Teacher

Ex. problem: NMSI super Problem (Good example)

NATIONAL MATH + SCIENCE INITIATIVE

AP CHEMISTRY

Redox and Galvanic Cells

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

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 16.00	9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 93.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 § (269)	111 § (272)	112 § (277)						

§Not yet named

*Lanthanide Series:	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
†Actinide Series:	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

AP Chemistry Equations & Constants

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

L, mL	= liter(s), milliliter(s)		mm Hg	= millimeters of mercury
g	= gram(s)		J, kJ	= joule(s), kilojoule(s)
nm	= nanometer(s)		V	= volt(s)
atm	= atmosphere(s)		mol	= mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy

ν = frequency

λ = wavelength

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

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

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

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

EQUILIBRIUM

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

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

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

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

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

$$= K_a \times K_b$$

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

$$14 = pH + pOH$$

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

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

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

$$PV = nRT$$

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

$$P_{total} = P_A + P_B + P_C + \ldots$$

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

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

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

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

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 J mol^{-1} K^{-1}

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

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

1 atm = 760 mm Hg

$\qquad$ = 760 torr

STP = 0.00 °C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

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

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

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

$$= -RT \ln K$$

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

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

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

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

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Electrochemistry
Redox and Galvanic Cells

What I Absolutely Have to Know to Survive the AP Exam
The following might indicate the question deals with electrochemical processes: $E°_{cell}$; 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

ELECTROCHEMICAL TERMS

Electrochemistry	the study of the interchange of chemical and electrical energy
OIL RIG	**O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain (of electrons)
LEO the lion says **GER**	**L**ose **E**lectrons in **O**xidation; **G**ain **E**lectrons in **R**eduction
Oxidation	the loss of electrons, increase in charge
Reduction	the gain of electrons, reduction of charge
Oxidation number	the assigned charge on an atom

Balancing Oxidation–Reduction Reactions: The half-reaction method

1	Split the overall reaction into its oxidation and reduction half-reactions.
2	One half-reaction at a time, balance the atoms, except hydrogen and oxygen.
3	Balance oxygen atoms by adding H_2O molecules to the side that is short atoms of oxygen.
4	Balance hydrogen atoms by adding H^+ ions to the side missing atoms of hydrogen.
5	Add up the total charge on each side of the half reactions. Then add electrons, to the side that is most positive, until the charge on both sides is equal.
6	Make sure both the oxidation and reduction half reactions have the same number of electrons. If not, multiply each half-reaction by the coefficient required to produce an equal number of electrons being transferred in the two half-reactions.
7	Add the two half-reactions; simplify by cancelation (often there are common species on both sides).
If the solution is neutral or acidic the reaction is balanced.	
If the solution is basic continue with step 8	
8	Add OH^- ions (equal to the number of H^+ ions) to **both** sides of the equation. One side of the equation will also have H^+; combine the OH^- ion with those H^+ and form H_2O. Water, which appears on both sides of the equation, can be canceled out.
NOTE: No electrons should appear in the final balanced equation!	

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Balancing Examples
Balance the following redox reactions
In acidic solution: $Cr_2O_7^{2-}(aq) + Cl^-(aq) \rightarrow Cr^{3+}(aq) + Cl_2(g)$

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	Reduction half-reaction
$Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+}$	The coefficient of 2 balances the Cr atoms
$Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$	The 7 H_2O molecules balance the O atoms
$14\ H^+ + Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$	The 14 H^+ ions balance the H atoms
$6\ e^- + 14\ H^+ + Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$	The 6 e^- are added because the charge on the left side of the reaction is +12 and the charge on the right is +6
$Cl^- \rightarrow Cl_2$	Oxidation half-reaction
$2\ Cl^- \rightarrow Cl_2$	The coefficient of 2 balances the Cl atoms
$2\ Cl^- \rightarrow Cl_2 + 2\ e^-$	The 2 e^- are added because the charge on the right side of the reaction is 0 and the charge on the left side is −2
$6\ Cl^- \rightarrow 3\ Cl_2 + 6\ e^-$	This half-reaction was multiplied by 3 so there are equal numbers of electrons being lost and gained
$14\ H^+ + Cr_2O_7^{2-} + 6\ Cl^- \rightarrow 2\ Cr^{3+} + 3\ Cl_2 + 7\ H_2O$	Balanced for atoms and charge

