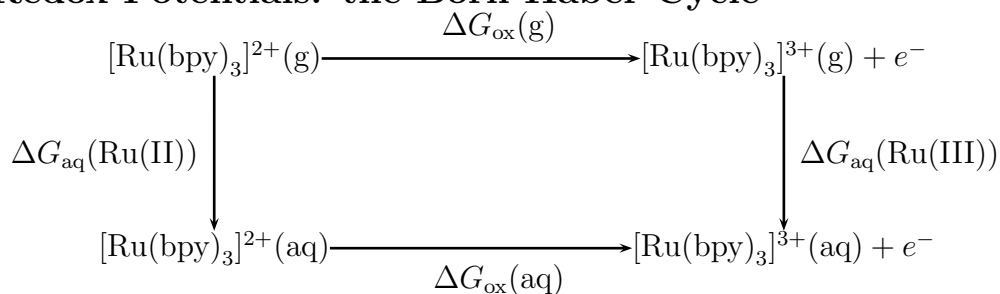


# Calculating Redox Potentials Using NWChem

## *Ab Initio* Redox Potentials: the Born-Haber Cycle



The redox potential ( $E_m^{(2+/3+)}$ ) is obtained from

$$\Delta G(\text{aq}) = -n F E_m^{(2+/3+)}$$

where  $n = 1$ , i.e. the number of electrons involved in the redox process,  $F = 96,500 \text{ C}$ ,

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

and

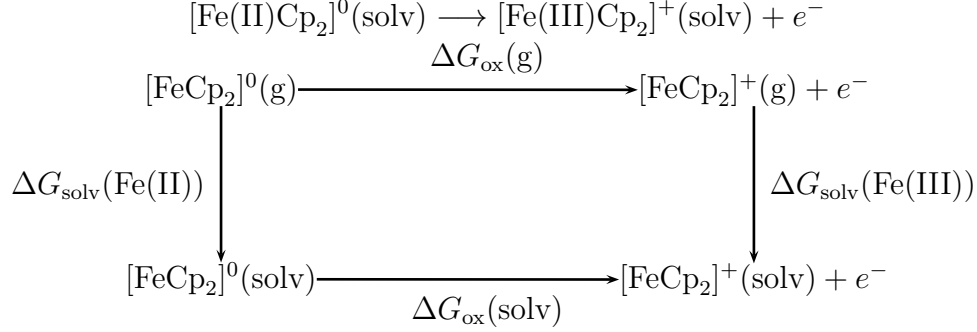
$$\Delta G_{\text{ox}}(\text{g}) = G[\text{Ru}(\text{bpy})_3^{3+}(\text{g})] - G[\text{Ru}(\text{bpy})_3^{2+}(\text{g})]$$

## 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



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			
$[\text{FeCp}_2]^0$		$[\text{FeCp}_2]^+$	
$E_g^{\text{scf}}(\text{Fe(II)})$	-510.439067386	$E_g^{\text{scf}}(\text{Fe(III)})$	-510.170289413
$G_{\text{Correction}}(\text{g, Fe(II)})$	0.134232	$G_{\text{Correction}}(\text{g, Fe(III)})$	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 $[\text{FeCp}_2]^0$

Experimental Determination of $E_m^{0/+}$	
$E^0$ (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  $[\text{MCp}_2]^{0/+}$ , and  $[\text{MCp}_2^*]^{0/+}$  where  $\text{M} = \text{Fe}, \text{Co}$ , and  $\text{Cp} = \eta - \text{C}_5\text{H}_5$ ,  $\text{Cp}^* = \eta - \text{C}_5\text{Me}_5$ .

1. Obtain minimum energy structures for  $[\text{CoCp}_2]^{0/+}$ ,  $[\text{FeCp}_2]^{0/+}$ , and  $[\text{FeCp}_2^*]^{0/+}$ , and compare them to the corresponding X-ray crystal structures.
2. Calculate the redox potential for the  $[\text{FeCp}_2]^{0/+}$  pair in acetonitrile ( $\text{CH}_3\text{-C}\equiv\text{N}$ ) which will act as the standard electrode for Question #3.
3. Calculate the redox potentials for the  $[\text{CoCp}_2]^{0/+}$  pair in acetonitrile ( $\text{CH}_3\text{-C}\equiv\text{N}$ ) relative to redox potential obtained for  $[\text{FeCp}_2]^{0/+}$  in Question #2.

Compare your results to the experimental values given in Connelly, N.G.; Geiger, W.E., *Chemical Reviews*. **1996**, **96**, **877-910**.

4. Construct an orbital interaction diagram for  $\text{FeCp}_2$ , and then use this to rationalize all the results obtained from Questions #1, #2, and #3.