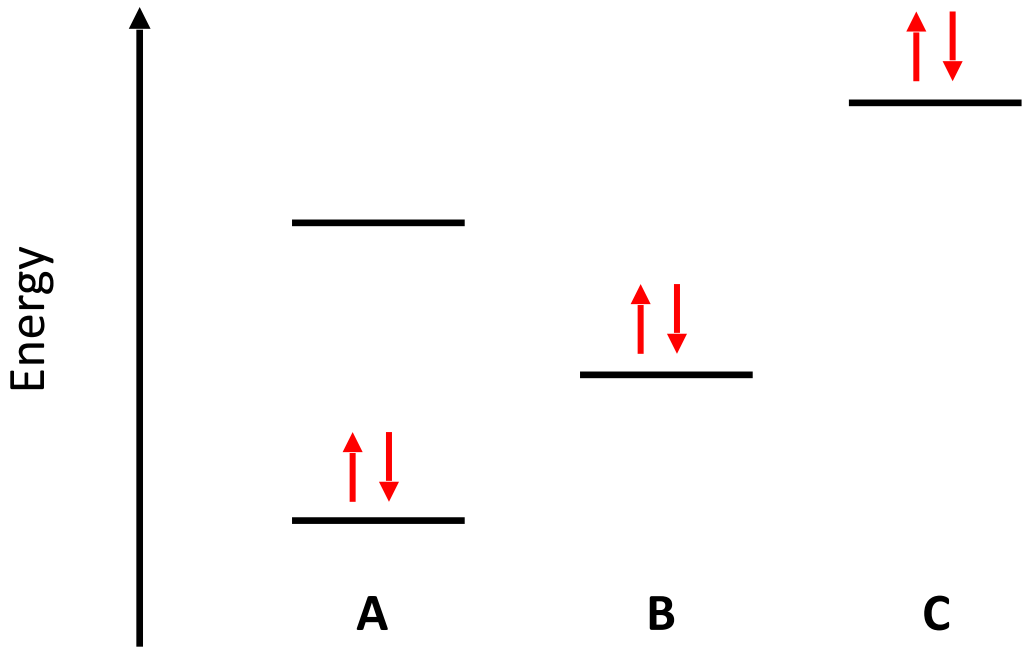
Redox Reaction



A^{2+}, A, A^{2-}, B, B^{2+}, C, C^{2+}

1. Which is the best oxidizing agent?
2. Which is the best reducing agent?
3. Which oxidizes A^{2-} but not A?
4. Which reduces B^{2+} but not C^{2+}?

- Jun-Ho YUM, junho.yum@epfl.ch

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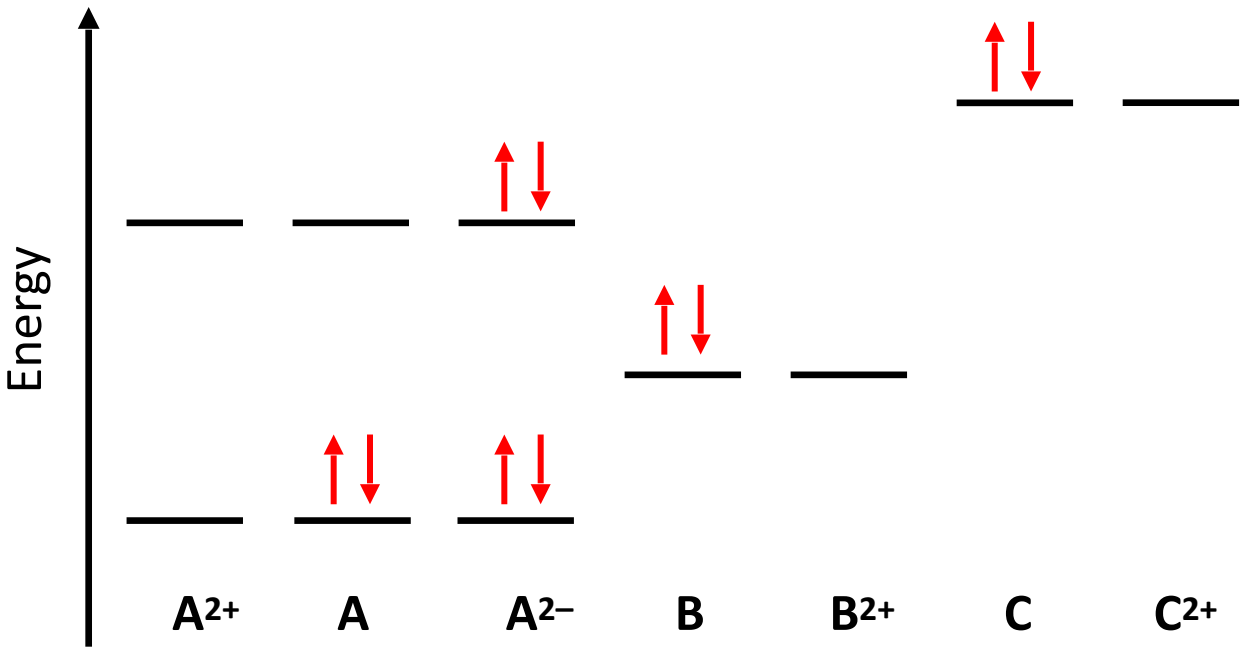

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Strong reducing agents have high-energy electrons, and strong oxidizing agents have unfilled orbitals at low energy: driving force for electron transfer

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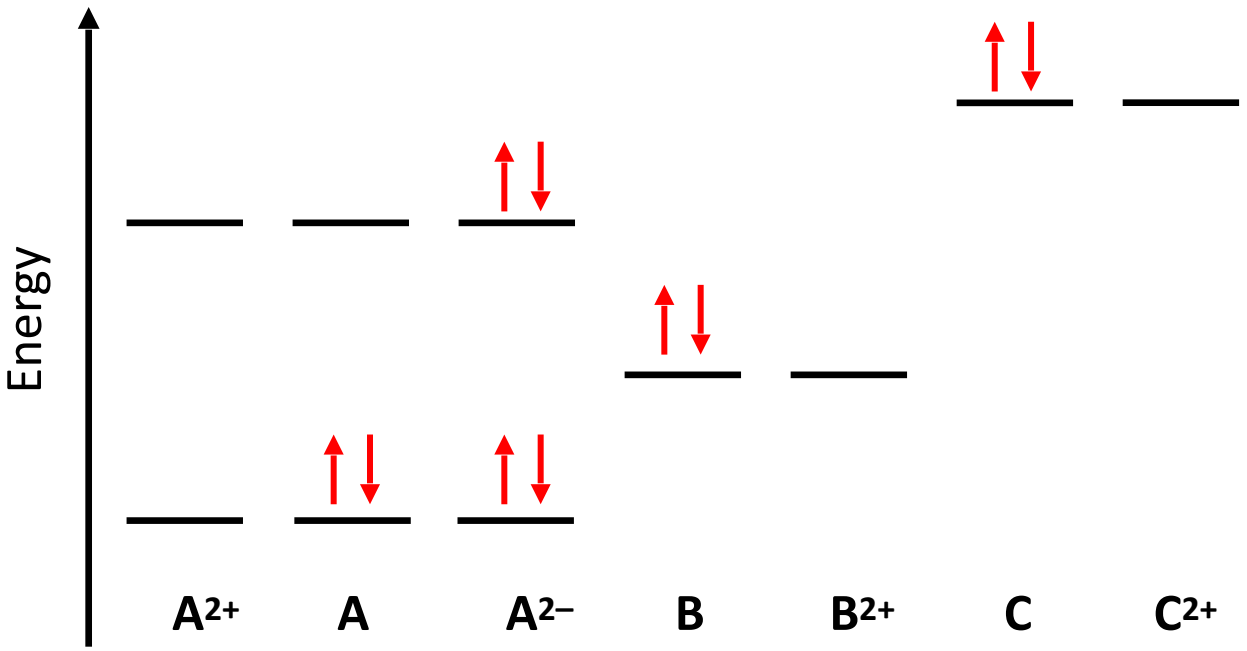

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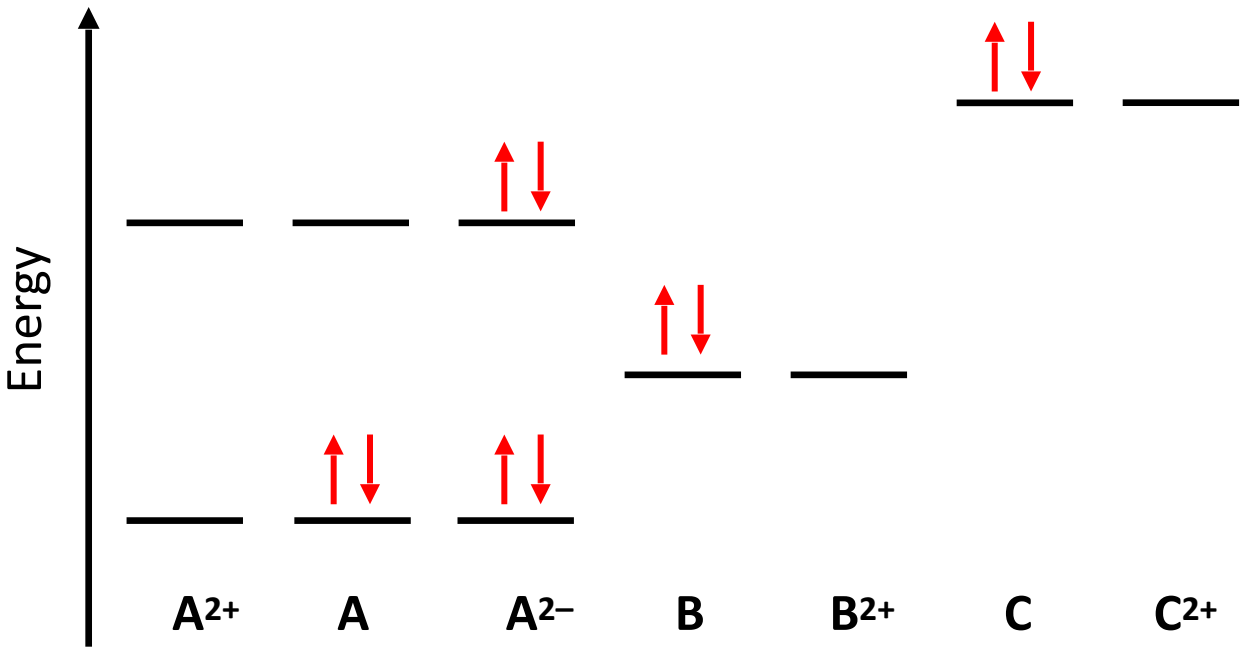

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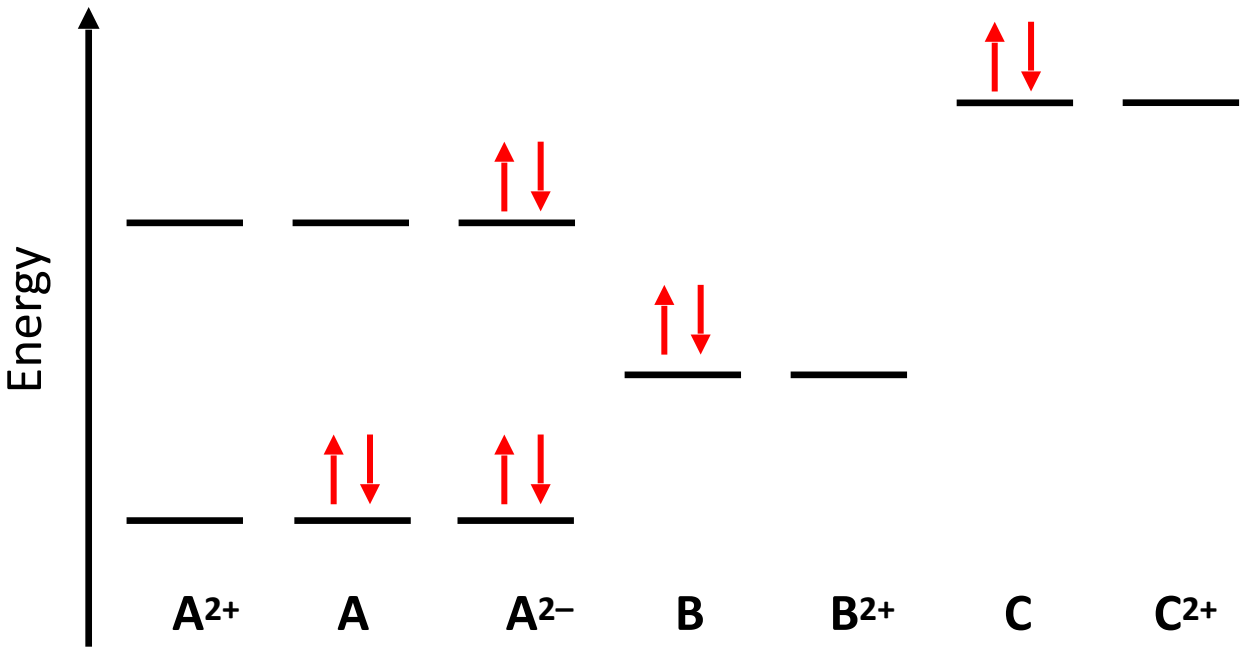

