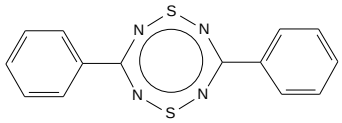
Chemistry 2740 Spring 2010 Test 2

Time: 50 minutes
Marks: 31
Aids allowed: calculator, 8.5×11-inch formula sheet
Useful data is given on the reverse of this page.
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).
If you use a graph to answer a question, make sure to provide a reasonable sketch of the graph, as well as a brief explanation of what information the graph provides.

1. What do the following symbols in the Nernst equation represent? Be specific. [1 mark each]
   (a) E
   (b) E°
   (c) ν_e

2. Taking non-ideal effects into account, what is the pH of a 0.0058 mol/L aqueous solution of HCl at 25°C? The permittivity of water at this temperature is $6.957 \times 10^{-10}\,\mathrm{C^2N^{-1}m^{-2}}$. [9 marks]

3. In a recent study, the electrochemistry of 1,5,2,4,6,8-dithiatetrazocine (R)



   and its radicals was studied by EPR spectroscopy.[1] In one experiment, the radical anion $\mathrm{R^{\cdot -}}$ was generated electrochemically, then its decay was followed by monitoring the intensity of the corresponding EPR signal, which is proportional to the concentration of the radical.

   (a) Is the formation of the radical anion from the neutral compound an example of oxidation or reduction? [1 mark]

   (b) The radical anion can decay by one of at least two mechanisms:
      i. $\mathrm{R^{\cdot -} + R^{\cdot -} \rightarrow R + R^{2-}}$
      ii. $\mathrm{R^{\cdot -} + S \rightarrow R + S^{\cdot -}}$,
   where S is the solvent. Explain why these two elementary processes would be expected to lead to different rate laws. What law of chemical kinetics is involved? What simplification(s) arise due to the reaction conditions? [4 marks]

[1] R. T. Boeré et al., *Inorg. Chem.* **46**, 5596 (2007).

(c) The following data were obtained for the decay of the radical in dichloromethane,[2] starting immediately after the electrolytic current generating the radical had been turned off:

t/s	14.68	27.80	40.92	54.04	67.16	80.28
I	4.28	1.29	0.56	0.35	0.18	0.09

On the basis of these data, can you determine which of the above two mechanisms is the correct one? If so, also calculate the rate constant. Otherwise, explain what the problem is. [14 marks]

Useful data

To convert degrees Celsius to Kelvin, add 273.15.

Debye-Hückel formulae: $\ln \gamma_i = -Az_i^2(\varepsilon T)^{-3/2}\sqrt{I_c}$
or $\ln \gamma_\pm = -A|z_+ z_-|(\varepsilon T)^{-3/2}\sqrt{I_c}$,
with $A = 1.107 \times 10^{-10}$.

[2] Thanks to Dr Tracey Roemmele for making the original data available.