## An Application: the Reaction of Metals with Acids

Some metals (e.g., Fe) dissolve in acid (e.g., HCl) to give  $H_2$  (g), others (e.g., Cu) do not. Why?

Consider:	M (s) +	2 H⁺ (aq) —	→ M <sup>2+</sup> (aq)	+	H <sub>2</sub> (g)
	stronger	stronger	weaker		weaker
	red. agent	ox. agent	ox. agent		red. agent

-- for the M (s) to react to give  $M^{2+}$  (aq) and  $H_2$  (g), the reaction has to be spontaneous left-to-right.

The half-reactions are:

$$\begin{array}{ll} M^{2+} (aq) + 2 e^{-} \rightarrow M (s) & E^{\circ}{}_{M} \\ 2 H^{+} (aq) + 2 e^{-} \rightarrow H_{2} (g) & (= SHE) \end{array}$$

For the reaction to occur spontaneously, the following must be true:

- (1) voltaic cell using these half-rxns must have  $E^{\circ}_{cell} > 0$  (i.e.  $\Delta G < 0$ )
- (2) M (s) must be a stronger reducing agent than  $H_2$  (g)
- (3)  $H^+$  (aq) must be a stronger oxidizing agent than  $M^{2+}$  (aq)

<u>All these are saying the same thing</u>! - and all require  $E^{\circ}_{half-rxn}$  for M (= $E^{\circ}_{M}$ ) to be smaller (less positive or more negative) than  $E^{\circ}_{half-rxn}$  for H<sup>+</sup> (=  $E^{\circ}_{H2}$ ) i.e.  $E^{\circ}_{M}$  is the anode, and  $E^{\circ}_{H2}$  is the cathode.



