Chemistry 153a
Winter 2020
Due 28 February, 2020

Problem Set 8

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

$$V^{3+/2+}, Cr^{3+/2+}, Mn^{3+/2+}, Fe^{3+/2+}, Co^{3+/2+}$$

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

$$M^{3+} + e^- \xrightarrow{\text{IP}} M^{2+}$$

$$\Delta G_S°(M^{3+}) \downarrow \qquad\qquad \downarrow \Delta G_S°(M^{2+})$$

$$M_{aq}^{3+} + e^- \xrightarrow{E°} M_{aq}^{2+}$$

a. Find the ionization potential for each M^{2+} ion, citing the reference used.

b. Find the Gibbs energies of hydration for each M^{2+} and M^{3+} ion, citing the reference used.

c. Use the foregoing cycle to calculate the standard reduction potentials ($E°$(calc), V vs NHE) for each M^{3+} ion. Find experimental values for each of these ($E°$(expt), V vs. NHE), citing the reference(s) used. Suggest possible reasons for any significant discrepancies.

d. Plot IP, $E°$(expt), $E°$(calc), $\Delta G_S°(M^{3+})$, and $\Delta G_S°(M^{3+})$ 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 $MnO_4^{-/2-}$ reduction potential, the pKa of $Mn(OH)O_3^-$, the dissociation enthalpy of H_2, and the solvation enthalpy of $H^\bullet$ to estimate the H–O bond dissociation enthalpy of $Mn(OH)O_3^-$.

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 $E°$ values for these redox couples in the literature. How do they compare? Suggest possible reasons for any significant discrepancies.

Couple	pKa	BDE (kcal/mol)
$HO^{\bullet/-}$	14	119.2
$CH_3O^{\bullet/-}$	16	104.4
$t\text{-}C_4H_9OO^{\bullet/-}$	4.5	89.4
$I^{\bullet/-}$	−10	71.4
$Br^{\bullet/-}$	−8.5	86.5
$Cl^{\bullet/-}$	−7	102
$F^{\bullet/-}$	3.45	134