

UNIT 5 – CHAPTER 16 STUDENT NOTES: ELECTROCHEMISTRY

Electrochemistry – interconversions of electrical and chemical energy

2 types of electrochemical cells

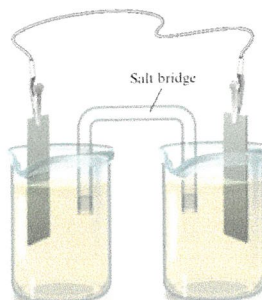
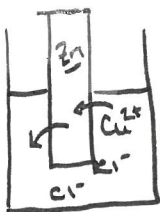
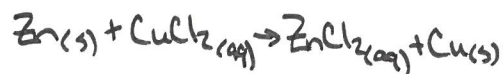
1. Voltaic – spontaneous reactions generate electrical energy
2. Electrolytic cells – electrical energy brings about nonspontaneous reaction

Voltaic Cells

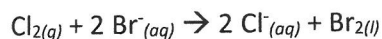
Oxidation – (more +) anode

Reduction – (more -) cathode

WHAT HAPPENS TO Zn METAL IN A $\text{CuCl}_2(\text{aq})$ SOLUTION?

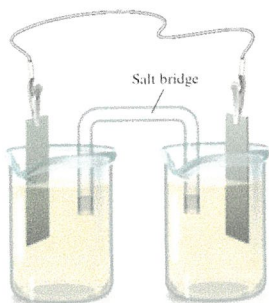


EX 1: When chlorine gas is bubbled through a water solution of NaBr, a spontaneous reaction occurs:

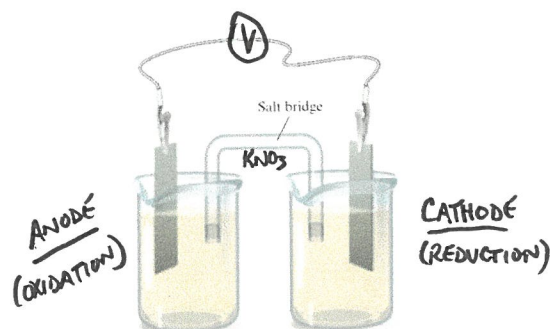
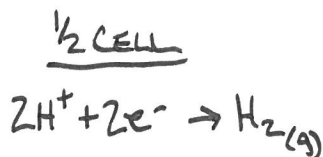
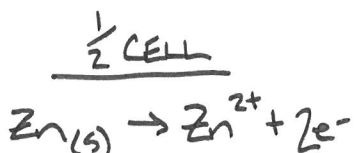
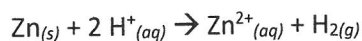


This reaction can serve as a source of electrical energy in a voltaic cell.

- a) Draw the voltaic cell.
- b) What is the cathode reaction? Anode reaction?
- c) Which way do the e^{-} move in the external circuit?
- d) Which way do the anions move? Which way do the cations move?



EX 2: Do the same as before for the following reaction:



Summary of voltaic cells

1. Voltaic cells consist of two half-cells. They are joined by an external electrical circuit through which electrons move and a salt bridge through which ions move.
2. Each half-cell consists of an electrode dipping into a water solution. If a metal participates in the cell reaction, either as a product or a reactant, it is ordinarily used as the electrode; otherwise an inert electrode such as platinum is used.
3. In one half-cell, oxidation happens at the anode and reduction occurs at the cathode.

End 5.1

Standard voltages

SKIP FOR A BIT

Standard voltage – current flow is zero ions and molecules in solution at standard conditions (1 M for solutions, 1 atm for gases)

Zn-H⁺ cell as an example

You need two half-cells to measure a voltage

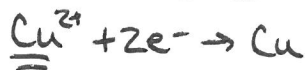
EX 3: What is the E^0_{red} for Cu^{2+} if E^0 for $\text{Zn}-\text{Cu}^{2+}$ is +1.101 V?