# Standard Electrode (Half-Cell) Potentials

Strength of Oxidizing and Reducing Agents

> Increasing oxidizing strength

$\begin{array}{llllllllllllllllllllllllllllllllllll$	Half-Reaction	<i>E</i> ° (V)
$\begin{aligned} O_3(g) + 2H^*(aq) + 2e^- \bigoplus O_2(g) + H_2O(l) & +207 \\ Co^{3^+}(aq) + e^- \bigoplus Co^{2^+}(aq) & +182 \\ H_2O_2(aq) + 2H^*(aq) + 2e^- \supseteq 2H_2O(l) & +177 \\ PbO_2(s) + 3H^*(aq) + HSO_4^-(aq) + 2e^- \bigoplus PbSO_4(s) + 2H_2O(l) & +170 \\ Ce^{4^+}(aq) + e^- \bigoplus Ce^{3^+}(aq) & +180 \\ AmO_4^-(aq) + 8H^*(aq) + 5e^- \bigoplus Mn^{2^+}(aq) + 4H_2O(l) & +151 \\ Au^{3^+}(aq) + 3e^- \bigoplus Au(s) & +150 \\ Cl_2(g) + 2e^- \bigoplus 2CI^-(aq) & +134 \\ Cl_2(g) + 2e^- \bigoplus 2CI^-(aq) & +2H_2O(l) & +133 \\ MnO_2(s) + 4H^*(aq) + 2e^- \bigoplus Mn^{2^+}(aq) + 2H_2O(l) & +123 \\ MnO_2(s) + 4H^*(aq) + 4e^- \bigoplus 2H_2O(l) & +123 \\ Br_2(h) + 2e^- \bigoplus 2Br^-(aq) & +10f \\ NO_3^-(aq) + 4H^+(aq) + 3e^- \bigoplus NO(g) + 2H_2O(l) & +109 \\ Hg_2^{3^+}(aq) + 2e^- \bigoplus Hg_2^{2^+}(aq) & +088 \\ Ag^*(aq) + e^- \bigoplus Fe^{2^+}(aq) & +088 \\ Fa^{3^+}(aq) + e^- \bigoplus Fe^{2^+}(aq) & +007 \\ O_2(g) + 2H^+(aq) + 2e^- \bigoplus Hg_2O_2(aq) & +007 \\ MnO_4^-(aq) + 2H_2O(l) + 3e^- \bigoplus MnO_2(s) + 4OH^-(aq) & +059 \\ Hg_2(h) + 2e^- \bigoplus 2Lr^-(aq) & +005 \\ MnO_4^-(aq) + 2H_2O(l) + 4e^- \bigoplus 4OH^-(aq) & +059 \\ I_2(s) + 2e^- \bigoplus CU(s) & +034 \\ AgCl(s) + e^- \bigoplus Ag(s) + CI^-(aq) & +0.13 \\ O_2(g) + 2H^+(aq) + 2e^- \bigoplus CU(s) & +0.14 \\ AgCl(s) + e^- \bigoplus Ag(s) + CI^-(aq) & +0.15 \\ Sn^{4^+}(aq) + 2e^- \bigoplus Sn^{4^+}(aq) & +2e^- \bigoplus SO_2(g) + 2H_2O(l) & +0.20 \\ Cu^{2^+}(aq) + 2e^- \bigoplus Ni(s) & -0.14 \\ N_2(g) + 5H^+(aq) + 4e^- \bigoplus N_2H_5^+(aq) & -0.13 \\ Ni^{2^+}(aq) + 2e^- \bigoplus Ni(s) & -0.25 \\ Co^{2^+}(aq) + 2e^- \bigoplus Ni(s) & -0.25 \\ PbSO_4(s) + H^+(aq) + 2e^- \bigoplus Pb(s) + HSO_4^-(aq) & -0.33 \\ Mn^{2^+}(aq) + 2e^- \bigoplus Ni(s) & -0.25 \\ Co^{2^+}(aq) + 2e^- \bigoplus Ni(s) & -0.25 \\ C$	$F_2(g) + 2e^- \Longrightarrow 2F^-(aq)$	+2.87
$\begin{aligned} & Co^{3^+}(aq) + e^{-1} Co^{2^+}(aq) & +182 \\ & H_2O_2(aq) + 2H^+(aq) + 2e^{-1} 2H_2O(l) & +177 \\ & PbO_2(s) + 3H^-(aq) + HSO_4(aq) + 2e^{-1} PbSO_4(s) + 2H_2O(l) & +1.77 \\ & Ce^{4^+}(aq) + e^{-1} Ce^{3^+}(aq) + 5e^{-1} Mn^{2^+}(aq) + 4H_2O(l) & +1.51 \\ & MnO_4^-(aq) + 8H^+(aq) + 5e^{-1} Mn^{2^+}(aq) + 4H_2O(l) & +1.51 \\ & Au^{3^+}(aq) + 3e^{-1} 2Cr^{3^+}(aq) + 7H_2O(l) & +1.33 \\ & MnO_2(s) + 4H^+(aq) + 2e^{-1} Mn^{2^+}(aq) + 2H_2O(l) & +1.23 \\ & DnO_2(s) + 4H^+(aq) + 2e^{-1} 2H_2O(l) & +1.23 \\ & DnO_3(aq) + 4H^+(aq) + 3e^{-1} NO(g) + 2H_2O(l) & +1.23 \\ & DnO_3(aq) + 4H^+(aq) + 3e^{-1} NO(g) + 2H_2O(l) & +1.23 \\ & DnO_3(aq) + 2e^{-1} Hg_2^{3^-}(aq) & +00g \\ & 2Hg^{2^+}(aq) + 2e^{-1} Hg_2^{3^-}(aq) & +00g \\ & 2Hg^{2^+}(aq) + 2e^{-1} Hg_2^{3^-}(aq) & +00g \\ & Hg_2^{2^+}(aq) + 2e^{-1} Hg_2^{3^-}(aq) & +00g \\ & Hg_2^{2^+}(aq) + 2e^{-1} Hg_2^{3^-}(aq) & +00g \\ & Hg_2^{3^+}(aq) + e^{-1} Fe^{2^+}(aq) & +00g \\ & Hg_2^{3^+}(aq) + e^{-1} Fe^{2^+}(aq) & +00g \\ & MnO_4(aq) + 2H_2O(l) + 3e^{-1} MnO_2(s) + 4OH^-(aq) & +0.59 \\ & J_2(s) + 2H_2O(l) + 3e^{-1} MnO_2(s) + 4OH^-(aq) & +0.59 \\ & J_2(s) + 2H_2O(l) + 3e^{-1} MnO_2(s) + 4OH^-(aq) & +0.25 \\ & SO_2(aq) + 4H^+(aq) + 2e^{-1} SO_2(g) + 2H_2O(l) & +0.22 \\ & SO_2^{-2}(aq) + 4H^+(aq) + 2e^{-1} SO_2(g) + 2H_2O(l) & +0.22 \\ & SO_2^{-2}(aq) + 4H^+(aq) + 2e^{-1} SO_2(g) + 2H_2O(l) & +0.22 \\ & SO_2^{-2}(aq) + 2e^{-1} Sn(s) & -0.14 \\ & N_2(g) + 5H^+(aq) + 2e^{-1} Sn(s) & -0.14 \\ & N_2(g) + 5H^+(aq) + 2e^{-1} Sn(s) & -0.25 \\ & Co^{2^+}(aq) + 2e^{-1} Sn(s) &$	$O_3(g) + 2H^+(aq) + 2e^- = O_2(g) + H_2O(l)$	+2.07
$\begin{aligned} & + 2 P_{2} O_{2}(aq) + 2 H^{+}(aq) + 2 e^{-1} 2 H_{2} O_{2}(l) & + 177 \\ & + 177 \\ PbO_{2}(s) + 3 H^{+}(aq) + HSO_{4}^{-}(aq) + 2 e^{-1} PbSO_{4}(s) + 2 H_{2} O_{2}(l) & + 177 \\ & + 177 \\ PbO_{2}(s) + 3 H^{+}(aq) + 4 e^{-1} Au(s) & + 150 \\ & + 150 \\ & + 150 \\ C_{12}(a) + 2 e^{-1} 2 C_{1}(aq) & + 2 e^{-1} Mn^{2}(aq) + 4 H_{2} O_{2}(l) & + 133 \\ & + 136 \\ C_{12}O_{2}^{-1}(aq) + 14 H^{+}(aq) + 2 e^{-1} Mn^{2}(aq) + 2 H_{2} O_{2}(l) & + 133 \\ & + 123 $	$\operatorname{Co}^{3^+}(aq) + e^- \longrightarrow \operatorname{Co}^{2^+}(aq)$	+1.82
$\begin{aligned} & PbO_{1}(s) + 3H^{-}(aq) + HSO_{4}^{-}(aq) + 2e^{-} \implies PbSO_{4}(s) + 2H_{2}O(l) & +1.70 \\ Ce^{+}(aq) + e^{-} \implies Ce^{3+}(aq) + Sm^{2+}(aq) + 4H_{2}O(l) & +1.51 \\ & MnO_{4}^{-}(aq) + 8H^{-}(aq) + 5e^{-} \implies Mn^{2+}(aq) + 4H_{2}O(l) & +1.51 \\ & Au^{3+}(aq) + 3e^{-} \implies Au(s) & +1.50 \\ Cr_{2}O_{2}^{-}(aq) + 14H^{+}(aq) + 6e^{-} \ge 2Cr^{3+}(aq) + 7H_{2}O(l) & +1.33 \\ & MnO_{2}(s) + 4H^{-}(aq) + 2e^{-} \implies Mn^{2+}(aq) + 2H_{2}O(l) & +1.23 \\ & Dr_{2}(b) + 4H^{-}(aq) + 4e^{-} \ge 2H_{2}O(l) & +1.23 \\ & Dr_{3}(aq) + 4H^{+}(aq) + 3e^{-} \implies NO(g) + 2H_{2}O(l) & +0.53 \\ & Dr_{3}(aq) + 4H^{+}(aq) + 3e^{-} \implies NO(g) + 2H_{2}O(l) & +0.54 \\ & Hg^{2+}(aq) + 2e^{-} \implies Hg^{2+}(aq) & +0.57 \\ & Hg^{2+}(aq) + 2e^{-} \implies Hg^{2+}(aq) & +0.57 \\ & Hg^{2+}(aq) + 2e^{-} \implies