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NATIONAL MATH + SCIENCE INITIATIVE

AP CHEMISTRY

Electrolysis and Electroplating

2016 EDITION

Click on the following link or scan the QR code to complete the evaluation for the Study Session https://www.surveymonkey.com/r/S_SSS



Periodic Table of the Elements

2 He 4.0026	10 Ne 20.179	18 Ar 39.948	36 Kr 83.80	54 Xe 131.29	86 Rn (222)	= -
	9 F 19.00	17 Cl 35.453	35 Br 79.90	53 126.91	85 At (210)	
	8 O 16.00	16 S 32.06	34 Se 78.96	52 Te 127.60	84 Po (209)	
	7 N 14.007	15 P 30.974	33 As 74.92	51 Sb 121.75	83 Bi 208.98	рөг
	6 C 12.011	14 Si 28.09	32 Ge 72.59	50 Sn 118.71	82 Pb 207.2	§Not yet named
	5 B 10.811	13 Al 26.98	31 Ga 69.72	49 In 114.82	81 TI 204.38	§Not
			30 Zn 65.39	48 Cd 112.41	80 Hg 200.59	112 § (277)
			29 Cu 63.55	47 Ag 107.87	79 Au 196.97	111 § (272)
			28 Ni 58.69	46 Pd 106.42	78 Pt 195.08	110 § (269)
			27 Co 58.93	45 Rh 102.91	77 Ir 192.2	109 Mt (266)
			26 Fe 55.85	44 Ru 101.1	76 Os 190.2	108 Hs (265)
			25 Mn 54.938	43 Tc (98)	75 Re 186.21	107 Bh (262)
			24 Cr 52.00	42 Mo 93.94	74 W 183.85	106 Sg (263)
			23 V 50.94	41 Nb 92.91	73 Ta 180.95	105 Db (262)
			22 Ti 47.90	40 Zr 91.22	72 Hf 178.49	104 Rf (261)
_			21 Sc 44.96	39 Y 88.91	, 57 La 138.91	88 89 Ra [†] Ac 226.02 227.03
	4 Be 9.012	12 Mg 24.30	20 Ca 40.08	38 Sr 87.62	56 Ba 137.33	88 Ra 226.02
1 H 1.0079	3 Li 6.941	11 Na 22.99	19 K 39.10	37 Rb 85.47	55 Cs 132.91	87 Fr (223)

_		_			_
71	n Lr	174.97	103	۲	(260)
20	Υp	173.04	102	ž	(259)
69	T	168.93	101	Md	(258)
99	ங்	167.26	100	Fm	(257)
29	웃	164.93	66	Es	(252)
99	à	162.50	86	ర	(251)
65	Д	~	26	崙	(247)
64	g d	157.25	96	Cm	(247)
63	En	151.97	92	Am	(243)
62	Sm	150.4	94	Pu	(244)
61	Pm	(145)	93	ď	
09	PZ	144.24	92	⊃	238.03
29	ቯ	140.12 140.91 144.2	91	Ъа	232.04 231.04 238.0
58	Çe	140.12	06	드	232.04

*Lanthanide Series:

†Actinide Series:

AP Chemistry Electrochemistry: Electrolytic Cells and Electroplating AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)

g = gram(s)

nm = nanometer(s)

atm = atmosphere(s)

mm Hg = millimeters of mercury

J, kJ = joule(s), kilojoule(s)

V = volt(s)

mol = mole(s)

ATOMIC STRUCTURE

$$E = h \nu$$

$$c = \lambda v$$

E = energy

v = frequency

 λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34} \,\mathrm{J}\,\mathrm{s}$

Speed of light, $c = 2.998 \times 10^8 \,\text{m s}^{-1}$

Avogadro's number = $6.022 \times 10^{23} \text{ mol}^{-1}$

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$
, where $a A + b B \rightleftharpoons c C + d D$

$$K_p = \frac{(P_{\rm C})^c (P_{\rm D})^d}{(P_{\rm A})^a (P_{\rm B})^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[\mathrm{OH}^-][\mathrm{HB}^+]}{[\mathrm{B}]}$$

$$K_w = [\mathrm{H^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \ \mathrm{at} \ 25^{\circ}\mathrm{C}$$

$$= K_a \times K_b$$

$$pH = -log[H^+], pOH = -log[OH^-]$$

$$14 = pH + pOH$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pK_a = -\log K_a$$
, $pK_b = -\log K_b$