In basic solution: $Cl_2(g) \rightarrow Cl^-(aq) + OCl^-(aq)$

$Cl_2 \rightarrow Cl^-$	Reduction half-reaction
$Cl_2 \rightarrow 2\ Cl^-$	The coefficient of 2 balances the Cl atoms
$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$	The 2 e^- are added because the charge on the right side of the reaction is 0 and the charge on the left side is −2
$Cl_2 \rightarrow OCl^-$	Oxidation half-reaction
$Cl_2 \rightarrow 2\ OCl^-$	The coefficient of 2 balances the Cl atoms
$2\ H_2O + Cl_2 \rightarrow 2\ OCl^-$	The 2 H_2O molecules balance the O atoms
$2\ H_2O + Cl_2 \rightarrow 2\ OCl^- + 4\ H^+$	The 4 H^+ ions balance the H atoms
$2\ H_2O + Cl_2 \rightarrow 2\ OCl^- + 4\ H^+ + 2\ e^-$	The 2 e^- are added because the charge on the left side of the reaction is 0 and the charge on the right side is +2
$4\ OH^- + 2\ H_2O + 2\ Cl_2 \rightarrow 2\ Cl^- + 2\ OCl^- + 4\ H^+ + 4\ OH^-$	The 4 OH^- ions are added to neutralize the H^+ ions in the basic solution.
$4\ OH^- + 2\ H_2O + 2\ Cl_2 \rightarrow 2\ Cl^- + 2\ OCl^- + 4\ H_2O$	The 4 OH^- ions and the 4 H^+ ions combine
$4\ OH^- + 2\ Cl_2 \rightarrow 2\ Cl^- + 2\ OCl^- + 2\ H_2O$	
$2\ OH^- + Cl_2 \rightarrow Cl^- + OCl^- + H_2O$	Balanced for atoms and charge

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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^-
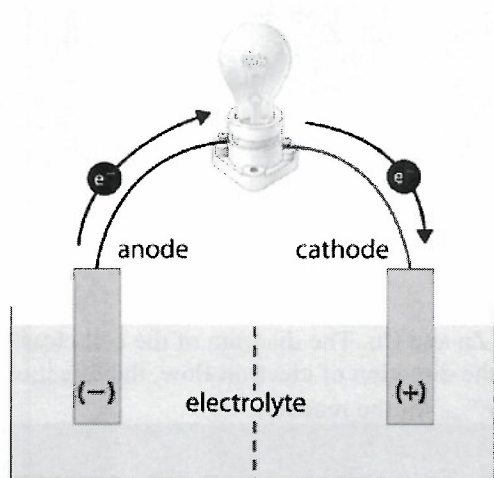
GALVANIC CELL