Hg^{2+}(aq) & +0.57 \\ & Ag^{*}(aq) + e^{-} \implies Ag(s) & Fe^{2+}(aq) & +0.57 \\ & Pg^{2+}(aq) + 2e^{-} \implies Hg^{2}(l) + 3e^{-} \implies MnO_{2}(s) + 4OH^{-}(aq) & +0.53 \\ & O_{2}(g) + 2H^{+}(aq) + 2e^{-} \implies H_{2}O_{2}(aq) & +0.57 \\ & D_{3}(g) + 2H^{+}(aq) + 2e^{-} \implies MO^{-}(aq) & +0.53 \\ & O_{2}(g) + 2H_{2}O(l) + 4e^{-} \implies 4OH^{-}(aq) & +0.53 \\ & O_{2}(g) + 2H_{2}O(l) + 4e^{-} \implies Ag(s) + C^{-}(aq) & +0.53 \\ & O_{2}(g) + 2H_{2}O(l) + 4e^{-} \implies Ag(s) + C^{-}(aq) & +0.53 \\ & O_{4}^{-}(aq) + e^{-} \implies Cu^{*}(aq) & +0.53 \\ & O_{4}^{-}(aq) + e^{-} \implies Cu^{*}(aq) & +0.53 \\ & O_{4}^{-}(aq) + e^{-} \implies Cu^{*}(aq) & +0.53 \\ & O_{4}^{-}(aq) + 4e^{-} \implies Dr(s) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Sn^{2}(aq) & +0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Sn^{2}(aq) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Sn(s) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Sn(s) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Pb(s) + HSO_{4}^{-}(aq) & -0.23 \\ & Nn^{2}^{+}(aq) + 2e^{-} \implies Pb(s) + HSO_{4}^{-}(aq) & -0.23 \\ & Nn^{2}^{+}(aq) + 2e^{-} \implies Fe(s) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Pb(s) + HSO_{4}^{-}(aq) & -0.23 \\ & Nn^{2}^{+}(aq) + 2e^{-} \implies Fe(s) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Fe(s) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Fe(s) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Fe(s) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Fe(s) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Fe(s) & -0.13 \\ & Sn^{+}(aq) + 2e^{-} \implies Fe(s$	$H_2O_2(aq) + 2H^+(aq) + 2e \longrightarrow 2H_2O(l)$	+1.77
$\begin{aligned} & \text{Ce}^{4+}(aq) + e^{-} \bigoplus Ce^{3+}(aq) & \text{mn}^{2+}(aq) + 4\text{H}_2O(l) & \text{mn}^{4+}(la) + 15l \\ & \text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^{-} \bigoplus \text{Mn}^{2+}(aq) + 4\text{H}_2O(l) & \text{mn}^{4+}(la) \\ & \text{MnO}_4^-(aq) + 8e^{-} \bigoplus 2C\Gamma^{3+}(aq) + 7\text{H}_2O(l) & \text{mn}^{4+}(la) \\ & \text{Cr}_2O_7^{-2}(aq) + 14\text{H}^+(aq) + 2e^{-} \bigoplus \text{Mn}^{2+}(aq) + 2\text{H}_2O(l) & \text{mn}^{4+}(la) \\ & \text{MnO}_2(s) + 4\text{H}^+(aq) + 2e^{-} \bigoplus \text{Mn}^{2+}(aq) + 2\text{H}_2O(l) & \text{mn}^{4+}(la) \\ & \text{Sr}_2(l) + 2e^{-} \bigoplus 2\text{Br}^-(aq) & \text{mn}^{2+}(aq) + 2\text{H}_2O(l) & \text{mn}^{4+}(la) \\ & \text{Sr}_2(l) + 2e^{-} \bigoplus 2\text{Br}^-(aq) & \text{mn}^{2+}(aq) & \text{mn}^{4+}(la) \\ & \text{Sr}_2(l) + 2e^{-} \bigoplus 2\text{Br}^-(aq) & \text{mn}^{2+}(aq) & \text{mn}^{4+}(la) \\ & \text{Sr}_2^{-1}(aq) + 2e^{-} \bigoplus 2\text{Hg}(l) & \text{mn}^{4+}(la) & \text{mn}^{4+}(la) \\ & \text{Sr}_2^{-1}(aq) + 2e^{-} \bigoplus 2\text{Hg}(l) & \text{mn}^{4+}(la) & \text{mn}^{4+}(la) & \text{mn}^{4+}(la) & \text{mn}^{4+}(la) \\ & \text{Sr}_2^{-1}(aq) + 2e^{-} \bigoplus 2\text{Hg}(l) & \text{mn}^{4+}(la) & $	$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \implies PbSO_4(s) + 2H_2O(l)$	+1.70
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$\operatorname{Ce}^{4+}(aq) + e^{-} = \operatorname{Ce}^{3+}(aq)$	+1.61
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-} \implies Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$Au^{3+}(aq) + 3e^{-} \Longrightarrow Au(s)$	+1.50
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\operatorname{Cl}_2(g) + 2e \Longrightarrow 2\operatorname{Cl}(aq)$	+1.36
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$Cr_2O_7^2(aq) + 14H^+(aq) + 6e \implies 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$O_2(g) + 4H^+(aq) + 4e^- = 2H_2O(l)$	+1.23
$NO_{3}^{-}(aq) + 4H^{+}(aq) + 3e^{-} NO(g) + 2H_{2}O(l) + 0.96$ $2H_{g}^{2+}(aq) + 2e^{-} H_{g}^{2+}(aq) + 0.85$ $Ag^{+}(aq) + 2e^{-} Ag(s) + 0.85$ $Ag^{+}(aq) + e^{-} Ag(s) + 0.85$ $Ag^{+}(aq) + e^{-} Ag(s) + 0.85$ $Ag^{+}(aq) + e^{-} Ag(s) + 0.85$ $MnO_{4}^{-}(aq) + 2e^{-} Ag(s) + 0.77$ $O_{2}(g) + 2H^{+}(aq) + 2e^{-} H_{2}O_{2}(aq) + 0.77$ $O_{2}(g) + 2H^{+}(aq) + 2e^{-} MnO_{2}(s) + 4OH^{-}(aq) + 0.59$ $I_{2}(s) + 2e^{-} 2I^{-}(aq) + 0.61$ $Ag(s) + 2e^{-} Cu(s) + 4OH^{-}(aq) + 0.40$ $Cu^{2+}(aq) + 2e^{-} Cu(s) + 4OH^{-}(aq) + 0.22$ $SO_{4}^{-2}(aq) + 4H^{+}(aq) + 2e^{-} SO_{2}(g) + 2H_{2}O(l) + 0.22$ $Cu^{2+}(aq) + 2e^{-} Cu^{+}(aq) + 0.13$ $2H^{-}(aq) + 2e^{-} Cu^{+}(aq) + 0.13$ $2H^{-}(aq) + 2e^{-} Sn(s) + 0.13$ $Sn^{2+}(aq) + 2e^{-} Sn(s) + 0.13$ $Sn^{2+}(aq) + 2e^{-} Sn(s) + 0.25$ $Co^{2+}(aq) + 2e^{-} Cd(s) + 0.26$ $Ag^{2+}(aq) + 2e^{-$	$Br_2(l) + 2e \implies 2Br(aq)$	+1.07
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$NO_3^{-}(aq) + 4H^+(aq) + 3e^- > NO(g) + 2H_2O(l)$	+0.96