Equilibrium Constants

 K_c (molar concentrations)

 K_p (gas pressures)

 K_a (weak acid)

 K_b (weak base)

 K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

 $t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A$$
, where $X_A = \frac{\text{moles A}}{\text{total moles}}$

$$P_{total} = P_{A} + P_{B} + P_{C} + \dots$$

$$n = \frac{m}{M}$$

$$K = {}^{\circ}C + 273$$

$$D = \frac{m}{V}$$

$$KE$$
 per molecule = $\frac{1}{2}mv^2$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n =number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

 $= 0.08206 L atm mol^{-1} K^{-1}$

 $= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$

1 atm = 760 mm Hg

= 760 torr

STP = 0.00 °C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^{\circ} = \sum S^{\circ}$$
 products $-\sum S^{\circ}$ reactants

$$\Delta H^{\circ} = \sum \Delta H_f^{\circ}$$
 products $-\sum \Delta H_f^{\circ}$ reactants

$$\Delta G^{\circ} = \sum \Delta G_f^{\circ} \text{ products } -\sum \Delta G_f^{\circ} \text{ reactants}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

$$= -RT \ln K$$

$$= -n F E^{\circ}$$

$$I = \frac{q}{t}$$

q = heat

m = mass

c =specific heat capacity

T = temperature

 S° = standard entropy

 H° = standard enthalpy

 G° = standard free energy

n = number of moles

 E° = standard reduction potential

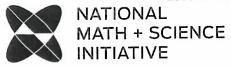
I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Faraday's constant, F = 96,485 coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$



Electrochemistry

Electrolytic Cells and Electroplating

What I Absolutely Have to Know to Survive the AP Exam

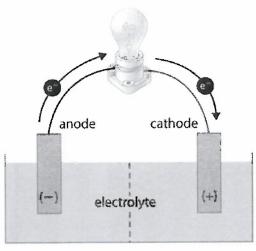
The following might indicate the question deals with electrochemical processes:

 E°_{cell} ; cell potential; reduction or oxidation; anode; cathode; salt bridge; electron flow; voltage; electromotive force; galvanic/voltaic; electrode; battery; current; amps; time; grams (mass); plate/deposit; electroplating; identity of metal; coulombs of charge

ELECTROCHEMICAL TERMS		
Electrochemistry	the study of the interchange of chemical and electrical energy	
OIL RIG	Oxidation Is Loss, Reduction Is Gain (of electrons)	
LEO the lion says GER	Lose Electrons in Oxidation; Gain Electrons in Reduction	
Oxidation	the loss of electrons, increase in charge	
Reduction	the gain of electrons, reduction of charge	
Oxidation number	the assigned charge on an atom	

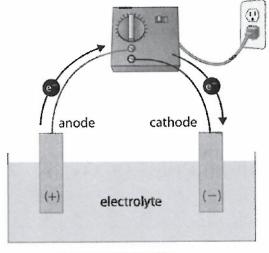
ELECTROCHEMICAL CELLS

Electrochemical Cells: A Comparison					
Galvanic (voltaic) cells	spontaneous oxidation-reduction reaction	Is separated into 2 half-cells	Electrodes made from metals (inert Pt or C if ion to ion or gas)	Battery – its cell potential drives the reaction and thus the e ⁻	
Electrolytic cells	non-spontaneous oxidation-reduction reaction	Usually occurs in a single container	Usually inert electrodes	Battery charger – requires an external energy source to drive the reaction and e ⁻	



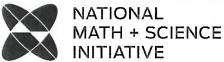
GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.



ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.



Electrolysis and Non-spontaneous Cells

The Electrolytic Cell: What is what and what to know

An electrolytic cell is an electrochemical cell in which the reaction occurs only after adding electrical energy; thus it is *not thermodynamically favorable* – it requires a driving force

Electrolytic reactions often occur in a single container; not 2 separate ½ cells like Voltaic cells

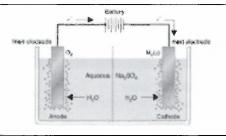
The calculated E° for an electrolytic cell is negative (i.e. that is the amount of potential required to drive the reaction).

This driving force causes the electrons to travel from the positive electrode to the negative electrode, the exact opposite of what you would expect. Remember: **EPA** – **Electrolytic Positive Anode**

<u>Anode</u> – the electrode where *oxidation* occurs.

Cathode – the electrode where *reduction* occurs.

Electron Flow - From Anode To CAThode



- Electrolytic reactions typically occur aqueous solutions (or in molten liquids)
 - If there is no water present, you have a pure molten ionic compound thus
 - the cation will be reduced
 - the anion will be oxidized
 - If water is present, you have an aqueous solution of the ionic compound, thus
 - You must decide which species is being oxidized and reduced; the ions or the water!
 - No alkali or alkaline earth metal can be reduced in an aqueous solution water is more easily reduced.
 - Polyatomic ions are typically NOT oxidized in an aqueous solution water is more easily oxidized.
- When it comes to water, be familiar with the following
 - REDUCTION OF WATER:

$$2 \text{ H}_2\text{O}(\ell) + 2 \text{ e}^- \rightarrow \text{H}_2(g) + 2 \text{ OH}^ E^\circ = -0.83 \text{ V}$$

OXIDATION OF WATER:

$$2 \text{ H}_2\text{O}(\ell) \rightarrow \text{O}_2(g) + 4 \text{ H}^+ + 4 \text{ e}^- \qquad E^\circ = -1.23 \text{ V}$$

Electrolysis: What to Do and How to Do it!

An electric current is applied to a 1.0 M KI solution. The possible *reduction* half reactions are listed in the table.

Reduction Half Reactions	$E^{\circ}(V)$
$2 \text{ H}_2\text{O}(\ell) + 2 e^- \rightarrow \text{H}_2(g) + 2 \text{ OH}^-$	-0.83 V
$O_2(g) + 4 H^+ + 4 e^- \rightarrow 2 H_2O(\ell)$	+1.23 V
$I_2(g) + 2 e^- \rightarrow 2 I^-$	+0.53 V
$K^+ + e^- \rightarrow K(s)$	-2.92 V

- (A) Write the balanced half-reaction for the reaction that takes place at the anode.
- (B) Write the balanced overall reaction for the reaction that takes place.
- (C) Which reaction takes place at the cathode?

First realize the solution contains 3 important species: K⁺, I⁻, and H₂O. From those 3 species, you must decide which is being oxidized and which is being reduced.

Where to start – Water can be both oxidized and reduced in an aqueous solution.

The I⁻ cannot be further reduced (it has a 1- charge)

The K⁺ cannot be further oxidixed (it has a 1+ charge)

For OXIDATION: either I or H₂O will be OXIDIZED... Write the oxidation half-reactions - Remember. the more positive oxidation potential will be oxidized.

$$2 \text{ H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{ H}^+ + 4 e^- \qquad E^\circ = -1.23 \text{ V}$$

$$E^{\circ} = -1.23 \text{ V}$$

$$2 I^{-} \rightarrow I_{2} + 2 e^{-}$$

$$E^{\circ} = -0.53 \text{ V}$$
 (will be oxidized)

Must decide which is being reduced, K⁺ or H₂O... The more positive reduction potential gets to be reduced; plus a great rule of thumb to remember is NO alkali metal will be reduced in aqueous solution - water will be.

