Chemistry 2000 review problems on thermodynamics

Useful data is provided on the last page of this problem set.

1. An initially *p*H-neutral solution of cysteine ($C_3H_7NO_2S$) reacts with solid HgO to form cystine ($C_6H_{12}N_2O_4S_2$) and metallic mercury. Balance the reaction.

2. What is the *p*H of a 1.3×10^{-3} mol/L solution of sodium hydroxide in water at **20**°C?

3. Dimethylphenols are gaseous pollutants generated during combustion of fuels such as gasoline and wood. The Henry's law constant for 2,5-dimethylphenol in water varies with temperature as follows:[1]

T (K)	283	293
K_H ($\mathrm{mol\,L^{-1}atm^{-1}}$)	3981	1270

   (a) Calculate the enthalpy change for dissolving 2,5-dimethylphenol in water.

   (b) If the maximum allowable concentration of 2,5-dimethylphenol in water is 2000 μg/L, what is the maximum partial pressure of this pollutant at 20°C? The molar mass of 2,5-dimethylphenol is 122.16 g/mol.

4. Formamide decomposes to ammonia and carbon monoxide at high temperatures:

$$\mathrm{HCONH_{2(g)} \rightleftharpoons NH_{3(g)} + CO_{(g)}}$$

   At 400 K, the equilibrium constant for this reaction is 157. If we put 3.5 bar of formamide into a sealed flask at 400 K, what are the equilibrium pressures of all the gases?

[1] P. Diévart et al., *Phys. Chem. Chem. Phys.* **8**, 1714 (2006).

5. The solubility of lead (II) fluorochloride (PbFCl, molar mass 136.086 g/mol) in water at 25°C is 0.37 g/L.

   (a) Write down a balanced chemical reaction for the dissolution process.

   Hint: What would you write down for PbF_2 or for $PbCl_2$?

   (b) Calculate the solubility product of this compound.

   (c) Calculate the standard free energy of formation of solid PbFCl.

6. There are two common iron chlorides, namely $FeCl_2$ and $FeCl_3$. Suppose that we put a piece of solid iron into a sealed container with 0.6 bar of chlorine gas at 25°C. Use a thermodynamic argument to determine which of the iron chlorides, if any, you would expect to produce under these conditions.

   Note: This is a harder problem. Start by thinking about one of these compounds, and whether you expect it to be formed. Then think about the second compound.

7. An electrochemical cell is constructed that uses the following two half-reactions:

$$\begin{aligned} &\text{Anode:} && \mathrm{Pb_{(s)} \rightarrow Pb^{2+}_{(aq)}(0.10\,M) + 2e^-} \\ &\text{Cathode:} && \mathrm{VO^{2+}_{(aq)}(0.10\,M) + 2H^+_{(aq)}(0.10\,M) + e^-} \\ & && \mathrm{\rightarrow V^{3+}_{(aq)}(1.0 \times 10^{-5}\,M) + H_2O_{(l)}} \end{aligned}$$

   The cell produces 0.67 V at 25°C at the concentrations listed above. What is the standard reduction potential corresponding to the second half-reaction?

   Note: For the anode, the given half-cell potential is the oxidation potential.

8. Suppose that you want to generate an electrical current from the following half-reactions:

$$\mathrm{Fe(CN)}^{3-}_{6(\mathrm{aq})} + \mathrm{e}^- \rightarrow \mathrm{Fe(CN)}^{4-}_{6(\mathrm{aq})} \qquad E^\circ = 0.356\,\mathrm{V}$$

$$\mathrm{Cu}^{2+}_{(\mathrm{aq})} + 2\mathrm{e}^- \rightarrow \mathrm{Cu}_{(\mathrm{s})} \qquad E^\circ = 0.340\,\mathrm{V}$$

The standard reduction potentials are given for a temperature of 298.15 K.

(a) Describe the apparatus you would need to obtain electricity from these reactions. A carefully labeled sketch is adequate.

(b) Suppose that a coworker has prepared the following solutions:

Solution 1: 0.4 mol/L $\mathrm{Fe(CN)}^{3-}_{6(\mathrm{aq})}$ and 0.03 mol/L $\mathrm{Fe(CN)}^{4-}_{6(\mathrm{aq})}$
Solution 2: 0.5 mol/L $\mathrm{Cu}^{2+}_{(\mathrm{aq})}$

What is the spontaneous overall reaction that occurs in the apparatus you described above and what voltage is produced at 298.15 K?

9. For the reaction

$$2\mathrm{Cr}^{3+}_{(\mathrm{aq})} + 3\mathrm{Mn}_{(\mathrm{s})} \rightarrow 2\mathrm{Cr}_{(\mathrm{s})} + 3\mathrm{Mn}^{2+}_{(\mathrm{aq})}$$

$E^\circ = 0.44\,\mathrm{V}$ at 298.15 K.

(a) Calculate the equilibrium constant for this reaction.

(b) If we start with 10 L of a 2.5 mol/L solution of chromium(III) chloride, what mass of solid chromium is produced if an excess of manganese is tossed into the solution?

Data

Autoionization constant of water				
T (°C)	10	20	25	30
K_w	0.29×10^{-14}	0.68×10^{-14}	1.01×10^{-14}	1.47×10^{-14}

Standard thermodynamic data		
Species	$\dfrac{\Delta_f H^\circ_m}{\mathrm{kJ\,mol^{-1}}}$	$\dfrac{\Delta_f G^\circ_m}{\mathrm{kJ\,mol^{-1}}}$
$\mathrm{Cl^-_{(aq)}}$	−167.080	−131.218
$\mathrm{F^-_{(aq)}}$	−335.35	−281.52
$\mathrm{FeCl_{2(s)}}$	−341.83	−302.35
$\mathrm{FeCl_{3(s)}}$	−399.41	−333.91
$\mathrm{Pb^{2+}_{(aq)}}$	0.92	−24.24

Standard reduction potentials at 25 °C	
Reduction process	E°/V
$\mathrm{Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}}$	−0.13