Redox Potential Calculations Using NWChem

Example Calculation: Redox Potential for $[\mathbf{FeCp_2}]^{0/+}$

As an example of how to do this part of the assignment, we will compute the redox potential

$$\Delta G(\mathrm{aq}) = -\mathrm{n\ F\ E}_m^{(0/+)}$$

from a calculation for the Gibbs free energy change, $\Delta G_{\mathrm{ox}}(\mathrm{sol})$, for the reaction

$$[\mathrm{Fe(II)Cp_2}]^0(\mathrm{solv}) \longrightarrow [\mathrm{Fe(III)Cp_2}]^+(\mathrm{solv}) + e^-$$

The Born-Haber Cycle

$$\begin{tikzcd}
{[\mathrm{FeCp_2}]^0(\mathrm{g})} \arrow[r, "\Delta G_{\mathrm{ox}}(\mathrm{g})"] \arrow[d, "\Delta G_{\mathrm{solv}}(\mathrm{Fe(II)})"'] & {[\mathrm{FeCp_2}]^+(\mathrm{g}) + e^-} \arrow[d, "\Delta G_{\mathrm{solv}}(\mathrm{Fe(III)})"] \\
{[\mathrm{FeCp_2}]^0(\mathrm{solv})} \arrow[r, "\Delta G_{\mathrm{ox}}(\mathrm{solv})"'] & {[\mathrm{FeCp_2}]^+(\mathrm{solv}) + e^-}
\end{tikzcd}$$

Using the Born-Haber Cycle, we obtain:

$$\Delta G_{\mathrm{ox}}(\mathrm{solv}) = \Delta G_{\mathrm{ox}}(\mathrm{g}) + \Delta G_{\mathrm{solv}}(\mathrm{III}) - \Delta G_{\mathrm{solv}}(\mathrm{II})$$

where

$$\Delta G_{\mathrm{solv}}(\mathrm{II}) = \mathrm{E}_{\mathrm{solv}}^{\mathrm{scf}}(\mathrm{II}) - \mathrm{E}_{\mathrm{g}}^{\mathrm{scf}}(\mathrm{II})$$

$$\Delta G_{\mathrm{solv}}(\mathrm{III}) = \mathrm{E}_{\mathrm{solv}}^{\mathrm{scf}}(\mathrm{III}) - \mathrm{E}_{\mathrm{g}}^{\mathrm{scf}}(\mathrm{III})$$

$$\Delta G_{\mathrm{ox}}(\mathrm{g}) = \left(\mathrm{E}_{\mathrm{g}}^{\mathrm{scf}}(\mathrm{III}) + \mathrm{G}_{\mathrm{Correction}}(\mathrm{g,\ III})\right) - \left(\mathrm{E}_{\mathrm{g}}^{\mathrm{scf}}(\mathrm{II}) + \mathrm{G}_{\mathrm{Correction}}(\mathrm{g,\ II})\right)$$

The correction for the free energy $\mathrm{G}_{\mathrm{Correction}}$ because of temperature is given by $G^0 = H^0 - TS^0$ where H^0 is the molecular enthalpy obtained from the minimum energy structure, and S^0 is the molecular entropy obtained from a frequency calculation.

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Tabulated Energies (au) from Calculations			
$[\mathrm{FeCp_2}]^0$		$[\mathrm{FeCp_2}]^+$	
$\mathrm{E}_{\mathrm{g}}^{\mathrm{scf}}(\mathrm{Fe(II)})$	-510.439067386	$\mathrm{E}_{\mathrm{g}}^{\mathrm{scf}}(\mathrm{Fe(III)})$	-510.170289413
$\mathrm{G}_{\mathrm{Correction}}$ (g, Fe(II))	0.134232	$\mathrm{G}_{\mathrm{Correction}}$ (g, Fe(III))	0.132483
$\mathrm{E}_{\mathrm{solv}}^{\mathrm{scf}}(\mathrm{Fe(II)})$	-510.444248948	$\mathrm{E}_{\mathrm{solv}}^{\mathrm{scf}}(\mathrm{Fe(III)})$	-510.239713457

Calculated Free Energy Values (au)	
$\Delta G_{\mathrm{solv}}(\mathrm{Fe(II)})$	-0.005181562
$\Delta G_{\mathrm{solv}}(\mathrm{Fe(III)})$	-0.069424027
$\Delta G_{\mathrm{ox}}(\mathrm{g})$	+0.267028973
$\Delta G_{\mathrm{ox}}(\mathrm{solv})$	+0.202786508

$$\mathrm{E}_{\mathrm{m}}^{0/+} = -\frac{\text{(-0.202786508 au)} \times 627.51\ \text{kcal/mol)}}{(1) \times 96500\ \text{C/mol}} \times \frac{4186\ \text{J}}{\text{kcal}} \times \frac{1\ \text{V}}{\text{J/C}} \approx 5.52\ \text{V}$$

Experimental Determination of $E_m^{0/+}$ for $[FeCp_2]^0$

E^0 (Absolute Reduction Potential, NHE)	4.60 V
E^0(Saturated Calomel Electrode (SCE), Relative to NHE)	0.26 V
$E_m^{0/+}$(Relative to SCE)	0.43 V
$E_m^{0/+}$(Relative to NHE)	5.29 V

Notes on Comparing Calculated and Experimental Redox Potentials

- Experimental redox potentials are reported relative to a standard electrode.
- If the standard is the **Normal Hydrogen Electrode (NHE)** , then 4.60 V is either subtracted from the absolute reduction potential (i.e. the cost of free electron) or added to the absolute oxidation potential (return of remove electron) in order to determine the potential.
- Adjustment to other standard electrodes is straightforward, since their potentials relative to the NHE is known.

Exercises

Consider the redox pairs $[FeCp_2]^{0/+}$ and $[FeCp_2^*]^{0/+}$ where $Cp = \eta - C_5H_5$ and $Cp^* = \eta - C_5Me_5$.

1. Obtain minimum energy structures for $[FeCp_2]^{0/+}$ and $[FeCp_2^*]^{0/+}$. Compare them to the corresponding X-ray crystal structures.
2. Calculate the redox potential for the $[FeCp_2]^{0/+}$ pair in water (H_2O), acetonitrile ($CH_3 - C \equiv N$), and dimethyl sulfoxide ($(CH_3)_2S = O$).

   Compare the calculated results to the experimental values given in Connelly, N.G.; Geiger, W.E., *Chemical Reviews*. ***1996, 96, 877-910***.
3. Construct an orbital interaction diagram for $FeCp_2$, and then use this to rationalize all the results obtained for exercise #2.