Strength of oxidizing-reducing agents

Oxidizing agent (reduction) – gains e^-

$\oplus$ CATHODE

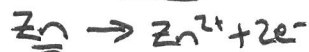
OXIDIZING AGENT IS REDUCED



Reducing agent (oxidation) – releases e^-

$\ominus$ ANODE

REDUCING AGENT IS OXIDIZED



EX 4: Consider the following species in acidic solutions:



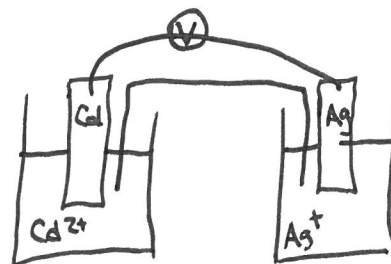
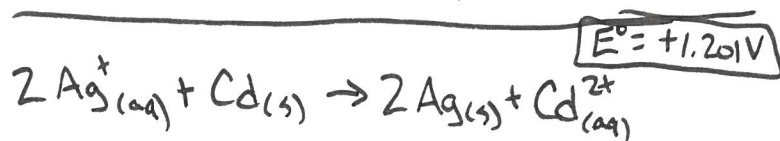
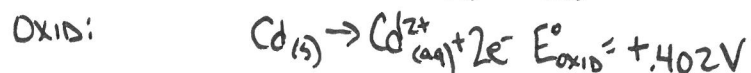
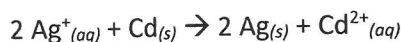
Using the table of standard potentials:

- Classify each of these as an oxidizing and/or a reducing agent.
- Arrange the oxidizing agents in order of increasing strength.
- Arrange the reducing agents in order of increasing strength.

To calculate the E^0 from the E^0_{red} and E^0_{ox}

$$E^0 = E^0_{red} + E^0_{ox}$$

EX 5: Using the table of standard potentials, calculate the E^0 for a voltaic cell in which the reaction is:



2 general points

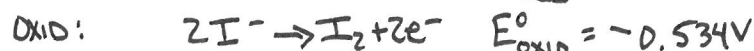
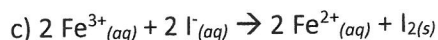
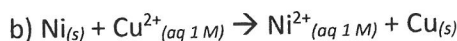
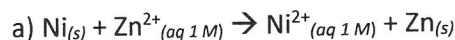
- The calculated voltage, E^0 , is always a (+) quantity for a reaction taking place in a voltaic cell.
- The quantities E^0 , E^0_{red} , and E^0_{ox} are independent of how the equation for the cell reaction is written. You never multiply the voltage by the coefficients of the balanced equation.

Spontaneity of redox reactions

To determine whether a given redox reaction is spontaneous, apply a simple principle:

If the calculated voltage for a redox reaction is (+), the reaction will be spontaneous. If (-), the reaction will not be spontaneous.

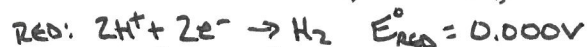
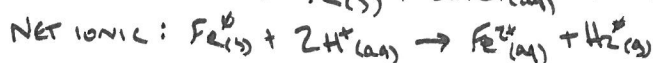
EX 6: Determine if the following reactions are spontaneous.



*Both Pull e^{-} ,
 Fe^{3+} Pulls HARDER*

$E^{\circ} = +0.235\text{V}$ SPONTANEOUS

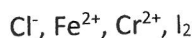
d) $\text{Fe}_{(s)}$ will oxidize to Fe^{2+} by treatment of hydrochloric acid. (The H^{+} is only used because Cl^{-} cannot be reduced). Will this reaction occur?



