Answers to Practice Test Questions 9
Redox Reactions and Electrochemistry

1.

(a) -2

Sulfur is more electronegative than both C and H. As such, when calculating oxidation state, the electrons in the $S-C$ and $S-H$ bonds are all assigned to S (along with the four electrons from its lone pairs). This gives it an oxidation state of $6-8=-2$.

(b) -1

Sulfur is more electronegative than C. As such, when calculating oxidation state, the electrons in the $S-C$ bond are assigned to S (along with the four electrons from its lone pairs). The electrons in the $S-S$ bond are divided equally between the two sulfur atoms (one each). This gives each sulfur atom an oxidation state of $6-7=-1$.

(c) iv. The sulfur atom in the cysteine residue is oxidized.

For this to occur, it must react with an oxidizing agent.

Since the oxidation state of sulfur gets less negative, it is "losing electrons" therefore it is oxidized.

2.

Oxidation: $Ag_{(s)} \rightarrow Ag^{+}_{(aq)} + e^{-}$

multiply by 6

Reduction: $Cr_2O^{2-}_{7(aq)} + 14\,H^{+}_{(aq)} + 6\,e^{-} \rightarrow Cr^{3+}_{(aq)} + 7\,H_2O_{(l)}$

Overall: $6\,Ag_{(s)} + Cr_2O^{2-}_{7(aq)} + 14\,H^{+}_{(aq)} \rightarrow 6\,Ag^{+}_{(aq)} + Cr^{3+}_{(aq)} + 7\,H_2O_{(l)}$

3.

(a)

Oxidation: $Ca_{(s)} \rightarrow Ca^{2+}_{(aq)} + 2\,e^{-}$

Reduction: $2\,CO_{2(g)} + 2\,e^{-} \rightarrow C_2O^{2-}_{4(aq)}$

Overall: $Ca_{(s)} + 2\,CO_{2(g)} \rightarrow Ca^{2+}_{(aq)} + C_2O^{2-}_{4(aq)}$

(b) Ca

4.

(a)

Oxidation: $2\,Rh_{(s)} + 3\,H_2O_{(l)} \rightarrow Rh_2O_{3(s)} + 6\,H^{+}_{(aq)} + 6e^{-}$

Reduction: $H_5IO_{6(aq)} + H^{+}_{(aq)} + 2\,e^{-} \rightarrow IO^{-}_{3(aq)} + 3\,H_2O_{(l)}$ multiply by 3

Overall: $2\,Rh_{(s)} + 3\,H_5IO_{6(aq)} \rightarrow Rh_2O_{3(s)} + 3\,IO^{-}_{3(aq)} + 3\,H^{+}_{(aq)} + 6\,H_2O_{(l)}$

(b) **Step 1: Identify stoichiometric coefficient for electrons (ν_e)**

This is the number of electrons canceled out when adding the oxidation and reduction half-reactions to obtain the overall balanced redox equation.

$\nu_e = 6$

Step 2: Calculate standard free energy change from standard potential

Recall that $1\,V = 1\,\frac{J}{C}$

$\Delta_r G° = -\nu_e F E°$

$\Delta_r G° = -(6)\left(96\,485\,\frac{C}{mol}\right)\left(0.73\,\frac{J}{C}\right)$

$\Delta_r G° = -4.2 \times 10^5\,\frac{J}{mol} \times \frac{1\,kJ}{1000\,J} = -4.2 \times 10^2\,\frac{kJ}{mol}$

Step 3: Check your work

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

Standard cell potential was positive (reaction thermodynamically allowed under standard conditions) therefore standard free energy change should be negative.

5.

Oxidation: $2\,C_3H_7NO_2S \rightarrow C_6H_{12}N_2O_4S_2 + 2\,H^+ + 2e^-$

Reduction: $HgO + 2\,H^+_{(aq)} + 2\,e^- \rightarrow Hg + H_2O$

Overall: $2\,C_3H_7NO_2S + HgO \rightarrow C_6H_{12}N_2O_4S_2 + Hg + H_2O$

6.

(a) $Sn_{(s)}\left|Sn^{2+}_{(aq)}\right\|Cr_2O^{2-}_{7\,(aq)}, H^+_{(aq)}, Cr^{3+}_{(aq)}\left|C_{(s)}\right.$

(b)+(c)

Oxidation: $Sn_{(s)} \longrightarrow Sn^{2+}_{(aq)} + 2e^-$ multiply by 3

Reduction: $Cr_2O^{2-}_{7\,(aq)} + 14\,H^+_{(aq)} + 6\,e^- \longrightarrow 2\,Cr^{3+}_{(aq)} + 7\,H_2O_{(l)}$

Overall: $3\,Sn_{(s)} + Cr_2O^{2-}_{7\,(aq)} + 14\,H^+_{(aq)} \longrightarrow 3\,Sn^{2+}_{(aq)} + 2\,Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

7.

(a)

Oxidation: $NO_{(g)} + 4\,OH^-_{(aq)} \longrightarrow NO^-_{3\,(aq)} + 2\,H_2O_{(l)} + 3\,e^-$ multiply by 2

Reduction: $Cl_{2(g)} + 2\,e^- \longrightarrow 2\,Cl^-_{(aq)}$ multiply by 3

Overall: $2\,NO_{(g)} + 8\,OH^-_{(aq)} + 3\,Cl_{2(g)} \longrightarrow 2\,NO^-_{3\,(aq)} + 6\,Cl^-_{(aq)} + 4\,H_2O_{(l)}$

(b) *Standard potential for a reaction can be calculated from standard free energy change for the reaction.*

Step 1: Write a balanced chemical equation for the reaction (or phase change)

This was done in part (a).

