

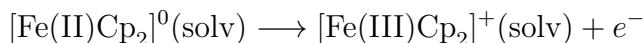
Redox Potential Calculations Using NWChem

Example Calculation: Redox Potential for $[\text{FeCp}_2]^{0/+}$

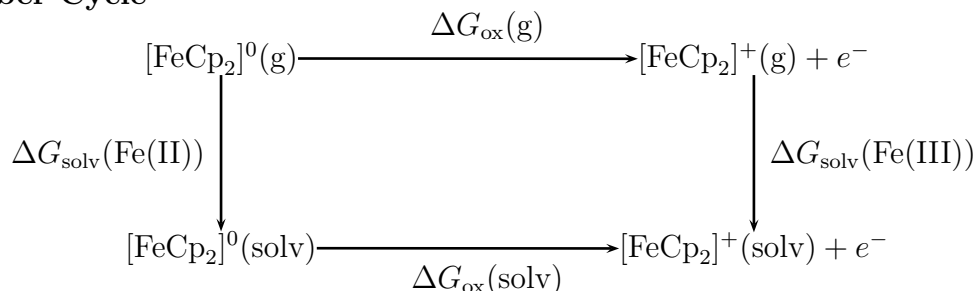
As an example of how to do this part of the assignment, we will compute the redox potential

$$\Delta G(\text{aq}) = -n F E_m^{(0/+)}$$

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



The Born-Haber Cycle



Using the Born-Haber Cycle, we obtain:

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

where

$$\Delta G_{\text{solv}}(\text{II}) = E_{\text{solv}}^{\text{scf}}(\text{II}) - E_{\text{g}}^{\text{scf}}(\text{II})$$

$$\Delta G_{\text{solv}}(\text{III}) = E_{\text{solv}}^{\text{scf}}(\text{III}) - E_{\text{g}}^{\text{scf}}(\text{III})$$

$$\Delta G_{\text{ox}}(\text{g}) = (E_{\text{g}}^{\text{scf}}(\text{III}) + G_{\text{Correction}}(\text{g}, \text{III})) - (E_{\text{g}}^{\text{scf}}(\text{II}) + G_{\text{Correction}}(\text{g}, \text{II}))$$

The correction for the free energy $G_{\text{Correction}}$ 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.

Example Calculation: Redox Potential for $[\text{FeCp}_2]^{0/+}$

Tabulated Energies (au) from Calculations			
$[\text{FeCp}_2]^0$		$[\text{FeCp}_2]^+$	
$E_{\text{g}}^{\text{scf}}(\text{Fe(II)})$	-510.439067386	$E_{\text{g}}^{\text{scf}}(\text{Fe(III)})$	-510.170289413
$G_{\text{Correction}}(\text{g}, \text{Fe(II)})$	0.134232	$G_{\text{Correction}}(\text{g}, \text{Fe(III)})$	0.132483
$E_{\text{solv}}^{\text{scf}}(\text{Fe(II)})$	-510.444248948	$E_{\text{solv}}^{\text{scf}}(\text{Fe(III)})$	-510.239713457

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

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

Experimental Determination of $E_m^{0/+}$ for $[\text{FeCp}_2]^0$

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 $[\text{FeCp}_2]^{0/+}$ and $[\text{FeCp}_2^*]^{0/+}$ where $\text{Cp} = \eta - \text{C}_5\text{H}_5$ and $\text{Cp}^* = \eta - \text{C}_5\text{Me}_5$.

1. Obtain minimum energy structures for $[\text{FeCp}_2]^{0/+}$ and $[\text{FeCp}_2^*]^{0/+}$. Compare them to the corresponding X-ray crystal structures.
2. Calculate the redox potential for the $[\text{FeCp}_2]^{0/+}$ pair in water (H_2O), acetonitrile ($\text{CH}_3 - \text{C} \equiv \text{N}$), and dimethyl sulfoxide ($(\text{CH}_3)_2\text{S} = \text{O}$).

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.