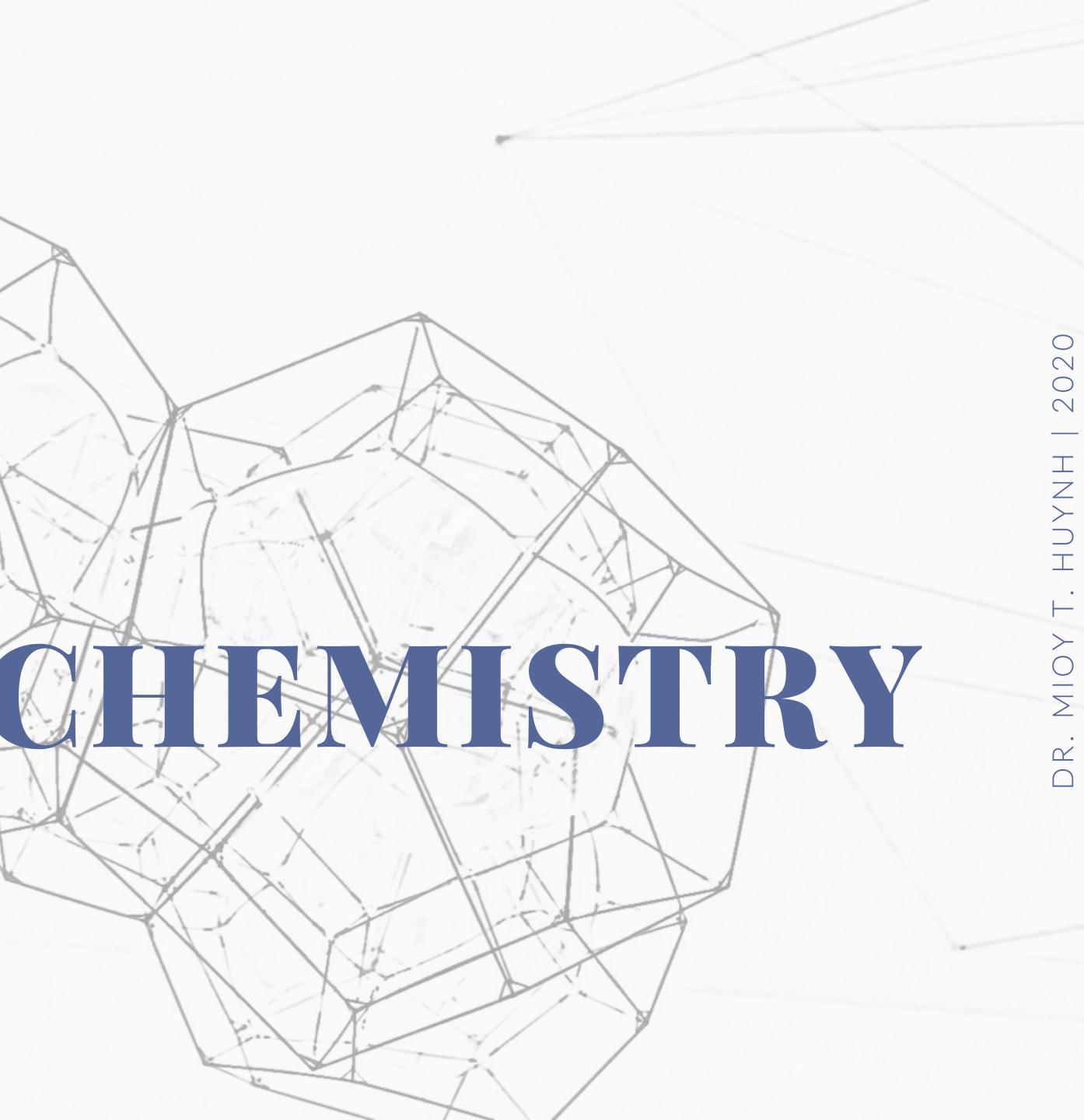
# ELECTROCHEMICAL CELLS

CHEMISTRY 165 // SPRING 2020



Consider a Galvanic (voltaic) cell consisting of the reaction above. Write the cell notation/diagram for this cell.

- answer -

 $2 \text{ Cr (s)} + 3 \text{ Cu}^{2+} (aq) \rightarrow 2 \text{ Cr}^{3+} (aq) + 3 \text{ Cu (s)}$ 

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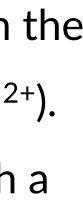
We can deconstruct the overall net ionic reaction taking place in the cell into the reduction (cathode) and oxidation (anode) reactions by considering the oxidation states of the reactants and products.

