CHAPTER 20 – Electrochemistry

Section 20.1 – Oxidation States and Oxidation-Reduction Reactions

(a) One mnemonic device used to help students remember the role of electrons in redox reactions is the following: OIL RIG. This mnemonic device reminds the student that

Oxidation involves the ___________ of electrons, and

Reduction involves the ___________ of electrons.

(b) Write a balanced, net-ionic equation for the reaction between zinc metal and aqueous hydrochloric acid.

(c) In the reaction that you wrote in part (b),

zinc (loses gains) electrons, so it is (oxidized reduced).

hydrogen (loses gains) electrons, so it is (oxidized reduced).

(d) For each of the following reactions, classify them as redox equations (or not.) If a reaction is redox, assign oxidation numbers to each element on both sides of the equation. Identify the species that is oxidized and the species that is reduced.

(i) $PCl_3 + 3\ H_2O \rightarrow H_3PO_3 + 3\ HCl$

(ii) $2\ PH_3 + 4\ O_2 \rightarrow P_2O_5 + 3\ H_2O$

(iii) $NH_4Br + NaOH \rightarrow NaBr + NH_3 + H_2O$

(iv) $Br_2 + 5\ Cl_2 + 6\ H_2O \rightarrow 2\ HBrO_3 + 10\ HCl$

Section 20.2 – Balancing Redox Equations

The method of half reactions helps to ensure that the electrons gained (from a reduction half reaction) are equal to the electrons lost (from an oxidation half reaction.)

In the tables below, combine the two half reactions and write the overall balanced redox equation.

(a)

Reduction Half Reaction	Oxidation Half Reaction
Fe^{3+} + e^- → Fe^{2+}	Sn^{2+} → Sn^{4+} + 2 e^-
Overall Redox Equation	

(b)

Reduction Half Reaction	Oxidation Half Reaction
NO_3^- + 4 H^+ + 3 e^- → NO + 2 H_2O	5 H_2O + As_2O_3 → 2 H_3AsO_4 + 4 H^+ + 4 e^-
Overall Redox Equation	

$$MnO_4^- \quad + \quad C_2O_4^{2-} \quad \rightarrow \quad Mn^{2+} \quad + \quad CO_2$$

(c) In the reaction shown above, __________ is reduced from __________ to ________, and

__________ is oxidized from __________ to ________.

(d) Follow steps (a) – (d) listed on the bottom of page 830 to balance each half reaction under acidic conditions. Write the balanced half reactions in the boxes below.

Reduction half reaction:

Oxidation half reaction:

(e) After following steps 3 – 5 on the top of page 831 to combine the two half reactions together, you should get the following balanced redox equation.

Balance each of the following redox reactions using the half-reaction method.
These reactions occur in acidic solution.

(f) $Cu + NO_3^- \rightarrow Cu^{2+} + NO_2$

(g) $Mn^{2+} + BiO_3^- \rightarrow Bi^{3+} + MnO_4^-$

(h) $MnO_4^- + CH_3OH \rightarrow Mn^{2+} + HCO_2H$

Section 20.3 – Voltaic Cells

(a) When a strip of zinc metal is placed in a solution of $CuSO_4$, a reddish-brown solid appears on the surface of the zinc. Write a balanced chemical equation for this reaction.

(b) In this reaction, zinc is (reduced oxidized), and copper is (reduced oxidized).

(c) When a strip of copper metal is placed in a solution of $ZnSO_4$, a chemical reaction (does doesn't) take place. This is because zinc (loses gains) electrons more readily than copper does. (Hint: See Table 4.5 on page 136.)

(d) In a voltaic (or galvanic) cell, the transfer of _________________ takes place through an ___________________ pathway rather than directly between reactants present in the same reaction vessel.

(e) Electrons flowing through a __________ and ions moving in solution both constitute an electrical current. This flow of electrical charge can be used to accomplish electrical work.

(f) The two solid metals connected by the external circuit are called ___________________.

(g) In a galvanic cell, oxidation always occurs at the _____________, and reduction occurs at the ___________________. A mnemonic device to help you remember this fact is "the vowels go together (O and A) and the consonants go together (R and C)."

(h) As the galvanic cell runs over time, the mass of the anode (decreases increases) because the atoms of the metal are going into solution, becoming aqueous ions.

(i) As the galvanic cell runs over time, the mass of the cathode (decreases increases) because the aqueous ions of the metal are converted into atoms and deposited on the surface of the cathode.

(j) Figure 20.5 on page 836 shows a zinc – copper galvanic cell.

The half-reaction that occurs at the anode is ______________________________________

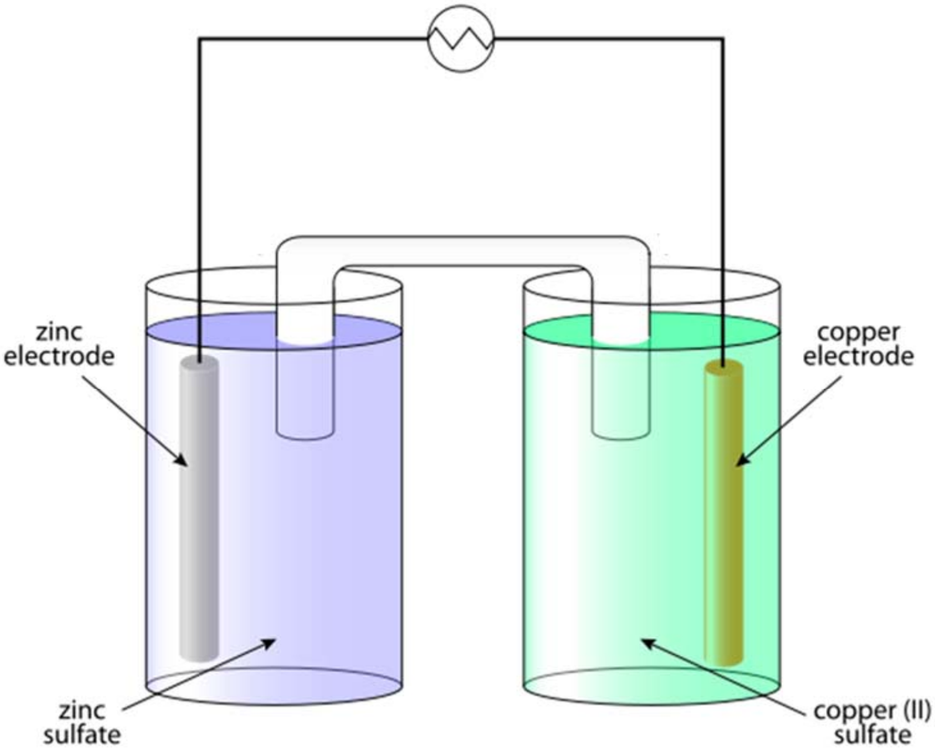
The half-reaction that occurs at the cathode is _____________________________________

(k) In the diagram below, label the following.

anode cathode salt bridge voltmeter.

In addition, draw an arrow to indicate the direction in which electrons are flowing through the wire.

Electrons do not flow through the salt bridge. Only ions flow through the salt bridge.



(l) For a galvanic cell to work, the solutions in the two half-cells must remain electrically

________________. A porous glass disc or U-shaped tube acts as a salt bridge so that ions can travel through the electrolyte solution from one side to the other.

(m) The anions always migrate toward the (anode cathode) and the cations always migrate toward the (anode cathode).

(n) The electrons flow from the (anode cathode) toward the (anode cathode).

Electrons do NOT flow through the salt bridge! This is a common misconception.

(o) Identify the anode and the cathode for each of the following galvanic cells.

Overall Reaction	Anode	Cathode
$2\ Ag^+ + Sn \rightarrow 2\ Ag + Sn^{2+}$		
$2\ Al + 3\ Sn^{2+} \rightarrow 2\ Al^{3+} + 3\ Sn$		
$Cu^{2+} + Sn \rightarrow Cu + Sn^{2+}$		
$2\ Ag^+ + Cu \rightarrow 2\ Ag + Cu^{2+}$		
$2\ Al + 3\ Cu^{2+} \rightarrow 2\ Al^{3+} + 3\ Cu$		

(p) Based on the information in part (o), which of the four metals (Ag, Sn, Al, or Cu) seems to lose electrons most easily? Which metal seems to gain electrons most easily?

(q) Only one of the following reactions actually occurs. Write a balanced net-ionic equation for the chemical reaction that does occur.

aluminum metal plus silver nitrate → ?   silver metal plus aluminum nitrate → ?

Section 20.4 – Cell Potentials Under Standard Conditions

The reason that electrons flow from a Zn atom to a Cu^{2+} ion is based on a difference in potential energy. In general, which electrode (anode or cathode) has the *higher potential energy* in a galvanic cell?

(a) The potential energy of electrons is higher in the ________________ than in the ________________. Thus, the electrons always flow from the _______________ to the ________________.

(b) The difference in potential energy per electrical charge (the potential difference) between two electrodes is measured in units of _______________.

(c) The potential difference between two electrodes of a galvanic cell is called the ____________ ____________________, denoted by E_{cell}. It is also called the electromotive force, or emf. It is also commonly called the __________________ of the cell because it is measured in volts.

(d) The cell potential of any galvanic cell is (positive negative).

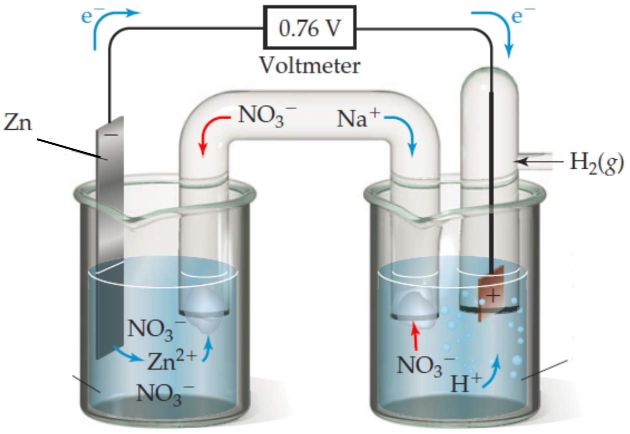
(e) Under standard conditions, the temperature is ______ °C, the pressure is _____ atm, and the concentration of reactants and products in solution is _______ mol/L.

(f) For the Zn-Cu galvanic cell mentioned in the last section, E^{o}_{cell} = ___________ V

(g) By convention, the potential associated with each electrode is chosen to be the potential for reduction at that electrode. Thus, standard half-cell potentials are tabulated for reduction reactions, which means they are __________________ __________________ potentials, denoted E^{o}_{red} .

(h) Write Equation 20.8 on page 839. ____

(i) It is not possible to measure the standard reduction potential of a half reaction directly. The reference half reaction is the reduction of H^+(*aq*) to H_2(*g*) under standard conditions, which is assigned a standard reduction potential of exactly __________ V.



(j) Identify the half reactions that occur at each electrode in the diagram above.

Anode: ____

Cathode: ____

(k) In the galvanic cell shown above, the nitrate ions migrate toward the _______________, and the sodium ions migrate toward the ___________________.

(l) If a potassium sulfate solution were used inside the salt bridge, the potassium ions would migrate toward the _________________, and the sulfate ions would migrate toward the ____________________.

Electrons do NOT flow through the salt bridge! This is a common misconception.

A table of standard reduction potentials is on p. 841. A more complete list is on p. 1064.

(m) If an equation is multiplied by N, the value of ΔH^o_{rxn} or ΔS^o_{rxn} is also multiplied by N. The values of standard reduction potentials are intensive properties. If we multiply a redox equation or the equation for a half reaction by N, the cell potential E^o_{cell} (is isn't) multiplied by N.

Half-Reaction	E° (V)
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	–1.66
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.14

(n) Use the data in the table above to calculate the standard cell potential (E^o_{cell}) for each of the following reactions.

Redox Reaction	E^o_{cell} (V)
$2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$	
$2Al + 3Sn^{2+} \rightarrow 2Al^{3+} + 3Sn$	

(o) Using the four half reactions listed in the table above part (n), write the balanced net ionic equation for the redox reaction that would generate the largest value for E^o_{cell}. Determine the value of E^o_{cell} for that redox reaction.

Redox Reaction	E^o_{cell} (V)

(p) A standard galvanic cell is set up using chromium and nickel. Based on the information below, determine which half-reaction occurs at the anode and which half-reaction occurs at the cathode. Calculate the standard cell potential for the cell.

