Standard Reduction Potentials

Cell	E^o / V vs. NHE
NHE // Cd^{2+} / Cd $Cd^{2+} + H_2 \leftrightharpoons Cd + 2H^+$	-0.4025 ($\Delta G^o > 0$)
NHE // Ag^+ / Ag $2Ag^+ + H_2 \leftrightharpoons 2Ag + 2H^+$	0.7991 ($\Delta G^o < 0$)
NHE // Li^+ / Li $2Li^+ + H_2 \leftrightharpoons 2Li + 2H^+$ $\Uparrow$ E right side vs. left side	-3.045 ($\Delta G^o > 0$)

Under standard conditions,

- Cd is a stronger reductant than H_2
- H_2 is a stronger reductant than Ag
- Li is a stronger reductant than H_2
- Li is a stronger reductant than Ag
- Ag^+ is a stronger oxidant than Li^+

(-)

e- energy

(+)

1/2 reaction	E^o / V vs. NHE
$Li^+ + e^- \leftrightharpoons Li$	-3.045
$Cd^{2+} + 2e^- \leftrightharpoons Cd$	-0.4025
$Ag^+ + e^- \leftrightharpoons Ag$	0.7991
$O + ne^- \leftrightharpoons R$	

R more reducing

O more oxidizing

Question.

1/2 reaction	E^o / V vs. NHE
$\mathrm{RuL_3^{2+} + e^- \leftrightharpoons RuL_3^+}$	-1.30
$\mathrm{TCNQ^{\cdot-} + e^- \leftrightharpoons TCNQ^{2-}}$	-0.29

Which is the stronger reductant, $\mathrm{RuL_3^{2+}}$ or $\mathrm{TCNQ^{\cdot-}}$?

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Which is the stronger reductant, RuL_3^{2+} or $TCNQ^{\cdot-}$?

Can't answer. These are the O forms acting as oxidants in the 1/2 reaction.

1/2 reaction	E^o / V vs. NHE
$RuL_3^{3+} + e^- \leftrightharpoons RuL_3^{2+}$	1.32
$TCNQ + e^- \leftrightharpoons TCNQ^{\cdot-}$	0.13

$TCNQ^{\cdot-}$ is the stronger reductant.

What is E^o good for?

1. Can rank oxidizing/reducing power.
2. More quantitatively can calculate ΔG for redox reactions.

What is ΔG for the following reaction?

$$\mathrm{Cd^{2+} + 2Ag \leftrightharpoons Cd + 2Ag^+}$$

$$\begin{array}{r} \mathrm{Cd^{2+} + 2e^- \leftrightharpoons Cd} \\ \mathrm{-2(Ag^+ + e^- \leftrightharpoons Ag)} \\ \hline \mathrm{Cd^{2+} + 2Ag \leftrightharpoons Cd + 2Ag^+} \end{array}$$

$$E^o_{cell} = E^o(Cd^{2+}/Cd) - 2E^o(Ag^+/Ag)$$
$$E^o_{cell} = -0.4 - 2(0.8) = -2.0V$$

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WRONG!

$$\begin{array}{r} \mathrm{Cd^{2+}} + 2\mathrm{e^-} \leftrightharpoons \mathrm{Cd} \\ -2[\mathrm{Ag^+} + \mathrm{e^-} \leftrightharpoons \mathrm{Ag}] \\ \hline \mathrm{Cd^{2+}} + 2\mathrm{Ag} \leftrightharpoons \mathrm{Cd} + 2\mathrm{Ag^+} \end{array} \qquad \begin{array}{r} \Delta G^o = -2F(-0.4) = 0.8F \\ \Delta G^o = -2[-F(0.8)] = 1.6F \\ \hline \Delta G^o = 0.8F + 1.6F = 2.4F \end{array}$$

For overall 2 electron reaction:

$$E^o = -\frac{\Delta G^o}{nF} = -\frac{2.4F}{2F} = -1.2V$$

$$\mathrm{Ag/Ag^+//Cd^{2+}/Cd}$$

$$E_{cell} = E_{right} - E_{left}$$

$$E_{cell} = E_{cathode} - E_{anode}$$

regardless of n for each 1/2 reaction and overall reaction. Again, work in terms of ΔG and you won't mess this up.

Nernst Equation

Above we dealt with electrochemical cells and redox reactions with all reactants and products at standard states (unit activity).

For $O + ne^- \leftrightharpoons R$

$$E = E^o - \frac{RT}{nF} ln \frac{a_R}{a_O}$$

(increase activity of R more reducting, more negative)

If $a_R = a_O$, then $E = E^o$, suggests method for measuring E^o

1. Start with O or R
2. Drive electrochemistry to convert O to R or R to O
3. Identify signature of data that tells you when $a_R = a_O$ then $E = E_o$

Note: Book defines $E^{o'}$ as E when [O] = [R] since activities hard to measure. We will use E^o in place of $E^{o'}$

Oxidation vs. Reduction Potentials

Consider a determination of E^o where you begin with all R.

- To perform the measurement you proceed by oxidizing R.
- This leads many to call the measured E^o an oxidation potential. IT IS NOT!

Reduction potential	Oxidation potential
NHE // $O + ne^- \leftrightharpoons R$ / Pt	NHE // $O + ne^- \leftrightharpoons R$ / Pt
$\Uparrow$	$\Uparrow$
Measure right side vs. left.	Measure left side vs. right.

- The standard reduction potential characterizes the free energy for oxidation and the reduction.
- Oxidation vs. reduction potential is a sign convention in regards to the measurement of potentials.