$\begin{aligned} &Hg_2^{2+}(aq) + 2e^{-} \implies 2Hg(l) & +0.85 \\ &Ag^{*}(aq) + e^{-} \implies Ag(s) & +0.80 \\ &Fe^{3+}(aq) + e^{-} \implies Fe^{2^{*}}(aq) & +0.77 \\ &0_2(g) + 2H^{*}(aq) + 2e^{-} \implies H_2O_2(aq) & +0.77 \\ &0_2(g) + 2H^{*}(aq) + 2e^{-} \implies MnO_2(s) + 4OH^{-}(aq) & +0.53 \\ &0_2(g) + 2H_2O(l) + 4e^{-} \implies 4OH^{-}(aq) & +0.53 \\ &0_2(g) + 2H_2O(l) + 4e^{-} \implies 4OH^{-}(aq) & +0.43 \\ &AgCl(s) + e^{-} \implies Ag(s) + Cl^{-}(aq) & +0.22 \\ &SO_4^{-2}(aq) + 4H^{+}(aq) + 2e^{-} \implies SO_2(g) + 2H_2O(l) & +0.20 \\ Cu^{2^{*}}(aq) + 2e^{-} \implies Cu^{*}(aq) & +0.13 \\ &2H^{+}(aq) + 2e^{-} \implies Sn^{2^{*}}(aq) & +0.13 \\ Sn^{2^{+}}(aq) + 2e^{-} \implies Sn(s) & -0.13 \\ Sn^{2^{+}}(aq) + 2e^{-} \implies Sn(s) & -0.13 \\ Sn^{2^{+}}(aq) + 2e^{-} \implies Sn(s) & -0.25 \\ Co^{2^{*}}(aq) + 2e^{-} \implies Fe(s) & -0.28 \\ PbSO_4(s) + H^{+}(aq) + 2e^{-} \implies Pb(s) + HSO_4^{-}(aq) & -0.31 \\ Ca^{2^{+}}(aq) + 2e^{-} \implies Fe(s) & -0.74 \\ Zn^{2^{+}}(aq) + 2e^{-} \implies Fe(s) & -0.74 \\ Zn^{2^{+}}(aq) + 2e^{-} \implies H_2(g) + 2OH^{-}(aq) & -0.74 \\ Zn^{2^{+}}(aq) + 2e^{-} \implies H_2(g) + 2OH^{-}(aq) & -0.74 \\ Zn^{2^{+}}(aq) + 2e^{-} \implies Mi(s) & -1.18 \\ Al^{3^{+}}(aq) + 3e^{-} \implies Al(s) & -1.18 \\ Al^{3^{+}}(aq) + 2e^{-} \implies Ma(s) & -2.71 \\ Ca^{2^{+}}(aq) + 2e^{-} \implies Ma(s) & -2.81 \\ Sn^{2^{+}}(aq) + 2e^{-} \implies Ma(s) & -2.81 \\ Sn^{2^{+}}(aq) + 2e^{-} \implies Ma(s) & -2.71 \\ Ca^{2^{+}}(aq) + 2e^{-} \implies Ma(s) & -2.81 \\ Sn^{2^{+}}(aq) + 2e^{-} \implies Sn(s) & -2.81 \\ Sn^{2^{+}}(aq) + 2e^{-} \implies Sn(s) & -2.81 \\$	$2Hg^{2+}(aq) + 2e^{-} \longrightarrow Hg_{2}^{2+}(aq)$	+0.92
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$Hg_2^{2+}(aq) + 2e^- \Longrightarrow 2Hg(l)$	$\pm 0.85$
$Fe^{3+}(aq) + e^{-} \implies Fe^{2+}(aq) + 10^{-1}(aq) + 10^{-1$	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$Fe^{3+}(aq) + e^- \Longrightarrow Fe^{2+}(aq)$	+0.80
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$O_2(g) + 2H^+(ag) + 2e^- \implies H_2O_2(ag)$	+0.77
$I_{2}(s) + 2e = 2I^{-}(aq) + 4e^{-}(aq) + 2e^{-}(aq) + 4e^{-}(aq) + 2e^{-}(aq) + 4e^{-}(aq) + 2e^{-}(aq) + 4e^{-}(aq) + 2e^{-}(aq) + $	$MnO_4(aa) + 2H_2O(l) + 3e \longrightarrow MnO_2(s) + 4OH(aa)$	+0.08
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$I_2(s) + 2e \rightleftharpoons 2I(aa)$	+0.39
$\begin{aligned} & \text{Cu}^{2+}(aq) + 2e^{-} \rightleftharpoons \text{Cu}(s) & \text{Hore}(aq) & \text$	$O_2(g) + 2H_2O(l) + 4e^{-1} = 4OH^{-1}(ag)$	+0.33
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$Cu^{2+}(aa) + 2e^{-} \Longrightarrow Cu(s)$	+0.40
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$AgCl(s) + e \implies Ag(s) + Cl^{-}(ag)$	+0.34
$\begin{aligned} & \text{Cu}^{2+}(aq) + e^{-} \implies \text{Cu}^{+}(aq) & \text{Cu}^{2-}(aq) & \text{cu}^{2-}$	$SO_{1}^{2}(aq) + 4H^{+}(aq) + 2e^{-1} - SO_{1}(a) + 2H_{1}O(b)$	+0.22
$\begin{aligned} & (aq) + 2e^{-} \iff Cl^{-}(aq) & (aq) & (a$	$Cu^{2+}(aq) + a^{-} \longrightarrow Cu^{+}(aq)$	+0.20
$\begin{aligned} & \text{H}^{-1}(aq) + 2e  \longrightarrow  \text{H}^{-1}(aq) \\ & \text{Pb}^{2+}(aq) + 2e  \longrightarrow  \text{Pb}(s) \\ & \text{Sn}^{2+}(aq) + 2e  \longrightarrow  \text{Pb}(s) \\ & \text{Sn}^{2+}(aq) + 2e  \longrightarrow  \text{Sn}(s) \\ & \text{N}_{2}(g) + 5H^{+}(aq) + 4e  \longrightarrow  \text{N}_{2}H_{5}^{+}(aq) \\ & \text{N}_{2}(g) + 5H^{+}(aq) + 4e  \longrightarrow  \text{N}_{2}H_{5}^{+}(aq) \\ & \text{N}_{2}(g) + 5H^{+}(aq) + 4e  \longrightarrow  \text{N}_{2}H_{5}^{+}(aq) \\ & \text{N}_{2}(aq) + 2e  \longrightarrow  \text{Ni}(s) \\ & \text{Co}^{2+}(aq) + 2e  \longrightarrow  \text{Co}(s) \\ & \text{PbSO}_{4}(s) + H^{+}(aq) + 2e  \longrightarrow  \text{Pb}(s) + \text{HSO}_{4}^{-}(aq) \\ & \text{Cd}^{2+}(aq) + 2e  \longrightarrow  \text{Cd}(s) \\ & \text{Cd}^{2+}(aq) + 2e  \longrightarrow  \text{Cd}(s) \\ & \text{Cd}^{2+}(aq) + 2e  \longrightarrow  \text{Fe}(s) \\ & \text{Cr}^{3+}(aq) + 3e  \longrightarrow  \text{Cr}(s) \\ & \text{Zn}^{2+}(aq) + 2e  \longrightarrow  \text{Fe}(s) \\ & \text{Ch}^{2+}(aq) + 2e  \longrightarrow  \text{Fe}(s) \\ & \text{Mn}^{2+}(aq) + 2e  \longrightarrow  \text{Mn}(s) \\ & \text{Mn}^{2+}(aq) + 2e  \longrightarrow  \text{Mn}(s) \\ & \text{Mn}^{2+}(aq) + 2e  \longrightarrow  \text{Mn}(s) \\ & \text{Mn}^{2+}(aq) + 2e  \longrightarrow  \text{Mg}(s) \\ & \text{Sn}^{2+}(aq) + 2e  \longrightarrow  \text{Mg}(s) \\ & \text{Sn}^{2+}(aq) + 2e  \longrightarrow  \text{Mg}(s) \\ & \text{Sn}^{2+}(aq) + 2e  \longrightarrow  \text{Sn}(s) \\ & \text{Sn}^{2+}(aq) + 2e  \longrightarrow $	$\operatorname{Sn}^{4+}(aq) + 2q^{-} \longrightarrow \operatorname{Sn}^{2+}(aq)$	+0.15
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$3\Pi^+(uq) + 2e^- \longrightarrow H^+(q)$	+0.13
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Ph^{2+}(aq) + 2e^{-} \longrightarrow Ph(s)$	0.00
$\begin{aligned} & -0.14 \\ N_2(g) + 5H^+(aq) + 4e^- \implies N_2H_5^+(aq) & -0.23 \\ Ni^{2^+}(aq) + 2e^- \implies Ni(s) & -0.25 \\ Co^{2^+}(aq) + 2e^- \implies Co(s) & -0.28 \\ PbSO_4(s) + H^+(aq) + 2e^- \implies Pb(s) + HSO_4^-(aq) & -0.31 \\ Cd^{2^+}(aq) + 2e^- \implies Cd(s) & -0.40 \\ Cr^{2^+}(aq) + 2e^- \implies Fe(s) & -0.44 \\ Cr^{3^+}(aq) + 3e^- \implies Cr(s) & -0.74 \\ Zn^{2^+}(aq) + 2e^- \implies Fe(s) & -0.76 \\ 2H_2O(l) + 2e^- \implies H_2(g) + 2OH^-(aq) & -0.83 \\ Mn^{2^+}(aq) + 2e^- \implies Mn(s) & -1.18 \\ Al^{3^+}(aq) + 3e^- \implies Al(s) & -1.66 \\ Mg^{2^+}(aq) + 2e^- \implies Mg(s) & -2.37 \\ Na^+(aq) + 2e^- \implies Na(s) & -2.37 \\ Na^+(aq) + 2e^- \implies Ca(s) & -2.87 \\ Sr^{2^+}(aq) + 2e^- \implies Sr(s) & -2.89 \\ Ba^{2^+}(aq) + 2e^- \implies Ba(s) & -2.93 \\ K^+(aq) + e^- \implies K(s) & -2.93 \\ K^+(aq) + e^- \implies Li(s) & -2.93 \\ K^+(aq) + E^- \implies Li(s$	$Sn^{2+}(aq) + 2e^{-1} Sn(s)$	-0.13
$\begin{aligned} & -2.63 + 511 (aq) + 2e \longrightarrow Ni(s) & -0.23 \\ & Ni^{2+}(aq) + 2e \bigoplus Co(s) & -0.28 \\ & PbSO_4(s) + H^+(aq) + 2e \bigoplus Cb(s) + HSO_4^-(aq) & -0.31 \\ & Cd^{2+}(aq) + 2e \bigoplus Cd(s) & -0.40 \\ & Cd^{2+}(aq) + 2e \bigoplus Cd(s) & -0.44 \\ & Cr^{3+}(aq) + 2e \bigoplus Cr(s) & -0.74 \\ & Zn^{2+}(aq) + 2e \bigoplus Cr(s) & -0.76 \\ & 2H_2O(l) + 2e \bigoplus H_2(g) + 2OH^-(aq) & -0.83 \\ & Mn^{2+}(aq) + 2e \bigoplus Mn(s) & -1.18 \\ & Al^{3+}(aq) + 3e \bigoplus Al(s) & -2.37 \\ & Na^+(aq) + 2e \bigoplus Mg(s) & -2.37 \\ & Na^+(aq) + 2e \bigoplus Sr(s) & -2.87 \\ & Sr^{2+}(aq) + 2e \bigoplus Sr(s) & -2.89 \\ & Ba^{2+}(aq) + 2e \bigoplus Ba(s) & -2.93 \\ & K^+(aq) + e \bigoplus K(s) & -2.93 \\ & K^+(aq) + E \bigoplus K(s) & -2.93 \\ & K^+(aq) + E \bigoplus K(s) & -2.93 \\ & K^+(aq) + E \bigoplus K(s) & -2.93 \\ & K^+(aq) + E \bigoplus K(s) & -2.93 \\ & K^+(aq) + E \bigoplus K(s) & -2.93 \\ & K^+(aq) + E \bigoplus K(s) & -2.93 \\ & K^+(aq) + E \bigoplus K(s) & -2.93 \\ & K^+(aq) + E \bigoplus K(s) & -2.93 \\ & K^+$	$N_{2}(q) + 5H^{+}(qq) + 4e^{-} \longrightarrow N_{2}H_{2}^{++}(qq)$	-0.14
$\begin{aligned} & -0.25 \\ & -0.25 \\ & Co^{2^+}(aq) + 2e & Co(s) \\ & -0.28 \\ PbSO_4(s) + H^+(aq) + 2e & Pb(s) + HSO_4^-(aq) \\ & -0.31 \\ Cd^{2^+}(aq) + 2e & Cd(s) \\ & -0.40 \\ Cr^{3^+}(aq) + 2e & Fe(s) \\ & -0.44 \\ Cr^{3^+}(aq) + 3e^- & Cr(s) \\ & -0.74 \\ Zn^{2^+}(aq) + 2e^- & H_2(g) + 2OH^-(aq) \\ & -0.76 \\ 2H_2O(l) + 2e^- & H_2(g) + 2OH^-(aq) \\ & -0.83 \\ Mn^{2^+}(aq) + 2e^- & Mn(s) \\ Mn^{2^+}(aq) + 3e^- & Al(s) \\ Mg^{2^+}(aq) + 2e^- & Mg(s) \\ Na^+(aq) + e^- & Na(s) \\ Ca^2^+(aq) + 2e^- & Ca(s) \\ Sr^{2^+}(aq) + 2e^- & Sr(s) \\ Sr^{2^+}(aq) + 2e^- & Sr(s) \\ Ba^{2^+}(aq) + 2e^- & Ba(s) \\ K^+(aq) + e^- & K(s) \\ $	$Ni^{2+}(aq) + 2a^{-} Ni(a)$	-0.23
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\operatorname{Co}^{2+}(aq) + 2e \longrightarrow \operatorname{Co}(r)$	-0.25
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$PbSO_{1}(s) + H^{+}(as) + 2e^{-1} = Pb(s) + HSO_{1}(as)$	-0.28
$\begin{array}{c} Ca^{2}(aq) + 2e^{-1} & Ca(s) & -0.40 \\ -0.40 \\ Cr^{3+}(aq) + 3e^{-1} & Cr(s) & -0.74 \\ Cr^{3+}(aq) + 2e^{-1} & Cr(s) & -0.76 \\ 2H_2O(l) + 2e^{-1} & H_2(g) + 2OH^{-}(aq) & -0.83 \\ Mn^{2+}(aq) + 2e^{-1} & Mn(s) & -1.18 \\ Al^{3+}(aq) + 3e^{-1} & Al(s) & -1.66 \\ Mg^{2+}(aq) + 2e^{-1} & Mg(s) & -2.37 \\ Na^{+}(aq) + e^{-1} & Na(s) & -2.71 \\ Ca^{2+}(aq) + 2e^{-1} & Ca(s) & -2.87 \\ Sr^{2+}(aq) + 2e^{-1} & Ba(s) & -2.89 \\ Ba^{2+}(aq) + 2e^{-1} & Ba(s) & -2.93 \\ K^{+}(aq) + e^{-1} & K(s) & -2.93 \\ L^{+}(aq) + e^{-1} & Li(s) & $	$Cd^{2+}(aq) + 2e^{-10(s)} + 110(s) + 1130_4 (aq)$	-0.31
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$Fe^{2+}(aa) + 2e^{-} \longrightarrow Fe(s)$	-0.40
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$Cr^{3+}(aq) + 3e^{-} \implies Cr(s)$	-0.44
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$Zn^{2+}(aq) + 2e = Zn(s)$	-0.74
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$2H_2O(l) + 2e^{-1} H_2(g) + 2OH^{-1}(gg)$	-0.76
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$Mn^{2+}(nq) + 2e^{-} \longrightarrow Mn(c)$	-0.05
$Mg^{2^{+}}(aq) + 2e^{-} Mg(s) -2.37$ $Na^{-}(aq) + e^{-} Na(s) -2.71$ $Ca^{2^{+}}(aq) + 2e^{-} Ca(s) -2.87$ $Ba^{2^{+}}(aq) + 2e^{-} Ba(s) -2.89$ $Ba^{2^{+}}(aq) + 2e^{-} Ba(s) -2.90$ $K^{+}(aq) + e^{-} K(s) -2.93$ $L^{+}(aq) + e^{-} L^{+}(s) -2.93$	$Al^{3+}(aa) + 3e \implies Al(s)$	-1.18
$\begin{aligned} & \text{Na}^{+}(aq) + e^{-} & \text{Na}(s) & -2.37 \\ & \text{Na}^{+}(aq) + 2e^{-} & \text{Na}(s) & -2.71 \\ & \text{Ca}^{2^{+}}(aq) + 2e^{-} & \text{Ca}(s) & -2.87 \\ & \text{Sr}^{2^{+}}(aq) + 2e^{-} & \text{Sr}(s) & -2.89 \\ & \text{Ba}^{2^{+}}(aq) + 2e^{-} & \text{Ba}(s) & -2.90 \\ & \text{K}^{+}(aq) + e^{-} & \text{K}(s) & -2.93 \\ & \text{K}^{+}(aq) + e^{-} & \text{Li}(s) & -2.93 \end{aligned}$	$Mg^{2+}(aq) + 2e^{-} \longrightarrow Mg(q)$	-1.00
$Ca^{2+}(aq) + 2e^{-} Ca(s) -2.87$ $Sr^{2+}(aq) + 2e^{-} Sr(s) -2.89$ $Ba^{2+}(aq) + 2e^{-} Ba(s) -2.90$ $K^{+}(aq) + e^{-} K(s) -2.93$ $L^{+}(aq) + e^{-} Li(s) -2.93$	$Na^+(aq) + e \longrightarrow Na(s)$	-2.3/
$Sr^{2+}(aq) + 2e \implies Sr(s) \qquad -2.89$ $Ba^{2+}(aq) + 2e \implies Ba(s) \qquad -2.90$ $K^{+}(aq) + e \implies K(s) \qquad -2.93$ $L^{+}(aq) + e \implies Li(s) \qquad -2.93$	$Ca^{2+}(aa) + 2e^{-} \Longrightarrow Ca(s)$	-2.71
$Ba^{2+}(aq) + 2e^{-} Ba(s) -2.99$ $Ba^{2+}(aq) + e^{-} K(s) -2.93$ $Li^{+}(aq) + e^{-} Li(s) -2.93$	$\operatorname{Sr}^{2+}(aa) + 2e \Longrightarrow \operatorname{Sr}(x)$	-2.8/
$\mathbf{K}^{+}(aq) + \mathbf{e} \stackrel{-}{\longrightarrow} \mathbf{K}(s) \qquad -2.93$	$Ba^{2+}(aq) + 2e^{-} \Longrightarrow Ba(s)$	-2.09
$Li^+(aa) + e^- \implies Li(s)$	$K^+(aa) + e \implies K(s)$	-2.90
	$Li^+(aa) + e^- \Longrightarrow Li(s)$	-2.93

#### Increasing reducing strength



*e.g.*, 
$$E^{\circ}_{cell} = E^{\circ}_{cat} - E_{ano} = E^{\circ}_{H2} - E^{\circ}_{M} = 0.00 - E^{\circ}_{M}$$

 $\therefore$  for  $E^{\circ}_{cell}$  to be positive,  $E^{\circ}_{M}$  must be < 0.00 (i.e. negative)

i.e.,  $E_{M}^{\circ} < E_{H2}^{\circ}$  i.e.  $E_{M}^{\circ} < 0.00 V$ 

- **So**, M(s) must be a stronger reducing agent than  $H_2(g)$  $\therefore$  M must be listed <u>below</u>  $H_2$  in Table 21.2 or App D
- OR H<sup>+</sup> (aq) must be a stronger oxidizing agent than M<sup>2+</sup> (aq) ∴ H<sup>+</sup> must be listed above M half-cell in Table 21.2 or App D

∴ Co, Mn, Na, Zn, Mg, Al, etc. dissolve in (react with) acid whereas Cu, Hg, Au, Ag, etc. do <u>not</u>



Figure 21.8 The reaction of calcium in water.

Oxidation half-reaction Ca(s)  $\rightarrow$  Ca<sup>2+</sup>(aq) + 2e<sup>-</sup> Reduction half-reaction  $2H_2O(I) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ 



Overall (cell) reaction Ca(s) + 2H<sub>2</sub>O(*I*)  $\rightarrow$  Ca<sup>2+</sup>(*aq*) + H<sub>2</sub>(*g*) + 2OH<sup>-</sup>(*aq*)





#### Section 21.4. Free Energy and Work

We saw earlier that:

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$

F = Faraday Constant = 9.65 x 10<sup>4</sup> J/V. mol e<sup>-</sup> = 9.65 x 10<sup>4</sup> C/mol e<sup>-</sup>

since we also saw that  $\Delta G^{\circ} = -RT \ln K$  in Chapter 20

 $\therefore \quad \mathsf{E^{o}}_{cell} = \frac{\mathsf{RT}}{\mathsf{nF}} \ln \mathsf{K}$ 

Thus, we can relate  $\Delta G^{\circ}$ , K and  $E^{\circ}_{cell}$  !!



Figure 21.10



#### Sample Problem 21.5

Consider the reaction:

Pb (s) + 2 Ag<sup>+</sup> (aq) 
$$\rightarrow$$
 Pb<sup>2+</sup> (aq) + 2 Ag (s)  
Calculate E<sup>o</sup><sub>cell</sub>, K and  $\Delta G^{\circ}$  at 25 °C.  
Pb (s)  $\rightarrow$  Pb<sup>2+</sup> (aq) + 2 e<sup>-</sup> (anode)  
2 Ag<sup>+</sup> + 2 e<sup>-</sup>  $\rightarrow$  2 Ag (s) (cathode)  
E<sup>o</sup><sub>cell</sub> = E<sup>o</sup><sub>cat</sub> - E<sup>o</sup><sub>ano</sub> = 0.80 V - (-0.13 V)  $\therefore$  E<sup>o</sup><sub>cell</sub> = 0.93 V  
 $\therefore$  InK =  $\frac{nF}{RT}$  E<sup>o</sup><sub>cell</sub> = 0.93 V = 72.45  
K = 3.0 × 10<sup>31</sup> [book gets 2.6 × 10<sup>31</sup> because it converts to log<sub>10</sub>  
(answers the same within rounding errors)]

