Chemistry 2740 Spring 2016 Test 3

Time: 50 minutes
Marks: 33
Aids allowed: calculator, 8.5×11-inch formula sheet
Useful data is given on the last page of this test.
Instructions: You can answer the questions in any order, but make sure that you clearly label each of your answers with the question number in your exam booklet(s).
For any advanced calculator procedures, make sure to clearly indicate in your exam booklet what you did (e.g. "I used the equation solver in my calculator to solve this equation.").

1. Free hemoglobin in the bloodstream presents a number of dangers, notably its ability, due to the iron(III) ion it carries, to catalyze reactions that result in the formation of highly damaging hydroxyl radicals. Haptoglobin (Hp) binds free hemoglobin (Hb) in the bloodstream, inhibiting the latter's catalytic properties. The binding stoichiometry is 1:1:
$$\mathrm{Hp} + \mathrm{Hb} \rightleftharpoons \mathrm{Hp}\cdot\mathrm{Hb}$$
For this process, $\Delta_r H^\circ = -138\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_r S^\circ = -305\,\mathrm{J\,K^{-1}mol^{-1}}$.[1]
   (a) Calculate the equilibrium constant for this association at 37 °C. [4 marks]
   (b) The circulating concentration (the total concentration in the bloostream in all forms) of haptoglobin is $25\,\mu\mathrm{mol\,L^{-1}}$.[2] For a normal individual, the circulating concentration of hemoglobin is $6\,\mu\mathrm{mol\,L^{-1}}$. Assuming equilibrium, what percentage of hemoglobin remains free in the bloodstream? Relate your answer back to the danger posed by the ability of hemoglobin to catalyze the formation of hydroxyl radicals. [9 marks]

2. The Grove cell is an early voltaic cell that was mainly used to power the American telegraph system during the period 1840 to 1860. Figure 1 provides a schematic diagram of a Grove cell. The **unbalanced** half-cell reactions are
$$\mathrm{Zn_{(s)}} + \mathrm{SO^{2-}_{4(aq)}} \rightarrow \mathrm{ZnSO_{4(s)}}$$
$$\mathrm{NO^{-}_{3(aq)}} \rightarrow \mathrm{NO_{2(g)}}$$
The production of toxic nitrogen dioxide gas is the major disadvantage of the Grove cell and the reason it was eventually abandoned.
   (a) Balance this reaction. [4 marks]
   (b) In which direction do electrons flow? [1 mark]

[1] P. D. Ross and S. Subramanian, *Biochemistry* **20**, 3096 (1981).
[2] R. L. Nagel and Q. H. Gibson, *J. Biol. Chem.* **246**, 69 (1971).

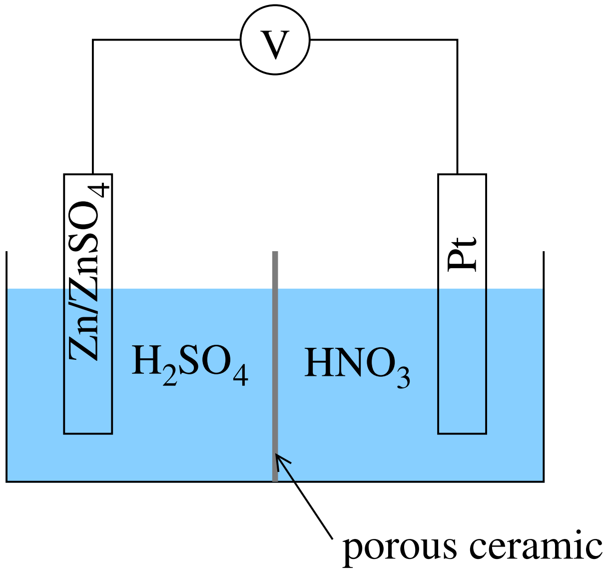

Figure 1: Schematic diagram of a Grove cell. The zinc/zinc sulfate electrode bathes in a dilute sulfuric acid solution, while the platinum electrode is immersed in nitric acid. A porous ceramic barrier, which allows ion flow, separates the two half-cells.

(c) Calculate E° for the Grove cell. [5 marks]

(d) Suppose that, in the left half-cell, the concentration of sulfuric acid is $0.0025\,\mathrm{mol\,L^{-1}}$. At this concentration of sulfuric acid, the activity of the sulfate ion is 0.0013. In the right half-cell, the concentration of nitric acid is $0.0078\,\mathrm{mol\,L^{-1}}$. Suppose that the cell has a cover, and that, at a particular point in time, the NO_2 pressure inside the right half-cell reaches 0.38 bar. Use Debye-Hückel theory to calculate the EMF generated by this cell at 25 °C. The permittivity of water at this temperature is $6.939 \times 10^{-10}\,\mathrm{C^2N^{-1}m^{-2}}$. [10 marks]

Bonus: I calculated the activity of the sulfate ion in the left half-cell using Debye-Hückel theory. Outline the calculation you would have to do to get this activity.

Useful data

$F = 96\,485.342\,\mathrm{C\,mol^{-1}}$
$R = 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}$
To convert degrees Celsius to Kelvin, add 273.15.

$$\left.\begin{array}{l}\ln\gamma_i = -Az_i^2(\varepsilon T)^{-3/2}\sqrt{I_c}\\ \ln\gamma_\pm = -A|z_+z_-|(\varepsilon T)^{-3/2}\sqrt{I_c}\end{array}\right\}\text{ with } A = 1.107\times10^{-10}$$

Standard thermodynamic data at 298.15 K		
Species	$\frac{\Delta_f H^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta_f G^\circ}{\mathrm{kJ\,mol^{-1}}}$
$H_2O_{(l)}$	−285.830	−237.140
$NO_{2(g)}$	33.2	51.32
$NO^-_{3(aq)}$	−207.4	−111.4
$SO^{2-}_{4(aq)}$	−909.34	−744.00
$ZnSO_{4(s)}$	−982.8	−874.4