$Cr^{3+}(aq) + 3\ e^- \rightarrow Cr(s)$ $E^o = -0.74$ V

$Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$ $E^o = -0.28$ V

Anode: ____

Cathode: ______________________________________

E^o_{cell}: __________________

(q) Use the table of standard reduction potentials on page 1064 to help you write a balanced chemical equation for each of the following reactions. A positive value of E^o_{cell} should be generated. Calculate the standard cell potential for each reaction.

Chemicals Involved	Balanced Redox Equation	E^o_{cell} (V)
MnO_4^- and Mn^{2+} Fe^{3+} and Fe^{2+}		
NO_3^- and NO Cu^{2+} and Cu		
Al^{3+} and Al H^+ and H_2		

Section 20.5 – Free Energy and Redox Reactions

(a) Write Equation 20.10 on page 845. ____

(b) A positive value for the potential, E^o, for a certain redox equation indicates that the process

(is isn't) thermodynamically favored.

A negative value for the potential, E^o, for a certain redox equation indicates that the process

(is isn't) thermodynamically favored.

(c) Use the table of standard reduction potentials on page 1064 to calculate the potential for each redox reaction and determine if the reaction is favored or not favored under standard conditions.

Redox Reaction	E^o (V)	favored or not favored?
$3\ Ag + Al^{3+} \rightarrow 3\ Ag^+ + Al$		
$Sn^{2+} + 2\ Fe^{3+} \rightarrow Sn^{4+} + 2\ Fe^{2+}$		
$2\ H^+ + Ca \rightarrow H_2 + Ca^{2+}$		
$2\ Na^+ + 2\ Br^- \rightarrow 2\ Na + Br_2$		

(d) Write Equation 20.12 on page 847. ____

(e) In this equation, *n* is a positive number without units that represents the number of

______________ of ____________________ transferred according to the balanced equation

for the reaction.

Figure 20.14 on page 847 summarizes the relationships among E^o, ΔG°, and *K*.

(f) Calculate the value of E^o, ΔG^o (in units of kJ/mol$_{rxn}$) and *K* for the following reaction under standard conditions.

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

<u>Section 20.6 – Cell Potentials Under Nonstandard Conditions</u>

(a) As a galvanic cell is discharged, the concentrations of the ions in solution, originally at 1.0 *M* in each half-cell, will change gradually over time. As the cell runs,

the concentration of the reactants (decreases increases), and

the concentration of the products (decreases increases).

(b) As the cell runs, the voltage progressively (decreases increases) over time.

When the cell reaches equilibrium, the value of E becomes equal to ___________ V, and the value of ΔG becomes equal to ________ kJ.

The value of E under nonstandard conditions can be calculated with the **Nernst equation**, which can be written as follows:

$$E = E^o - \frac{0.0592}{n}\log Q \quad @\ 25^oC$$

The AP Chemistry exam does not require students to use the Nernst equation to do calculations involving E, and the Nernst equation is not included on the list of equations and constants given to students on the exam.

The following information comes from the AP Chemistry Course and Exam Description.

> Many real systems do not operate at standard conditions and the electrical potential determination must account for the effect of concentrations.
>
> The qualitative effects of concentration on the cell potential can be understood by considering the cell potential as a driving force toward equilibrium, in that the farther the reaction is from equilibrium, the greater the magnitude of the cell potential.
>
> The standard cell potential, E^o, corresponds to the standard conditions of $Q = 1$.
>
> As the system approaches equilibrium, the magnitude (i.e., absolute value) of the cell potential decreases, reaching zero at equilibrium (when $Q = K$).
>
> Deviations from standard conditions that take the cell further from equilibrium than $Q = 1$ will increase the magnitude of the cell potential relative to E^o.
>
> Deviations from standard conditions that take the cell closer to equilibrium than $Q = 1$ will decrease the magnitude of the cell potential relative to E^o.
>
> In concentration cells, the direction of spontaneous electron flow can be determined by considering the direction needed to reach equilibrium.
>
> The Nernst equation is beyond the scope of this course and the AP Exam.
>
> Rationale: Qualitative reasoning about the effects of concentration on cell potential is part of the course. However, inclusion of algorithmic calculations was not viewed as the best way to deepen understanding of the big ideas.

