Electrochemistry: Intro

Redox reactions:

e.g. the copper-silver system

$$2Ag^{+} + Cu(s) \Rightarrow 2Ag(s) + Cu^{2+}$$

Redox reactions:

e.g. the permanganate-oxalate system

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \Rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Schematics of Cells e.g. the galvanic cell:

$Cu|Cu^{2+}(0.0200\ M)||Ag^{+}(0.0200M)|Ag$

By convention:
- Anode is on the left
- Cathode on the right

- Vertical line: Interface at which a potential develops. (e.g. interface between Cu(s) and the Cu^{2+} solution)

- Double vertical line: two interfaces. (One at each end of the salt bridge, where a liquid-junction potential develops)

CATHODE: Electrode where reduction occurs. (Ag)

ANODE: Where oxidation takes place. (Cu)

Potential of a cell $E_{cell} = E_{cathode} - E_{anode}$

Nernst Equation

for the reaction: $aA + bB + ... + ne^{-} \text{---->} cC + dD + ...$

The electrode potential is: $$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d...}{[A]^a[B]^b...}$$

E^0 = standard electrode potential

$R = 8.314\ JK^{-1}mol^{-1}$

T = Temperature in K

n = Number of moles of e^- involved

F = Faraday constant = 96,485 C

$\ln = 2.303\log$

At 25°C:

$$E = E^0 - \frac{0.0592}{n} \log \frac{[C]^c[D]^d...}{[A]^a[B]^b}$$

TABLE 3.4 PARAMETER *a* AND INDIVIDUAL ION ACTIVITY COEFFICIENTS

Ion Size Parameter, a (Å)[a]	Ion	Activity Coefficients Calculated with (2) of Table 3.3 for Ionic Strength				
		10^{-4}	10^{-3}	10^{-2}	0.05	10^{-1}
9	H^+	0.99	0.97	0.91	0.86	0.83
	Al^{3+}, Fe^{3+}, La^{3+}, Ce^{3+}	0.90	0.74	0.44	0.24	0.18
8	Mg^{2+}, Be^{2+}	0.96	0.87	0.69	0.52	0.45
6	Ca^{2+}, Zn^{2+}, Cu^{2+}, Sn^{2+}, Mn^{2+} Fe^{2+}	0.96	0.87	0.68	0.48	0.40
5	Ba^{2+}, Sr^{2+}, Pb^{2+}, CO_3^{2-}	0.96	0.87	0.67	0.46	0.39
4	Na^+, HCO_3^-, $H_2PO_4^-$, CH_3COO^-	0.99	0.96	0.90	0.81	0.77
	SO_4^{2-}, HPO_4^{2-}	0.96	0.87	0.66	0.44	0.36
	PO_4^{3-}	0.90	0.72	0.40	0.16	0.10
3	K^+, Ag^+, NH_4^+, OH^-, Cl^- ClO_4^-, NO_3^-, I^-, HS^-	0.99	0.96	0.90	0.80	0.76

[a] After J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937). Reproduced with permission from American Chemical Society.

Example: for the reaction

$$MnO_4^- + 5e^- + 8H^+ \text{ -----> } Mn^{2+} + 4H_2O$$

$$E = E^0 - \frac{0.0592}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

The Nernst equation reflects the number of moles of electrons exchanged:

e.g. i) $Cu^{2+} + 2e^- \text{--->} Cu(s)$ $E^0 = +0.337$

ii) $3Cu^{2+} + 6e^- \text{--->} 3Cu(s)$ $E^0 = +0.337$

$$\text{i) } E = 0.337 - \frac{0.0592}{2} \log \frac{1}{[Cu^{2+}]}$$

$$\text{ii) } E = 0.337 - \frac{0.0592}{6} \log \frac{1}{[Cu^{2+}]^3}$$

Galvanic (Voltaic) Cells:

- Reactions proceed spontaneously

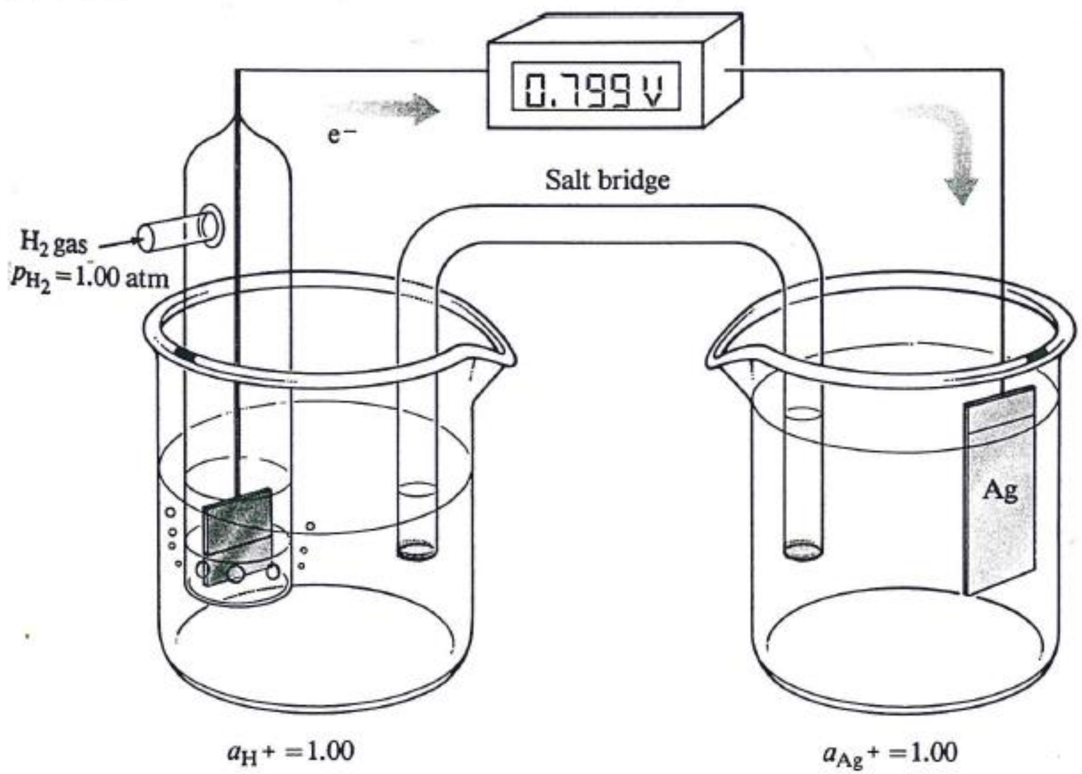
- A flow of electrons is produced from the anode to the cathode via an external conductor.

- Allow for storage of electrical energy.

Standard Electrode Potential of a Half-Reaction, E_o

Definition: Potential of a cell composed of a working electrode (1 M cation activity) as the cathode and SHE as the anode.

$$Pt, H_2(p=1 atm) | ([H^+]=1M) || ([Ag^+]=1M) | Ag$$



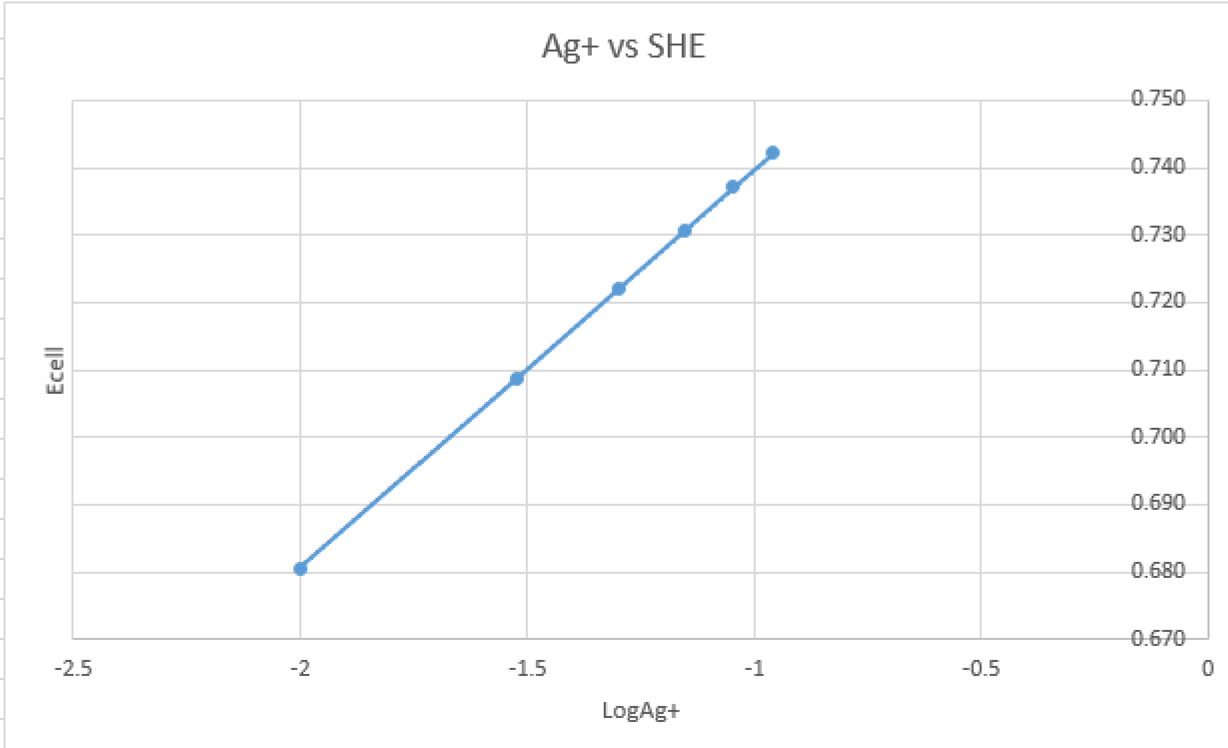
Half-Reaction	Standard Electrode Potential, V
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	+0.000
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763

Potentiometric measurements

$$SHE||[Ag^{+}]=xM|Ag(s)$$

$$SCE||[Zn^{2+}]=xM|Zn(s)$$

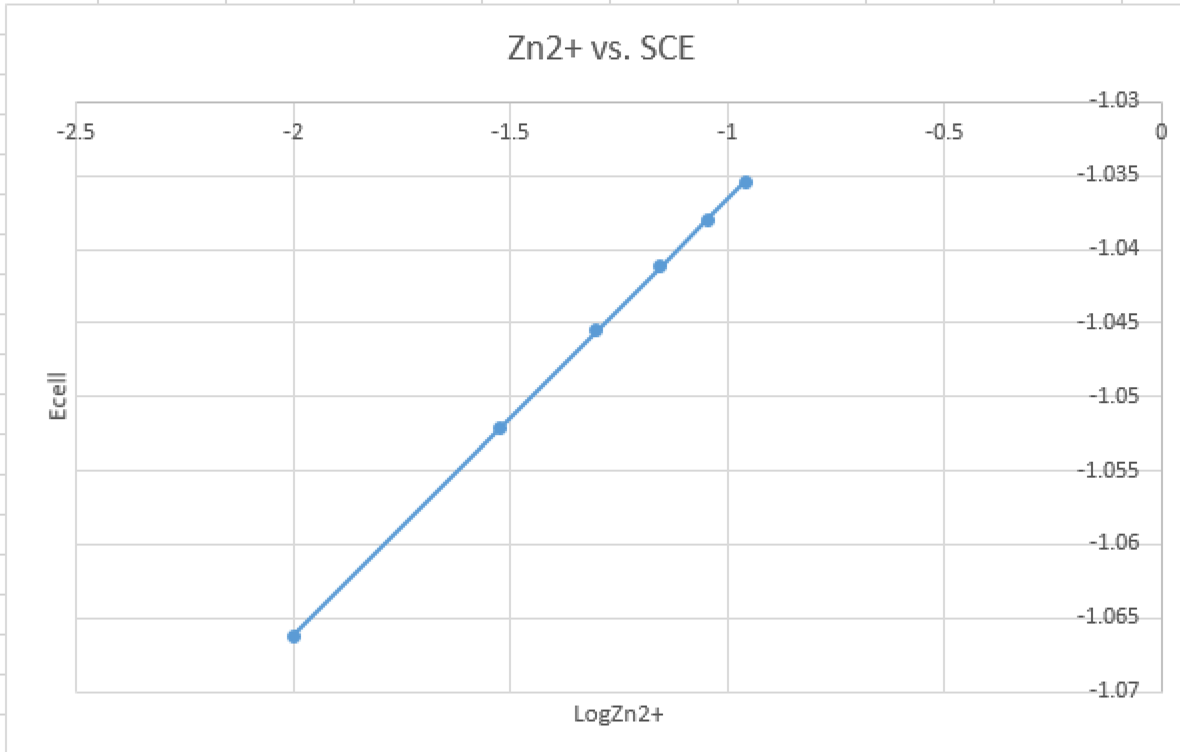
logAg+	Ecell	Ag+
-2	0.681	0.01
-1.523	0.709	0.03
-1.301	0.722	0.05
-1.155	0.731	0.07
-1.046	0.737	0.09
-0.959	0.742	0.11



Slope: 0.0605

Intercept: 0.801

logZn2+	Ecell	Zn2+
-2	-1.0662	0.01
-1.523	-1.05208	0.03
-1.301	-1.04551	0.05
-1.155	-1.04119	0.07
-1.046	-1.03795	0.09
-0.959	-1.03537	0.11



Slope: 0.0300

Intercept: -1.0056

pH measurements

SCE||HE system

SCE:

$Hg_2Cl_2(s) + 2e^- \dashrightarrow 2Hg(l) + 2Cl^-(aq)$

$E^0 = 0.2444$ V

HE:

$2H^+ + 2e^- \dashrightarrow H_2(g)$

$E^0 = 0.000$ when $P_{H2} = 1$ atm and $[H^+] = 1$ M

For variable pH values: $E = -\frac{0.0592}{2} \log \frac{P_{H2}}{[H^+]^2}$

P_{H2} = constant = 1atm

Inert metallic electrodes

Pt, Au, Pd, C are *inert conductors*.

Electrodes made of these materials respond to the potential of redox systems with which they are in contact.

The E value of a Pt electrode in a solution of Ce^{4+} and Ce^{3+} is:

$$E = E^0_{Ce4+} - 0.0592 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

Redox Titrations

Example: Titration of 50.00 mL of 0.025 M U^{4+} with 0.1000 M Ce^{4+}

Half-reactions: $Ce^{4+} + e^- \longrightarrow Ce^{3+}$

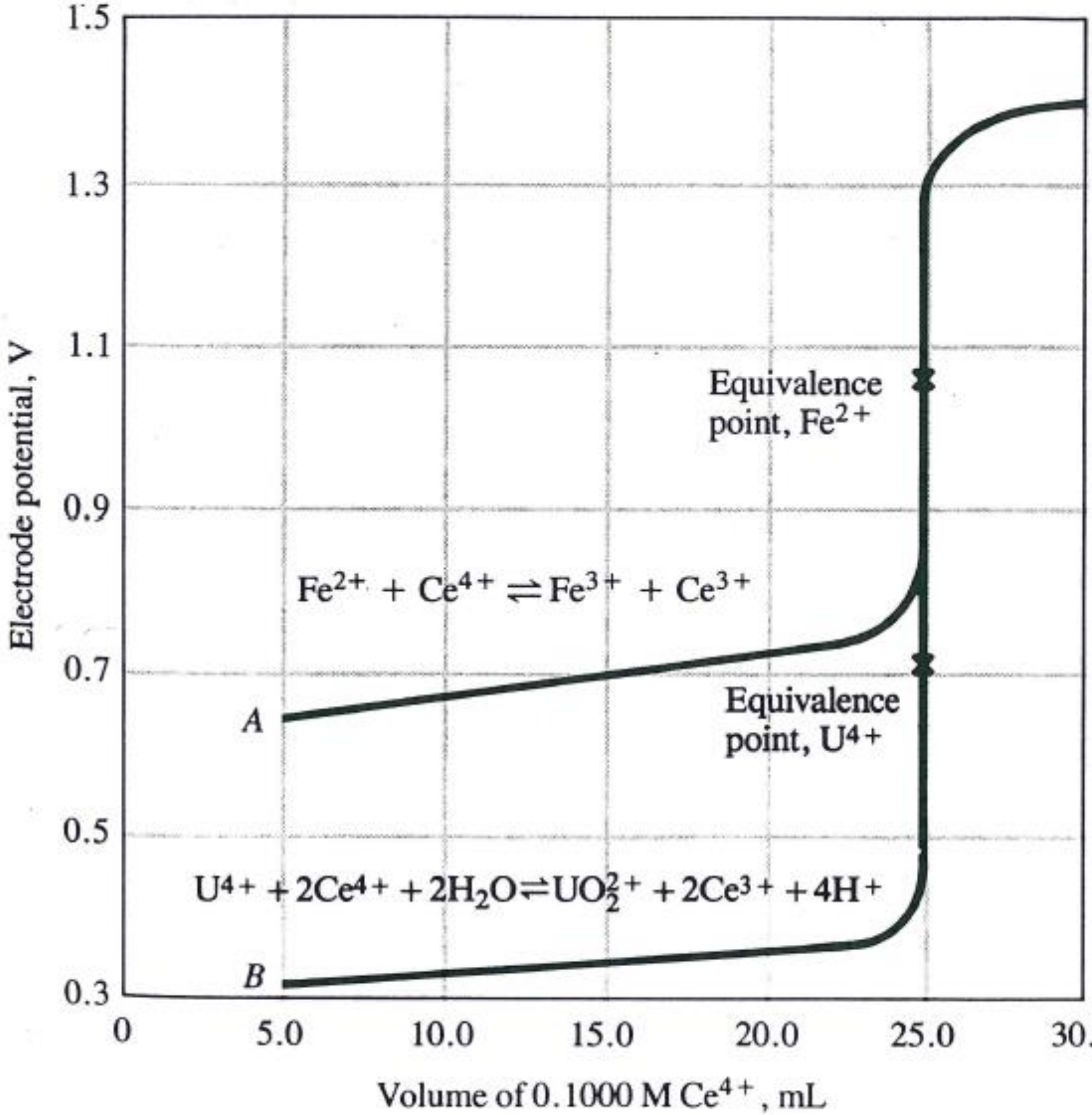
$$E^0_{Ce} = +1.44 \text{ V}$$

$$UO_2^{2+} + 4H^+ + 2e^- \longrightarrow U^{4+} + 2H_2O$$

$$E^0_U = +0.334 \text{ V}$$

Overall reaction:

$$U^{4+} + 2H_2O + 2Ce^{4+} \longrightarrow UO_2^{2+} + 2Ce^{3+} + 4H^+$$



1.5
1.3
1.1
0.9
0.7
0.5
0.3
Electrode potential, V
Equivalence
point, Fe2+
Fe2+ + Ce4+ ⇌ Fe3+ + Ce3+
A
Equivalence
point, U4+
U4+ + 2Ce4+ + 2H2O ⇌ UO22+ + 2Ce3+ + 4H+
B
0
5.0
10.0
15.0
20.0
25.0
30.
Volume of 0.1000 M Ce4+, mL

Questions

1. Calculate E° for the reaction:

$2Na(s) + ClO_4^- + H_2O \rightarrow 2Na^+ + ClO_3^- + 2OH^-$

a) +2.88 V b) +2.54 V c) -2.54 V d) -5.59 V e) - 2.88 V

Standard electrode potentials in aqueous solution at 25°C

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04
$K^+(aq) + e^- \rightarrow K(s)$	-2.92
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	-2.76