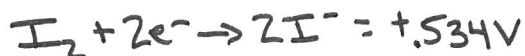
$E^{\circ} = +0.409\text{V}$

E° is (+) $\therefore$
 SPONTANEOUS,
 WILL REACT

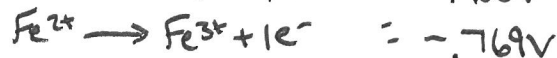
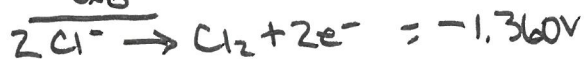
e) Will a reaction occur when the following species are mixed in an acidic solution:



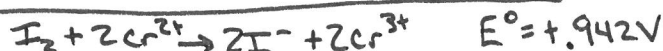
E°_{red} :



E°_{ox} :



ONLY COMBINATIONS TO PRODUCE (+) E° :



END 5.2

Relations between E° , ΔG° , and K

$$\Delta G^\circ = -nFE^\circ$$

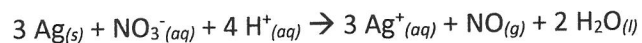
$$E^\circ = \left(\frac{0.0257}{n} \right) \cdot \ln K$$

ΔG° = Free energy ($-\Delta G^\circ$ is spontaneous)

K = equilibrium constant ($K > 1$ is spontaneous)

E° is a measure of the spontaneity of a cell reaction

EX 7: For the reaction:

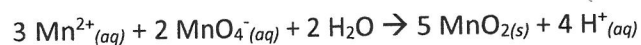


Calculate:

a) ΔG°

b) K

EX 8: Calculate E° , ΔG° and K for the reaction:



Effect of concentration on voltage

We have only worked with standard voltages (E^0) – (1 M solutions and 1 atm pressure). **When concentrations change, so does the voltage.**

Direction in which voltage shifts is predicted when you realize cell voltage is directly related to reaction spontaneity.

Voltage increases when [] reactant increases or [] product decreases

Voltage decreases when [] reactant decreases or [] product increases

After time, voltage drops and becomes zero as redox reaction reaches equilibrium

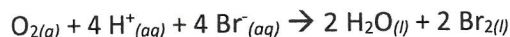
Comparing cell voltage (E) to concentration

Nernst equation – $E = E^0 - \frac{(0.0257 \text{ V})}{n} \ln Q$

Q = reaction quotient

$$E = E^0 - \frac{(0.0592 \text{ V})}{n} \log Q$$

EX 9: Consider a voltaic cell in which the following reaction occurs:



Calculate the cell voltage (E) when $\text{O}_2 = 1 \text{ atm}$ and $[\text{H}^+] = [\text{Br}^-] = 0.10 \text{ M}$

EX 10: Consider a voltaic cell at 25°C in which the following reaction takes place.



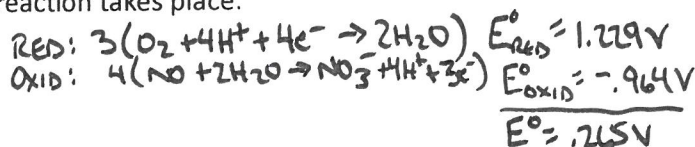
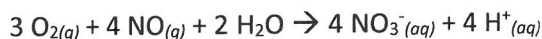
Calculate E^0

Write the Nernst equation for the cell.

Calculate E when $[\text{Au}^{3+}] = 0.250 \text{ M}$, $[\text{H}^+] = 1.25 \text{ M}$, $[\text{H}_2\text{O}_2] = 1.50 \text{ M}$.

Use of Nernst equation with pH

EX 11: Consider a voltaic cell at 25°C in which the following reaction takes place.



Calculate E° .

Write the Nernst equation for the cell.

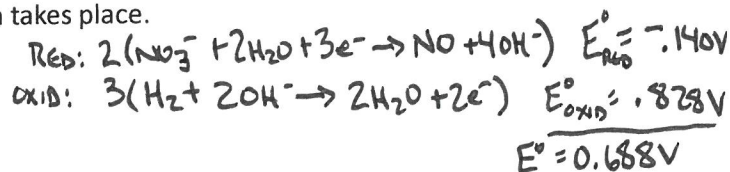
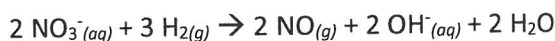
Calculate E when $[\text{NO}_3^-] = 0.250 \text{ M}$, $P_{\text{NO}} = 0.493 \text{ atm}$, $P_{\text{O}_2} = 0.315 \text{ atm}$, $\text{pH} = 4.85$.

