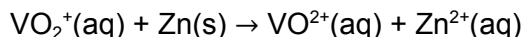


Electrochemistry R and R Worksheet

7/29/24

1) Balance the net ionic equation for the reaction of the dioxovanadium(V) ion, VO_2^+ , with zinc in acid solution to form VO^{2+} .



Step 1. Recognize the reaction as an oxidation–reduction reaction.

The oxidation number of V changes from +5 in VO_2^+ to +4 in VO^{2+} . The oxidation number of Zn changes from 0 in the metal to +2 in Zn^{2+} .

Step 2. Separate the process into half-reactions.

Oxidation: $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq})$
(Zn(s) is oxidized and is the reducing agent.)

Reduction: $\text{VO}_2^+(\text{aq}) \rightarrow \text{VO}^{2+}(\text{aq})$
($\text{VO}_2^+(\text{aq})$ is reduced and is the oxidizing agent.)

Step 3. Balance the half-reactions for mass.

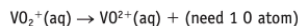
Begin by balancing all atoms except H and O. (These atoms are always the last to be balanced because they often appear in more than one reactant or product.)

Zinc half-reaction: $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq})$

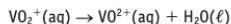
The zinc half-reaction is already balanced for mass.

Vanadium half-reaction: $\text{VO}_2^+(\text{aq}) \rightarrow \text{VO}^{2+}(\text{aq})$

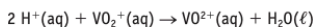
The V atoms in this half-reaction are already balanced. An oxygen-containing species must be added to the right side of the equation to achieve an O atom balance, however.



In acid solution, add H_2O to the side requiring O atoms, one H_2O molecule for each O atom required.



There are now two unbalanced H atoms on the right. Because the reaction occurs in an acidic solution, H^+ ions are present. Therefore, a mass balance for H can be achieved by adding H^+ to the side of the equation deficient in H atoms. Here, two H^+ ions are added to the left side of the equation, and the equation is balanced for mass.



Step 4. Balance the half-reactions for charge by adding electrons to the more positive side to make the charges equal on both sides.

Two electrons are added to the right side of the zinc half-reaction to bring its charge down to the same value as is present on the left side (in this case, zero).

Zinc half-reaction: $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^-$

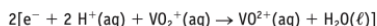
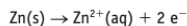
The mass-balanced VO_2^+ equation has a net charge of 3+ on the left side and 2+ on the right. Therefore, 1 e^- is added to the more positive left side, giving a net charge of 2+ on both sides of the equation.

Vanadium half-reaction: $\text{e}^- + 2 \text{H}^+(\text{aq}) + \text{VO}_2^+(\text{aq}) \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\ell)$

As a check on your work, notice that the vanadium atom changes in oxidation number from +5 to +4 and so needs to acquire one electron for each vanadium atom reduced.

Step 5. Multiply the half-reactions by appropriate factors so that the reducing agent supplies as many electrons as the oxidizing agent consumes.

Here, the oxidation half-reaction supplies two electrons per Zn atom, and the reduction half-reaction consumes one electron per VO_2^+ ion. Therefore, the reduction half-reaction must be multiplied by two. Now two ions of the oxidizing agent (VO_2^+) consume the two electrons provided per atom of the reducing agent (Zn).



Step 6. Add the half-reactions to give the balanced, overall equation.

Oxidation half-reaction: $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^-$

Reduction half-reaction: $2 \text{e}^- + 4 \text{H}^+(\text{aq}) + 2 \text{VO}_2^+(\text{aq}) \rightarrow 2 \text{VO}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\ell)$

Net ionic equation: $\text{Zn}(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{VO}_2^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{VO}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\ell)$

Step 7. Simplify by eliminating reactants and products that appear on both sides.

This step is not required here.

2) Aluminum metal is oxidized in aqueous base, with water serving as the oxidizing agent. The products of the reaction are $[\text{Al}(\text{OH})_4]^{-}(\text{aq})$ and $\text{H}_2(\text{g})$. Write a balanced net ionic equation for this reaction.

Step 1. Recognize the reaction as an oxidation–reduction reaction.

The unbalanced equation is



Here, aluminum is oxidized, with its oxidation number changing from 0 to +3. Hydrogen is reduced, with its oxidation number decreasing from +1 to zero.

Step 2. Separate the process into half-reactions.



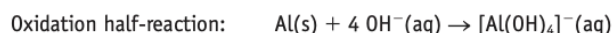
(Al oxidation number increased from 0 to +3.)



(H oxidation number decreased from +1 to 0.)

Step 3. Balance the half-reactions for mass.

Addition of OH^{-} or OH^{-} and H_2O is required for mass balance in both half-reactions. In the case of the aluminum half-reaction, add OH^{-} ions to the left side.

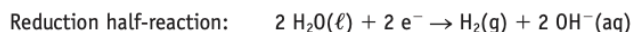
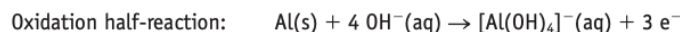


To balance the half-reaction for water reduction for mass, notice that an oxygen-containing species must appear on the right side of the equation. Because H_2O is a reactant, use OH^{-} , which is present in this basic solution, as the other product.



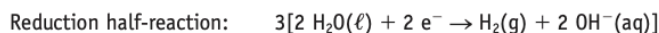
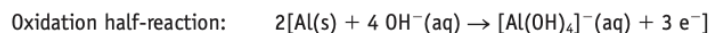
Step 4. Balance the half-reactions for charge.