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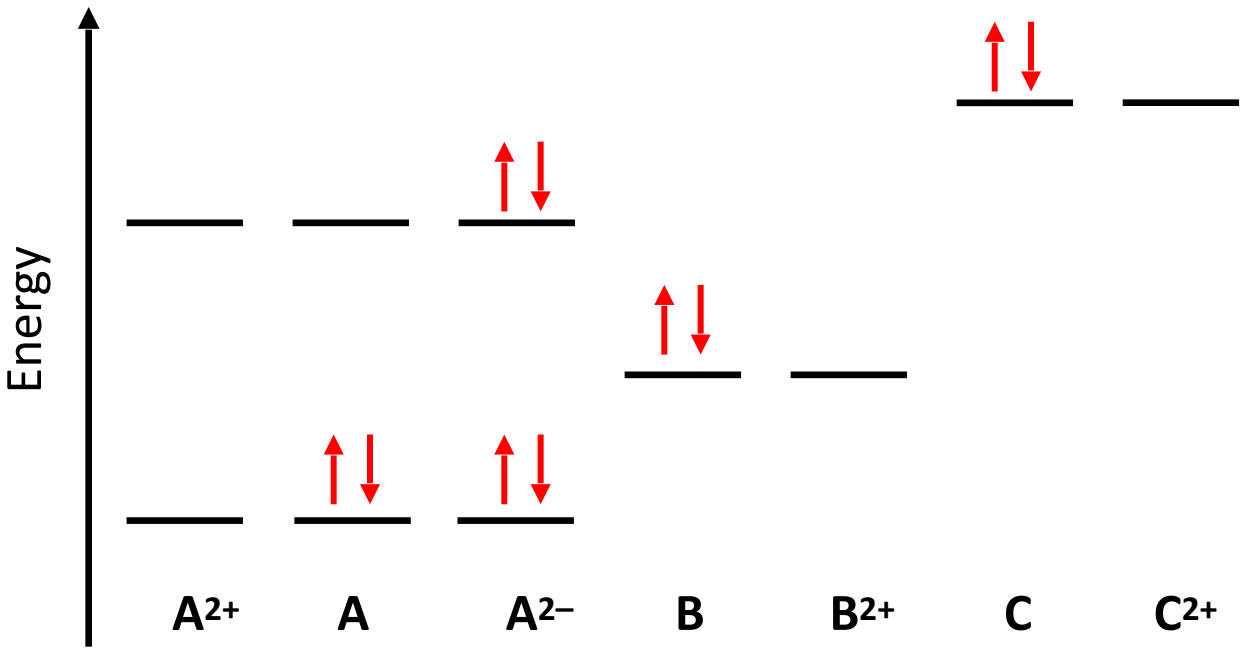

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A^{2-}

Nernst Equation

Ex) What is the cell potential of the following reaction at 298 K?

$2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$

$[Al^{3+}] = 0.1M \; and \; [Cu^{2+}] = 3M$

Reaction	E^0 (V) (SHE)	Reaction	E^0 (V) (SHE)
$Li^+ + e^- \rightleftharpoons Li$	−3.045	$HgO + H_2O + 2e^- \rightleftharpoons Hg + 2OH^-$	0.098
$K^+ + e^- \rightleftharpoons K$	−2.935	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0.154
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	−2.866	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	0.153
$Na^+ + e^- \rightleftharpoons Na$	−2.714	$AgCl + e^- \rightleftharpoons Ag + Cl^-$	0.2224
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.363	$HgCl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	0.2676
$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.662	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	0.337
$Ti^{2+} + e^- \rightleftharpoons 2e^- \rightleftharpoons Ti$	−1.628	$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	0.36
$Zn(OH)_2 + 2e^- \rightleftharpoons Zn + 2OH^-$	−1.245	$Cu^{2-} + e^- \rightleftharpoons Cu$	0.521
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	−1.180	$I_2 + 2e^- \rightleftharpoons 2I^-$	0.536
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^{2-}$	−0.822	$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.682
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.764	$Fe^{3+} + e^- \rightleftharpoons e^- \rightleftharpoons Fe^{2+}$	0.771
$S + 2e^- \rightleftharpoons S^{2-}$	−0.48	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.065
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.441	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.229
$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0.403	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.358
$Ni^{2-} + 2e^- \rightleftharpoons Ni$	−0.250	$PbO_2 + 4H^+ + e^- \rightleftharpoons Pb^{2+} + 2H_2O$	1.455
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.136	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	1.61
$2H^+ + 2e^- \rightleftharpoons H_2$	0.0000	$F_2 + 2e^- \rightleftharpoons 2F^-$	1.87

