

Ch153a
Winter 2019
Due 8 February, 2019

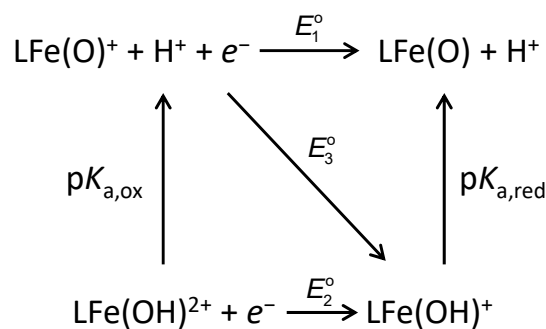
Problem Set 5

1. Jim Mayer and coworkers examined the reactions of permanganate with a variety of H-atom donors (*Inorg. Chem.* **1997**, *36*, 2069-2078). They used a thermodynamic cycle based on the $\text{MnO}_4^{-/2-}$ reduction potential, the $\text{p}K_{\text{a}}$ of $\text{Mn}(\text{OH})\text{O}_3^-$, the dissociation enthalpy of H_2 , and the solvation enthalpy of H^\bullet to estimate the H–O bond dissociation enthalpy of $\text{Mn}(\text{OH})\text{O}_3^-$.

Develop an analogous thermodynamic cycle for the couples in the Table below. Using the bond-dissociation enthalpies and $\text{p}K_{\text{a}}$ values given in the Table below, estimate the reduction potentials for the couples given in the Table. Try to find E° values for these redox couples in the literature. How do they compare? Suggest possible reasons for any significant discrepancies.

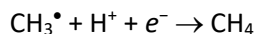
Couple	$\text{p}K_{\text{a}}$	BDE (kcal/mol)
$\text{HO}^{\bullet/-}$	14	119.2
$\text{CH}_3\text{O}^{\bullet/-}$	16	104.4
$\text{CH}_3^{\bullet/-}$	50	104.9
$\text{t-C}_4\text{H}_9\text{OO}^{\bullet/-}$	4.5	89.4
$\text{I}^{\bullet/-}$	-10	71.4
$\text{Br}^{\bullet/-}$	-8.5	86.5
$\text{Cl}^{\bullet/-}$	-7	102
$\text{F}^{\bullet/-}$	3.45	134

2. Consider an iron-oxo complex $\text{LFe}(\text{O})^+$ (where L is a dianionic ligand) that undergoes electron and proton transfer reactions as described by the diagram on the right. Assume that the potentials are defined with respect to the reference electrode potential E_{ref}° .



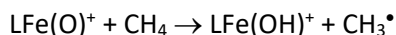
- (a) Express $\Delta E^\circ \equiv E_1^\circ - E_2^\circ$ as a function of $\text{p}K_{\text{a,red}}$ and $\text{p}K_{\text{a,ox}}$.
- (b) Express E_3° as a function of E_1° and $\text{p}K_{\text{a,red}}$.
- (c) Express E_3° as a function of E_2° and $\text{p}K_{\text{a,ox}}$.

3. The pK_a values for alkanes are generally assumed to be ~ 50 .
- (a) Use the value obtained for $E^\circ(\text{CH}_3^{\bullet/-})$ in problem (1) to estimate the standard potential for the following half-reaction:

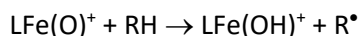


- (b) For the $\text{LFe}(\text{O})^+$ complex of problem 2, assume that $E_1^\circ = 1.0 \text{ V}$ vs NHE, and $pK_{a,\text{red}} = 10$. Calculate the value of E_3° .

- (c) On the basis of your answers to (a) and (b), would the following reaction be spontaneous?



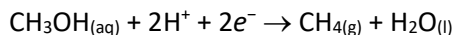
- (d) If the reaction in part (c) is not spontaneous, what would the C-H BDE have to be in order for the following reaction to be spontaneous (assume the alkane $pK_a = 50$):



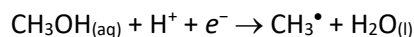
4. The standard free energies of formation of $\text{CH}_3\text{OH}_{(\text{aq})}$, $\text{H}_{2(\text{g})}$, $\text{CH}_{4(\text{g})}$ and $\text{H}_2\text{O}_{(\text{l})}$ are given in the Table.

	ΔG_f° (kcal mol ⁻¹)
$\text{CH}_3\text{OH}_{(\text{aq})}$	-41.7
$\text{H}_{2(\text{g})}$	0
$\text{CH}_{4(\text{g})}$	-12.1
$\text{H}_2\text{O}_{(\text{l})}$	-56.7

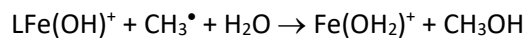
- (a) Use the data in the Table to define the standard reduction potential for the following half reaction:



- (b) Use your results from 3(a) and 4(a) to estimate the standard reduction potential for the following half reaction:



- (c) Consider the following reaction:



In order for this reaction to be spontaneous, what standard potential is required for the following half-reaction:

