UNIVERSITY OF MANITOBA

**CHEM 3590 Final examination 2016 Instructor : Dr. Hélène Perreault**
**Tuesday December 13, 6-9 pm, University College – Great Hall**

**Questions 1-15** have multiple choices (50 pts). Please answer on the bubble sheet.
**Questions 16-25** must be answered in the examination booklet (50 pts).

**Question 1: membranes (NOT COVERED)**

A city's water demand is 26.5 metric tons/day (1 metric ton = 1000 kg). What is the source water (feed water) flow required for a reverse osmosis system if the plant recovery is 78%, and what is the feed water volume delivered per day?

a) 21 tons/day, 2100 L/day

b) 34 tons/day, 34000 L/day

c) 3 tons/day, 30000 L/day

d) 26.5 tons/day, 2.65 x $10^6$ L/day

**Question 2**

In ICP, two detectors can be used in line: an OES system and a mass spectrometer. What is the main advantage of this combination?

a) All elements M produce $M^+$ ions and emit light at the same wavelength
b) Elements that have the same mass emit light at different wavelengths
c) The OES can be used only in the axial configuration, yielding more intensity
d) It is not possible to combine ICP with both OES and MS
e) No calibration is needed

**Question 3**

Given the following anions: $Cl^-$, $Br^-$, $C_6H_6O_7^{2-}$ (citrate) and $HCO_3^-$ (bicarbonate), predict their migration order in capillary zone electrophoresis (CZE), if the apparatus is operated from + to – at high pH. The order is given from first to last to reach the detector.

a) $Cl^-$, $Br^-$, $HCO_3^-$, and $C_6H_6O_7^{2-}$

b) $Br^-$, $Cl^-$, $C_6H_6O_7^{2-}$ and $HCO_3^-$

c) $C_6H_6O_7^{2-}$, $HCO_3^-$, $Br^-$, and $Cl^-$

d) $C_6H_6O_7^{2-}$, $Br^-$, $HCO_3^-$, and $Cl^-$

e) These ions would not come out of the capillary

**Question 4 (NOT COVERED)**

An unstable nucleus decays by beta emission, then two nuclei of the product are combined in a reactor to produce $^{24}Mg$ plus an alpha particle. Determine the nature of the original isotope.

a) Beryllium b) Lithium c) Carbon d) Nitrogen e) Aluminum

**Question 5**

Calculate $E^o$ for the reaction:

$2Ce^{3+} + Br_2 \rightarrow 2Br^- + 2Ce^{4+}$

a) -0.37 V b) +2.51 V c) -0.7 V d) -5.59 V e) +0.37 V

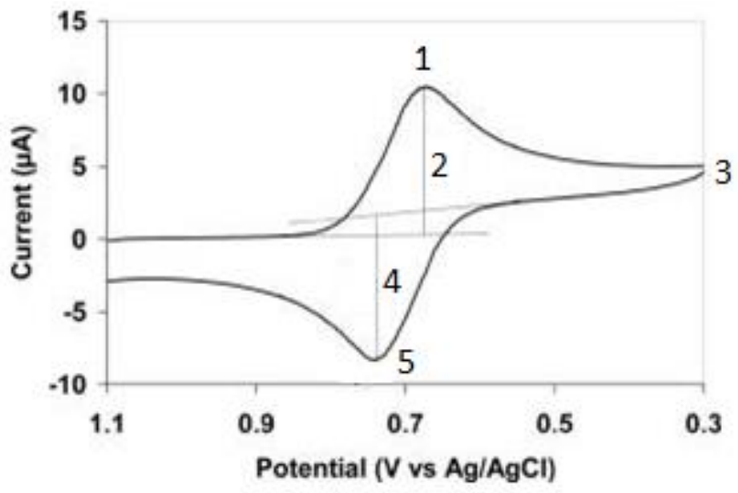
**Question 6**

In a potentiostatic coulometric experiment, the amount of charge used to transform $UO_2^{2+}$ into $U^{4+}$ in a 200 mL solution is 5782 C. What is the uranium concentration?

1 Faraday = 96368 C/mol.

a) 0.150 M b) 0.075 M c) 0.03 M d) 0.06 M e) none of these

**Question 7**

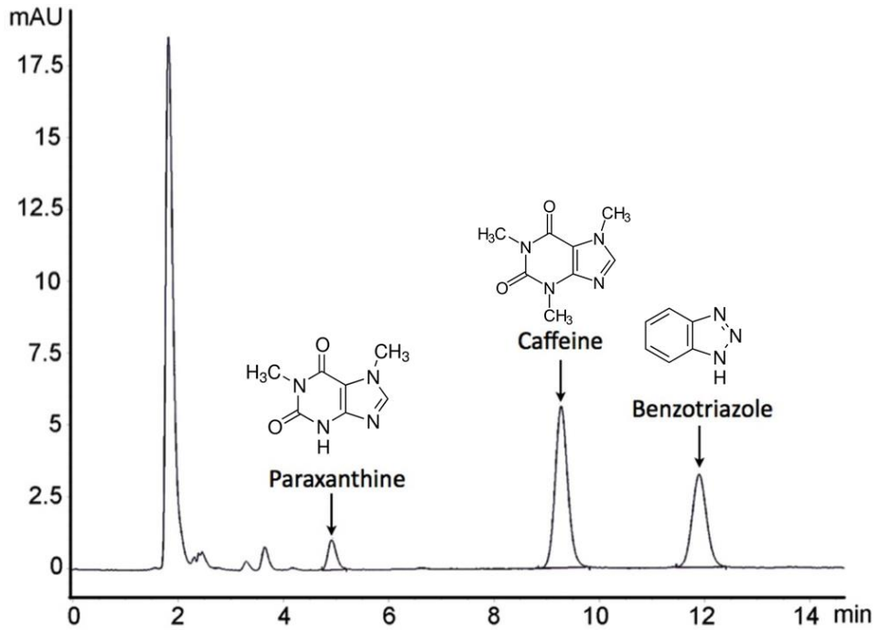



$E^o_{Ag,AgCl}$ = +0.199 V

According to this voltammogram:

a) The analyte is first oxidized, then reduced and its reduction potential is 0.67 V
b) The analyte is neither reduced nor oxidized as the reaction is reversible.
c) The analyte is first reduced, then oxidized and its reduction potential is 0.90 V
d) Ag(s) in the reference electrode is oxidized at an oxidation potential of 0.72 V
e) None of these answers

**Question 8**




From the order of elution of compounds in the chromatogram above, what technique was used for separation?

a) Gas chromatography with flame ionization detection
b) Normal phase HPLC with fluorescence detection
c) Reversed phase HPLC with UV detection
d) Gel permeation chromatography with UV detection
e) None of these modes

**Question 9**

When preparing a full 500-mL column for size exclusion chromatography, the gel used swells to 1.75x its volume when mixed with solvent. What volume of dry gel will be needed to fill the column?

a) 50 mL b) 175 mL c) 500 mL d) 88 mL e) 286 mL

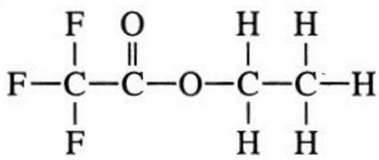
**Question 10**

Given the following compounds, what would be their elution order on an anion exchange column at pH 7? Diethylamine; phosphoric acid; glycine (an amino acid); acetic acid.

a) phosphoric acid, diethylamine, glycine, acetic acid.
b) diethylamine, glycine, acetic acid, phosphoric acid
c) acetic acid, phosphoric acid, diethylamine, glycine
d) glycine, diethylamine, phosphoric acid, acetic acid
e) None of these compounds would be retained on an anion exchange resin

**Question 11**

Photoelectron spectroscopy: for the following molecule, give the order of increasing binding energies for carbon 1s photoelectrons.



a) C=O, $CF_3$, $CH_3$, $CH_2$

b) $CH_3$, $CH_2$, C=O, $CF_3$

c) $CH_2$, C=O, $CF_3$, $CH_3$

d) $CF_3$, C=O, $CH_2$, $CH_3$

e) All 1s binding energies are equivalent

**Question 12 (NOT COVERED)**

A 1-g sample of pure neutron activated $^{28}Al$ emits a beta radiation rate of 2500 decays/min.