 $\Delta G^{\circ} = -nFE^{\circ}_{cell} = -(2 \text{ mol } e^{-})(9.65 \times 10^{4} \text{ J/V mol } e^{-})(0.93 \text{ V})$ 

 $\Delta G^{\circ} = -1.8 \times 10^5 \text{ J} = -1.8 \times 10^2 \text{ kJ}$ 



#### Effect of Concentration on Cell Potentials

The concentrations are not always going to be standard ones (1 M): this will alter  ${\rm E^o}_{\rm cell}$  to  ${\rm E}_{\rm cell}$ 

Since 
$$\Delta G = \Delta G^{\circ} + RT \ln Q$$
 and  $\Delta G^{\circ} = -nFE^{\circ}_{cell}$ ,  

$$\therefore \qquad E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln Q$$
or
$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592V}{n} \log Q$$
remember,  $Q = \frac{[product]}{[reactants]}$ 

$$\therefore Q < 1, \quad \log Q < 0, \quad E_{cell} > E^{\circ}_{cell}$$

$$Q > 1, \quad \log Q < 0, \quad E_{cell} < E^{\circ}_{cell}$$

$$Q = 1, \quad \log Q = 0, \quad E_{cell} = E^{\circ}_{cell}$$
Figure 21.11A



## Figure 21.11A The relation between $E_{cell}$ and log Q for the zinccopper cell.



If the reaction starts with  $[Zn^{2+}] < [Cu^{2+}] (Q < 1)$ ,  $E_{cell}$  is higher than the standard cell potential.

As the reaction proceeds,  $[Zn^{2+}]$  increases and  $[Cu^{2+}]$  decreases, so  $E_{cell}$  drops. Eventually the system reaches equilibrium and the cell can no longer do work.

21-8

**<u>Problem</u>**: Voltaic cell: Zn (s)/ Zn<sup>2+</sup> anode and H<sup>+</sup>/H<sub>2</sub> (gas) cathode.

What is  $E_{cell}$  if  $[Zn^{2+}] = 0.010 \text{ M}$ ,  $[H^+] = 2.5 \text{ M}$  and  $p(H_2) = 0.30 \text{ atm}$  at 25 °C?

Answer: Calculate 
$$E^{\circ}_{cell}$$
 and Q, and use  $E_{cell} = E^{\circ}_{cell} - \frac{0.0592V \log Q}{n}$   
Zn (s) + 2 H<sup>+</sup> (aq)  $\rightarrow$  Zn<sup>2+</sup> (aq) + H<sub>2</sub> (g)  
 $E^{\circ}_{cell} = 0.00 V - (-0.76 V) = 0.76 V$   
Q =  $\frac{[Zn^{2+}]p(H_2)}{[H^+]^2} = \frac{(0.010)(0.30)}{(2.5)^2} = 4.8 \times 10^{-4}$ 

$$\therefore E_{cell} = 0.76 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \text{ Q} = 0.86 \text{ V} \qquad \text{E}_{cell} = 0.86 \text{ V}$$



<u>Problem</u>. Voltaic cell: Fe (s) + Cu<sup>2+</sup> (aq)  $\rightarrow$  Fe<sup>2+</sup> (aq) + Cu (s) Calculate E°<sub>cell</sub>. Then, if [Cu<sup>2+</sup>] = 0.30 M, calculate [Fe<sup>2+</sup>] needed to give E<sub>cell</sub> that is 0.25 V bigger than E°<sub>cell</sub>.

$$E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{ano} = 0.34 \text{ V} - (-0.44 \text{ V}) = 0.78 \text{ V}$$

Need [Fe<sup>2+</sup>] to give  $E_{cell} = E_{cell}^{\circ} + 0.25 V = 1.03 V$ 

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0592}{n} \log Q = E_{cell}^{\circ} - \frac{0.0592}{2} \log \frac{[Fe^{2+}]}{[Cu^{2+}]}$$

$$\therefore 1.03 \text{ V} = 0.78 \text{ V} - \frac{0.0592}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]}$$
$$\therefore \frac{0.0592}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} = -0.25 \text{ V} \therefore \log \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} = -8.446$$

 $\therefore \frac{[Fe^{2+}]}{[Cu^{2+}]} = 3.6 \times 10^{-9} \qquad \therefore \ [Fe^{2+}] = 1.1 \times 10^{-9} \text{ M}$ 



## Variation of E<sub>cell</sub> with Concentrations

Consider Zn (s) + Cu<sup>2+</sup> (aq) 
$$\rightarrow$$
 Zn<sup>2+</sup> (aq) + Cu (s)  

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} [Note: Do not include M (s)]$$

At equilibrium, Q = K and  $E_{cell}$  = 0.00 V. We say the voltaic cell has fully discharged or the battery is dead or flat.

Another way of looking at it:

Q < K,  $E_{cell}$  is positive. When Q = K, reached equil and  $E_{cell} = 0$ .

If Q > K, reaction will run in reverse until Q = K.



#### **Concentration Cells**

If we use the same half-reaction on both sides but with different [ $M^{2+}$ ], we can get a current.

*e.g.*,  $Cu(s) | Cu^{2+}(aq, 0.10 \text{ M}) || Cu^{2+}(aq, 1.0 \text{ M}) | Cu(s)$ 

e's will flow until  $[Cu^{2+}]$  the same on both sides. Figure 21.12

pH meters are concentration cells. A non-zero  $E_{cell}$  results if reference [H<sup>+</sup>] is different from unknown [H<sup>+</sup>] - measured and converted into pH.



## Figure 21.12 A concentration cell based on the Cu/Cu<sup>2+</sup> half-reaction.



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 $E_{cell}$  > 0 as long as the half-cell concentrations are different. The cell is no longer able to do work once the concentrations are equal.



21-13

### Section 21.7. Electrolytic Cells

Electrical energy from an external source is used to drive a non-spontaneous reaction.

Consider the tin-copper voltaic cell.  $E_{cell}^{\circ} = 0.48 V$  Fig. 21.26

We can drive the reaction in its non-spontaneous direction by using an external source with  $E^\circ$  > 0.48 V

: instead of Sn (s) +  $Cu^{2+}$  (aq)  $\rightarrow$  Sn<sup>2+</sup> (aq) + Cu (s), we can make reaction go backwards, *i.e.*, Sn (s) forms at cathode and Cu (s) dissolves at anode.

This is the principle of rechargeable batteries where we wait until the battery is "flat" and then drive it backwards to recharge it.

<u>Electrolysis</u> is the splitting (lysing) of a substance by the input of electrical energy and is often used to decompose a compound into its elements.

e.g. Al(s) from  $Al_2O_3(s)$  (the industrial production of aluminum metal)  $H_2(g)$  and  $O_2(g)$  from  $H_2O$ , etc.