The Nernst equation can be used to calculate the voltage produced by a galvanic cell under nonstandard conditions. For example, consider the following reaction

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \rightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$$

In this case, $n = 2$ because 2 electrons are transferred from Zn to Cu^{2+}.

Under standard conditions, the galvanic cell has the following properties. Note that the reaction is favored (negative ΔG) and the equilibrium constant K is very large (i.e., product-favored).

$[\mathrm{Cu}^{2+}]$ (M)	$[\mathrm{Zn}^{2+}]$ (M)	Q	E (V)	ΔG (kJ/mol$_{rxn}$)	K
1.0	1.0	**1.0**	**1.10**	–212	1.5×10^{37}

When this galvanic cell reaches equilibrium, $Q = K$, and the cell has the following properties.

$[\mathrm{Cu}^{2+}]$ (M)	$[\mathrm{Zn}^{2+}]$ (M)	Q	E (V)	ΔG (kJ/mol$_{rxn}$)
very small	very large	1.5×10^{37}	0	0

The following tables illustrate the effect of changes in concentration (of reactants or products) on the voltage (E) of the galvanic cell.

Increasing the Concentration of the Reactants: $Q < 1$ and $E > E^o$

$[\mathrm{Cu}^{2+}]$ (M)	$[\mathrm{Zn}^{2+}]$ (M)	Q	E (V)	ΔG (kJ/mol$_{rxn}$)
10.0	1.0	**0.10**	**1.13**	–218

Decreasing the Concentration of the Products: $Q < 1$ and $E > E^o$

$[\mathrm{Cu}^{2+}]$ (M)	$[\mathrm{Zn}^{2+}]$ (M)	Q	E (V)	ΔG (kJ/mol$_{rxn}$)
1.0	**0.010**	**0.010**	**1.16**	–224

Increasing the Concentration of the Products: $Q > 1$ and $E < E^o$

$[\mathrm{Cu}^{2+}]$ (M)	$[\mathrm{Zn}^{2+}]$ (M)	Q	E (V)	ΔG (kJ/mol$_{rxn}$)
1.0	**10.0**	**10**	**1.07**	–206

Decreasing the Concentration of the Reactants: $Q > 1$ and $E < E^o$

$[\mathrm{Cu}^{2+}]$ (M)	$[\mathrm{Zn}^{2+}]$ (M)	Q	E (V)	ΔG (kJ/mol$_{rxn}$)
0.010	1.0	**100**	**1.04**	–201

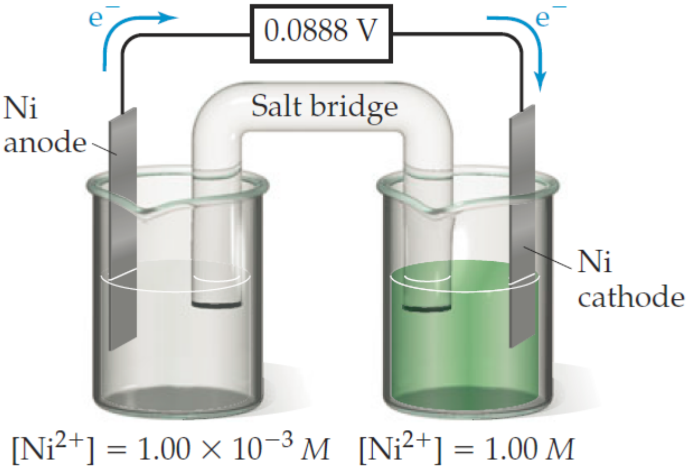
Summary of Cell Potentials Under Nonstandard Conditions

Increasing the concentration of reactants or decreasing the concentration of products increases the driving force for the reaction, resulting in a voltage that is GREATER than E^o.

If $Q < 1$, you are FURTHER AWAY FROM EQUILIBRIUM than $Q = 1$ and E is GREATER than E^o.

Decreasing the concentration of reactants or increasing the concentration of products decreases the driving force for the reaction, resulting in a voltage that is LESS than E^o.

If $Q > 1$, you are CLOSER TO EQUILIBRIUM than $Q = 1$ and E is LESS than E^o.