$2\,NO_{(g)} + 8\,OH^-_{(aq)} + 3\,Cl_{2(g)} \longrightarrow 2\,NO^-_{3\,(aq)} + 6\,Cl^-_{(aq)} + 4\,H_2O_{(l)}$

Step 2: Determine stoichiometric coefficient for electrons (ν_e)

$\nu_e = 6$

Step 3: Convert temperature to Kelvin (if necessary)

$T = 25\ ℃ = 298.15\ K$ *"standard conditions" means exactly* 25 ℃ *so infinite sig. fig.*

Step 4: Calculate the standard free energy change for the reaction

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = \left[2\,\Delta_f G°\left(NO^-_{3(aq)}\right) + 6\,\Delta_f G°\left(Cl^-_{(aq)}\right) + 4\,\Delta_f G°\left(H_2O_{(l)}\right)\right]$
$\qquad -\left[2\,\Delta_f G°\left(NO_{(g)}\right) + 8\,\Delta_f G°\left(OH^-_{(aq)}\right) + 3\,\Delta_f G°\left(Cl_{2(g)}\right)\right]$

$\Delta_r G° = \left[2\left(-110.5\frac{kJ}{mol}\right) + 6\left(-131.0\frac{kJ}{mol}\right) + 4\left(-237.1\frac{kJ}{mol}\right)\right]$
$\qquad -\left[2\left(86.55\frac{kJ}{mol}\right) + 8\left(-157.2\frac{kJ}{mol}\right) + 3\left(0\frac{kJ}{mol}\right)\right]$

$\Delta_r G° = -870.9\frac{kJ}{mol}$

Step 5: Calculate standard potential from standard free energy change

$\Delta_r G° = -\nu_e F E°$

$E° = -\frac{\Delta_r G°}{\nu_e F}$

$E° = -\frac{\left(-870.9\frac{kJ}{mol}\right)}{(6)\left(96\,485\frac{C}{mol}\right)} \times \frac{1000\ J}{1\ kJ}$

$E° = +1.504\ \frac{J}{C} = +1.504\ V$

Step 6: Check your work

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

Standard free energy change was negative (reaction thermodynamically allowed under standard conditions) therefore standard potential should be positive.

(c) Yes. $E° > 0$

(d) *Calculate potential under nonstandard conditions from standard potential using Nernst equation Stoichiometric coefficient (ν_e) is known from part (b).*

Step 1: Determine activities for all reactants and products

$a_{NO_{(g)}} = \frac{0.2\ bar}{1\ bar} = 0.2$ $\qquad$ $a_{NO^-_{3(aq)}} = \frac{0.01\ M}{1\ M} = 0.01$

$a_{OH^-_{(aq)}} = \frac{0.03\ M}{1\ M} = 0.03$ $\qquad$ $a_{Cl^-_{(aq)}} = \frac{0.8\ M}{1\ M} = 0.8$

$a_{Cl_{2(g)}} = \frac{0.05\ bar}{1\ bar} = 0.05$ $\qquad$ $a_{H_2O_{(l)}} = 1$

Step 2: Calculate reaction quotient

$$Q = \frac{\left(a_{NO_{3(aq)}^-}\right)^2\left(a_{Cl_{(aq)}^-}\right)^6\left(a_{H_2O_{(l)}}\right)^4}{\left(a_{NO_{(g)}}\right)^2\left(a_{OH_{(aq)}^-}\right)^8\left(a_{Cl_{2(g)}}\right)^3} = \frac{(0.01)^2(0.8)^6(1)^4}{(0.2)^2(0.03)^8(0.05)^3} = 7.99 \times 10^{12}$$

Step 3: Calculate potential for reaction under nonstandard conditions

$$E = E° - \frac{RT}{\nu_e F} lnQ$$

$$E = (1.504\ V) - \frac{\left(8.314\ 462 \frac{J}{mol \cdot K}\right)(298.15\ K)}{(6)\left(96\ 485 \frac{C}{mol}\right)} ln(7.99 \times 10^{12}) \times \frac{1\ V}{1\ \frac{J}{C}}$$

$$E = 1.504\ V - 0.12722\ V$$

$$E = 1.377\ V$$

Step 4: Check your work

Does your answer seem reasonable?

Step 5: Answer the question!

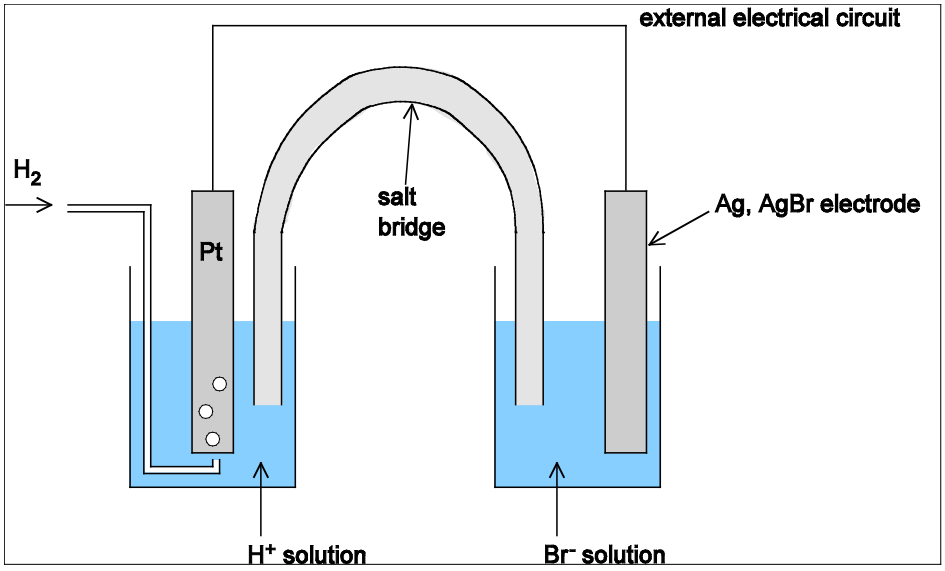
There was a verbal question attached to this calculation. It's easy to forget about that. Always re-read the question when you think you're done to make sure you answered everything!

Yes, the reaction is thermodynamically allowed under these conditions. $E > 0$

It is also acceptable to use Q to calculate $\Delta_r G$ from $\Delta_r G°$ using $\Delta_r G = \Delta_r G° + RTlnQ$. In that case, $\Delta_r G = -797.3\ \frac{kJ}{mol}$ and, since , $\Delta_r G < 0$, the reaction is still thermodynamically allowed.