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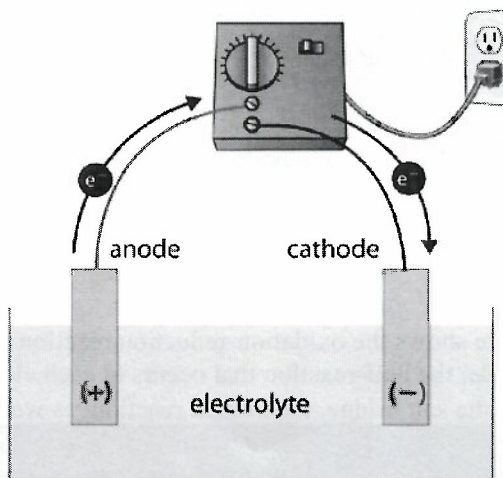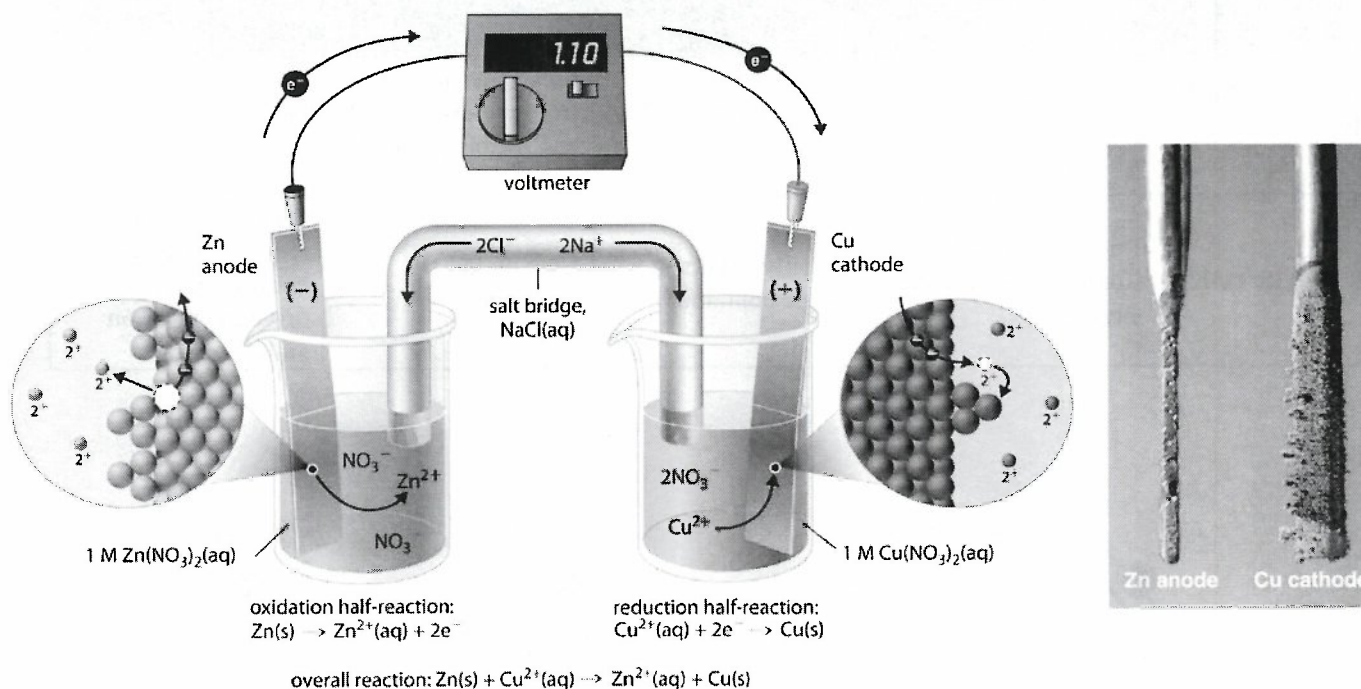
ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

The Galvanic Cell: *What is what and what to know?*	
ANODE: AN OX	Anode – the electrode where *oxidation* occurs. Over time the mass of the anode may decrease as the metal is oxidized into ions.
CATHODE: RED CAT	Cathode – the electrode where *reduction* occurs. Over time the mass of the cathode may increase as the metal ions in the solution are reduced and plated onto it.
FAT CAT	Electron Flow – From Anode To CAThode
Ca + hode	Cathode is + galvanic cells
Salt Bridge	Salt Bridge – provides ions to balance the charge in each cell; contains a neutral salt that is very soluble (avoids precipitation issues). The salt cations flow into the cathode and the salt anions flow into the anode.

The Galvanic Cell: *How it Works!*

oxidation half-reaction:
Zn(s) → Zn²⁺(aq) + 2e⁻

reduction half-reaction:
Cu²⁺(aq) + 2e⁻ → Cu(s)

overall reaction: Zn(s) + Cu²⁺(aq) → Zn²⁺(aq) + Cu(s)

The above picture shows the oxidation-reduction reaction between Zn and Cu. The diagram of the cell clearly shows: the anode and cathode; the half-reaction that occurs at each electrode, the direction of electron flow, the direction of ion movement from the salt bridge, the overall reaction, as well as the $E°_{cell}$ for the reaction.
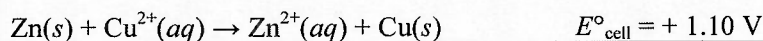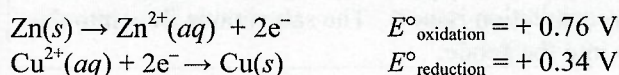
Calculating Standard Cell Potential ($E°_{cell}$)	
The difference in electrical potential between the two half-reactions is measured with a voltmeter. The difference between the cell potentials of the two half-reactions determines the overall cell potential for the reaction.	
1	Look at a table of Standard Reduction Potentials (or the reduction potentials that are provided). Write both **reduction** reactions from the table with their voltages.
2	THE MORE POSITIVE REDUCTION POTENTIAL IS REDUCED. *THE LEAST POSITIVE IS OXIDIZED.*
3	Reverse the equation that will be oxidized; be sure to change the sign of the voltage [this is now $E°_{oxidation}$]
4	Balance and add the two half-reactions together.
5	Now add the two cell potentials together. $E°_{cell} = E°_{oxidation} + E°_{reduction}$
	° indicates *standard conditions* (1 atm, 25°C; 1 *M*)

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E°_{reduction} = -0.76$ V
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E°_{reduction} = +0.34$ V
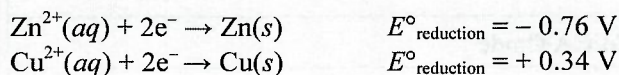
More positive is reduced (+ 0.34 V > – 0.76 V) – Cu^{2+} (+0.34) is reduced and Zn oxidized

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E°_{oxidation} = +0.76$ V
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E°_{reduction} = +0.34$ V

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ $E°_{cell} = +1.10$ V

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Non Standard Conditions

- The pressure, the temperature or the concentration changes from 1 atm, 25°C, or 1M...

- Typically a concentration change from 1 M will result in a change in the cell potential
  - THINK about the changes in concentration – they only affect the ions in solution (aq)
    - $$\frac{[\text{PRODUCT}^{ion}]}{[\text{REACTANT}^{ion}]}$$
    - If the ratio of ions increases compared to standard conditions, the reverse reaction will become thermodynamically favored
    - If the ratio of ions decreases compared to standard conditions, the forward reaction will become thermodynamically favored

Non Standard Conditions Example
For the cell

$$2\ Al(s) + 3\ Mn^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Mn(s)$$
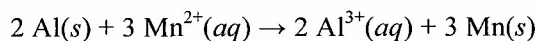
The reaction above was carried out at 25°C. The concentration of the aluminum ion (Al^{3+}) is 2.0 M, and the concentration of the manganese ion (Mn^{2+}) is 1.00 M. Indicate whether E_{cell} will increase, decrease, or remain the same (compared to the standard cell potential, $E°_{cell}$). Justify your answer.

For the cell
$$X(s) + Y^{2+}(aq) \rightarrow X^{2+}(aq) + Y(s)$$
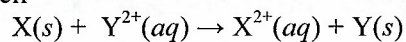
The concentration of the X ion is 0.20 M, and the concentration of the Y ion is 0.30 M. Indicate whether E_{cell} will increase, decrease, or remain the same (compared to $E°_{cell}$). Justify your answer.

CELL POTENTIAL, ELECTRICAL WORK, EQUILIBRIUM & FREE ENERGY

Work

The electromotive force (*emf*) or cell potential (E_{cell}) is the driving force responsible for the movement of electrons from the anode to the cathode in a voltaic cell. The unit for this potential is the Volt (V) – by definition, it requires 1 joule of energy (work) to transport 1 coulomb of electrical charge across a potential of 1 volt.

$$emf(V) = \frac{work(J)}{charge(C)}$$

Summary OF Gibb's Free Energy and Cell Potential	
$E°_{cell} = -$	Implies non-spontaneous reaction ($\Delta G° = +$ and $K < 1$)
$E°_{cell} = +$	Implies spontaneous reaction ($\Delta G° = -$ and $K > 1$)
$E°_{cell} = 0$	Reaction is at equilibrium (dead battery)
The larger the $E°_{cell}$	The more spontaneous the reaction

Gibb's Free Energy and Cell Potential: Relevant Equations	
$\Delta G° = -n \Im E°$	ΔG = Gibb's free energy change n = number of moles of electrons. $\Im$ = Faraday's constant $\dfrac{96500\,C}{mol\,e^-}$
$\Delta G° = -RT \ln K$	ΔG = Gibb's free energy change R = Gas constant 8.315×10^{-3} kJ mol^{-1} K^{-1} K = equilibrium constant T = Temperature (K)

Free Energy, Equilibrium, and Cell Potential

$\Delta G°$	K	$E°$
0	at equilibrium	0
negative	>1, products favored	+
positive	<1, reactants favored	−

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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

