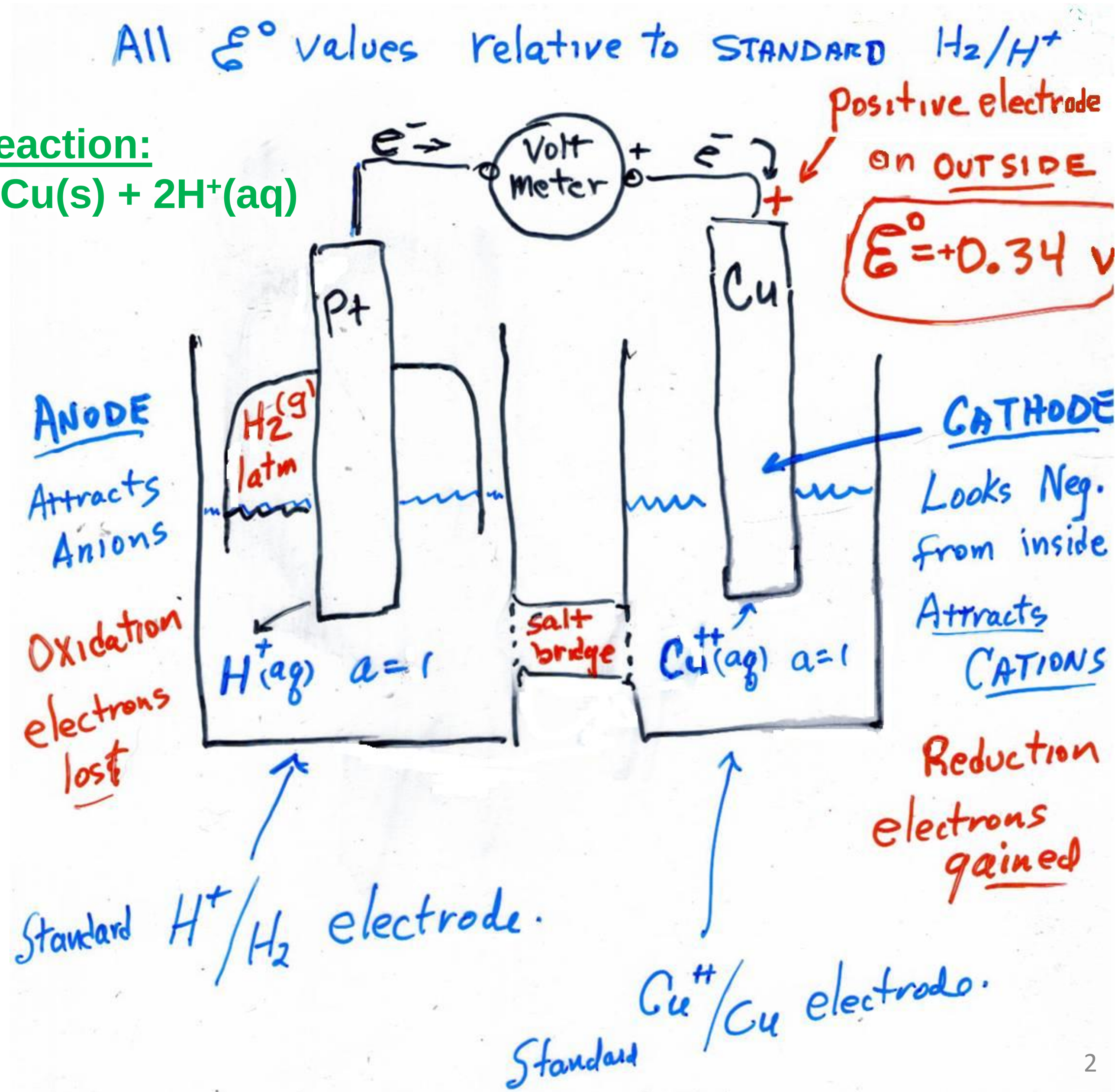
Why are these more negative ??
(use LeChatelier)

reactions less spontaneous at pH 7, if H^+ on left

Notice where **Na metal silver**, **O_2** and **F_2** are in table

Actual chemical reaction:

$Cu^{++}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$



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

NOT BALANCED →

$$H_3C-\underset{H}{\overset{H}{C}}-\overset{H}{O} + Fe^{+3} \longrightarrow H_3C-\underset{H}{C}=O + Fe + 2H^+$$

ethanol — acetaldehyde (ethanal)

(a) What is $\mathcal{E}^{0\prime}$ for this reaction as written?