$$E = 0.265 \text{ V} - \left(\frac{0.0257}{12}\right) \cdot \ln \frac{[\text{H}^+]^4 \cdot [\text{NO}_3^-]^4}{(P_{\text{O}_2})^3 \cdot (P_{\text{NO}})^4}$$

$$\begin{aligned} * \text{pH} &= -\log[\text{H}^+] \\ [\text{H}^+] &= \text{ANTILOG}(-\text{pH}) \\ &= \text{ANTILOG}(-4.85) \\ [\text{H}^+] &= 1.41 \times 10^{-5} \text{ M} \end{aligned}$$

$$E = 0.359 \text{ V}$$

EX 12: Consider a voltaic cell in which the following reaction takes place.



Calculate E° .

Write the Nernst equation for the cell.

Calculate E when $[\text{NO}_3^-] = 0.015 \text{ M}$, $P_{\text{NO}} = 0.722 \text{ atm}$, $P_{\text{H}_2} = 0.237 \text{ atm}$, $\text{pH} = 9.50$

$$E = 0.688 \text{ V} - \left(\frac{0.0257}{6}\right) \cdot \ln \frac{(P_{\text{NO}})^2 \cdot [\text{OH}^-]^2}{[\text{NO}_3^-]^2 \cdot (P_{\text{H}_2})^3}$$

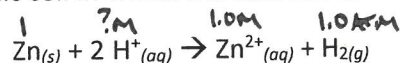
$$\begin{aligned} * \text{pH} + \text{pOH} &= 14 \\ \text{pOH} &= 14 - 9.50 \\ \text{pOH} &= 4.5 \\ [\text{OH}^-] &= \text{ANTILOG}(-4.5) \\ [\text{OH}^-] &= 3.16 \times 10^{-5} \text{ M} \end{aligned}$$

$$E = 0.725 \text{ V}$$

Use of the Nernst equation to determine ion concentration

In chemistry, the most important use of the Nernst equation lies in the experimental determination of the concentration of ions in solution. Suppose you measure the cell voltage, E , and know all but one species in the two half-cells. It should then be possible to calculate the concentration of that species using the Nernst equation.

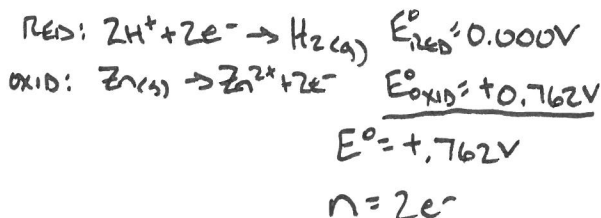
EX 13: Consider a voltaic cell in which the reaction is:



$$E = 0.560 \text{ V}$$

It is found that the voltage is +0.560 V when $[\text{Zn}^{2+}] = 1.0 \text{ M}$, $\text{pH}_2 = 1.0 \text{ atm}$, what must be the concentration of H^+ in the $\text{H}_2\text{-H}^+$ half-cell?

CALCULATE E° AND n :



"PLUG + CHUG"

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

$$0.560 = 0.762 \text{ V} - \left(\frac{0.0257}{2}\right) \cdot \ln Q$$

$$0.560 = 0.762 \text{ V} - \left(\frac{0.0257}{2}\right) \cdot \ln \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

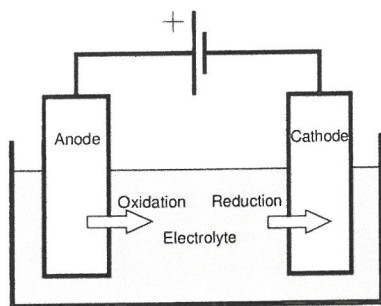
$$-0.202 = -\left(\frac{0.0257}{2}\right) \cdot \ln \frac{1}{[\text{H}^+]^2} \rightarrow 15.72 = \ln \frac{1}{[\text{H}^+]^2}$$

$$67.14932 \cdot 649 = \frac{1}{[\text{H}^+]^2} \rightarrow [\text{H}^+]^2 = 1.49 \times 10^{-7} \rightarrow [\text{H}^+] = 3.86 \times 10^{-4} \text{ M}$$

$$(\text{pH of } 3.41)$$

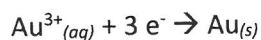
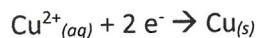
END 5.4