### Galvanic or Voltaic Cell Relationships

Cathode is **+** galvanic cells	OIL RIG – oxidation is loss of e⁻; reduction is gain
"the more positive reduction potential gets to be reduced"	FATCAT – e⁻ from the anode to the cathode
ANOX – oxidation at the anode	REDCAT – reduction at the cathode
Be able to… label the parts of a galvanic cell; such as the anode; cathode; salt bridge; electron flow; half reactions; overall reaction; direction of ions from salt bridge	The cathode will gain mass because it is the site of reduction; the anode will lose mass because it is the site of oxidation. (only true when electrodes are metals – not true of inert electrodes)
$E°_{cell}$ = +; thermodynamically favored ΔG = (−); K>1	$E°_{cell}$ = −; non thermodynamically favored ΔG = (+); K<1
<u>Salt Bridge</u> – provides ions to balance the charge in each ½ cell; contains a neutral salt that is very soluble (avoids precipitation issues). The salt cations flow into the cathode and the salt anions flow into the anode.	Be able to explain whether E_{cell} increases or decreases or remains the same when the concentrations of ions change from $1M$ solutions. Justify by describing which direction is more thermodynamically favorable (OR USE the Nernst equation.
For the Nernst Equation you MUST be able to relate how the sign of log Q affects the overall cell potential. If Q is greater than 1 then the log of Q is positive; thus $E°_{cell}$ − (+) decreases the E_{cell} If Q is greater less 1 then the log of Q is negative; thus $E°_{cell}$ − (−) increases the E_{cell}	The Nernst Equation – NOT required for the EXAM but it is very helpful in solving for cell potential under non-standard conditions $$E_{cell} = E°_{cell} - \frac{RT}{n\mathfrak{I}} \ln Q$$

Connections

| Thermo and Equilibrium	Stoichiometry
Connects EQUILIBRIUM to ELECTRO and THERMO $E°_{cell}$ = 0 at equilibrium thus ΔG = 0	Connects THERMO to ELECTRO $\Delta G°$ = −$n\mathfrak{I} E°$
Use this to connect EQUILIBRIUM to THERMO (and then THERMO to ELECTRO $\Delta G°$ = −$RT \ln K$	

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

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Electrochemistry – Redox and Galvanic Cells
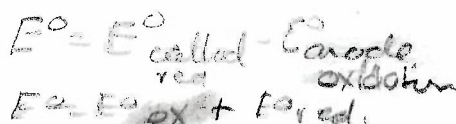
NMSI SUPER PROBLEM

Answer the questions below, which relate to reactions involving copper, Cu and copper(II) ion, Cu^{2+}.

A standard voltaic cell is constructed using copper and metal X. The standard reduction potential for Cu is given below.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$E^\circ = 0.34$ V
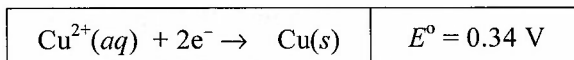
Immediately after closing the switch, the Voltmeter shows a reading of 0.47 V. Several minutes later it was noted that small flakes were adhering to the Cu electrode.
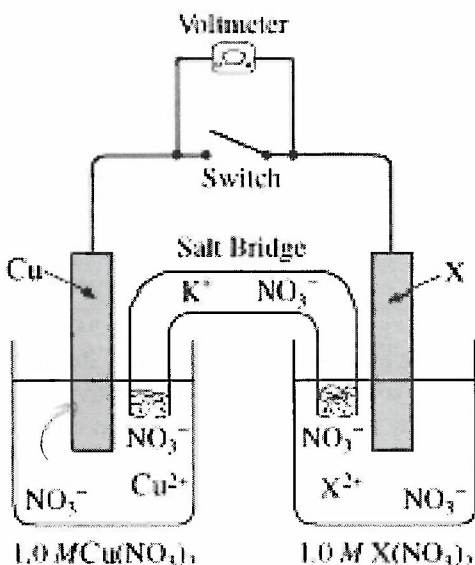
(a) Which metal, Cu or X, is the anode? Justify your answer.

(b) In the diagram of the cell shown above, label the

    i.   cathode

    ii.   direction of electron flow

(c) Which substance is being oxidized, Cu or X? Explain

(d) Determine the standard *reduction potential* for the X^{2+}/X half-cell.

(e) Using the information provided, select the *metal* that was used for the X electrode. Explain your choice.

