Answers to Exercise 9.4 Standard Potential for Electrochemical Cells

1. A positive standard potential indicates that the reaction is thermodynamically allowed under standard conditions.

The corollary is that a negative standard potential indicates that the reaction is not thermodynamically allowed under standard conditions. A standard potential of zero would mean that the system reaches equilibrium under standard conditions.

If the system is not under standard conditions, you must calculate potential under those conditions (e.g. from the standard potential and the reaction quotient) before assessing whether or not the reaction is thermodynamically allowed.

2.
$$(a) + (b)$$

Oxidation:
$$2I_{(aq)}^{-} \rightarrow I_{2(s)} + 2e^{-}$$
 $E^{\circ} = -0.5355 V$
Reduction: $Cl_{2(g)} + 2e^{-} \rightarrow 2Cl_{(aq)}^{-}$ $E^{\circ} = +1.35827 V$
Overall: $Cl_{2(g)} + 2I_{(aq)}^{-} \rightarrow 2Cl_{(aq)}^{-} + I_{2(s)}$ $E^{\circ} = +0.8228 V$

Therefore, $v_e = 2$

Remember to switch the sign of the standard reduction potential for the oxidation half reaction! In other words, if the half-cell potential for reducing I_2 to I^- is $+0.5355\,V$ then the half-cell potential for oxidizing I^- to I_2 is $-0.5355\,V$.

(c)
$$\Delta_r G^{\circ} = -\nu_e F E^{\circ}$$

 $\Delta_r G^{\circ} = -(2) \left(96 \ 485 \frac{c}{mol} \right) \left(0.8228 \ \frac{J}{c} \right)$
 $\Delta_r G^{\circ} = -1.588 \times 10^5 \frac{J}{mol} = -158.8 \frac{kJ}{mol}$

Remember that $1 V = 1 \frac{J}{c}$.

(d)
$$\Delta_{r}G^{\circ} = \Delta_{f}G^{\circ}(products) - \Delta_{f}G^{\circ}(reactants)$$

$$\Delta_{r}G^{\circ} = \left[2\Delta_{f}G^{\circ}(Cl_{(aq)}^{-}) + \Delta_{f}G^{\circ}(I_{2(s)})\right] - \left[\Delta_{f}G^{\circ}(Cl_{2(g)}) + 2\Delta_{f}G^{\circ}(I_{(aq)}^{-})\right]$$

$$-158.8 \frac{kJ}{mol} = \left[2\Delta_{f}G^{\circ}(Cl_{(aq)}^{-}) + \left(0 \frac{kJ}{mol}\right)\right] - \left[\left(0 \frac{kJ}{mol}\right) + 2\left(-51.67 \frac{kJ}{mol}\right)\right]$$

$$-158.8 \frac{kJ}{mol} = 2\Delta_{f}G^{\circ}(Cl_{(aq)}^{-}) - 2\left(-51.67 \frac{kJ}{mol}\right)$$

$$2\Delta_{f}G^{\circ}(Cl_{(aq)}^{-}) = 2\left(-51.67 \frac{kJ}{mol}\right) - 158.8 \frac{kJ}{mol}$$

$$\Delta_{f}G^{\circ}(Cl_{(aq)}^{-}) = \frac{2\left(-51.67 \frac{kJ}{mol}\right) - 158.8 \frac{kJ}{mol}}{2}$$

$$\Delta_{f}G^{\circ}(Cl_{(aq)}^{-}) = -131.1 \frac{kJ}{mol}$$

The value on the Table of Thermodynamic Data provided is $-131.0 \frac{kJ}{mol}$ which is within rounding error of this answer.

3.

(a)

Oxidation:
$$3 H_2 O_{(l)} \rightarrow O_{3(g)} + 6 H_{(aq)}^+ + 6 e^-$$
 multiply by 2 Reduction: $O_{2(g)} + 4 H_{(aq)}^+ + 4 e^- \rightarrow 2 H_2 O_{(l)}$ multiply by 3 Overall: $3 O_{2(g)} \rightarrow 2 O_{3(g)}$

Overall:

Therefore, $v_e = 12$

Step 1: Find v_e by balancing redox equation

done in part (a)

Step 2: Calculate the standard free energy change for the reaction

$$\Delta_r G^{\circ} = \sum \Delta_f G^{\circ}(products) - \sum \Delta_f G^{\circ}(reactants)$$

$$\Delta_r G^{\circ} = 2 \Delta_f G^{\circ} (O_{3(g)}) - 3 \Delta_f G^{\circ} (O_{2(g)})$$

$$\begin{split} &\Delta_r G^\circ = 2 \left(+163.2 \frac{kJ}{mol} \right) - 3 \left(0 \frac{kJ}{mol} \right) \\ &\Delta_r G^\circ = +326.4 \frac{kJ}{mol} \end{split}$$

$$\Delta_r G^\circ = +326.4 \frac{kJ}{mol}$$

Step 3: Calculate standard potential from standard free energy change

$$\Delta_r G^\circ = -\nu_e F E^\circ$$

$$E^{\circ} = -\frac{\Delta_r G^{\circ}}{\nu_{e} F}$$

$$E^{\circ} = -\frac{\left(326.4 \frac{kJ}{mol}\right)}{(12)\left(96485 \frac{C}{mol}\right)} \times \frac{1000 J}{1 kJ}$$

$$E^{\circ} = -0.2819 \frac{J}{c} = -0.2819 V$$

Step 4: Check your work

Does your answer seem reasonable? Are sig. fig. correct?