(c) Figure 20.15(a) on page 852 shows a galvanic cell that is set up differently from the other cells that we have seen so far. It is a ______________________ cell, a cell based solely on the voltage generated because of a difference in concentration. It consists of a strip of nickel immersed in a dilute solution of $Ni^{2+}(aq)$ and a strip of nickel immersed in a concentrated solution of $Ni^{2+}(aq)$.

(d) In this concentration cell, oxidation of Ni(*s*) occurs in the half-cell containing the (dilute concentrated) solution, and reduction of $Ni^{2+}(aq)$ occurs in the half-cell containing the (dilute concentrated) solution.

(e) If this galvanic cell had been set up under standard conditions, the concentration of $Ni^{2+}(aq)$ would be equal to ________ *M* in each half-cell, and the cell potential would be equal to __________ V. However, this cell operates under nonstandard conditions. This concentration cell will continue to operate until $[Ni^{2+}]_{anode}$ is ______________________ $[Ni^{2+}]_{cathode}$.

$$\begin{array}{lrcl} \textit{Anode:} & \mathrm{Ni}(s) & \longrightarrow & \mathrm{Ni}^{2+}(aq,\ \text{dilute}) + 2\,\mathrm{e}^- \\ \textit{Cathode:} & \mathrm{Ni}^{2+}(aq,\ \text{concentrated}) + 2\,\mathrm{e}^- & \longrightarrow & \mathrm{Ni}(s) \\ \hline \textit{Overall:} & \mathrm{Ni}^{2+}(aq,\ \text{concentrated}) & \longrightarrow & \mathrm{Ni}^{2+}(aq,\ \text{dilute}) \end{array}$$

(f) The Nernst equation can be used to calculate the voltage of a concentration cell.

In the example shown in Figure 20.15(a) on page 852, the value of n is equal to ________, the value of Q is equal to ____________, and the value of E is equal to ___________ V.

(g) As shown in Figure 20.15(b), the concentrations of $Ni^{2+}(aq)$ in these two half-cells will eventually become the same. When that happens, the value of Q would be equal to ________, and the value of E would be equal to _________ V.

Section 20.7 – Batteries and Fuel Cells

This section helps you to understand the variety of batteries that exist on the market today. However, you will not be responsible for memorizing the details from these examples.

Section 20.8 – Corrosion

(a) Corrosion reactions are spontaneous redox reactions in which a ______________ is attacked by some substance in its environment and converted to an unwanted compound.

(b) Some metals undergo very slow chemical corrosion because a thin coating of an oxide forms on the metal surface, which protects the underlying metal from further corrosion. Two examples of metals that experience this type of protection are _________ and _________.

(c) The rusting of ___________ requires both oxygen and water, and the process can be accelerated by other factors, such as _________, the presence of salts, and stress on the iron.

(d) Write the balanced half reactions involved in the rusting of iron.

Reduction at the cathode: ____

Oxidation at the anode: ____

(e) The reduction of O_2 requires H^+. Iron in contact with a solution whose pH is greater than 9

(does doesn’t) corrode.

(f) One way to protect iron from rusting is to cover the surface with a coat of _____________. Another option is to create galvanized iron, in which iron is coated with a thin layer of _____________, a metal that is more easily oxidized than iron.

(g) One method of protecting a metal from corrosion is called ______________________ protection. It is a process in which another metal is used as a sacrificial anode. For example, pieces of magnesium are buried near the iron pipe or storage tank and connected to it by a wire. In this way the magnesium is oxidized instead of the iron.

Section 20.9 – Electrolysis

(a) Galvanic cells are based on spontaneous (favorable) redox reactions. It is also possible for nonspontaneous redox reactions to occur by using _______________________________ to drive them.

(b) Write the balanced half reactions for the electrolysis of molten sodium chloride.

Reduction at the cathode: ____

Oxidation at the anode: ____

(c) The process of ________________________ uses electrolysis to deposit a thin layer of one metal on another metal to improve beauty or resistance to corrosion.

(d) The quantity of charge passing through an electrical circuit is measured in units of _______________________. This unit is abbreviated as C, and it can be calculated by multiplying (amperes) x (seconds). Note that 1 ampere = 1 C/s.

(e) Suppose that molten $AlCl_3$ undergoes electrolysis with a current of 10.0 A.

(i) How many grams of aluminum would be produced in one hour?

(ii) How many minutes would it take for 1.75 g Al to be produced?