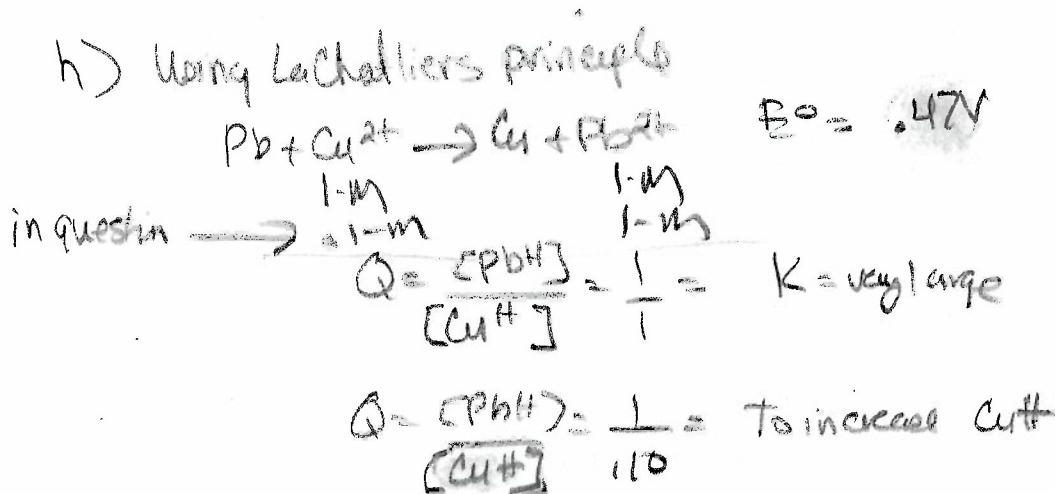| $Ag^+(aq) + e^- \rightarrow Ag(s)$	$E^\circ = 0.80$ V
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	$E^\circ = -0.13$ V
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	$E^\circ = -0.14$ V

(f) Write a balanced net ionic equation for this electrochemical cell.

(g) This galvanic cell has a salt bridge that is filled with a saturated solution of KNO_3.
     i.   As the cell operates, describe what happens in the salt bridge.

     ii.   Describe what you would observe in the anode half-cell if the salt bridge contained a saturated solution of KCl instead of KNO_3.

(h) In the original galvanic cell, if the $[Cu^{2+}]$ is changed from 1.0 M to 0.1 M, would the new cell potential, E_{cell}, at 25°C, increase, decrease, or remain the same. Justify your answer.

(i) For the original reaction in the galvanic cell above, indicate whether
     i. ΔG is positive or negative. Justify your choice. $\Delta G = -RT \ln K$

     ii.   the equilibrium constant, K, is greater than one or less than one. Justify your choice.

In another experiment, a 1.019 gram piece of Cu was cut from the electrode used above and added to 250. mL of 0.25 M nitric acid, HNO_3. An oxidation-reduction reaction between the copper and the nitrate ion occurs as indicated below.

$$Cu + NO_3^- \rightarrow Cu^{2+} + NO$$
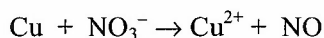
(j) Write a complete and balanced net ionic equation for this redox reaction. Show work to support your answer.

(k) Identify the limiting reactant. Show work to support your answer.

(l) On the basis of the limiting reactant identified above, calculate the value of the concentration of Cu^{2+} ions after the reaction is complete.

h) Using LeChatliers principle

$Pb + Cu^{2+} \longrightarrow Cu + Pb^{2+}$ $E° = .47V$

     1-M   1-M

in question $\longrightarrow$ ≈1-m   1-m

$Q = \dfrac{[PbH]}{[CuH]} = \dfrac{1}{1} =$ $K =$ very large

$Q = \dfrac{[PbH]}{[CuH]} = \dfrac{1}{.10} =$ To increase CuH

2012 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

6. In a laboratory experiment, Pb and an unknown metal Q were immersed in solutions containing aqueous ions of unknown metals Q and X. The following reactions summarize the observations.

$$\text{Observation 1: } Pb(s) + X^{2+}(aq) \rightarrow Pb^{2+}(aq) + X(s)$$
$$\text{Observation 2: } Q(s) + X^{2+}(aq) \rightarrow \text{ no reaction}$$
$$\text{Observation 3: } Pb(s) + Q^{2+}(aq) \rightarrow Pb^{2+}(aq) + Q(s)$$

(a) On the basis of the reactions indicated above, arrange the three metals, Pb, Q, and X, in order from least reactive to most reactive on the lines provided below.