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Ex) What is the cell potential of the following reaction at 298 K?

$2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$

$[Al^{3+}] = 0.1M \; and \; [Cu^{2+}] = 3M$

$Cu^{2+} + 2e^- \rightarrow$ Cu, $E^0 = 0.337$ V and $Al^{3+} + 3e^- \rightarrow$ Al, $E^0 = -1.662$ V

$$E^0 = 1.999\,V, Q = \frac{[Al^{3+}]^2}{[Cu^{2+}]^3} = \frac{0.1^2}{3^3} = 3.7 \times 10^{-4}, n = 6$$

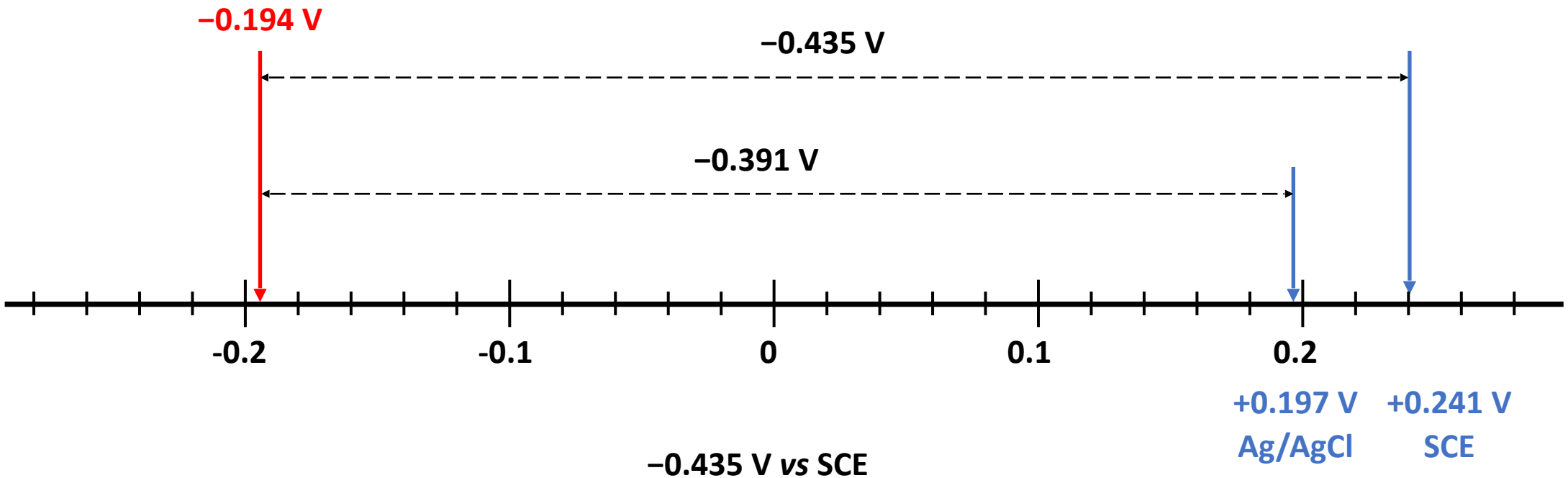
$$E = 1.999 - \frac{0.0592}{6}\log(3.7 \times 10^{-4}) = 2.033\,V$$

Reference Electrodes vs SHE

Ex) If an electrode has a potential of −0.435 V with respect to a SCE (sat), what is the potential with respect to a silver-silver chloride electrode (saturated KCl)? What would be the potential with respect to the SHE?

SCE: a saturated solution of KCl, the potential is +0.241 V *vs* SHE at RT

Ag/AgCl: a saturated solution of KCl, the potential is +0.197 V *vs* SHE at RT



−0.435 V *vs* SCE

−0.391 V *vs* Ag/AgCl

−0.194 V *vs* SHE