8.

(a)



(b) $H_{2(g)} + 2\ AgBr_{(s)} \rightarrow 2\ H^+_{(aq)} + 2\ Ag_{(s)} + 2\ Br^-_{(aq)}$

9.

(a)

Oxidation (Anode): $C_3H_{8(g)} + 20\,OH^-_{(aq)} \rightarrow 3\,CO_{2(g)} + 14\,H_2O_{(l)} + 20\,e^-$

Reduction (Cathode): $O_2 + 2\,H_2O_{(l)} + 4\,e^- \rightarrow 4\,OH^-_{(aq)}$

(b) *Calculate potential under standard conditions & reaction quotient (Q) then use Nernst equation.*

Step 1: Write a balanced chemical equation for the reaction

$C_3H_{8(g)} + 5\,O_2 \rightarrow 3\,CO_{2(g)} + 4\,H_2O_{(l)}$

Step 2: Determine stoichiometric coefficient for electrons (ν_e)

$\nu_e = 20$

Step 3: Convert temperature to Kelvin (if necessary)

$T = 25\,℃ = 298.15\,K$

Step 4: Calculate the standard free energy change for the reaction

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = \left[3\,\Delta_f G°(\,CO_{2(g)}) + 4\,\Delta_f G°(H_2O_{(l)})\right] - \left[\Delta_f G°(C_3H_{8(g)}) + 5\,\Delta_f G°(O_2)\right]$

$\Delta_r G° = \left[3\left(-394.4\frac{kJ}{mol}\right) + 4\left(-237.1\frac{kJ}{mol}\right)\right] - \left[\left(-23.3\frac{kJ}{mol}\right) + 5\left(0\frac{kJ}{mol}\right)\right]$

$\Delta_r G° = -2108.3\frac{kJ}{mol}$

Step 5: Calculate standard potential from standard free energy change

$\Delta_r G° = -\nu_e F E°$

$E° = -\frac{\Delta_r G°}{\nu_e F}$

$E° = -\frac{\left(-2108.3\frac{kJ}{mol}\right)}{(20)\left(96\,485\frac{C}{mol}\right)} \times \frac{1000\,J}{1\,kJ}$

$E° = +1.0926\,\frac{J}{C} = +1.0926\,V$

Step 6: Determine activities for all reactants and products

$a_{C_3H_{8(g)}} = \frac{1\,bar}{1\,bar} = 1$ $\qquad$ $a_{CO_{2(g)}} = \frac{0.05\,bar}{1\,bar} = 0.05$

$a_{O_{2(g)}} = \frac{0.2\,bar}{1\,bar} = 0.2$ $\qquad$ $a_{H_2O_{(l)}} = 1$

Step 7: Calculate reaction quotient

$Q = \frac{\left(a_{CO_{2(g)}}\right)^3\left(a_{H_2O_{(l)}}\right)^4}{\left(a_{C_3H_{8(g)}}\right)\left(a_{O_{2(g)}}\right)^5} = \frac{(0.05)^3(1)^4}{(1)(0.2)^5} = 0.4$

Step 8: Calculate potential for reaction under nonstandard conditions

$E = E° - \frac{RT}{\nu_e F} lnQ$

$E = (1.0926\,V) - \frac{\left(8.314\,462\frac{J}{mol\cdot K}\right)(298.15\,K)}{(20)\left(96\,485\frac{C}{mol}\right)} ln(0.4) \times \frac{1\,V}{1\,\frac{J}{C}}$

$E = 1.0926\,V + 0.001\,V$

$E = 1.094\,V$

Step 9: Check your work

Does your answer seem reasonable?

10.

(a) The cell potential is positive therefore the reaction will be spontaneous (since a positive cell potential corresponds to a negative free energy change for the reaction).

(b) **Step 1: Find ν_e by balancing redox equation**

Oxidation: $N_2H_{4(aq)} \rightarrow N_{2(g)} + 4\,H^+_{(aq)} + 4\,e^-$

Reduction: $O_{2(g)} + 4\,H^+_{(aq)} + 4e^- \rightarrow 2\,H_2O_{(l)}$

Overall: $N_2H_{4(aq)} + O_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(l)}$

ν_e is the number of electrons canceled out when adding the oxidation and reduction half-reactions to obtain the overall balanced redox equation.

Therefore, $\nu_e = 4$

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

$\Delta_r G° = -\nu_e F E°$

$\Delta_r G° = -(4)\left(96\,485\,\frac{C}{mol}\right)\left(1.559\,\frac{J}{C}\right)\left(\frac{1\,kJ}{1000\,J}\right)$

$\Delta_r G° = -601.7\ \frac{kJ}{mol}$

Step 3: Calculate the standard free energy of formation for $N_2H_{4(aq)}$

$\Delta_r G° = \Delta_f G°(products) - \Delta_f G°(reactants)$

$\Delta_r G° = \left[\Delta_f G°\left(N_{2(g)}\right) + 2\Delta_f G°\left(H_2O_{(l)}\right)\right] - \left[\Delta_f G°\left(N_2H_{4(aq)}\right) + \Delta_f G°\left(O_{2(g)}\right)\right]$

$\left(-601.7\,\frac{kJ}{mol}\right) = \left[\left(0\,\frac{kJ}{mol}\right) + 2\left(-237.1\,\frac{kJ}{mol}\right)\right] - \left[\Delta_f G°\left(N_2H_{4(aq)}\right) + \left(0\,\frac{kJ}{mol}\right)\right]$

$\left(-601.7\,\frac{kJ}{mol}\right) = 2\left(-237.1\,\frac{kJ}{mol}\right) - \Delta_f G°\left(N_2H_{4(aq)}\right)$

$\Delta_f G°\left(N_2H_{4(aq)}\right) = 2\left(-237.1\,\frac{kJ}{mol}\right) - \left(-601.7\,\frac{kJ}{mol}\right)$

$\Delta_f G°\left(N_2H_{4(aq)}\right) = 127.5\,\frac{kJ}{mol}$

Step 4: Check your work

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

11.

