Chemistry 2740 Spring 2020 Test 2

Time: 50 minutes
Marks: 34
Aids allowed: calculator, 8.5 × 11-inch formula sheet
Useful data is found on page 2.
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).

1. You may recall that boric acid [$B(OH)_3$] is a Lewis acid. Like many Lewis acids, boric acid reacts with water: **17 marks**

$$B(OH)_{3(aq)} + H_2O_{(l)} \rightleftharpoons B(OH)^-_{4(aq)} + H^+_{(aq)}.$$

The equilibrium constant for this reaction has been measured as a function of temperature. The results were as follows:[1]

$T/°C$	15	25	35	45
$K/10^{-10}$	4.70	5.80	6.89	7.89

Note: $K/10^{-10}$ means that the entry in the table is the result of dividing K by 10^{-10}. For example, the equilibrium constant at 15 °C is 4.70×10^{-10}.

(a) What is the standard free energy of reaction? [2 marks]

(b) Determine the standard enthalpy of reaction. [9 marks]

(c) What is the pH of a $0.013\,\text{mol}\,\text{L}^{-1}$ solution of boric acid in water at 45 °C assuming that boric acid and water both behave ideally? Give your answer to two decimal places. [6 marks]

Hint: The calculation is easier than it may first look. Start by thinking about what you need to calculate to get a pH.

[1] Selected data from B. B. Owen, *J. Am. Chem. Soc.* **56**, 1695 (1934)

2. Robert Bunsen (of Bunsen burner fame) was a versatile chemist who, among other things, invented the Bunsen voltaic cell, which has the following cell diagram: **17 marks**

$$\mathrm{Zn_{(s)}|H_2SO_4(0.0032\,mol/L), ZnSO_4(1.0\times10^{-5}\,mol/L)}\\ \mathrm{||HNO_3(3.539\,mol/L)|C_{(s)}, NO_2(0.24\,bar)}$$

   (a) At the anode, zinc metal is oxidized to zinc ions. At the cathode, nitrate ions react to form NO_2. (The latter is why this cell was not widely used, NO_2 being unpleasantly toxic.) Balance the reaction. [5 marks]

   (b) Calculate the EMF of this cell at 25 °C. Assuming that water behaves ideally. At the concentration of nitric acid in this cell, $\gamma_{H^+} = \gamma_{NO_3^-} = 0.968$. Use Debye-Hückel theory to calculate the activity coefficients of any remaining ions in your balanced reaction. The permittivity of water at this temperature is $6.939\times10^{-10}\,C^2J^{-1}m^{-1}$. [12 marks]

Useful data

Constants and conversion factors

$0\,K = -273.15\,°C$
$F = 96\,485.342\,C\,mol^{-1}$
$R = 8.314\,472\,J\,K^{-1}mol^{-1}$

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

Standard thermodynamic data at 298.15 K

Species	$\Delta_f H^\circ$ / kJ mol^{-1}	$\Delta_f G^\circ$ / kJ mol^{-1}
$H_2O_{(l)}$	−285.830	−237.140
$NO_{2(g)}$	33.2	51.32
$NO^-_{3(aq)}$	−205.0	−108.74
$Zn^{2+}_{(aq)}$	−153.39	−111.62