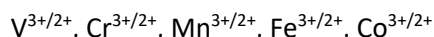


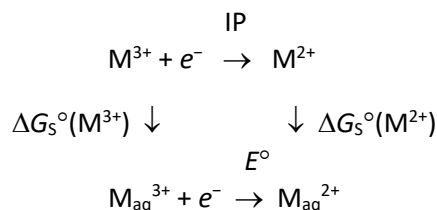
**Chemistry 153a**  
**Winter 2020**  
**Due 28 February, 2020**

**Problem Set 8**

1. Consider the following series of redox couples in aqueous solution:



The reduction potentials for these couples ( $E^\circ$ ) can be defined in terms of the ionization potentials for the gaseous ions (IP) and the Gibbs energy of hydration for the ions ( $\Delta G_S^\circ$ ), as suggested by the following Born-Haber cycle:



- Find the ionization potential for each  $M^{2+}$  ion, citing the reference used.
  - Find the Gibbs energies of hydration for each  $M^{2+}$  and  $M^{3+}$  ion, citing the reference used.
  - Use the foregoing cycle to calculate the standard reduction potentials ( $E^\circ(\text{calc})$ , V vs NHE) for each  $M^{3+}$  ion. Find experimental values for each of these ( $E^\circ(\text{expt})$ , V vs. NHE), citing the reference(s) used. Suggest possible reasons for any significant discrepancies.
  - Plot IP,  $E^\circ(\text{expt})$ ,  $E^\circ(\text{calc})$ ,  $\Delta G_S^\circ(M^{3+})$ , and  $\Delta G_S^\circ(M^{2+})$  vs. the atomic number of each metal. Explain the trends in terms of the electronic structures of the ions.
2. 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 pKa of  $\text{Mn}(\text{OH})\text{O}_3^-$ , the dissociation enthalpy of  $\text{H}_2$ , and the solvation enthalpy of  $\text{H}^\bullet$  to estimate the H–O bond dissociation enthalpy of  $\text{Mn}(\text{OH})\text{O}_3^-$ .

Using an analogous thermodynamic cycle, along with the bond-dissociation enthalpies and pKa values given in the Table below, estimate the reduction potentials for the couples given in the Table. Try to find  $E^\circ$  values for these redox couples in the literature. How do they compare? Suggest possible reasons for any significant discrepancies.

Couple	pKa	BDE (kcal/mol)
$\text{HO}^{\bullet/-}$	14	119.2
$\text{CH}_3\text{O}^{\bullet/-}$	16	104.4
$t\text{-C}_4\text{H}_9\text{OO}^{\bullet/-}$	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