_____ , _____ , _____

least reactive metal   most reactive metal

The diagram below shows an electrochemical cell that is constructed with a Pb electrode immersed in 100. mL of $1.0\ M$ $Pb(NO_3)_2(aq)$ and an electrode made of metal X immersed in 100. mL of $1.0\ M$ $X(NO_3)_2(aq)$. A salt bridge containing saturated aqueous KNO_3 connects the anode compartment to the cathode compartment. The electrodes are connected to an external circuit containing a switch, which is open. When a voltmeter is connected to the circuit as shown, the reading on the voltmeter is 0.47 V. When the switch is closed, electrons flow through the switch from the Pb electrode toward the X electrode.

(b) Write the equation for the half-reaction that occurs at the anode.

(c) The value of the standard potential for the cell, $E°$, is 0.47 V.

    (i) Determine the standard reduction potential for the half-reaction that occurs at the cathode.

    (ii) Determine the identity of metal X.

(d) Describe what happens to the mass of each electrode as the cell operates.

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2012 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

(e) During a laboratory session, students set up the electrochemical cell shown above. For each of the following three scenarios, choose the correct value of the cell voltage and justify your choice.

   (i) A student bumps the cell setup, resulting in the salt bridge losing contact with the solution in the cathode compartment. Is V equal to 0.47 or is V equal to 0 ? Justify your choice.

  (ii) A student spills a small amount of 0.5 M $Na_2SO_4(aq)$ into the compartment with the Pb electrode, resulting in the formation of a precipitate. Is V less than 0.47 or is V greater than 0.47 ? Justify your choice.

 (iii) After the laboratory session is over, a student leaves the switch closed. The next day, the student opens the switch and reads the voltmeter. Is V less than 0.47 or is V equal to 0.47 ? Justify your choice.

STOP

END OF EXAM

2010 AP® CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$
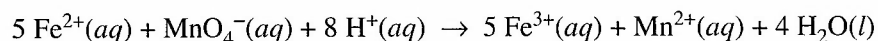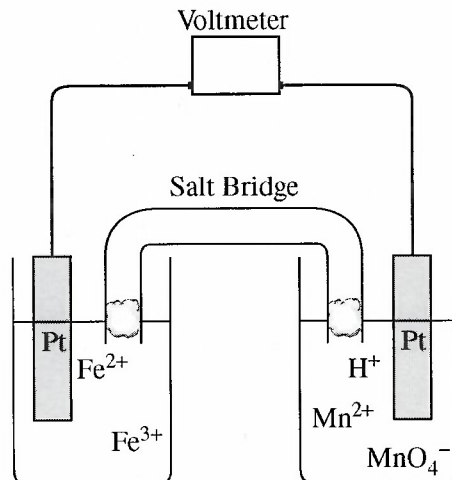
2. A galvanic cell and the balanced equation for the spontaneous cell reaction are shown above. The two reduction half-reactions for the overall reaction that occurs in the cell are shown in the table below.

Half-Reaction	$E°$ (V) at 298 K
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+ 0.77
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$	+1.49

(a) On the diagram, clearly label the cathode.

(b) Calculate the value of the standard potential, $E°$, for the spontaneous cell reaction.

(c) How many moles of electrons are transferred when 1.0 mol of $MnO_4^-(aq)$ is consumed in the overall cell reaction?

(d) Calculate the value of the equilibrium constant, K_{eq}, for the cell reaction at 25°C. Explain what the magnitude of K_{eq} tells you about the extent of the reaction.

Three solutions, one containing $Fe^{2+}(aq)$, one containing $MnO_4^-(aq)$, and one containing $H^+(aq)$, are mixed in a beaker and allowed to react. The initial concentrations of the species in the mixture are 0.60 M $Fe^{2+}(aq)$, 0.10 M $MnO_4^-(aq)$, and 1.0 M $H^+(aq)$.

(e) When the reaction mixture has come to equilibrium, which species has the higher concentration, $Mn^{2+}(aq)$ or $MnO_4^-(aq)$? Explain.

(f) When the reaction mixture has come to equilibrium, what are the molar concentrations of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$?