Cathode (Reduction)  $3 \text{ Cu}^{2+}(aq) + 6 e^{-} \rightarrow 3 \text{ Cu}(s)$ (Oxidation) 2 Cr (s)  $\rightarrow$  2 Cr<sup>3+</sup> (aq) + 6 e<sup>-</sup> Anode

Now we can construct the cell diagram. Start with the salt bridge ( || ) which separates the anode and cathode. The anode is on the left and cathode is on the right in the diagram. To the left/right of the salt bridge, we write the aqueous solutions ( $Cr^{3+}$  and  $Cu^{2+}$ ). Finally, we write the electrodes (Cr and Cu) on the far ends of the diagram, which is separated from the aqueous solutions with a phase-separating line (|).

- $2 \text{ Cr (s)} + 3 \text{ Cu}^{2+} (aq) \rightarrow 2 \text{ Cr}^{3+} (aq) + 3 \text{ Cu (s)}$

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Cr (s) | Cr<sup>3+</sup> (aq) || Cu<sup>2+</sup> (aq) | Cu (s)
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(a) What is the standard cell potential for a Galvanic (voltaic) cell consisting of the two half-reactions above?

(b) Write the cell diagram.

- answer -

- Au<sup>3+</sup> (aq) + 3 e<sup>-</sup>  $\rightarrow$  Au (s)  $E^{\circ} = +1.498$  V
- Ni<sup>2+</sup> (aq) + 2  $e^- \rightarrow$  Ni (s)  $E^\circ = -0.257 V$

- (a) What is the standard cell potential for a Galvanic (voltaic) cell consisting of the two half-reactions above?
- (b) Write the cell diagram.

- answer -

(a) Recognize that a Galvanic (voltaic) cell is one that is spontaneous, so  $\Delta G_{cell}^{o} < 0$  and  $E_{cell}^{o} > 0$  because  $\Delta G_{cell}^{o} = -nFE_{cell}^{o}$ . This means that the other half-reaction is the oxidation reaction (anode).

$$E_{\text{cell}}^{\text{o}} = E_{\text{cathode}}^{\text{o}} - E_{\text{anode}}^{\text{o}} = -$$

- $Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$   $E^{\circ} = +1.498 V$
- Ni<sup>2+</sup> (aq) + 2 e<sup>-</sup>  $\rightarrow$  Ni (s)  $E^{\circ} = -0.257 \text{ V}$

Generally, the reaction with the more positive value of  $E^{\circ}$  will be the reduction reaction (cathode)—remember that the E value is related to the spontaneity ( $\Delta G$ ) of the reaction, so we want to keep the more spontaneous reduction reaction as the cathode.

+1.498 V - (-0.257 V) = +1.755 V

- (a) What is the standard cell potential for a Galvanic (voltaic) cell consisting of the two half-reactions above?
- (b) Write the cell diagram.

- answer -

- (a) Recognize that a Galvanic (voltaic) cell is one that is spontaneous, so  $\Delta G_{cell}^{o} < 0$  and  $E_{cell}^{o} > 0$  because  $\Delta G_{cell}^{o} = -nFE_{cell}^{o}$ . This means that the other half-reaction is the oxidation reaction (anode).  $E_{\text{cell}}^{\text{o}} = E_{\text{cathode}}^{\text{o}} - E_{\text{anode}}^{\text{o}} = +$
- The overall reaction is then: 2 Cathode (Reduction): (b) Anode (Oxidation): Cell

And the cell diagram is: Ni (s) | Ni<sup>2+</sup> (1.0 M) || Au<sup>3+</sup> (1.0 M) | Au (s) Recall that standard conditions for electrochemistry are: T = 298.15 K; P = 1.0 atm; [] = 1.0 M

- $Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$   $E^{\circ} = +1.498 V$
- Ni<sup>2+</sup> (aq) + 2 e<sup>-</sup>  $\rightarrow$  Ni (s)  $E^{\circ} = -0.257 \text{ V}$

Generally, the reaction with the more positive value of  $E^{\circ}$  will be the reduction reaction (cathode)—remember that the E value is related to the spontaneity ( $\Delta G$ ) of the reaction, so we want to keep the more spontaneous reduction reaction as the cathode.

$$1.498 \text{ V} - (-0.257 \text{ V}) = +1.755 \text{ V}$$

Based on the following standard reduction potentials, which of the following is the strongest oxidizing agent?

- $F_{2}(g) + 2 e^{-} \rightarrow 2 F^{-}(aq) \qquad E^{\circ} = +2.866 V$ Cl<sub>2</sub>(g) + 2 e<sup>-</sup> → 2 Cl<sup>-</sup>(aq)  $E^{\circ} = +1.358 V$
- $Br_2(I) + 2e^- \rightarrow 2Br^-(aq)$   $E^\circ = +1.066V$

- answer -

Based on the following standard reduction potentials, which of the following is the strongest oxidizing agent?

- answer -

An oxidizing agent is a species that is reduced.

Recall that the larger the  $E^{\circ}$  value, the more spontaneous/favorable the reduction reaction. Therefore,  $F_2$  (g) is the strongest oxidizing agent.