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

From Table: 4.1

		$\mathcal{E}^{0\prime}$
ethanal / ethanol	$CH_3-\underset{H}{C}=O + 2H^+ + 2e^- \rightarrow CH_3-\underset{H}{\overset{H}{C}}-\overset{H}{O}$	-0.20
Fe^{+3}/Fe	$Fe^{+3} + 3e^- \rightarrow Fe$	-0.04

Remember: Watch the electrons as the reaction is <u>written</u>

Note that the electrons are on the **R**educed species

ALWAYS on the **RIGHT** in **R**eduction tables

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

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

$$\mathcal{E}^{o'}_{final} - \mathcal{E}^{o'}_{start} = \mathcal{E}^{o'}_{Fe} - \mathcal{E}^{o'}_{ethanol}$$

$$= -0.04 - (-0.20)$$

should be $NADP^+$/NADH

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 $\boxed{NADP/NADPH^+}$ 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:

$$GSSG + 2H^+ + 2e^- \rightarrow 2\,GSH \qquad \mathcal{E}^{\circ\prime} = -0.240\ V$$

$$NADP^+ + H^+ + 2e^- \rightarrow NADPH \qquad \mathcal{E}^{\circ\prime} = -0.339\ V$$

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

$$NADPH \rightarrow NADP^+ + H^+ + 2e^- \qquad \mathcal{E}^{\circ\prime} = +0.339\ V$$

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

(3) Add the reactions and the electrochemical potentials:

$$GSSG + H^+ + NADPH \rightarrow 2\,GSH + NADP^+ \qquad \mathcal{E}^{\circ\prime} = +0.099\ V$$

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

We do not include the H^+ concentration, since the activity of H^+ is defined as 1 at pH 7 in the biochemists' standard state. only true at pH7; a poor way to think

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

Read the following critique of this example <u>CAREFULLY</u>

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Critique:

The ***problem with this example*** is that it gives the ***<u>impression</u>*** that to find $\mathcal{E}^{0\prime}$ requires balancing the equation (which includes balancing the electrons).

<u>You do NOT need to have balanced electrons to find $\mathcal{E}^{0\prime}$ for the reaction. (That's the beauty of using $\mathcal{E}^{0\prime}$!</u>

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 $\mathcal{E}^{0\prime}$ for the reaction that is reversed and ***add*** the two $\mathcal{E}^{0\prime}$ values. In other words, the reaction $\mathcal{E}^{0\prime}$ is given by: $\mathcal{E}^{0\prime} = \mathcal{E}^{0\prime}_{\mathbf{NOTreversed}} - \mathcal{E}^{0\prime}_{\mathbf{reversed}}$

i.e., **subtract** the reversed one from the NOT-reversed one.

<u>No balancing needed</u> because $\mathcal{E}^{0\prime}$ is **<u>INTENSIVE.</u>**

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

Identify where the electrons are initially (NADPH) and finally (GSH). The reaction $\mathcal{E}^{0\prime}$ is given by:

$$\mathcal{E}^{0\prime} = \mathcal{E}^{0\prime}_{\mathbf{Final}} - \mathcal{E}^{0\prime}_{\mathbf{Initial}}$$

$$= -0.240 - (-0.339) = +0.099$$

(2) **<u>Balancing is a separate issue:</u>** 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**.

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

$$2Fe^{+3} + 6e^- \rightarrow 2Fe \quad \text{so, } n = 6$$

$$\Delta G^{o\prime} = -nF\mathcal{E}^{o\prime} = -6 \times 96{,}500 \times (+0.16)$$

$$= -93{,}200 \frac{J}{mol} = -93.2 \frac{kJ}{mol}$$

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(C) BALANCED EQUATION

HOW MANY MOLES ETHANOL ?

$3\times(CH_3CH_2\text{-}OH \longrightarrow CH_3CHO + 2H^+ + 2e^-)$

Need to accept $6\bar{e}$ $(n=6)$

So Multiply by 3

$$2Fe^{+3} + 6\bar{e} \longrightarrow 2Fe_{(s)}$$

$$3\ \text{ethanol} \longrightarrow 3\,CH_3CHO + 6H^+ + 6e^-$$

$$2Fe^{+3} + 3\,\text{ethanol} + \cancel{6\bar{e}} \rightarrow 2Fe + 3\ \text{acet.} + 6H^+ + \cancel{6\bar{e}}$$

(d) What is $\mathcal{E}^\circ$?