Chemistry 2740 Spring 2018 Test 3

Time: 50 minutes
Marks: 30
Aids allowed: calculator, 8.5×11-inch formula sheet
Useful data is given on page 3.
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. (a) When concentrated nitric acid reacts with copper, the copper is dissolved to copper(II) ions, and brown NO_2 gas is produced. Balance this reaction. [5 marks]

   (b) Calculate the standard reduction potential of nitric acid. [7 marks]

2. In pulse radiolysis, electrons are shot into a solution using a linear accelerator. This is one of the rare situations where one can talk of solvated electrons in aqueous solution. Relatively high (μM) concentrations of solvated electrons can be generated by pulse radiolysis. However, these electrons react very quickly with water and with species in solution to generate radicals. Typically these experiments are performed to study the reactions of radicals with other molecules in solution. All of the data in this question are at 20 °C.

   (a) The solvated electron is often written $e^-_{(aq)}$, but a (slightly) better representation is $e^- \cdot H_2O$ (by analogy to H_3O^+) since the electron is hydrated in aqueous solution. One of the reactions that removes solvated electrons from solution is

   $$e^- \cdot H_2O + e^- \cdot H_2O \longrightarrow H_{2(g)} + 2\,OH^-_{(aq)}$$

   (This reaction removes $e^-_{(aq)}$ from solution without forming any radicals, so it's actually an unwanted, if inevitable, process.) The rate constant for this reaction is $5.5 \times 10^9\,\mathrm{L\,mol^{-1}s^{-1}}$. If a pulse radiolysis experiment generates $1.8\,\mu\mathrm{mol\,L^{-1}}$ of solvated electrons, what is the initial rate of removal of electrons by this reaction? [2 marks]

   (b) This reaction is the one that initially removes electrons from solution most efficiently under the experimental conditions described above. Estimate the half-life of a solvated electron in this experiment. [2 marks]

   Hint: You actually need to use $2k$ instead of k in the half-life formula. Bonus mark if you can tell me why.

   (c) Again assuming that the above reaction is the one that removes electrons most rapidly, how long would it take for the concentration of electrons to drop to less than 1% of the initial concentration? [2 marks]

   Note: The same issue of using $2k$ instead of k in the appropriate equation arises here.

(d) There are over 30 reactions involved in the radiolysis of pure water. We're going to study a highly simplified mechanism for the initial production of the hydroxyl radical ($OH^\bullet$), which is often a radical of interest in studies of (for example) oxidative damage of biomolecules:

$$
\begin{aligned}
e^-_{(aq)} + H_2O_{(l)} &\xrightarrow{k_1} H^\bullet_{(aq)} + OH^-_{(aq)} \\
e^-_{(aq)} + H^+_{(aq)} &\xrightarrow{k_2} H^\bullet_{(aq)} \\
H^\bullet_{(aq)} + H_2O_{(l)} &\xrightarrow{k_3} H_{2(g)} + OH^\bullet_{(aq)}
\end{aligned}
$$

Derive a rate law for the rate of production of hydroxyl radicals. [9 marks]

Hints: I suggest you start by writing down the equation for the rate of production of hydroxyl radicals. Skip the step of trying to work out an overall reaction. (There are two reaction pathways that lead from the solvated electron to a hydroxyl radical, so you can get two different "overall reactions" from the elementary reactions given above. Both occur at the same time.)

Side note: The mechanism given above is not fully realistic. One important reaction I have left out is

$$H^\bullet_{(aq)} + H^\bullet_{(aq)} \longrightarrow H_{2(g)}.$$

Bonus mark if you can tell me why I left this reaction out, i.e. why the problem would be much harder if I added this reaction.

(e) In order to get interpretable data, it is critical to carry out these experiments in pH-buffered solutions. Why? [3 marks]

Useful data

Constants and conversion factors

$0\,\mathrm{K} = -273.15\,°\mathrm{C}$
$F = 96\,485.342\,\mathrm{C\,mol^{-1}}$

Standard thermodynamic data at 298.15 K

Species	$\frac{\Delta_f H^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta_f G^\circ}{\mathrm{kJ\,mol^{-1}}}$
$Cu^{2+}_{(aq)}$	65.69	65.6
$H_2O_{(l)}$	−285.830	−237.140
$HNO_{3(l)}$	−174.1	−80.7
$NO_{2(g)}$	33.2	51.32

Standard reduction potentials at 298.15 K

$$\mathrm{Cu^{2+}_{(aq)} + 2\,e^- \longrightarrow Cu_{(s)}} \qquad E^\circ = 0.3419\,\mathrm{V}$$