What would be the radiation rate of $^{28}Al$ in 15 g of $Al_2(SO_4)_3$?

a) 5950/min b) 3053/min c) 6150/min d) 2959/min e) unsolvable

**Question 13**

Only one of the following statements is true. Which one?

a) The GC/MS instrument in the MCAL laboratory has a magnetic sector for m/z analysis

b) The ICP-OES apparatus in MCAL vapourizes and atomizes elements in a flame.

c) Electron capture detectors are more sensitive for all compounds than flame ionization detectors

d) In MCAL, the Cary spectrophotometer can measure both absorbance and fluorescence

e) Diode array detectors in general can monitor several absorbance wavelengths at once

**Question 14**

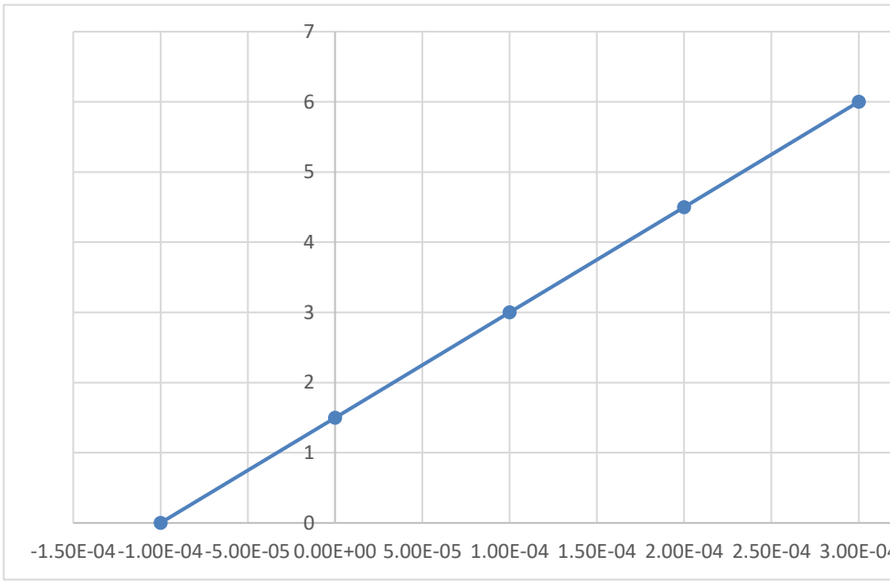
From the following data, determine which system was used for potentiometric analysis.

| Conc $M^{n+}$ | $E_{cell}$ |
|---|---|
| 0.01 | 0.281 |
| 0.03 | 0.295 |
| 0.05 | 0.301 |
| 0.07 | 0.306 |
| 0.09 | 0.309 |

a) SHE||$Mg^{2+}$|Mg(s)
b) SHE||$Al^{3+}$|Al(s)
c) SHE||$Cu^{2+}$|Cu(s)
d) SHE||$Fe^{3+}$|Fe(s)
e) SHE||$Ag^{+}$|Ag(s)

**Question 15**

The graph below was obtained using the method of standard additions. The x-axis represents the different concentrations of standard once added to the unknown, and the y-axis is the measured signal in arbitrary units. Determine the concentration of the unknown.