Oxidation: $Cr_2O^{2-}_{7(aq)} + 14\,H^+_{(aq)} + 6\,e^- \rightarrow 2\,Cr^{3+}_{(aq)} + 7\,H_2O_{(l)}$ multiply by 2

Reduction: $C_3H_7CH_2OH_{(aq)} + H_2O_{(l)} \rightarrow C_3H_7CO_2H_{(aq)} + 4\,H^+_{(aq)} + 4\,e^-$ multiply by 3

Overall: $2Cr_2O^{2-}_{7(aq)} + 3C_3H_7CH_2OH_{(aq)} + 16H^+_{(aq)} \rightarrow 4Cr^{3+}_{(aq)} + 11H_2O_{(l)} + 3C_3H_7CO_2H_{(aq)}$

12.

(a) $Sn_{(s)} + Pb^{2+}_{(aq)} \rightarrow Pb_{(s)} + Sn^{2+}_{(aq)}$

(b) *Calculate potential under standard conditions and reaction quotient (Q) then use Nernst equation to calculate potential under nonstandard conditions.*

Step 1: Write a balanced chemical equation for the reaction

This was done in part (a)

Step 2: Determine stoichiometric coefficient for electrons (ν_e)

$\nu_e = 2$

Step 3: Convert temperature to Kelvin (if necessary)

$T = 25\ ℃ = 298.15\ K$

Step 4: Calculate standard potential from standard reduction potentials of half-reactions

$E° = (-0.125\ V) + (+0.137\ V)$

$E° = +0.012\ V$

Step 5: Determine activities for all reactants and products

$a_{Sn_{(s)}} = 1$ $\qquad$ $a_{Pb_{(s)}} = 1$

$a_{Pb^{2+}_{(aq)}} = \frac{0.600\ M}{1\ M} = 0.600$ $\qquad$ $a_{Sn^{2+}_{(aq)}} = \frac{0.075\ M}{1\ M} = 0.075$

Step 6: Calculate reaction quotient

$$Q = \frac{\left(a_{Pb_{(s)}}\right)\left(a_{Sn^{2+}_{(aq)}}\right)}{\left(a_{Sn_{(s)}}\right)\left(a_{Pb^{2+}_{(aq)}}\right)} = \frac{(1)(0.075)}{(1)(0.600)} = 0.13$$

Step 7: Calculate potential for reaction under nonstandard conditions

$$E = E° - \frac{RT}{\nu_e F} lnQ$$

$$E = (0.012\ V) - \frac{\left(8.314\ 462 \frac{J}{mol \cdot K}\right)(298.15\ K)}{(2)\left(96\ 485 \frac{C}{mol}\right)} ln(0.13) \times \frac{1\ V}{1\ \frac{J}{C}}$$

$$E = 0.012\ V + 0.027\ V$$

$$E = 0.039\ V$$

Step 8: Check your work

Does your answer seem reasonable?

The reaction quotient is less than 1, so E ought to be more positive than E°.

(c) As the reaction proceeds, it approaches an equilibrium state. As a result, E_{cell} will decrease until it reaches 0 V at equilibrium.

13.

(a) **Step 1: Find ν_e by balancing redox equation**

Oxidation: $H_{2(g)} \rightarrow 2\,H^+_{(aq)} + 2\,e^-$ multiply by 2

Reduction: $O_{2(g)} + 4\,H^+_{(aq)} + 4e^- \rightarrow 2\,H_2O_{(l)}$

Overall: $2\,H_{2(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(l)}$

Therefore, $\nu_e = 4$

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

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = 2\,\Delta_f G°\left(H_2O_{(l)}\right) - \left[2\,\Delta_f G°\left(H_{2(g)}\right) + \Delta_f G°(O_2)\right]$

$\Delta_r G° = 2\left(-237.1\frac{kJ}{mol}\right) - \left[2\left(0\frac{kJ}{mol}\right) + \left(0\frac{kJ}{mol}\right)\right]$

$\Delta_r G° = -474.2\frac{kJ}{mol}$

Step 3: Calculate standard potential from standard free energy change

$\Delta_r G° = -\nu_e F E°$

$E° = -\frac{\Delta_r G°}{\nu_e F}$

$E° = -\frac{\left(-474.2\frac{kJ}{mol}\right)}{(4)\left(96\,485\frac{C}{mol}\right)} \times \frac{1000\,J}{1\,kJ}$

$E° = +1.229\,\frac{J}{C} = +1.229\,V$

Step 4: Check your work

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

(b) **Step 1: Convert temperature to Kelvin (if necessary)**

$T = 25\,℃ = 298.15\,K$

Step 2: Determine activities for all reactants and products

$a_{H_{2(g)}} = \frac{0.75\,bar}{1\,bar} = 0.75$ $\qquad$ $a_{H_2O_{(l)}} = 1$

$a_{O_{2(g)}} = \frac{0.15\,bar}{1\,bar} = 0.15$

Step 3: Calculate reaction quotient

$Q = \frac{\left(a_{H_2O_{(l)}}\right)^2}{\left(a_{H_{2(g)}}\right)^2\left(a_{O_{2(g)}}\right)} = \frac{(1)^2}{(0.75)^2(0.15)} = 12$

Step 4: Calculate potential for reaction under nonstandard conditions

$E = E° - \frac{RT}{\nu_e F} lnQ$

$E = (1.229\,V) - \frac{\left(8.314\,462\frac{J}{mol \cdot K}\right)(298.15\,K)}{(4)\left(96\,485\frac{C}{mol}\right)} ln(12) \times \frac{1\,V}{1\,\frac{J}{C}}$

$E = 1.229\,V - 0.0159\,V$

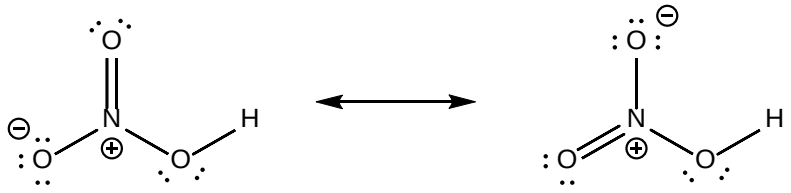
$E = 1.213\,V$

Step 5: Check your work

Does your answer seem reasonable?