Electrolytic cells: A **nonspontaneous** redox reaction is made to occur by pumping electrical energy into the system



- Battery acts as an electron pump, **pushing** e^- into the cathode and **removing** them from the anode
- Electrolysis – process of pumping e^- in the redox reaction

There is a simple relationship between the amount of electricity passed through an electrolytic cell and amounts of substance produced by oxidation and reduction at the electrodes.



You can deduce that:

1 mole $e^- \rightarrow$ 1 mole Ag (107.9 grams of Ag)

2 mole $e^- \rightarrow$ 1 mole Cu (63.55 grams of Cu)

3 mole $e^- \rightarrow$ 1 mole Au (197.0 grams of Au)

Terms

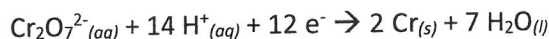
Coulomb (C): quantity of electrical charge (1 mole $e^- = 9.648 \times 10^4$ C)

Ampere (A): rate of current flow (1 A = 1 C/sec)

Joule (J): amount of electrical energy (1 J = 1 C · V)

Kilowatt hours (kWh): (1 kWh = 3.6×10^6 J)

EX 14: Chromium metal can be electroplated from a water solution of potassium dichromate. The reduction half-reaction is:



a) How many grams of chromium will be plated by 1.00×10^4 C?

b) How long will it take to plate 1 gram of chromium using a current of 6.00 A?

c) If the applied voltage is 4.5 V, how many kilowatt hours of electrical energy are required to plate 1.00 grams of Cr?

E^0 REDUCTION VALUES:
 * IF # IS NEGATIVE, THESE ARE ELEMENTS
 THAT DON'T "WANT" TO TAKE IN e^- *
 (OXIDATION ELEMENTS)