a) 1.5 M b) $10^{-4}$ M c) $5x10^{-5}$ M d) $3x10^{-4}$ M
e) unsolvable

**END OF THE MULTIPLE CHOICE SECTION**

**Question 16**

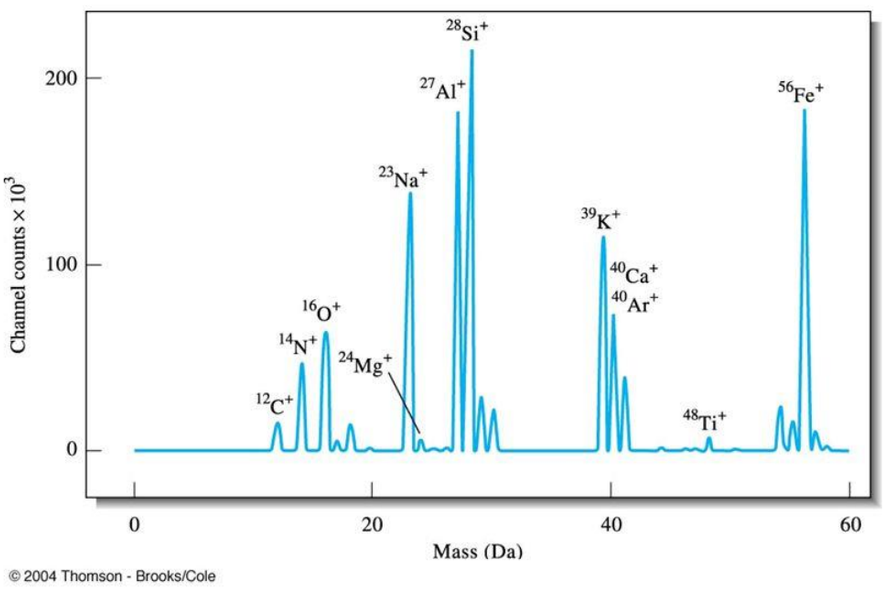
Trimethyl silylation (TMS) is commonly used for GC analysis of polar compounds.

a) Show an example of TMS reaction
b) What is the main advantage of using TMS reagents?

**Question 17**

The mass spectrum below was obtained by laser ablation ICP-MS with a low resolution mass spectrometer. Interference between Ar and Ca is observed at *m/z* 40.

Assuming that the background $Ar^+$ peak remains constant in all analyses, suggest and describe a method for the determination of $Ca^+$. Justify.




The mass spectrum of a standard rock sample obtained by laser ablation / ICP-MS.

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**Question 18 (NOT COVERED)**

A 0.25 M solution of radioactive $^{41}CaC_2O_4$ (50 mL) is measured for its gamma ray radiation intensity and the value obtained is 5823 units. This solution is poured into a large container of unknown volume and the well water is stirred mechanically. A 50-mL sample of the mixed water is then collected and measured for radiation at an intensity of 48 units.

a) Determine the volume of the container.
b) Would it matter if rate measurements were made a few minutes apart? Justify.

**Question 19**

Polycyclic aromatic compounds are in general non-polar and remain uncharged in solution.

Suggest and describe a capillary electrophoretic method that would make possible the analysis of these compounds by this technique.

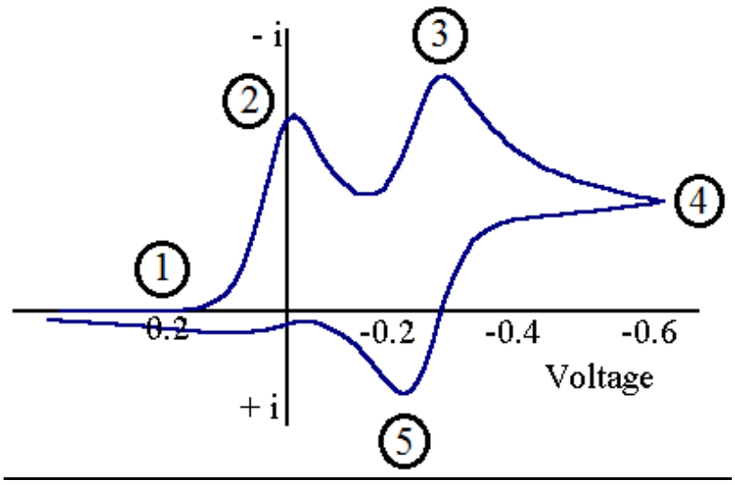
**Question 20**

In an affinity chromatography experiment, the analyte A forms a complex with the ligand L bound on the stationary phase. A and L do not protonate or deprotonate. The mobile phase is made up of aqueous sodium citrate buffer. Citric acid is a triprotic acid, $C_6H_8O_7$.