$$2 H_2O + 2 e^- \rightarrow H_2 + 2 OH^-$$

$$E^{\circ} = -0.83 \text{ V}$$
 (will be reduced)

$$K^+ + e^- \rightarrow K$$

$$E^{\circ} = -2.92 \text{ V}$$

Put BOTH half-reactions TOGETHER:

$$2 I^- \rightarrow I_2 + 2 e^-$$

$$E^{\circ} = -0.53 \text{ V}$$
 (oxidation) (occurs at the anode)

$$2 \text{ H}_2\text{O} + 2 \text{ e}^- \rightarrow \text{H}_2 + 2 \text{ OH}^-$$

$$2 \text{ H}_2\text{O} + 2 \text{ e}^- \rightarrow \text{H}_2 + 2 \text{ OH}^ E^\circ = -0.83 \text{ V}$$
 (reduction) (occurs at the cathode)

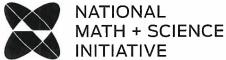
Balanced Overall Reaction:

$$2 I^{-} + 2 H_2O \rightarrow H_2 + 2 OH^{-} + I_2 E^{\circ} = -1.36 V$$

(D) What would you observe occurring at the cathode when current is applied to this solution?

Gas bubbles form from the production of hydrogen gas.

(E) Calculate the ΔG° for this reaction.



$$\Delta G^{\circ} = -n\Im E^{\circ}$$

$$\Delta G^{\circ} = -(2)(96500)(-1.36) = 262000 \frac{J}{\text{mol}}$$

$$\Delta G^{\circ} = 262 \frac{\text{kJ}}{\text{mol}}$$

(F) Is this reaction thermodynamically favorable or non-thermodynamically favorable? Justify your answer.

Since ΔG° is positive (and E°_{cell} is negative) the reaction is non-thermodynamically favorable.

The Electrical Energy of Electrolysis

When running an electrical current through a solution to cause electrolysis, you can measure that current and determine how much of what substance is going to be produced – think stoichiometry too! They will ask you "how many grams of a metal can be plated" or "how long it will take to plate a given mass"

The amount of electrical charge flowing through an electrochemical cell is measured in *coulombs* (c). The rate at which the charge flows (per *second*) is called the *current* and is measured in *amperes*, or *amps* symbolized by *I* for inductance. By definition,

$$amp(I) = \frac{Coulomb(c)}{sec(t)}$$

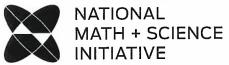
• A Faraday is the amount of charge associated with 1 mol of electrons. A Faraday has the value of 96,500 C.

Volt	$1 \frac{\text{Joule}(J)}{\text{Coulomb}(c)}$	
Amp	$1 \frac{\text{Coulomb}(c)}{\text{sec}(t)}$	
Faraday	$96,500 \frac{\text{Coulomb}(c)}{\text{mol of e}^-}$	
Balanced REDOX Equation	mol of e mol of substance	
# of Coulombs = IT or $c = IT$		
time (t) MUST BE IN SECONDS!!!!		

- Using these units you can measure how much substance is going to be produced, how many coulombs or how many amps were required, how long it takes, etc....
- A shortcut is the formula... $\frac{It}{n\Im}$ (Molar Mass) = grams plated

Calculate the mass of copper metal produced during the passage of 2.50 amps of current through a solution of copper(II) sulfate for 50.0 minutes.

$$\frac{It}{n\Im}$$
 (Molar Mass) = grams plated
 $\frac{(2.50)(50 \times 60)}{(2)(96500)}$ (63.55) = grams plated = 2.47g Cu

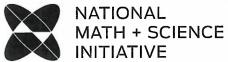


Electrochemistry Cheat Sheet

 E°_{cell} ; reduction and oxidizing agent; cell potential; reduction or oxidation; anode; cathode; salt bridge; electron flow; voltage; electromotive force; galvanic/voltaic; electrode; battery; current; amps; time; grams (mass); plate/deposit; electroplating; identity of metal; coulombs of charge

