Electrochemical Cell Voltage

How do changes in concentration within a cell change the voltage of the cell?

Why?

Batteries are simply electrochemical cells in a compact container. The most common are sold as 9-volt or 1.5-volt, but are these voltages reliable? Does the voltage of an electrochemical cell stay constant as the cell runs towards equilibrium? Can an electrochemical cell have a voltage other than its standard voltage?

Model 1 – Zinc and Copper Cell

$$Zn\,(s) + Cu^{2+}\,(aq) \leftrightarrow Zn^{2+}\,(aq) + Cu\,(s) \quad E° = 1.100\ V$$

Time (min)	$[Cu^{2+}]$ (M)	$[Zn^{2+}]$ (M)	Voltage (V)
1	1.750	0.250	1.123
2	1.500	0.500	1.113
3	1.250	0.750	1.106
4	1.000	1.000	1.100
5	0.750	1.250	1.094
6	0.500	1.500	1.087
7	0.250	1.750	1.077

1. Is the cell in Model 1 spontaneous or not? Use evidence from Model 1 to justify your answer.

   Yes, the cell is spontaneous. The standard voltage, and all of the voltages in the table, are positive.

2. Is the reaction in Model 1 favoring the reverse direction at any point during the experiment? Justify your answer.

   No, all of the voltages in the Model 1 are positive, so the reaction is always running in the forward direction.

3. Refer to Model 1.

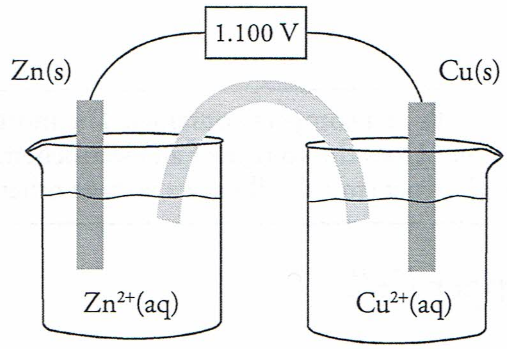
   a. What is the standard cell potential for the reaction between zinc and copper?

   E° = 1.100 V

   b. What are the concentrations of the zinc and copper solutions when the standard cell potential is obtained?

   The zinc and copper solutions are both 1.00 M when a voltage of 1.100 V is obtained.

4. Sketch how the Zn^{2+} (aq)/Cu (s) electrochemical cell in Model 1 may appear in a lab setup. Label the electrodes and solutions. Include a voltmeter in your drawing.



5. Is the reaction in Model 1 at equilibrium at any point during the experiment? If no, in which direction must the reaction proceed to reach equilibrium?

   No, the reaction is never at equilibrium. At equilibrium the voltage would be zero. The reaction must continue to run in the forward direction to reach equilibrium.

6. According to the data in Model 1, does an electrochemical cell provide a constant voltage as it proceeds?

   No, as the cell runs the voltage goes down.

7. Would you expect a 9-V battery to always provide 9 V? Justify your reasoning.

   No, a 9-V battery may start at 9 V, but as it runs, the voltage will decrease until it goes "dead" upon reaching equilibrium.

STOP

Model 2 – Concentration Effects in a Cell

$$\mathbf{Zn\,(s) + Cu^{2+}\,(aq) \leftrightarrow Zn^{2+}\,(aq) + Cu\,(s) \quad E° = 1.100\,V}$$

Trial	Initial $[Cu^{2+}]$ (M)	Initial $[Zn^{2+}]$ (M)	Voltage (V)
1	1.00	0.25	1.116
2	1.00	0.50	1.108
3	1.00	0.75	1.103
4	1.00	1.00	1.100
5	0.75	1.00	1.097
6	0.50	1.00	1.092
7	0.25	1.00	1.084

8. In trials 1–7 in Model 2, what variables in the cell have been changed?

   The concentrations of zinc and copper ions in solution have been changed.

9. Consider the data in Model 2.

   a. Based on the principles of LeChâtelier, in which direction would you predict the reaction to shift when the concentration of copper ions is decreased?