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.38
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.41
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	-0.40
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	-0.13
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	-0.04
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00 (ref)
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.16
$ClO_4^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_3^-(aq) + 2OH^-(aq)$	0.17
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.199 (ref)
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$ClO_3^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_2^-(aq) + 2OH^-(aq)$	0.35

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$IO^-(aq) + H_2O(l) + 2e^- \rightarrow I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightarrow Cu(s)$	0.52
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$ClO_2^-(aq) + H_2O(l) + 2e^- \rightarrow ClO^-(aq) + 2OH^-(aq)$	0.59
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \rightarrow Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq)$	0.90
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	1.44
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.49
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	1.78
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	1.82
$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$	2.01
$O_3(g) + 2H^+(aq) + 2e^- \rightarrow O_2(g) + H_2O(l)$	2.07
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87

2. From the following data, determine which system was used for potentiometric analysis. For SCE E_{ref} = 0.244 V.

- Mg^{2+}|Mg(s)||SHE
- Al^{3+}|Al(s)||SCE
- Cu^{2+}|Cu(s) ||SCE
- Fe^{3+}|Fe(s)||SHE
- Ag^{+}|Ag(s)||SHE

Conc M^{n+}	E_{cell}
0.01	-1.94333
0.03	-1.93395
0.05	-1.92959
0.07	-1.92671
0.09	-1.92457
0.11	-1.92285
0.13	-1.92143
0.15	-1.9202