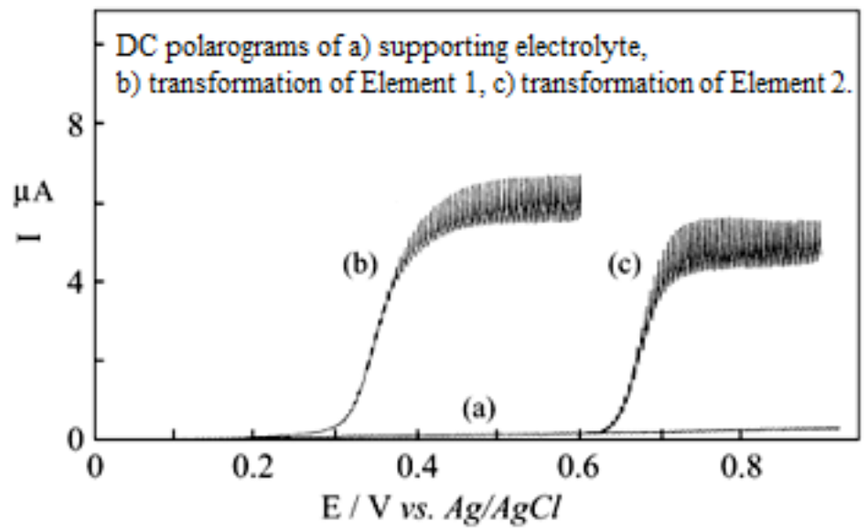
a) Write correct mass and charge balance equations for this system.
b) What is the usefulness of measuring equilibrium concentrations?

**Question 21**

Describe what you are seeing in the voltammogram shown below at points 1, 2, 3, 4, 5.




**Question 22**




a) What type of transformation(s) are Elements 1 and 2 subjected to?
b) Identify possible elements/ions corresponding to Elements 1 and 2, knowing that $E^{o}_{AgCl}$ is 0.199 V. Justify.

**Question 23**

In coulometry, the Karl-Fischer reaction is often used in many field of chemistry for the determination of moisture levels of different materials.

The main reaction is:

$C_5H_5N{\bullet}I_2 + C_5H_5N{\bullet}SO_2 + C_5H_5N + H_2O \rightarrow 2C_5H_5N{\bullet}HI + C_5H_5N{\bullet}SO_3$

$I_2$ is generated at the electrode from excess of $I^-$ present in the cell compartment.

a) What would be the total charge consumed (in coulombs) if 5 mg of NaI were used up to complete the coulometric titration? 1 Faraday = 96368 C.
b) Usually, methanol is added to the reagents. Why?

**Question 24 (NOT COVERED)**

A sample containing 10 g of $^{53}Mn$ (half-life 312 days) is irradiated with neutrons.

a) How many grams of $^{54}Mn$ are left in the sample after 90 days?
b) $^{54}Mn$ is a beta emitter. What is the product of radioactive decay?

