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**Problem 17.2.** Diagram the following galvanic cell, indicating the direction of flow of electrons in the external circuit and the motion of ions in the salt bridge.

$$Ni(s)|Ni^{2+}(aq)||HCl(aq)|H_2(g)|Pt(s)$$

Write a balanced equation for the overall reaction in this cell.

Solution:

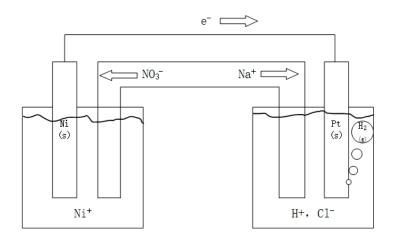


图 1: Problem 17.2 Diagram of the galvanic cell

The balanced equation for the overall reaction in this cell is  $Ni(s) + 2H^{+}(aq) \longrightarrow Ni^{2+}(aq) + H_{2}(g)$ 

**Problem 17.5.** A galvanic cell is constructed that has a zinc anode immersed in a  $Zn(NO_3)_2$  solution and a platinum cathode immersed in an NaCl solution equilibrated with  $Cl_2(g)$  at 1 atm and 25°C. A salt bridge connects the two half-cells.

- (a) Write a balanced equation for the cell reaction.
- (b) A steady current of 0.800 A is observed to flow for a period of 25.0 minutes. How much charge passes through the circuit during this time? How many moles of electrons is this charge equivalent to?
- (c) Calculate the change in mass of the zinc electrode.
- (d) Calculate the volume of gaseous chlorine generated or consumed as a result of the reaction.

## Solution:

- (a) The balanced equation for the cell reaction is  $\operatorname{Zn}(s) + \operatorname{Cl}_2(g) \longrightarrow \operatorname{Zn}^{2+}(aq) + \operatorname{Cl}^-(aq)$
- (b) The amount of charge passes through the circuit during this times is

$$Q = it = 0.800A \times (25.0 \times 60)s = \underline{1.20 \times 10^3 C}$$

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The number of moles of electrons is

$$n = \frac{Q}{F} = \frac{1.20 \times 10^3 C}{96485.34 C \cdot mol^{-1}} = \underline{0.0124 mol}$$

(c) Because the consumption of every mole of Zn corresponds to transfer of 2 mol electrons, the change in mass of the zinc electrode is

$$m(Zn) = M(Zn)\frac{n}{2} = 65.38g \cdot mol^{-1} \times \frac{0.0124mol}{2} = 0.407g$$

Therefore, the mass of zinc electrode decreased by 0.407 g.

(d) Because the consumption of every mole of gaseous chlorine corresponds to transfer of 2 mol electrons, the volume of gaseous chlorine consumed as a result of the reaction is

$$V(Cl_2) = \frac{\frac{n}{2}RT}{P} = \frac{\frac{0.0124mol}{2} \times 0.0821atm \cdot L \cdot mol^{-1} \cdot K^{-1} \times (25.0 + 273.15)K}{1atm} = \underline{0.152L}$$

**Problem 17.11.** A Ni|Ni<sup>2+</sup>||Ag<sup>+</sup>|Ag galvanic cell is constructed in which the standard cell potential is 1.03 V. Calculate the free energy change at 25°C when 1.00 g of silver plates out, if all concentrations remain at their standard value of 1 M throughout the process. What is the maximum electrical work done by the cell on its surroundings during this experiment?

Solution: The number of moles of Ag plates out through out the process is

$$n(Ag) = \frac{m(Ag)}{M(Ag)} = \frac{1.00g}{107.87g \cdot mol^{-1}} = 9.27 \times 10^{-3} mol$$

Because the generation of every mole of Ag corresponds to transfer of 1 mol electrons, the number of moles of electron transfered through out the process is

$$n = n(Ag) = 9.27 \times 10^{-3} mol$$

The change of the free energy change through out the process is

$$\Delta G^{\circ} = -nFE_{cell}^{\circ} = -9.27 \times 10^{-3} mol \times 96485C \cdot mol^{-1} \times 1.03V = -921J$$

Because  $w_{elec} = \Delta G^{\circ}$ , the maximum electrical work done by the cell on its surrounding during this experiment is <u>921 J</u>.

**Problem 17.25.** The following reduction potentials are measured at pH 0:

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$${\rm BrO_3}^- + 6 \, {\rm H_3O}^+ + 5 \, {\rm e}^- \longrightarrow \frac{1}{2} {\rm Br_2(l)} + 9 \, {\rm H_2O} \ E^\circ = 1.52V$$
  
 ${\rm Br_2(l)} + 2 \, {\rm e}^- \longrightarrow 2 \, {\rm Br}^- \ E^\circ = 1.065V$ 

- (a) Will bromine disproportionate spontaneously in acidic solution?
- (b) Which is the stronger reducing agent at pH 0: Br<sub>2</sub>(l) or Br<sup>-</sup>?

Solution:

(a) The equation of the disproportionation reaction of bromine in acidic solution and its standard cell potential is

$$3 \operatorname{Br}_{2}(1) + 9 \operatorname{H}_{2}O \longrightarrow 5 \operatorname{Br}^{-} + \operatorname{BrO}_{3}^{-} + 6 \operatorname{H}_{3}O^{+} E^{\circ} = -0.455V$$

The change of free energy change during the disproportionation reaction of bromine is positive

$$\Delta G^{\circ} = -nFE^{\circ} > 0$$

Therefore, bromine will not disproportionate in acidic solution.

(b) Because the standard potential of the reaction  $Br_2(l) + 2e^- \longrightarrow 2Br^-$  is positive, its change of free energy is negative, which means it can proceed spontaneously. In this reaction,  $Br_2(l)$  is reduced to  $Br^-$ . Therefore,  $Br^-$  is the stronger reducing agent.

**Problem 17.26.** The following reduction potentials are measured at pH 14:

$$ClO^{-} + H_2O + 2e^{-} \longrightarrow Cl^{-} + 2OH^{-} E^{\circ} = 0.90V$$
  
 $ClO_2^{-} + H_2O + 2e^{-} \longrightarrow ClO^{-} + 2HO^{-} E^{\circ} = 0.59V$ 

- (a) Will ClO<sup>-</sup> disproportionate spontaneously in basic solution?
- (b) Which is the stronger reducing agent at pH 14: ClO<sup>-</sup> or Cl<sup>-</sup>?

Solution:

(a) The equation of the disproportionation reaction of ClO<sup>-</sup> in basic solution and its standard cell potential is

$$2 \text{ ClO}^- \longrightarrow \text{Cl}^- + \text{ClO}_2^- \quad E^\circ = 0.31 V$$

The change of free energy change during the disproportionation reaction of bromine is negative

$$\Delta G^{\circ} = -nFE^{\circ} > 0$$

Therefore, bromine will disproportionate in acidic solution.

(b) Because the standard potential of the reaction  $ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$  is positive, its change of free energy is negative, which means it can proceed spontaneously. In this reaction,  $ClO^-$  is reduced to  $Cl^-$ . Therefore,  $\underline{Cl}^-$  is the stronger reducing agent.  $\Box$