NOTE: for this problem set, unless stated otherwise, all standard cell potentials and other standard thermodynamic values are assumed to be reported at 298 K.

- Consider the demonstration where a piece of copper wire is being immersed in a solution of AgNO₃.
 - a) What is the sign of ΔG° for the demonstration you are observing? Explain.

Negative. Reaction is spontaneous.

b) Write out a balanced overall reaction for the demonstration, including all phases and stoichiometric coefficients:

$$2 \text{ Ag}^*(aq) + \text{Cu}(s) \rightarrow 2 \text{ Ag}(s) + \text{Cu}^{2*}(aq)$$

c) In your engineering reference manual you find the following half-reactions:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
 $E^+ = +0.34 \text{ V}$
 $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^- = +0.80 \text{ V}$

Determine the standard cell potential associated (E°cell) associated with this reaction.

$$E^{0}_{cell} = E^{0}_{red} - E^{0}_{ox} = 0.80 - 0.34 = 0.46 \text{ V}$$

d) Calculate the value of ΔG° and K for the demonstration reaction at 298 K.

$$\Delta G^{\circ} = -n F E_{cell}^{0} = -2 \times 96485 C mol^{-1} \times 0.460 V = -88766 J$$

$$= -89 kJ$$

$$ln K = -\frac{\Delta G^{\circ}}{RT} = \frac{88766 J}{1 mol \times 8.3145 J mol^{-1} K^{-1} \times 298 K} = 35.83$$

$$K = e^{35.83} = 3.62 \times 10^{15}$$

 Use your knowledge of thermodynamics to predict what would happen if we were to carry out the opposite experiment – a piece of silver in Cu(NO₃)₂.

Because dipping Cu in AgNO₃ was a spontaneous process, that means the opposite process should be non-spontaneous.

Note: both this answer and that for part a) make a subtle assumption. Can you see what it is?

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M Mark

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