Electrolytic Cell Relationships

The Mnemonics apply to Electrolytic cells too: ANOX; REDCAT; FATCAT	Electrolytic Positive Anode	
"the more positive reduction potential gets to be reduced"	96,500 Coulombs = 1 mole of electrons	
"the more positive oxidation potential gets to be oxidized"	# electrons in balanced equations = # moles of electrons transferred	
Reduction of H_2O 2 $H_2O(\ell) + 2 e^- \rightarrow H_2(g) + 2 OH^ E^\circ = -0.83$	All time measurements must be in sec for electroplating/electrolysis problems	
Oxidation of H_2O 2 $H_2O \rightarrow O_2 + 4 H^+ + 4 e^ E^{\circ} = -1.23$	$V = \frac{It}{n\Im} (Molar Mass) = grams plated$	
No alkali or alkaline earth metal can be reduced in a aqueous solution - water is more easily reduced.	n Polyatomic ions are typically NOT oxidized in an aqueous solution - water is more easily oxidized.	
	$amp(I) = \frac{Coulomb(q)}{\sec(t)}$	
$E^{\circ}_{\text{cell}} = -$; not thermodynamically favored; $\Delta G = (+)$ $K < 1$	$\frac{\text{Volt} - 1}{\text{Coulomb}(c)}$	
$\Delta G^{\circ} = -n \Im E^{\circ}$	$Amp = \frac{Coulomb(c)}{sec(t)}$	
$\Delta G^{\circ} = -RT \ln K$	Faraday (3) = $96,500 \frac{\text{Coulomb}(c)}{\text{mol of e}^-}$	
Inert electrodes are typically used in gas and ion to i	on galvanic cells and in electrolytic cells	
Connections		
Thermo and Equilibrium	Stoichiometry	
Potential Pitfalls		
Watch signs on voltages!!	BE SURE units cancel out in your calculations.	
Balancing overall reactions – make sure # of electrons is the same in both half reactions.	Units on E°are volts	



NMSI SUPER PROBLEM

An electric current is applied to two separate solutions for 30 minutes, under the same conditions using inert electrodes. Observations are noted in the table below.

Solution A – 1.0 M K ₂ SO ₄	Solution B – 1.0 M CuSO ₄
Anode: gas bubbles	Anode: gas bubbles
Cathode: gas bubbles	Cathode: dark flakes formed on the electrode

In both reactions, water is oxidized according to the following oxidation half-reaction.

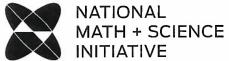
$$2 \text{ H}_2\text{O}(\ell) \rightarrow \text{O}_2(g) + 4 \text{ H}^+ + 4 \text{ e}^ E^\circ = -1.23 \text{ V}$$

- (a) Write the balanced equation for the half-reaction that occurs at the cathode in
 - (i) Solution A
 - (ii) Solution B
- (b) For Solution A, is the reaction thermodynamically favorable or not thermodynamically favorable? Justify your answer.
- (c) In the electrolysis of the K₂SO₄ solution, identify the gas produced and describe a test that can be used to identify the gas at the
 - (i) anode
 - (ii) cathode
- (d) Describe in the box below, what observations, if any, would be noted if a couple of drops of phenolphthalein indicator were added around the cathode of *both* solutions. Phenolphthalein indicator is colorless in acidic solutions and turns pink in basic solutions.

Justify your observations.

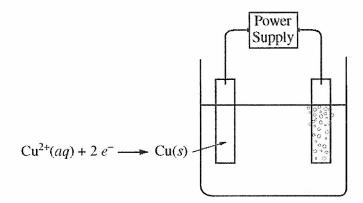
Solution A $- 1.0 M K_2 SO_4$	Solution B – 1.0 M CuSO ₄

2016 AP Chemistry - Electrochemistry: Electrolytic Cells and Electroplating



Electrochemistry - Electrolytic Cells and Electroplating

- (e) The dark flakes formed on the electrode in the electrolysis of Solution B were collected and dried. The mass of these flakes was determined to be 1.019 grams.
 - (i) Identify the flakes.
 - (ii) Calculate the amount of current that was passed through Solution B.