# Figure 21.26 The tin-copper reaction as the basis of a voltaic and an electrolytic cell.

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(1) Electrolysis of pure materials in molten state: easy to determine products: cation reduced, anion oxidized

e.g., CaCl<sub>2</sub>(I) ( at >782 °C to keep it molten):

2  $Cl^{-}(l) \rightarrow Cl_{2}(g) + 2 e^{-}$  (anode)  $Ca^{2+}(l) + 2 e^{-} \rightarrow Ca(s)$  (cathode)

 $Ca^{2+}(I) + 2 CI^{-}(I) \rightarrow Ca(s) + Cl_{2}(g)$ 

This is the non-spont direction of Ca (s) +  $Cl_2(g) \rightarrow Ca^{2+}(l) + 2 Cl^{-}(l)$ 

<u>Note</u>: We cannot use Tables of  $E^{\circ}_{half-rxn}$  to calculate  $E^{\circ}$  required because they are for *e.g.*,  $Ca^{2+}(aq) + 2 e \rightarrow Ca(s)$  under standard conditions.



## Stoichiometry of Electrolysis

Important type of calculation for electrolyses.

<u>Question:</u> How much metal will we get if we pass a certain current for a certain time?

<u>Faraday's Law of Electrolysis</u> = The amount of substance produced at each electrode is directly proportional to the amount of charge (electrons) flowing through the cell.

<u>Note</u>: 1 Faraday = 9.65 x 10<sup>4</sup> J/V.mol.e<sup>-</sup> = 9.65 x 10<sup>4</sup> C/mol.e<sup>-</sup>

 $\therefore$  1 Faraday = the charge (in coulombs C) of 1 mole of electrons.

Current = amount of charge moving per unit time

 $\therefore$  1 ampere (A) = 1 coulomb/second = 1 C/s

... To answer the question, calculate charge, convert to moles of electrons, and use half-reaction to see how many moles (and then mass) of metal produced. Figure 21.29









<u>Problem</u>: How much Cr(s) from electrolysis of molten  $Cr^{3+}$  salt for 60.0 minutes with a current of 10.0 amperes?

Charge = current (C/s) x time (s) = (10.0 C/s)(60.0 x 60 s) = 3.60 x 10<sup>4</sup> C moles of  $e^- = \frac{charge}{F} = \frac{3.60 \times 10^4 C}{9.65 \times 10^4 C/mole^-} = 0.373$  moles  $e^ Cr^{3+} + 3 e^- \rightarrow Cr$  (s)  $\therefore$  moles of Cr (s) produced =  $\frac{moles e^-}{3} = 0.124$  moles  $\therefore$  mass of Cr (s) produced = moles x M.W. = (0.124 mol)(52.0 g/mol)

: mass of Cr (s) = 6.47 g





(2) Electrolysis of water, aqueous solutions, or molten mixtures

In each case, there will be two (or more) cations and anions present. Therefore, we must be able to decide which will be oxidized or reduced. (a) Electrolysis of a mixture of molten NaBr and MgCl<sub>2</sub>

reduction: Nat or Mg<sup>2+</sup>?? Use E° half-rxn's as a 'guide'

$Mg^{2+}(I) + 2 e^{-} \rightarrow Mg(s)$	E° = -2.37 V
$Na^{+}(I) + e^{-} \rightarrow Na(s)$	E° = -2.71 V

The hardest to reduce (the weaker oxidizing agent) is  $Na^+$  ...  $Mg^{2+}$  is reduced ... Mg(s) obtained at the cathode

oxidation: Br- or Cl-??

$Cl_2(g) + 2 e^- \rightarrow 2 Cl^-(aq)$	E° = 1.36 V
$Br_2(I) + 2 e^- \rightarrow 2 Br^-(aq)$	E° = 1.07 V

The easier to oxidize (the stronger reducing agent) is  $Br^ \therefore Br^-$  is oxidized  $\therefore Br(I)$  obtained at the anode

 $\therefore$  The products are Mg (I) and Br<sub>2</sub> (I)



Electrolysis of water (+ inert Na<sub>2</sub>SO<sub>4</sub> to help conduct electricity)

$$\begin{array}{ll} \underbrace{\text{oxidation:}}_{(\text{anode})} & 2 \ \text{H}_2 O \ (\text{I}) \rightarrow O_2 \ (g) + 4 \ \text{H}^+ \ (\text{aq}) + 4 \ e^- & \text{E} = 0.82 \text{V} \\ \hline \text{(anode)} & 2 \ \text{H}_2 O \ (\text{I}) + 2 \ e^- \rightarrow \text{H}_2 \ (g) + 2 \ \text{OH}^- \ (\text{aq}) & \text{E} = -0.42 \text{V} \\ \hline \text{(cathode)} & \text{Overall:} & 2 \ \text{H}_2 O \ (\text{I}) \rightarrow 2 \ \text{H}_2 \ (g) + O_2 \ (g) & \text{(non-spont direction!)} \\ \hline \text{Figure 21.28} \end{array}$$

<u>Note</u>: E not E° since  $[H^+] = [OH^-] = 10^{-7} M \therefore$  <u>not</u> standard (1 M)

E = 0.82 V is for anode reaction with  $[H^+] = 10^{-7} \text{ M}, p(O_2) = 1 \text{ atm.}$ 

Use E = 0.82 V and -0.42 for aqueous solutions.



## Standard Electrode (Half-Cell) Potentials

Strength of Oxidizing and Reducing Agents

> Increasing oxidizing strength



#### Increasing reducing strength



## Figure 21.28The electrolysis of water.



Oxidation half-reaction  $2H_2O(I) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$  Reduction half-reaction  $2H_2O(I) + 4e^- \rightarrow 2H_2(g) + 2OH^-(aq)$ 





c) Electrolysis of aqueous solutions

First, we must realize the importance of <u>overvoltage</u>: formation of <u>gases</u> becomes less easy by ~ 0.4 to 0.6 V. Thus, it changes predicted products <u>sometimes</u>.

Example 1: Aqueous solution of KI (no overvoltage problem) oxidation:  $I^{-}(aq)$  or  $H_2O$ ? E° = 0.82 V  $O_2(q) + 4 H^+ + 4 e^- \rightleftharpoons 2 H_2O(l)$  $I_2$  (s) + 2 e<sup>-</sup>  $\Rightarrow$  2 I<sup>-</sup> (ag)  $F^{\circ} = 0.53 V$ I<sup>-</sup> is easier to oxidize (I<sup>-</sup> is the stronger reducing agent) .: I is oxidized  $\therefore$  I<sub>2</sub> (s) obtained at the anode <u>reduction</u>:  $K^{+}$  (aq) or  $H_2O(I)$ ?  $F^{\circ} = -2.93 V$  $K^+$  (ag) +  $e^- \rightarrow K$  (s)  $2 H_2O(I) + 2 e^- \rightarrow H_2(g) + 2 OH^-(aq)$  E = -0.42 V (~ -1V with overvoltage)  $\therefore$  H<sub>2</sub>O (I) is reduced  $\therefore$  H<sub>2</sub> (g) obtained at the cathode





The electrolysis of concentrated aqueous solutions of NaCl is how large amounts of  $Cl_2$  gas are made in industry.





## Figure 21.9 A dental "voltaic cell."

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Biting down with a filled tooth on a scrap of aluminum foil will cause pain. The foil acts as an active anode ( $E^{\circ}_{aluminum} = -1.66$  V), saliva as the electrolyte, and the filling as an inactive cathode as O<sub>2</sub> is reduced to H<sub>2</sub>O.