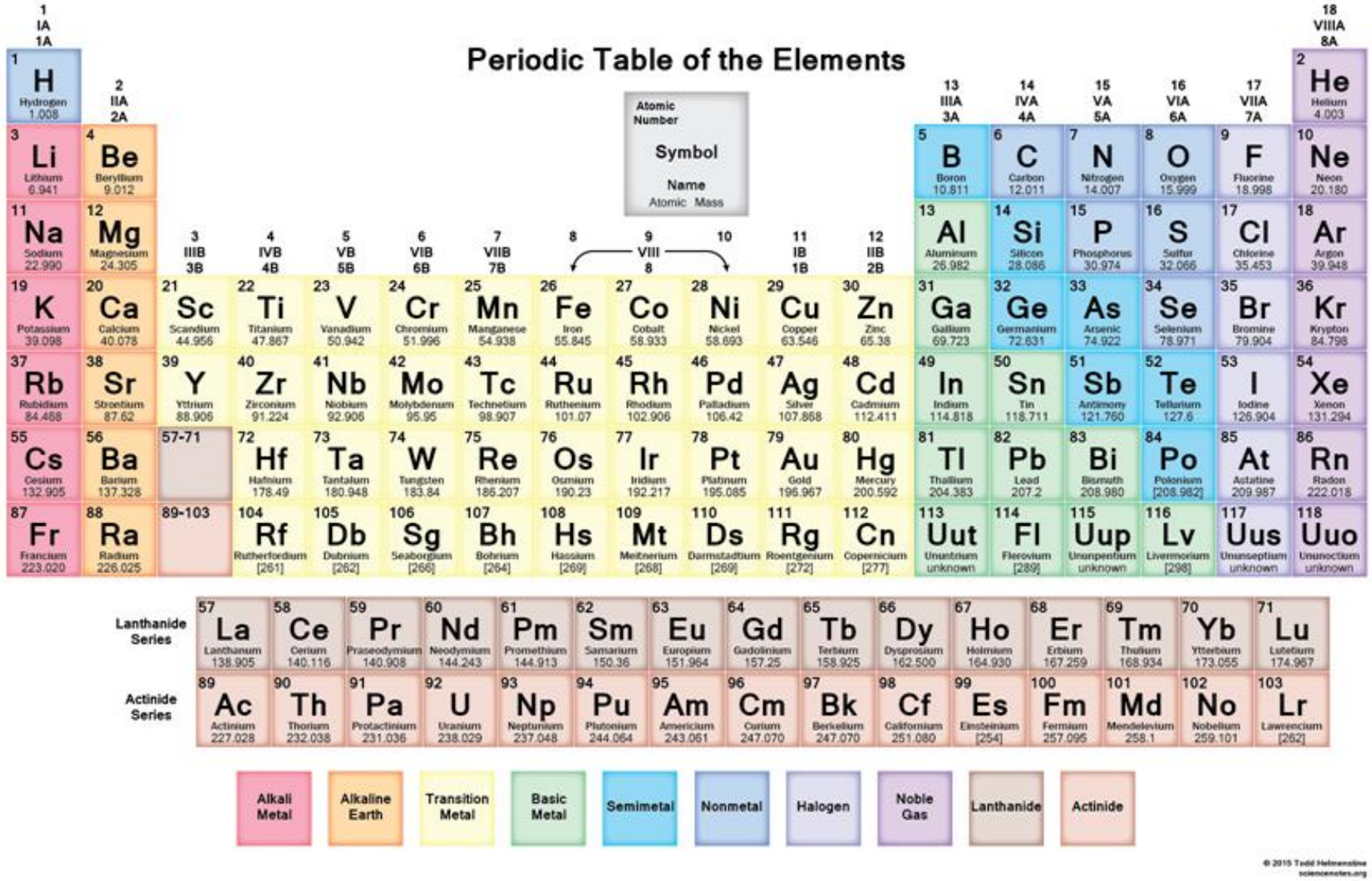
**Question 25**

Among all the techniques you have seen in this course, either in class or in the lab, which ones (pick 4) would you favour if you had to build your own analytical lab? Justify.

## Standard electrode potentials in aqueous solution at 25°C

| Cathode (Reduction) Half-Reaction | Standard Potential $E^\circ$ (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 $E^\circ$ (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 |