14.

(a)



oxidation state of N is +5

oxidation state of O is -2 *(for all of them)*

oxidation state of H is +1

(b) Gold (Au) is being oxidized (0 to +3)

(c) Nitrogen (N) is being reduced (+5 to +4)

(d)+(e)

Oxidation: $Au_{(s)} + 4\,HCl_{(aq)} \rightarrow HAuCl_{4\,(aq)} + 3\,H^{+}_{(aq)} + 3\,e^{-}$

Reduction: $HNO_{3(aq)} + H^{+}_{(aq)} + e^{-} \rightarrow NO_{2(g)} + H_2O_{(l)}$ multiply by 3

Overall: $Au_{(s)} + 3\,HNO_{3(aq)} + 4\,HCl_{(aq)} \rightarrow HAuCl_{4\,(aq)} + 3\,NO_{2(g)} + 3\,H_2O_{(l)}$

15.

(a)

Oxidation: $Mn^{2+}_{(aq)} + 4\,H_2O_{(l)} \longrightarrow MnO^{-}_{4\,(aq)} + 8\,H^{+}_{(aq)} + 5\,e^{-}$ multiply by 2

Reduction: $F_{2(g)} + 2e^{-} \longrightarrow 2\,F^{-}_{(aq)}$ multiply by 5

Overall: $2\,Mn^{2+}_{(aq)} + 8\,H_2O_{(l)} + 5\,F_{2(g)} \longrightarrow 2\,MnO^{-}_{4\,(aq)} + 16\,H^{+}_{(aq)} + 10\,F^{-}_{(aq)}$

(b) *Calculate potential under standard conditions and reaction quotient (Q) then use Nernst equation to calculate potential under nonstandard conditions.*

Step 1: Write a balanced chemical equation for the reaction

This was done in part (a)

Step 2: Determine stoichiometric coefficient for electrons (ν_e)

$\nu_e = 10$

Step 3: Convert temperature to Kelvin (if necessary)

$T = 25.00\ ℃ = 298.15\ K$

Step 4: Calculate the standard free energy change for the reaction

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = \left[2\,\Delta_f G°\left(MnO^{-}_{4(aq)}\right) + 16\,\Delta_f G°\left(H^{+}_{(aq)}\right) + 10\,\Delta_f G°\left(F^{-}_{(aq)}\right)\right]$

$\quad -\left[2\,\Delta_f G°\left(Mn^{2+}_{(aq)}\right) + 8\,\Delta_f G°\left(H_2O_{(l)}\right) + 5\,\Delta_f G°\left(F_{2(g)}\right)\right]$

$\Delta_r G° = \left[2\left(-425.1\frac{kJ}{mol}\right) + 16\left(0\frac{kJ}{mol}\right) + 10\left(-278.8\frac{kJ}{mol}\right)\right]$

$\quad -\left[2\left(-228.1\frac{kJ}{mol}\right) + 8\left(-237.1\frac{kJ}{mol}\right) + 5\left(0\frac{kJ}{mol}\right)\right]$

$\Delta_r G° = -1285.2 \frac{kJ}{mol}$

Step 5: Calculate standard potential from standard free energy change

$\Delta_r G° = -\nu_e F E°$

$E° = -\frac{\Delta_r G°}{\nu_e F}$

$E° = -\frac{\left(-1285.2\frac{kJ}{mol}\right)}{(10)\left(96\,485\frac{C}{mol}\right)} \times \frac{1000\ J}{1\ kJ}$

$E° = +1.332\ \frac{J}{C} = +1.332\ V$

Step 6: Determine activities for all reactants and products

$a_{Mn^{2+}_{(aq)}} = \frac{0.0320\ M}{1\ M} = 0.0320$

$a_{MnO^{-}_{4(aq)}} = \frac{0.010\ M}{1\ M} = 0.010$

$a_{H_2O_{(l)}} = 1$

$a_{H^{+}_{aq)}} = 10^{-pH} = 10^{-2.1} = 0.008$

$a_{F_{2(g)}} = \frac{0.110\ bar}{1\ bar} = 0.110$

$a_{F^{-}_{(aq)}} = \frac{0.0070\ M}{1\ M} = 0.0070$

Step 7: Calculate reaction quotient

$$Q = \frac{\left(a_{MnO^{-}_{4}(aq)}\right)^2\left(a_{H^{+}_{(aq)}}\right)^{16}\left(a_{F^{-}(aq)}\right)^{10}}{\left(a_{Mn^{2+}_{(aq)}}\right)^2\left(a_{H_2O_{(l)}}\right)^8\left(a_{F_{2(g)}}\right)^5} = \frac{(0.010)^2(10^{-2.1})^{16}(0.0070)^{10}}{(0.0320)^2(1)^8(0.110)^5} = 4.3 \times 10^{-52}$$

Step 8: Calculate potential for reaction under nonstandard conditions

$E = E° - \frac{RT}{\nu_e F} lnQ$

$E = (1.332\ V) - \frac{\left(8.314\,462\frac{J}{mol \cdot K}\right)(298.15\ K)}{(10)\left(96\,485\frac{C}{mol}\right)} ln(4.3 \times 10^{-52}) \times \frac{1\ V}{1\ \frac{J}{C}}$

$E = 1.332\ V + 0.304\ V$

$E = 1.636\ V$

Step 9: Check your work

Does your answer seem reasonable?

16.

Oxidation: $Sn^{2+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2\ e^-$ multiply by 4

Reduction: $IO^{-}_{4(aq)} + 8\ H^{+}_{(aq)} + 8\ e^- \longrightarrow I^{-}_{(aq)} + 4\ H_2O_{(l)}$

Overall: $4\ Sn^{2+}_{(aq)} + IO^{-}_{4(aq)} + 8\ H^{+}_{(aq)} \longrightarrow 4\ Sn^{4+}_{(aq)} + I^{-}_{(aq)} + 4\ H_2O_{(l)}$

17.