Electrons are added to balance charge.

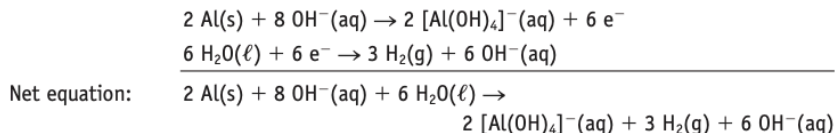


Step 5. Multiply the half-reactions by appropriate factors so that the reducing agent donates as many electrons as the oxidizing agent consumes.

Here, electron balance is achieved by using two Al atoms to provide six electrons, which are then acquired by six H_2O molecules.

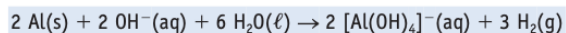


Step 6. Add the half-reactions.



Step 7. Simplify by eliminating reactants and products that appear on both sides.

Six OH^{-} ions can be canceled from the two sides of the equation:



Think about Your Answer The final equation is balanced for mass and charge.

Mass balance: 2 Al, 14 H, and 8 O on each side of the equation.

Charge balance: There is a net -2 charge on each side.

3) Consider the following half-reactions:

Half-Reaction	E° (V)
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66

a) Based on E° values, which metal is the most easily oxidized?

Aluminum, because it has the lowest standard reduction potential, which means it is most readily oxidized (or is the best reducing agent).

b) Which metals on this list are capable of reducing $\text{Fe}^{2+}(\text{aq})$ to $\text{Fe}(\text{s})$?

Aluminum and Zinc. For Iron to be reduced, it needs to react with a metal that has a lower standard reduction potential (weaker oxidizing agent / less readily reduced).

c) Write a balanced chemical equation for the reaction of $\text{Fe}^{2+}(\text{aq})$ with $\text{Sn}(\text{s})$. Is this reaction product-favored or reactant-favored at equilibrium?

Reduction Half Reaction: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$

Oxidation Half Reaction: $\text{Sn}(\text{s}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{e}^-$

Net Ionic Equation: $\text{Fe}^{2+}(\text{aq}) + \text{Sn}(\text{s}) \rightarrow \text{Fe}(\text{s}) + \text{Sn}^{2+}(\text{aq})$;

$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} + E^\circ_{\text{oxidation}} ; E^\circ_{\text{oxidation}} = -E^\circ_{\text{reduction}}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{reduction}}$$

$$E^\circ_{\text{cell}} = -0.44 \text{ V} - (-0.14 \text{ V}) = -0.30 \text{ V}$$

Since $E^\circ_{\text{cell}} < 0$, then $\Delta_r G^\circ > 0$, and thus $K \ll 1$ which means the reaction is reactant-favored at equilibrium.

d) Write a balanced chemical equation for the reaction of $\text{Zn}^{2+}(\text{aq})$ with $\text{Sn}(\text{s})$. Is this reaction product-favored or reactant-favored at equilibrium?

Reduction Half Reaction: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$

Oxidation Half Reaction: $\text{Sn}(\text{s}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{e}^-$

Net Ionic Equation: $\text{Zn}^{2+}(\text{aq}) + \text{Sn}(\text{s}) \rightarrow \text{Zn}(\text{s}) + \text{Sn}^{2+}(\text{aq})$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{cell}} = -0.76 \text{ V} - (-0.014 \text{ V}) = -0.62 \text{ V}$$

Since $E^\circ_{\text{cell}} < 0$, then $\Delta_r G^\circ > 0$, and thus $K \ll 1$ which means the reaction is reactant-favored at equilibrium.

4) Use standard reduction potentials for the half-reactions $\text{AgBr}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Br}^-(\text{aq})$ and $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ to calculate the value of K_{sp} for AgBr.

Reduction Half Reaction: $\text{AgBr}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Br}^-(\text{aq})$

Oxidation Half Reaction: $\text{Ag}(\text{s}) \rightarrow \text{Ag}^+(\text{aq}) + \text{e}^-$

Net Ionic Equation: $\text{AgBr}(\text{s}) \rightarrow \text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq})$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{cell}} = 0.0713 \text{ V} - (0.7994 \text{ V}) = -0.7281 \text{ V}$$

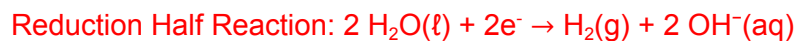
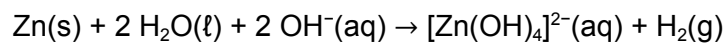
$$\ln(K) = nE^\circ / 0.0257$$

$$\ln(K) = (1)(-0.7281 \text{ V}) / 0.0257$$

$$K_{\text{sp}} = 4.97 \times 10^{-13}$$

5)

a) Calculate the standard cell potential delivered by a voltaic cell using the following reaction:



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$E^{\circ}_{\text{cell}} = -0.8277 \text{ V} - (-1.22 \text{ V})$$

$$E^{\circ}_{\text{cell}} = 0.3923 \text{ V}$$

b) If all dissolved species are $2.5 \times 10^{-2} \text{ M}$ and the pressure of H_2 is 1.0 bar, calculate the non-standard cell potential for the reaction above.

$$E = E^{\circ} - \frac{0.0257}{n} \ln(Q)$$

$$E = 0.3923 \text{ V} - \frac{0.0257}{2} \ln\left(\frac{1 \cdot .025}{.025^2}\right)$$

$$E = 0.34 \text{ V}$$