Periodic Table of the Elements
Atomic Number
Symbol
Name
Atomic Mass
1 IA 1A
2 IIA 2A
3 IIIB 3B
4 IVB 4B
5 VB 5B
6 VIB 6B
7 VIIB 7B
8
9 VIII 8
10
11 IB 1B
12 IIB 2B
13 IIIA 3A
14 IVA 4A
15 VA 5A
16 VIA 6A
17 VIIA 7A
18 VIIIA 8A
1 H Hydrogen 1.008
2 He Helium 4.003
3 Li Lithium 6.941
4 Be Beryllium 9.012
5 B Boron 10.811
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998
10 Ne Neon 20.180
11 Na Sodium 22.990
12 Mg Magnesium 24.305
13 Al Aluminum 26.982
14 Si Silicon 28.086
15 P Phosphorus 30.974
16 S Sulfur 32.066
17 Cl Chlorine 35.453
18 Ar Argon 39.948
19 K Potassium 39.098
20 Ca Calcium 40.078
21 Sc Scandium 44.956
22 Ti Titanium 47.867
23 V Vanadium 50.942
24 Cr Chromium 51.996
25 Mn Manganese 54.938
26 Fe Iron 55.845
27 Co Cobalt 58.933
28 Ni Nickel 58.693
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.631
33 As Arsenic 74.922
34 Se Selenium 78.971
35 Br Bromine 79.904
36 Kr Krypton 84.798
37 Rb Rubidium 84.468
38 Sr Strontium 87.62
39 Y Yttrium 88.906
40 Zr Zirconium 91.224
41 Nb Niobium 92.906
42 Mo Molybdenum 95.95
43 Tc Technetium 98.907
44 Ru Ruthenium 101.07
45 Rh Rhodium 102.906
46 Pd Palladium 106.42
47 Ag Silver 107.868
48 Cd Cadmium 112.411
49 In Indium 114.818
50 Sn Tin 118.711
51 Sb Antimony 121.760
52 Te Tellurium 127.6
53 I Iodine 126.904
54 Xe Xenon 131.294
55 Cs Cesium 132.905
56 Ba Barium 137.328
57-71
72 Hf Hafnium 178.49
73 Ta Tantalum 180.948
74 W Tungsten 183.84
75 Re Rhenium 186.207
76 Os Osmium 190.23
77 Ir Iridium 192.217
78 Pt Platinum 195.085
79 Au Gold 196.967
80 Hg Mercury 200.592
81 Tl Thallium 204.383
82 Pb Lead 207.2
83 Bi Bismuth 208.980
84 Po Polonium [208.982]
85 At Astatine 209.987
86 Rn Radon 222.018
87 Fr Francium 223.020
88 Ra Radium 226.025
89-103
104 Rf Rutherfordium [261]
105 Db Dubnium [262]
106 Sg Seaborgium [266]
107 Bh Bohrium [264]
108 Hs Hassium [269]
109 Mt Meitnerium [268]
110 Ds Darmstadtium [269]
111 Rg Roentgenium [272]
112 Cn Copernicium [277]
113 Uut Ununtrium unknown
114 Fl Flerovium [289]
115 Uup Ununpentium unknown
116 Lv Livermorium [298]
117 Uus Ununseptium unknown
118 Uuo Ununoctium unknown
Lanthanide Series
57 La Lanthanum 138.905
58 Ce Cerium 140.116
59 Pr Praseodymium 140.908
60 Nd Neodymium 144.243
61 Pm Promethium 144.913
62 Sm Samarium 150.36
63 Eu Europium 151.964
64 Gd Gadolinium 157.25
65 Tb Terbium 158.925
66 Dy Dysprosium 162.500
67 Ho Holmium 164.930
68 Er Erbium 167.259
69 Tm Thulium 168.934
70 Yb Ytterbium 173.055
71 Lu Lutetium 174.967
Actinide Series
89 Ac Actinium 227.028
90 Th Thorium 232.038
91 Pa Protactinium 231.036
92 U Uranium 238.029
93 Np Neptunium 237.048
94 Pu Plutonium 244.064
95 Am Americium 243.061
96 Cm Curium 247.070
97 Bk Berkelium 247.070
98 Cf Californium 251.080
99 Es Einsteinium [254]
100 Fm Fermium 257.095
101 Md Mendelevium 258.1
102 No Nobelium 259.101
103 Lr Lawrencium [262]
Alkali Metal
Alkaline Earth
Transition Metal
Basic Metal
Semimetal
Nonmetal
Halogen
Noble Gas
Lanthanide
Actinide
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