(a) **Step 1: Write a balanced chemical equation for the reaction (to give half reactions and ν_e)**

Oxidation: $H_{2(g)} \longrightarrow 2\,H^+_{(aq)} + 2\,e^-$

Reduction: $V^{2+}_{(aq)} + 2\,e^- \longrightarrow V_{(s)}$

Overall: $H_{2(g)} + V^{2+}_{(aq)} \longrightarrow 2\,H^+_{(aq)} + V_{(s)}$

Step 2: Determine stoichiometric coefficient for electrons (ν_e)

$\nu_e = 2$

Step 3: Convert temperature to Kelvin (if necessary)

$T = 25\ ℃ = 298.15\ K$

Step 4: Determine activities for all reactants and products

$a_{H_{2(g)}} = \frac{1\ bar}{1\ bar} = 1$ $\qquad$ $a_{H^+_{aq)}} = 10^{-pH} = 10^{-5.0} = 1 \times 10^{-5}$

$a_{V^{2+}_{(aq)}} = \frac{0.0010\ M}{1\ M} = 0.0010$ $\qquad$ $a_{V_{(s)}} = 1$

Step 5: Calculate reaction quotient

$$Q = \frac{\left(a_{H^+_{aq)}}\right)^2\left(a_{V_{(s)}}\right)}{\left(a_{H_{2(g)}}\right)\left(a_{V^{2+}_{(aq)}}\right)} = \frac{(1\times10^{-5})^2(1)}{(1)(0.0010)} = 1 \times 10^{-7}$$

Step 6: Calculate standard potential from nonstandard potential using Nernst equation

$E = E° - \frac{RT}{\nu_e F} lnQ$

$E° = E + \frac{RT}{\nu_e F} lnQ$

$$E° = (-0.97\ V) + \frac{\left(8.314\,462\frac{J}{mol\cdot K}\right)(298.15\ K)}{(2)\left(96\,485\frac{C}{mol}\right)} ln(1 \times 10^{-7}) \times \frac{1\ V}{1\frac{J}{C}}$$

$E° = -0.97\ V + (-0.21\ V)$

$E° = -1.18\ V$

Step 7: Calculate standard reduction potential for half-cell from standard cell potential

Oxidation: $H_{2(g)} \longrightarrow 2\,H^+_{(aq)} + 2\,e^-$ $\qquad$ $E°_{H_2/H^+} = 0\ V$

Reduction: $V^{2+}_{(aq)} + 2\,e^- \longrightarrow V_{(s)}$ $\qquad$ $E°_{V^{2+}/V} = ???$

Overall: $H_{2(g)} + V^{2+}_{(aq)} \longrightarrow 2\,H^+_{(aq)} + V_{(s)}$ $\qquad$ $E°_{cell} = -1.18\ V$

Since the half-reaction standard potentials add up to the overall standard potential, the standard potential for the reduction half-reaction must be $E°_{V^{2+}/V} = -1.18\ V$. Since it is the reduction half-reaction, this is also the standard reduction potential for $V^{2+}_{(aq)}$.

Step 8: Check your work

Does your answer seem reasonable?

(b) *To calculate the standard free energy of formation of $V^{2+}_{(aq)}$, first calculate the standard free energy change for the overall reaction. As long as you know (or can look up) standard free energies of formation for all other products/reactants, you can then calculate the missing standard free energy of formation.*

You will need to use ν_e and the standard potential calculated in part (a).

Step 1: Calculate the standard free energy change for the reaction from standard potential

$\Delta_r G° = -\nu_e F E°$

$\Delta_r G° = -(2)\left(96\,485 \frac{C}{mol}\right)\left(-1.18 \frac{J}{C}\right)\left(\frac{1\ kJ}{1000\ J}\right)$

$\Delta_r G° = +227\ \frac{kJ}{mol}$

Step 2: Calculate the standard free energy of formation for $N_2H_{4(aq)}$

$\Delta_r G° = \Delta_f G°(products) - \Delta_f G°(reactants)$

$\Delta_r G° = \left[2\ \Delta_f G°\left(H^+_{(aq)}\right) + \Delta_f G°\left(V_{(s)}\right)\right] - \left[\Delta_f G°\left(H_{2(g)}\right) + \Delta_f G°\left(V^{2+}_{(aq)}\right)\right]$

$\left(+227 \frac{kJ}{mol}\right) = \left[2\left(0 \frac{kJ}{mol}\right) + \left(0 \frac{kJ}{mol}\right)\right] - \left[\left(0 \frac{kJ}{mol}\right) + \Delta_f G°\left(V^{2+}_{(aq)}\right)\right]$

$\left(+227 \frac{kJ}{mol}\right) = -\Delta_f G°\left(V^{2+}_{(aq)}\right)$

$\Delta_f G°\left(V^{2+}_{(aq)}\right) = -227 \frac{kJ}{mol}$

Step 3: Check your work

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

18. *The equilibrium constant for a reaction can be calculated from the standard free energy change for the reaction. This, in turn, can be calculated from the standard potential.*

Standard potential for the overall reaction can be calculated by adding the standard potentials for the two half-reactions.

Step 1: Calculate standard cell potential from half-cell potentials

Oxidation:	$Hg_{(l)} \longrightarrow Hg^{2+}_{(aq)} + 2\,e^-$	$E°_{Hg/Hg^{2+}} = -0.851\ V$
Reduction:	$Hg^{2+}_{2(aq)} + 2\,e^- \longrightarrow 2\,Hg_{(l)}$	$E°_{Hg_2^{2+}/Hg} = +0.7973\ V$
Overall:	$Hg^{2+}_{2(aq)} \longrightarrow Hg^{2+}_{(aq)} + Hg_{(l)}$	$E°_{cell} = ???$

Note that the standard potential for the oxidation half-reaction is equal to the corresponding standard reduction potential $(+0.851\ V)$ multiplied by -1. Any time you 'flip' a reaction or half-reaction, you have to change the sign of the corresponding potential (or free energy or enthalpy or entropy).