   When the copper ion concentration is decreased, the reaction should shift left.

   b. What happens to the cell's potential (voltage) when the concentration of copper ions is decreased?

   The cell's potential decreases when the concentration of copper ions is decreased.

   c. Based on the principles of LeChâtelier, in which direction would you predict the reaction to shift when the concentration of zinc ions is decreased?

   When the zinc ion concentration is decreased, the reaction should shift right.

   d. What happens to the cell's potential when the concentration of zinc ions is decreased?

   STOP *The cell's potential increases when the concentration of zinc ions is decreased.*

10. Predict the effect on the cell's potential when the concentration of copper ions is increased. Use LeChâtelier's Principle to justify your prediction.

    When the concentration of copper ions is increased, the reaction would shift right, which would increase the cell's potential.

11. Using the reaction in Model 1, estimate the conditions that would be required to achieve a cell potential of 1.00 V.

    The concentration of zinc ions would need to be higher than 1.75 M and the copper ion concentration would need to be less than 0.25 M. ***Note:*** *Students are not expected to use the Nernst equation here to find the exact concentrations. However, they should be able to follow the trend in the table and realize that there would need to be a significant change in concentration of the two ions in order to have a potential of 1.00 V.*

12. Consider the following reaction:

$$F_2(g) + 2Cl^{1-}(aq) \leftrightarrow 2F^{1-}(aq) + Cl_2(g) \quad E° = 1.51\ V$$

   a. Describe the conditions that would provide a voltage of 1.51 V.

   The chloride and fluoride ions would need to have a concentration of 1.00 M. The fluorine and chlorine gases would need to have a partial pressure of 1.00 atm.

   b. Identify two changes to the cell that would increase the potential of the cell.

   Possible answers include: increase the concentration of chloride ion, increase the partial pressure of fluorine gas, decrease the concentration of fluoride ion, decrease the partial pressure of chlorine gas.

   c. Identify two changes to the cell that would decrease the potential of the cell.

   Possible answers include: decrease the concentration of chloride ion, decrease the partial pressure of fluorine gas, increase the concentration of fluoride ion, increase the partial pressure of chlorine gas.

STOP

Extension Questions

Model 3 – Chromium and Zinc

$$3Zn\,(s) + 2Cr^{3+}\,(aq) \leftrightarrow 2Cr\,(s) + 3Zn^{2+}\,(aq) \quad E^\circ = 0.020\ V$$

Trial	Initial $[Cr^{3+}]$ (M)	Initial $[Zn^{2+}]$ (M)	Voltage (V)
1	1.00×10^{-3}	1.00	−0.034
2	1.00×10^{-2}	1.00	−0.016
3	1.00×10^{-1}	1.00	0.002
4	1.00	1.00	0.020
5	1.00	1.00×10^{-1}	0.047
6	1.00	1.00×10^{-2}	0.074
7	1.00	1.00×10^{-3}	0.101

13. Under standard conditions, is the reaction in Model 3 spontaneous? Justify your answer.

    The standard cell potential for the reaction is positive, so under standard conditions, it is spontaneous.

14. Describe a set of estimated conditions that would allow the reaction in Model 3 to be at equilibrium.

    The cell potential would reach zero at equilibrium. In one possible set of conditions, the concentration of zinc ions would be 1.00 M and the concentration of chromium ions would be between 0.0100 M and 0.100 M.

15. According to Model 3, is it possible to make the reaction in Model 3 nonspontaneous? If yes, what was done to make this happen?

    Yes, the cell's potential became negative (nonspontaneous) when the concentration of chromium ions was decreased.

16. Are the data in Model 3 consistent with LeChâtelier's principle? Justify your reasoning.

    When the concentration of chromium ions is decreased, the reaction will shift to the left. If it shifts sufficiently, it could cause the reaction to no longer be spontaneous and begin to require voltage.

Faraday's Law

How can one predict the amount of product made in an electrolytic reaction?

Why?