3. An external direct-current power supply is connected to two platinum electrodes immersed in a beaker containing $1.0 \, M$ CuSO₄(aq) at 25°C, as shown in the diagram above. As the cell operates, copper metal is deposited onto one electrode and O₂(g) is produced at the other electrode. The two reduction half-reactions for the overall reaction that occurs in the cell are shown in the table below.

Half-Reaction	E ^o (V)
$O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$	+1.23
$Cu^{2+}(aq) + 2 e^{-} \rightarrow Cu(s)$	+0.34

- (a) On the diagram, indicate the direction of electron flow in the wire.
- (b) Write a balanced net ionic equation for the electrolysis reaction that occurs in the cell.
- (c) Predict the algebraic sign of ΔG° for the reaction. Justify your prediction.
- (d) Calculate the value of ΔG° for the reaction.

An electric current of 1.50 amps passes through the cell for 40.0 minutes.

- (e) Calculate the mass, in grams, of the Cu(s) that is deposited on the electrode.
- (f) Calculate the dry volume, in liters measured at 25°C and 1.16 atm, of the $O_2(g)$ that is produced.

STOP

If you finish before time is called, you may check your work on this part only.

Do not turn to the other part of the test until you are told to do so.

Question 7 - Modified into a Short Free Response

Explain each of the following.

- (a) When an aqueous solution of NaCl is electrolyzed, $Cl_2(g)$ is produced at the anode, but no Na(s) is produced at the cathode.
- (b) The mass of Fe(s) produced when 1 faraday is used to reduce a solution of $FeSO_4$ is 1.5 times the mass of Fe(s) produced when 1 faraday is used to reduce a solution of $FeCl_3$.

8.

The compound NaI dissolves in pure water according to the equation NaI(s) \rightarrow Na⁺(aq) + I⁻(aq). Some of the information in the table of standard reduction potentials given below may be useful in answering the questions that follow.

Half-reaction	<i>E</i> ° (V)
$O_2(g) + 4 H^+ + 4 e^- \rightarrow 2 H_2O(l)$	1.23
$I_2(s) + 2e^- \rightarrow 2I^-$	0.53
$2 H_2O(l) + 2 e^- \rightarrow H_2(g) + 2 OH^-$	-0.83
$Na^+ + e^- \rightarrow Na(s)$	-2.71

- (d) An electric current is applied to a 1.0 M NaI solution.
 - (i) Write the balanced oxidation half-reaction for the reaction that takes place.
 - (ii) Write the balanced reduction half-reaction for the reaction that takes place.
 - (iii) Which reaction takes place at the anode, the oxidation reaction or the reduction reaction?
 - (iv) All electrolysis reactions have the same sign for ΔG° . Is the sign positive or negative? Justify your answer.

Question 3

In an electrolytic cell, a current of 0.250 ampere is passed through a solution of a chloride of iron, producing Fe(s) and $Cl_2(g)$.

- (a) Write the equation for the reaction that occurs at the anode.
- (b) When the cell operates for 2.00 hours, 0.521 gram of iron is deposited at one electrode. Determine the formula of the chloride of iron in the original solution.
- (c) Write the balanced equation for the overall reaction that occurs in the cell.
- (d) How many liters of Cl₂(g), measured at 25 °C and 750 mmHg, are produced when the cell operates as described in part (b)?
- (e) Calculate the current that would produce chlorine gas at a rate of 3.00 grams per hour.

2007 AP® CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l)$$

- 3. In a hydrogen-oxygen fuel cell, energy is produced by the overall reaction represented above.
 - (a) When the fuel cell operates at 25°C and 1.00 atm for 78.0 minutes, 0.0746 mol of $O_2(g)$ is consumed. Calculate the volume of $H_2(g)$ consumed during the same time period. Express your answer in liters measured at 25°C and 1.00 atm.
 - (b) Given that the fuel cell reaction takes place in an acidic medium,
 - (i) write the two half reactions that occur as the cell operates,
 - (ii) identify the half reaction that takes place at the cathode, and
 - (iii) determine the value of the standard potential, E° , of the cell.
 - (c) Calculate the charge, in coulombs, that passes through the cell during the 78.0 minutes of operation as described in part (a).