$E°_{cell} = (-0.851\ V) + (+0.7973\ V)$

$E°_{cell} = -0.054\ V$

Step 2: Determine stoichiometric coefficient for electrons (ν_e)

$\nu_e = 2$

Step 3: Convert temperature to Kelvin (if necessary)

$T = 25\ ℃ = 298.15\ K$

Step 4: Calculate standard free energy change from standard cell potential

$\Delta_r G° = -\nu_e F E°$

$\Delta_r G° = -(2)\left(96\,485\frac{C}{mol}\right)\left(-0.054\frac{J}{C}\right)\left(\frac{1\,kJ}{1000\,J}\right)$

$\Delta_r G° = 10\ \frac{kJ}{mol}$

Step 5: Calculate equilibrium constant from standard free energy change

$\Delta_r G° = -RTlnK$

$lnK = -\frac{\Delta_r G°}{RT}$

$lnK = -\frac{\left(10\frac{kJ}{mol}\right)}{\left(8.314\,462\frac{J}{mol\cdot K}\right)(298.15\,K)} \times \frac{1000\,J}{1\,kJ}$

$lnK = -4.2$

$K = e^{-4.2}$

$K = 0.015$

Step 5: Check your work

Does your answer seem reasonable?

Step 6: Answer the question!

There was a verbal question attached to this calculation. It's easy to forget about that. Always re-read the question when you think you're done to make sure you answered everything!

The equilibrium concentration of $Hg^{2+}_{(aq)}$ is smaller than that of $Hg^{2+}_{2(aq)}$.

$K = \frac{\left(a_{Hg^{2+}_{(aq)}}\right)\left(a_{Hg_{(l)}}\right)}{\left(a_{Hg^{2+}_{2(aq)}}\right)}$ and $a_{Hg_{(l)}} = 1$. Therefore, since $K < 1$, it follows that $a_{Hg^{2+}_{(aq)}} < a_{Hg^{2+}_{2(aq)}}$.

19.

(a) *Use the equilibrium constant expression to relate the activity (and therefore the concentration) of $Hg^{2+}_{(aq)}$ to the equilibrium constant provided.*

$K = \frac{\left(a_{Hg^{2+}_{(aq)}}\right)\left(a_{HS^{-}_{(aq)}}\right)\left(a_{OH^{-}_{(aq)}}\right)}{\left(a_{HgS_{(s)}}\right)\left(a_{H_2O_{(l)}}\right)}$

We know that the activities of the solid HgS and liquid water are both 1.

In neutral water, the concentration of hydroxide is $10^{-7}M$ therefore the activity of hydroxide in a neutral solution is 10^{-7}.

Since every molecule of HgS that reacts with water generates one $Hg^{2+}_{(aq)}$ ion and one $HS^{-}_{(aq)}$ ion, the activities of those two ions are equal. I will represent that activity as 'x'.

Therefore:

$K = \frac{(x)(x)(10^{-7})}{(1)(1)} = (10^{-7})(x^2)$

$x = \sqrt{\frac{K}{10^{-7}}} = \sqrt{\frac{2\times10^{-53}}{10^{-7}}} = 1.4 \times 10^{-23}$ *but only 1 sig. fig.*

Since the concentration of $Hg^{2+}_{(aq)}$ is equal to its activity multiplied by $1\ M$, that means that the concentration of $Hg^{2+}_{(aq)}$ is $1.4 \times 10^{-23}\ M$.

The question asked for concentration in molecules/L, though, not moles/L. Use Avogadro's number to convert from moles/L to molecules/L.

$$c_{Hg^{2+}_{(aq)}} = 1.4 \times 10^{-23}\ \frac{mol}{L} \times \frac{6.022\ 141 \times 10^{23}\ molecules}{1\ mol} = 9\ \frac{molecules}{L}$$

In other words, we only expect to find nine molecules of HgS dissolved in 1 L of water. This equilibrium constant was clearly not measured by measuring a concentration of dissolved material!

(b) We might try something analogous to the AgCl solubility measurement. We could make up an Hg|HgS electrode. (This is not quite the same as an Ag|AgCl electrode since Hg is a liquid, but in principle we could make something like this.) The likely half-cell reaction would be:

$$HgS_{(s)} + H_2O_{(l)} + 2\,e^- \rightarrow Hg_{(l)} + HS^-_{(aq)} + OH^-_{(aq)}$$

Having made this electrode, we could measure its half-cell potential and calculate the corresponding standard reduction potential. Then, combining this standard reduction potential with the standard reduction potential of Hg^{2+} to Hg (which is already available), we could calculate the equilibrium constant for the solubility equilibrium.

20.

(a)

Oxidation: $Cd_{(s)} + 2\,OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + 2\,e^-$ $\quad E°_{Cd/\,Cd(OH)_2} = +0.809\ V$

Reduction: $Zn^{2+}_{(aq)} + 2\,e^- \longrightarrow Zn_{(s)}$ $\quad E°_{Zn^{2+}/Zn} = -0.7618\ V$

Overall: $Cd_{(s)} + Zn^{2+}_{(aq)} + 2\,OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + Zn_{(s)}$ $\quad E°_{cell} = ???$

(b) Calculate the potential generated by this cell at 25 °C.

Standard reduction potentials for the two half-reactions are provided on the Table of Standard Reduction Potentials. Add them to get the potential for the reaction under standard conditions then use the Nernst equation to calculate the potential under nonstandard conditions. Remember that the standard potential for the oxidation half-reaction is equal to the corresponding standard reduction potential $(-0.809\ V)$ multiplied by -1. For clarity, standard half-cell potentials are noted in the answer to part (a) even though they weren't needed for part (a).