In an electrolytic reaction, an electrical current is used to run a nonspontaneous redox reaction. This might be separating a metal from molten alloy or electroplating an object submersed in a metal cation solution. It may even be the electrolysis of water to collect oxygen and hydrogen gas. In any case, it is helpful to know how long the reaction will need to run to get the desired amount of product.

Model 1 – Collecting Pure Metal from Alloy

Experiment A

Trial	Run Time (hrs)	Current (Amperes)	Mass Ag Collected (g)	Moles Ag Collected
1	1.00	2.00	8.05	*0.075*
2	2.00	2.00	16.10	*0.149*
3	3.00	2.00	24.15	*0.224*
4	4.00	2.00	32.20	*0.299*
5	5.00	2.00	40.25	*0.373*
6	6.00	2.00	48.30	*0.448*

Experiment B

Trial	Run Time (hrs)	Current (Amperes)	Mass Na Collected (g)	Moles Na Collected
1	1.00	2.00	1.72	*0.075*
2	2.00	2.00	3.43	*0.149*
3	3.00	2.00	5.15	*0.224*
4	4.00	2.00	6.86	*0.299*
5	5.00	2.00	8.58	*0.373*
6	6.00	2.00	10.29	*0.448*

1. Model 1 shows data collected from two experiments where electric current was run through molten alloy containing the desired metal.

   a. Will the desired metal be collected at the anode or the cathode of the cell?

   The desired metal will be collected at the cathode.

   b. Write the half reaction that occurs as the metals are collected on the electrode.

   Experiment A electrode: $Ag^{1+} + e^- \rightarrow Ag(s)$

   Experiment B electrode: $Na^{1+} + e^- \rightarrow Na(s)$

2. Consider Experiment A of Model 1.

   a. Identify each of the following variables:

Independent	Dependent	Controlled
The time the cell is run.	*Mass of Ag collected.*	*Current of the cell.*

   b. Describe the relationship between the independent and dependent variable in this experiment. Linear? Inverse? Exponential? Logarithmic? Justify your answer.

   The relationship is a direct linear proportion. The slope of the line graphed would be constant. When another hour is added, an additional 8.05 g of silver is collected.

3. When the time and electrical current were identical in Experiments A and B, was the same mass of metal collected? Support your answer with evidence from Model 1.

   No, much less sodium is collected compared to silver with the same conditions of time and current. Trial 2 of experiment A yielded 16.10 g of silver while trial 2 of experiment B yielded only 3.43 g of sodium.

4. For each trial of Experiments A and B, calculate the moles of metal collected. Add these data points to Model 1 by adding a column to each of the tables. Divide the work among group members.

   See Model 1.

5. When the time and electrical current were identical in Experiments A and B, was the same amount of metal, in moles, collected? Support your answer with evidence from Model 1.

   Yes, when the conditions in the two experiments are identical, the same amount of metal, in moles, is collected. In trial 1 of both experiments, 0.075 moles of metal are collected.

STOP

Model 2 – A New Variable

Experiment C

Trial	Run Time (hrs)	Current (Amperes)	Ag Collected (mole)
1	1.00	1.00	0.037
2	1.00	2.00	0.075
3	1.00	3.00	0.112
4	1.00	4.00	0.149
5	1.00	5.00	0.187
6	1.00	6.00	0.224

6. Consider Experiment C of Model 2.

   a. Identify each of the following variables.

Independent	Dependent	Controlled
The current of the cell.	*The moles of Ag collected.*	*The time the cell is run.*

b. Describe the relationship between the independent and dependent variable in this experiment. Linear? Inverse? Exponential? Logarithmic? Justify your answer.

Current and moles of Ag collected have a direct linear relationship. The slope of the line would be constant at 0.038 mole/hour. For each additional Ampere, 0.038 mole of additional Ag are collected per hour.

7. Did any of the trials in Experiment C result in the same number of moles of metal being collected as that in Experiments A and B? If yes, list the time and current conditions for those that produced the same amounts of metal.

Yes, 2.00 hours at 2.00 Amperes yields the same moles of metal as 1.00 hour at 4.00 Amperes, and 3.00 hours at 2.00 Amperes yields the same moles of metal as 1.00 hour at 6.00 Amperes.