Standard Potential in Water Solution at 25°C

Acidic Solution, $[H^+] = 1 M$

	$E^0_{red} (V)$		$E^0_{red} (V)$
$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$	-3.040	$SO_4^{2-}_{(aq)} + 4 H^+ + 2e^- \rightarrow SO_{2(g)} + 2 H_2O$	0.155
$K^+_{(aq)} + e^- \rightarrow K_{(s)}$	-2.936	$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^{1+}_{(aq)}$	0.161
$Ba^{2+}_{(aq)} + 2e^- \rightarrow Ba_{(s)}$	-2.906	$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	0.339
$Ca^{2+}_{(aq)} + 2e^- \rightarrow Ca_{(s)}$	-2.869	$Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$	0.518
$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$	-2.714	$I_{2(s)} + 2e^- \rightarrow 2 I^-_{(aq)}$	0.534
$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg_{(s)}$	-2.357	$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$	0.769
$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$	-1.68	$Hg_2^{2+}_{(aq)} + 2e^- \rightarrow 2 Hg_{(l)}$	0.796
$Mn^{2+}_{(aq)} + 2e^- \rightarrow Mn_{(s)}$	-1.182	$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$	0.799
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$	-0.762	$2 Hg^{2+}_{(aq)} + 2e^- \rightarrow Hg_2^{2+}_{(aq)}$	0.908
$Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$	-0.744	$NO_3^-_{(aq)} + 4 H^+ + 3e^- \rightarrow NO_{(g)} + 2 H_2O$	0.964
$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$	-0.409	$AuCl_4(aq) + 3e^- \rightarrow Au_{(s)} + 4 Cl^-_{(aq)}$	1.001
$Cr^{3+}_{(aq)} + e^- \rightarrow Cr^{2+}_{(aq)}$	-0.408	$Br_{2(l)} + 2e^- \rightarrow 2 Br^-_{(aq)}$	1.007
$Cd^{2+}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$	-0.402	$O_{2(g)} + 4 H^+_{(aq)} + 2e^- \rightarrow 2 H_2O_{(l)}$	1.229
$PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}_{(aq)}$	-0.356	$MnO_{2(s)} + 4 H^+_{(aq)} + 2e^- \rightarrow Mn^{2+}_{(aq)} + 4 H_2O$	1.229
$Tl^+_{(aq)} + e^- \rightarrow Tl_{(s)}$	-0.336	$Cr_2O_7^{2-}_{(aq)} + 14 H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7 H_2O$	1.33
$Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}$	-0.282	$Cl_{2(aq)} + 2e^- \rightarrow 2 Cl^-_{(aq)}$	1.360
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$	-0.236	$ClO_3^-_{(aq)} + 6 H^+ + 5e^- \rightarrow \frac{1}{2} Cl_{2(g)} + 3 H_2O_{(l)}$	1.458
$AgI_{(s)} + e^- \rightarrow Ag_{(s)} + I^-_{(aq)}$	-0.152	$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$	1.498
$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$	-0.141	$MnO_4^-_{(aq)} + 8 H^+ + 5e^- \rightarrow Mn^{2+}_{(aq)} + 2 H_2O_{(l)}$	1.512
$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$	-0.127	$PbO_{2(s)} + SO_4^{2-}_{(aq)} + 4 H^+ + 2e^- \rightarrow PbSO_{4(s)} + 2 H_2O$	1.687
$2 H^+_{(aq)} + e^- \rightarrow H_{2(g)}$	0.000	$H_2O_{2(aq)} + 2 H^+ + 2e^- \rightarrow 2 H_2O_{(l)}$	1.763
$AgBr_{(s)} + e^- \rightarrow Ag_{(s)} + Br^-_{(aq)}$	0.073	$Co^{3+}_{(aq)} + e^- \rightarrow Co^{2+}_{(aq)}$	1.953
$S_{(s)} + 2H^+ + 2e^- \rightarrow H_2S_{(aq)}$	0.144	$F_{2(g)} + 2e^- \rightarrow 2 F^-_{(aq)}$	2.889
$Sn^{4+}_{(aq)} + 2e^- \rightarrow Sn^{2+}_{(aq)}$	0.154		

Basic Solution, $[OH^-] = 1 M$

	$E^0_{red} (V)$		$E^0_{red} (V)$
$Fe(OH)_{2(s)} + 2e^- \rightarrow Fe_{(s)} + 2 OH^-_{(aq)}$	-0.891	$NO_3^-_{(aq)} + H_2O + 2e^- \rightarrow NO_2^-_{(aq)} + 2 OH^-_{(aq)}$	0.004
$2 H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2 OH^-_{(aq)}$	-0.828	$ClO_4^-_{(aq)} + H_2O + 2e^- \rightarrow ClO_3^-_{(aq)} + 2 OH^-_{(aq)}$	0.394
$Fe(OH)_{3(s)} + 2e^- \rightarrow Fe(OH)_{2(s)} + 2 OH^-_{(aq)}$	-0.547	$O_{2(g)} + 2 H_2O + 4e^- \rightarrow 4 OH^-_{(aq)}$	0.401
$S_{(s)} + 2e^- \rightarrow S^{2-}_{(aq)} + 2 OH^-_{(aq)}$	-0.445	$ClO_3^-_{(aq)} + 3H_2O + 6e^- \rightarrow Cl^-_{(aq)} + 6 OH^-_{(aq)}$	0.614
$NO_3^-_{(aq)} + 2H_2O + 3e^- \rightarrow NO_{(g)} + 4 OH^-_{(aq)}$	-0.140	$ClO^-_{(aq)} + H_2O + 2e^- \rightarrow Cl^-_{(aq)} + 2 OH^-_{(aq)}$	0.890