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2009 AP® CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

6. Answer the following questions about electrochemical cells.
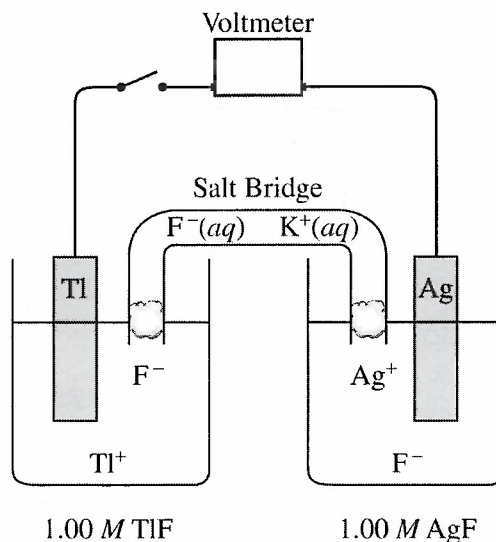
It is observed that when silver metal is placed in aqueous thallium(I) fluoride, TlF, no reaction occurs. When the switch is closed in the cell represented above, the voltage reading is +1.14 V.

(a) Write the reduction half-reaction that occurs in the cell.

(b) Write the equation for the overall reaction that occurs in the cell.

(c) Identify the anode in the cell. Justify your answer.

(d) On the diagram above, use an arrow to clearly indicate the direction of electron flow as the cell operates.

(e) Calculate the value of the standard reduction potential for the Tl^+/Tl half-reaction.

The standard reduction potential, $E°$, of the reaction $Pt^{2+} + 2\,e^- \rightarrow Pt$ is 1.20 V.

(f) Assume that electrodes of pure Pt, Ag, and Ni are available as well as 1.00 M solutions of their salts. Three different electrochemical cells can be constructed using these materials. Identify the two metals that when used to make an electrochemical cell would produce the cell with the largest voltage. Explain how you arrived at your answer.

(g) Predict whether Pt metal will react when it is placed in 1.00 M $AgNO_3(aq)$. Justify your answer.

STOP

END OF EXAM

2004 AP® CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)
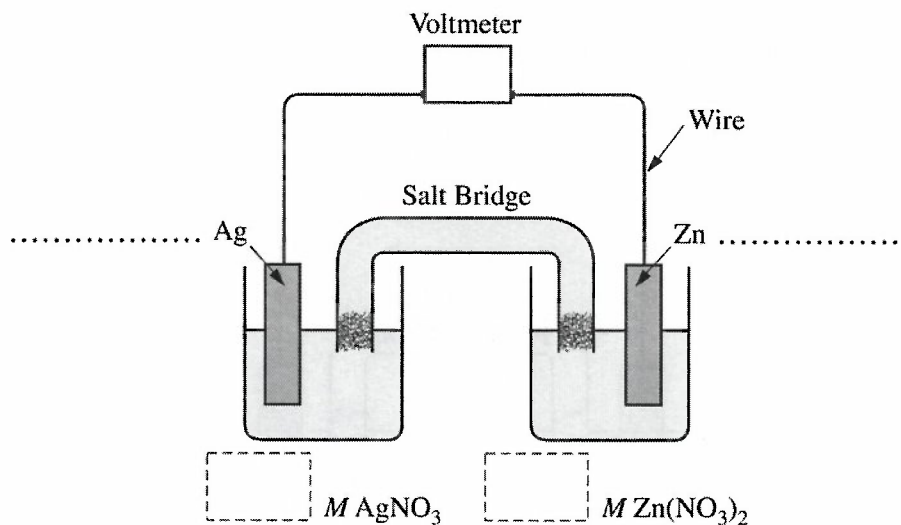
6. The following questions refer to the electrochemical cell shown in the diagram above.

    (a) Write a balanced net ionic equation for the spontaneous reaction that takes place in the cell.

    (b) Calculate the standard cell potential, $E°$, for the reaction in part (a).

    (c) In the diagram above,

        (i) label the anode and the cathode on the dotted lines provided, and

        (ii) indicate, in the boxes below the half-cells, the concentration of $AgNO_3$ and the concentration of $Zn(NO_3)_2$ that are needed to generate $E°$.

    (d) How will the cell potential be affected if KI is added to the silver half-cell? Justify your answer.

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