Read This!

Electrical current, a measure of the rate of electrons moving through a wire, can be thought of as water in a river passing a defined point. Electrical current is measured in Amperes. One amp is equal to one coulomb (unit of charge) per second. More coulombs (charge) will therefore move through a wire in an hour than in a minute at a given current. Similarly, more river water will move past a bridge in an hour than in a minute at a given current. As the magnitude of the current increases, more water (or charge) will pass a bridge (or move through a circuit) than at smaller currents in a given time span.

8. Discuss with your group how the total charge might be calculated for each of the trials in Experiment C. Propose an equation for finding total charge of an electrolytic cell using the variables t for time, q for charge and I for current. *Hint:* Consider the base units of a Coulomb.

Current (in Amperes) $\times$ *time (in seconds)* = *charge (in Coulombs)*

$I \times t = q$

9. Do the trials in Experiments A and C that produced the same number of moles of metal have the same total charge?

Yes.

2.00 hours $\times$ *3600 sec/hr* $\times$ *2.00 C/s* = *14400 C*

1.00 hour $\times$ *3600 sec/hr* $\times$ *4.00 C/s* = *14400 C*

10. The experiment was done two more times:

Experiment D

Trial	Run Time (hrs)	Current (Amperes)	Moles Zn
1	1.00	2.00	0.037
2	2.00	2.00	0.075
3	3.00	2.00	0.112
4	4.00	2.00	0.149
5	5.00	2.00	0.187

Experiment E

Trial	Run Time (hrs)	Current (Amperes)	Moles Al
1	1.00	2.00	0.025
2	2.00	2.00	0.050
3	3.00	2.00	0.075
4	4.00	2.00	0.100
5	5.00	2.00	0.124

a. Write the half reaction that occurs at the electrode as these metals are collected.

Experiment D electrode: $Zn^{2+} + 2e^- \rightarrow Zn(s)$

Experiment E electrode: $Al^{3+} + 3e^- \rightarrow Al(s)$

b. Compare the moles of metal collected in Experiments D and E with the moles of metal collected in Experiments A and B under the same conditions of time and electrical current. Was the same number of moles of metal collected when conditions were equal? Justify your answer with data from the four experiments.

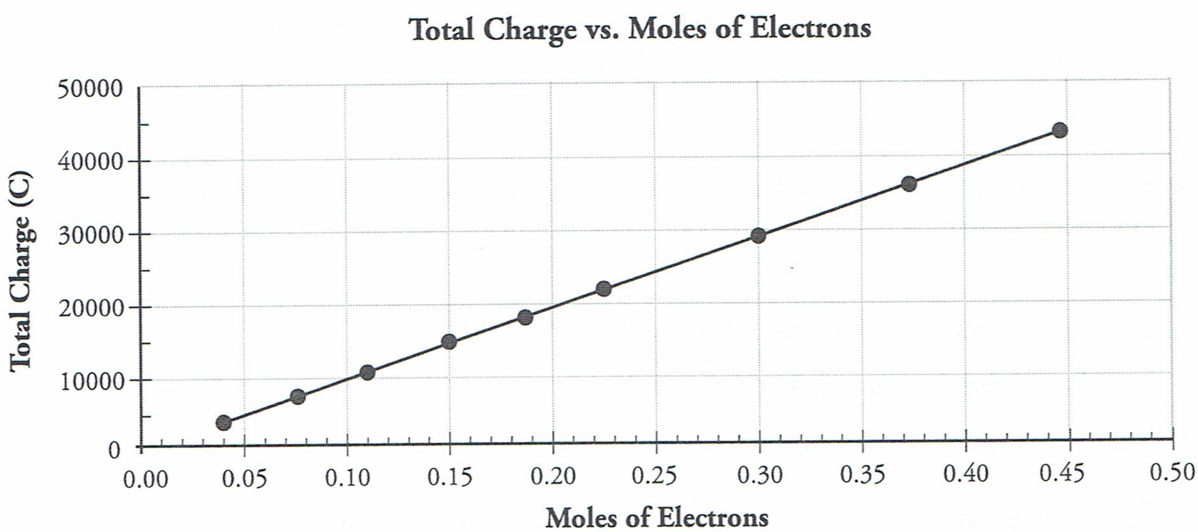
No, each of these experiments yielded less metal than Experiments A and B under the same conditions. The results of trial 1 in all four experiments have the same conditions of time and current, but in Experiments A and B, 0.075 mole of metal was produced. In Experiment D, only 0.037 mole was produced, and in Experiment E, only 0.25 mole of metal was produced.

