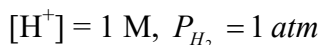# Chemistry 225 Semester 04-2016
# Homework for Submission #7 - Key

Answer the following questions and submit them for marking on or before 6 pm on Monday 5th December. Only answers showing full working can attract full marks. Express your answer to the correct number of significant figures. Answers showing evidence of copying will attract zero marks. Place your answers neatly in the spaces provided on this question paper.
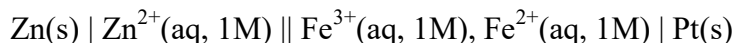
The following is a list of some standard electrode potentials at 298K. The arrangement is alphabetical.

| HALF-CELL | $E^0$/Volt |
|---|---|
| $Zn^{2+}(aq) \mid Zn(s)$ | -0.7618 |
| $Cu^{2+}(aq) \mid Cu(s)$ | +0.3419 |
| $Fe^{3+}(aq) \mid Fe^{2+}(aq)$ | +0.771 |
| $I_2(s) \mid I^-(aq)$ | +0.5355 |
| $Ni^{2+}(aq) \mid Ni(s)$ | -0.257 |
| $Sr^{2+}(aq) \mid Sr(s)$ | -2.889 |
| $Sn^{4+}(aq) \mid Sn^{2+}(aq)$ | +0.151 |
| $Cu^{2+}(aq) \mid Cu^+(aq)$ | +0.153 |

1)  The above potentials are measured relative to the standard electrode potential for the standard hydrogen half-cell (SHE): $Pt(s)|H^+(aq)|H_2(g)$ at 25°C. Precisely what is meant by the term *standard* in this context?
(2 marks)

$$[H^+] = 1 \text{ M}, \ P_{H_2} = 1 \ atm$$

2)  Consider the cell:
$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Fe^{3+}(aq, 1M), Fe^{2+}(aq, 1M) \mid Pt(s)$$

a)  Calculate the e.m.f. of the cell, $E^{\circ}_{cell}$ and state which electrode is the source of electrons for the external circuit.
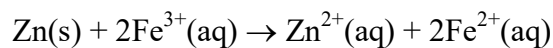(4 marks)

$E^{\circ}_{red}(Zn^{2+} \mid Zn) = -0/7618v$

$\therefore E^{\circ}_{ox}(Zn \mid Zn^{2+}) = +0/7618v$

$E^{\circ}_{red}(Fe^{3+} \mid Fe^{2+}) = -0/771v$

$\therefore E^{\circ}_{cell} = E^{\circ}_{red}(Fe^{3+} \mid Fe^{2+}) + E^{\circ}_{ox}(Zn \mid Zn^{2+}) = 0.771v + 0.7618v = 1.5328v = \underline{1.533v \ to \ 3 \ d.p.}$

The Zn electrode is the source of electrons. (Since oxidation occurs here, releasing electrons.)

b) Write down a balanced equation for the reaction occurring in the cell. (Make sure that you have the correct **direction** of reaction.) (2 marks)

$$Zn(s) + 2Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$$

c) Calculate the equilibrium constant for the reaction at 298 K. (3 marks)

$$E^\circ = \frac{RT}{nF} Ln(K) = \frac{8.31 \times 298}{2 \times 96500} Ln(K) = 1.5328v$$

$$\therefore Ln(K) = 1.5328 \times \frac{2 \times 96500}{8.31 \times 298} = 119.4608259...$$

$$\therefore K = e^{119.4608259} = 7.60637 \times 10^{51} = \underline{7.61 \times 10^{51}} \ to \ 3 \ s.f.$$

(In reality the answer is not correct to 3 s.f.: only to an order of magnitude.)

d) Calculate the e.m.f. of the cell which is 0.100 M in $Zn^{2+}$, $Fe^{2+}$ and $Fe^{3+}$ at 298 K. (3 marks0

$$E = E^\circ - \frac{RT}{nF} Ln(Q) = 1.5328 - \frac{8.31 \times 298}{2 \times 96500} Ln\left( \frac{[Fe^{2+}]^2[Zn^{2+}]}{[Fe^{3+}]^2} \right)$$

$$= 1.5328 - 0.0128309 \times Ln\left( \frac{0.1^2 0.1}{0.1^2} \right) = 1.56234... = \underline{1.562v \ to \ 3 \ d.p.}$$

e) Calculate ΔG for situation described in (d). What does the sign of ΔG tell you? (3 marks)

$$\Delta G = -nFE = -2 \times 96500 \times 1.56234... = -301532.47...J = \underline{-302 \ kJ \ mol^{-1}} \ to \ 3 \ s.f.$$
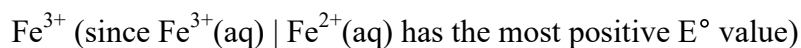
The negative sign of ΔG tells us that the reaction is spontaneous in the forward direction under these conditions.

3) From the table pick out the species which is
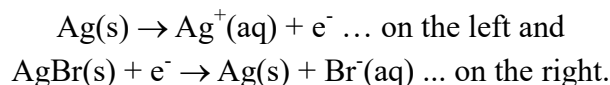   a) the strongest reducing agent and (1 mark)

$$Sr(s) \ (since \ Sr^{2+}(aq) \mid Sr(s) \ has \ the \ most \ negative \ E^\circ \ value)$$

   b) the strongest oxidizing agent. (1 mark)

$$Fe^{3+} \ (since \ Fe^{3+}(aq) \mid Fe^{2+}(aq) \ has \ the \ most \ positive \ E^\circ \ value)$$

Consider the cell:
$$Ag(s)|Ag^+(aq,1M)||Br^-(aq, 1M)|Cl^-(aq, 1M)|AgBr(s)|Ag(s)$$

The half reactions are:
$$Ag(s) \rightarrow Ag^+(aq) + e^- \dots \text{ on the left and}$$
$$AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq) \dots \text{ on the right.}$$

Given also that, at 298 K:
$$E^\circ_{red}(AgBr \mid Ag, Br^-) = 0.0711$$
$$E^\circ_{red}(Ag^+ \mid Ag) = 0.7999$$

a) Write the overall equation for the cell reaction.  (1 mark)

$$AgBr(s) \rightarrow Ag^+(aq) + Br^-(aq)$$
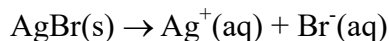
b) Calculate the solubility product of AgBr at 298 K.  (4 marks)

Since the overall reaction of the cell is the defining reaction for the solubility product of silver bromide, the associated equilibrium constant is the solubility product of silver bromide.

$$E^\circ_{ox}(Ag \mid Ag^+) = -E^\circ_{red}(Ag^+ \mid Ag) = -0.7999v$$
$$E^\circ_{red} = (AgBr \mid Ag, Br^-) = 0.0711v$$
$$\therefore E^\circ_{cell} = E^\circ_{red} = (AgBr \mid Ag, Br^-) + E^\circ_{ox}(Ag \mid Ag^+) = 0.0711 + (-0.7999) = -0.72879$$
$$But\ E^\circ = \frac{RT}{nF} Ln(K)$$
$$\therefore Ln(K) = E^\circ \times \frac{nF}{RT} = -0.72879 \times \frac{1 \times 96500}{8.31 \times 298} = -28.3996\dots$$
$$\therefore K = K_{sp}(AgBr) = e^{-28.3996} = \underline{\underline{4.64 \times 10^{-13}}}\ to\ 3\ s.f.$$

(This compares reasonably well with the published value of $5.0 \times 10^{-13}$ at 298 K. It also shows again that "significant figures" are not always to be trusted, particularly when exponentiation is involved.)