Step 1: Calculate standard potential for overall reaction by adding standard potentials for half-reactions

$E°_{cell} = (+0.809\ V) + (-0.7618\ V)$

$E°_{cell} = +0.047\ V$

Step 2: Determine stoichiometric coefficient for electrons (ν_e)

$\nu_e = 2$

Step 3: Convert temperature to Kelvin (if necessary)

$T = 25\ ℃ = 298.15\ K$

Step 4: Determine activities for all reactants and products

$a_{Cd_{(s)}} = 1$ $\qquad$ $a_{Cd(OH)_{2(s)}} = 1$

$a_{Zn^{2+}_{(aq)}} = \frac{0.11\ M}{1\ M} = 0.11$ $\qquad$ $a_{Zn_{(s)}} = 1$

$a_{OH^-_{(aq)}} = \frac{0.023\ M}{1\ M} = 0.023$

Step 5: Calculate reaction quotient

$$Q = \frac{\left(a_{Cd(OH)_{2(s)}}\right)\left(a_{Zn_{(s)}}\right)}{\left(a_{Cd_{(s)}}\right)\left(a_{Zn^{2+}_{(aq)}}\right)\left(a_{OH^-_{(aq)}}\right)^2} = \frac{(1)(1)}{(1)(0.11)(0.023)^2} = 1.7 \times 10^4$$

Step 6: Calculate standard potential from nonstandard potential using Nernst equation

$$E = E° - \frac{RT}{\nu_e F} lnQ$$

$$E = (0.047\ V) - \frac{\left(8.314\ 462 \frac{J}{mol \cdot K}\right)(298.15\ K)}{(2)\left(96\ 485 \frac{C}{mol}\right)} ln(1.7 \times 10^4) \times \frac{1\ V}{1\ \frac{J}{C}}$$

$$E = 0.047\ V - (0.125\ V)$$

$$E = -0.078\ V$$

Step 7: Check your work

Does your answer seem reasonable?

The only species with activities other than 1 are both reactants, and their activities are both significantly less than 1. As such, Q is expected to be significantly larger than 1 (more products and/or less reactants compared to standard conditions) and therefore the reaction is expected to be less thermodynamically favourable (in this case, more negative cell potential) than under standard conditions.

(c) The reaction is not thermodynamically allowed as written because the cell potential is negative.

It would have been thermodynamically allowed under standard conditions because the standard cell potential was positive.

21. The half-cell reactions are:

Oxidation: $2\ I^-_{(aq)} \longrightarrow I_{2(s)} + 2\ e^-$ $\qquad$ $E°_{I^-/I_2} = ???$

Reduction: $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$ (multiply by 2) $\qquad$ $E°_{Fe^{3+}/Fe^{2+}} = +0.771\ V$

Overall: $2\ Fe^{3+}_{(aq)} + 2\ I^-_{(aq)} \longrightarrow 2\ Fe^{2+}_{(aq)} + I_{2(s)}$ $\qquad$ $E°_{cell} = ???$

(a) The anode (from oxidation half-reaction) goes at the left. The cathode (from reduction half-reaction) goes at the right.

$$I_{2(s)} \left| I^-_{(aq)} \right\| Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)}$$

(b) *Since the standard potential for the overall reaction was not provided, it will have to be calculated from the standard free energy change for the reaction. That is, in turn, calculated from standard free energies of formation.*

Step 1: Write a balanced chemical equation for the reaction (to give half reactions and ν_e)

see answer key before part (a)

Step 2: Determine stoichiometric coefficient for electrons (ν_e)

$\nu_e = 2$

Step 3: Convert temperature to Kelvin (if necessary)

$T = 25\ ℃ = 298.15\ K$

Step 4: Calculate the standard free energy change for the reaction

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = \left[2\ \Delta_f G°\left(Fe^{2+}_{(aq)}\right) + \Delta_f G°\left(I_{2(s)}\right)\right] - \left[2\ \Delta_f G°\left(Fe^{3+}_{(aq)}\right) + \ 2\ \Delta_f G°\left(I^-_{(aq)}\right)\right]$

$\Delta_r G° = \left[2\left(-84.94\frac{kJ}{mol}\right) + \left(0\frac{kJ}{mol}\right)\right] - \left[2\left(-10.5\frac{kJ}{mol}\right) + 2\left(-51.67\frac{kJ}{mol}\right)\right]$

$\Delta_r G° = -45.5\frac{kJ}{mol}$

Step 5: Calculate standard potential from standard free energy change

$\Delta_r G° = -\nu_e F E°$

$E° = -\frac{\Delta_r G°}{\nu_e F}$

$E° = -\frac{\left(-45.5\ \frac{kJ}{mol}\right)}{(2)\left(96\ 485\frac{C}{mol}\right)} \times \frac{1000\ J}{1\ kJ}$

$E° = +0.236\ \frac{J}{C} = +0.236\ V$

Step 6: Calculate standard reduction potential for half-cell from standard cell potential

Oxidation:	$2\ I^-_{(aq)} \longrightarrow\ I_{2(s)} + \ 2\ e^-$	$E°_{I^-/I_2} = ???$
Reduction:	$Fe^{3+}_{(aq)}\ +\ e^- \longrightarrow\ Fe^{2+}_{(aq)}$	$E°_{Fe^{3+}/Fe^{2+}} = +0.771\ V$
Overall:	$2\ Fe^{3+}_{(aq)}\ +\ 2\ I^-_{(aq)} \longrightarrow\ 2\ Fe^{2+}_{(aq)}\ +\ I_{2(s)}$	$E°_{cell} = \ +0.236\ V$

$E°_{cell} = \ E°_{I^-/I_2} + \ E°_{Fe^{3+}/Fe^{2+}}$

$E°_{I^-/I_2} = E°_{cell} - \ E°_{Fe^{3+}/Fe^{2+}}$

$E°_{I^-/I_2} = (+0.236\ V) - \ (+0.771\ V)$

$E°_{I^-/I_2} = -0.535\ V$

HOWEVER, the question asked about the standard reduction potential for I_2. This is the standard potential for oxidation of I^- to I_2 (the reverse reaction). When reversing the direction of the reaction, we must also switch the sign for the potential.

The standard reduction potential for I_2 is the standard potential for:

$I_{2(s)} + \ 2\ e^- \longrightarrow\ 2\ I^-_{(aq)}$

$E°_{I_2/I^-} = +0.535\ V$

Step 7: Check your work

Does your answer seem reasonable?

It matches the value in the Table of Standard Reduction Potentials in the text.

Generally speaking, standard reduction potentials should have values between $+3\ V$ *and* $-3\ V$.