11. Consider the number of electrons that are needed to reduce the molten ions in Experiments A–E to neutral atoms. Explain why the trials which have the same amount of total charge going through the cell produce different numbers of moles of metal when the charges on the ions are different.

STOP

When the charge on the ion is larger, it takes more electrons to reduce the ion. Therefore, the same charge results in fewer solid atoms being formed.

Model 3 – Faraday's Constant



12. Calculate the total charge for each of the trials in Experiments A and C. Graph the data from Experiments A and C in Model 3.

See Model 3.

13. Calculate the slope of the trend line for the graph in Model 3, including units. This ratio of total charge to moles of electrons is called **Faraday's constant.**

The slope is 96485 C/mole e^-.

14. How many moles of electrons would be moved through the electrolytic cell if it ran for 45.0 minutes at a constant current of 3.85 Amperes?

$$\frac{(45.0\ min)(60\ s/min)(3.85\ C/s)}{96485\ C/mole\ e^-} = 0.108\ mole\ e^-$$

15. How many moles of solid copper could be produced by electrolysis of molten $CuSO_4$ under the conditions in Question 14?

$$0.108\ mole\ e^- \times \frac{1\ mole\ Cu}{2\ moles\ e^-} = 0.0540\ mole\ Cu$$

16. Molten aluminum hydroxide is electrolyzed for 8.00 hours at 4.27 Amperes. Calculate the mass of aluminum metal that will be produced.

$$\left(\frac{(8.00\ hr)\left(\frac{3600\ s}{1.00\ hr}\right)(4.27\ amp)}{96485\ C/mole\ e^-}\right)\left(\frac{1\ mole\ Al}{3\ moles\ e^-}\right)\left(\frac{26.982\ g}{1\ mole\ Al}\right) = 11.5\ g\ Al$$

Extension Questions

Model 4 – Electrolysis of Aqueous Solutions

Experiment F

Trial	$[AgNO_3]$ (M)	Run Time (hrs)	Current (Amperes)	Ag Collected (mole)
1	0.20	1.00	3.00	0.11
2	0.40	1.00	3.00	0.11
3	0.60	1.00	3.00	0.11
4	0.80	1.00	3.00	0.11
5	1.00	1.00	3.00	0.11

17. Consider Experiment F in Model 4.

a. Identify each of the following variables:

Independent	Dependent	Controlled
The $[Ag^{1+}]$ in solution.	*The moles of Ag collected.*	*Time and current.*

b. Describe the relationship between the independent and dependent variable in this experiment. Linear? Inverse? Exponential? Logarithmic? Justify your answer.

The concentration of silver ions in the solution has no effect on the amount of solid metal collected in the cell.

18. Propose an atomic level explanation for the data in Experiment F.

The amount of silver collected is not dependent on what is in solution, but rather the availability of electrons that are being added to the silver ions at the cathode. The current and time determine the availability of the electrons and since they were constant, the amount of silver collected was constant.

19. What is the minimum voltage needed for Trial 5 of Experiment F to work?

The half-cell reactions will be:

$Ag^{1+}(aq) + e^- \rightarrow Ag(s)$ $\qquad E° = 0.80\ V$

$2H_2O \rightarrow + O_2(g) + 4H^+(aq) + 4e^-$ $\qquad E° = 1.23\ V$

Therefore the total cell voltage must be $E°$ cell $= -0.43$ V.

For the reaction to work, the cell voltage must be exceeded.