- $F_2(g) + 2 e^- \rightarrow 2 F^-(aq)$   $E^\circ = +2.866 V$
- $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$   $E^\circ = +1.358V$
- $Br_2(I) + 2e^- \rightarrow 2Br^-(aq)$   $E^\circ = +1.066V$

- $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$   $E^\circ = +1.358V$
- $Br_2(I) + 2e^- \rightarrow 2Br^-(aq)$   $E^\circ = +1.066V$

(a) Write the cell diagram for a Galvanic (voltaic) cell constructed at standard conditions from the two reactions above. (b) Calculate the standard Gibbs free energy change of the cell ( $\Delta G_{cell}^{o}$ ).

- answer -

 $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$   $E^\circ = +1.358V$ 

- (a) Write the cell diagram for a Galvanic (voltaic) cell constructed at standard conditions from the two reactions above. (b) Calculate the standard Gibbs free energy change of the cell ( $\Delta G_{cell}^{o}$ ). - answer -

Cathode (Reduction):	Cl <sub>2</sub> (g
Anode (Oxidation):	
Cell	

Therefore, the cell diagram is: Pt (s) |  $Br_2$  (l) |  $Br^-$  (1.0 M) || Cl<sup>-</sup> (1.0 M) | Cl<sub>2</sub> (1.0 atm) | Pt (s) Recall that standard conditions for electrochemistry are: T = 298.15 K; P = 1.0 atm; [] = 1.0 M phase-separating line (|) to separate the aqueous phases ( $Br^-$  and  $CI^-$ ) from the others ( $Br_2$  and  $CI_2$ ).

 $Br_2(I) + 2e^- \rightarrow 2Br^-(aq)$   $E^\circ = +1.066V$ 

(a) Recognize that a Galvanic (voltaic) cell is one that is spontaneous, so  $\Delta G_{cell}^{o} < 0$  and  $E_{cell}^{o} > 0$  because  $\Delta G_{cell}^{o} = -nFE_{cell}^{o}$ .  $(g) + 2e^- \rightarrow 2Cl^-(aq)$  $2 \operatorname{Br}^{-}(\operatorname{aq}) \rightarrow \operatorname{Br}_{2}(I) + 2 \operatorname{e}_{-}$  $Cl_2(g) + 2 Br^-(aq) \rightarrow Br_2(l) + 2 Cl^-(aq)$ 

- In this case, we need to use an inert solid electrode (Pt) because  $Br_2$  and  $Cl_2$  are not solid. In addition, we need to use an addition



 $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$   $E^\circ = +1.358V$ 

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Cell

Cathode (Reduction):	Cl <sub>2</sub> (g
Anode (Oxidation):	

(a) Recognize that a Galvanic (voltaic) cell is one that is spontaneous, so  $\Delta G_{cell}^{o} < 0$  and  $E_{cell}^{o} > 0$  because  $\Delta G_{cell}^{o} = -nFE_{cell}^{o}$ .  $(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$  $2 \operatorname{Br}^{-}(\operatorname{aq}) \rightarrow \operatorname{Br}_{2}(I) + 2 \operatorname{e}^{-}$  $Cl_2(g) + 2 Br^-(aq) \rightarrow Br_2(l) + 2 Cl^-(aq)$ 

Therefore, the cell diagram is: Pt (s) |  $Br_2$  (l) |  $Br^-$  (1.0 M) || Cl<sup>-</sup> (1.0 M) | Cl<sub>2</sub> (1.0 atm) | Pt (s) Recall that standard conditions for electrochemistry are: T = 298.15 K; P = 1.0 atm; [] = 1.0 M In this case, we need to use an inert solid electrode (Pt) because  $Br_2$  and  $Cl_2$  are not solid. In addition, we need to use an addition phase-separating line (|) to separate the aqueous phases ( $Br^-$  and  $CI^-$ ) from the others ( $Br_2$  and  $CI_2$ ).

(b) The standard cell potential is  $E_{\text{cell}}^{\text{o}} = E_{\text{cathode}}^{\text{o}} - E_{\text{anode}}^{\text{o}} = +1.358 \text{ V} - 1.066 \text{ V} = +0.292 \text{ V}.$ The standard Gibbs free energy change can now be calculated using 1 V = 1 J/C:

$$\Delta G_{\text{cell}}^{0} = -nFE_{\text{cell}}^{0} = -(2 \text{ mol } e^{-}) \left(96500 \frac{\text{C}}{\text{mol } e^{-}}\right) \left(0.292 \frac{\text{J}}{\text{C}}\right) = -56400 \text{ J} = -56.4 \text{ kJ}$$

 $Br_2(I) + 2e^- \rightarrow 2Br^-(aq)$   $E^\circ = +1.066V$ 

