



Topic 4

Electrochem

The study of
interchange energy
chemical ↔ electrical

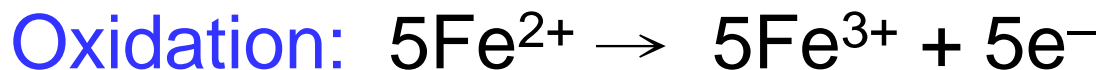
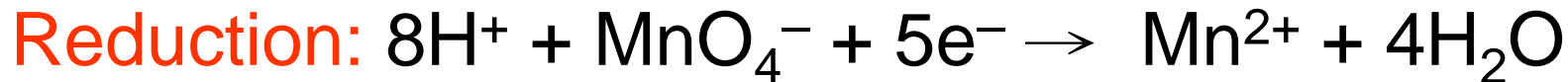
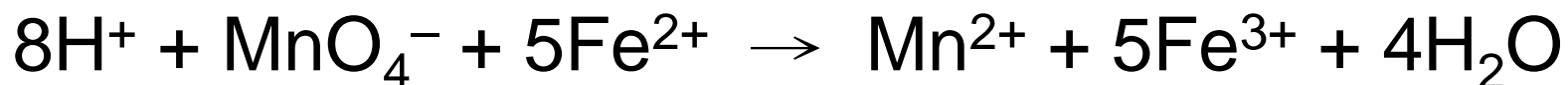


Review of Terms

- Oxidation–reduction (redox) reaction – involves a transfer of electrons from the reducing agent to the oxidizing agent
- Oxidation – **loss** of electrons
- Reduction – **gain** of electrons
- Reducing agent – electron **donor**
- Oxidizing agent – electron **acceptor**

Half-Reactions

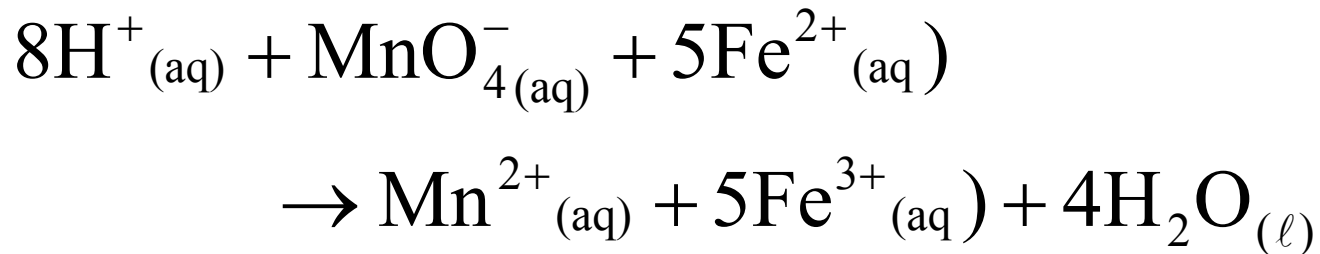
- The overall reaction is split into two half-reactions, one involving oxidation and one reduction.



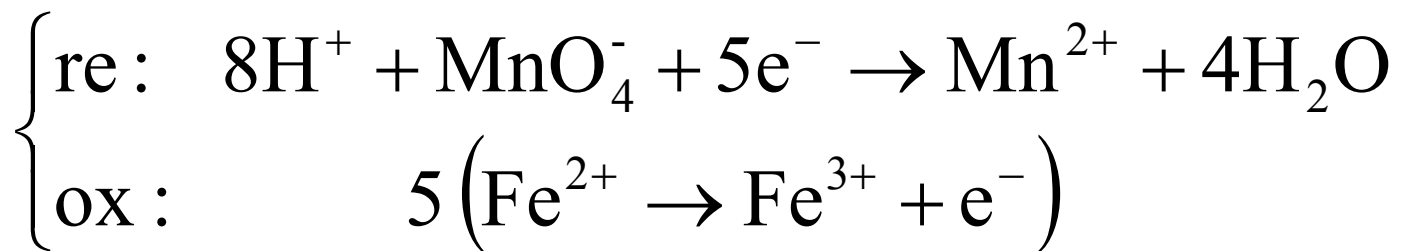
Electrochemical (Galvanic) Cell

- Device in which chemical energy is changed to electrical energy.
- Uses a spontaneous redox reaction to produce a current that can be used to do work.

1) oxidation-reduction (redox) reaction rxn:



half-reactions:



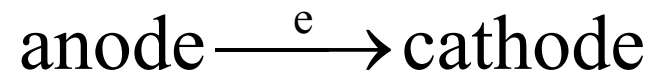
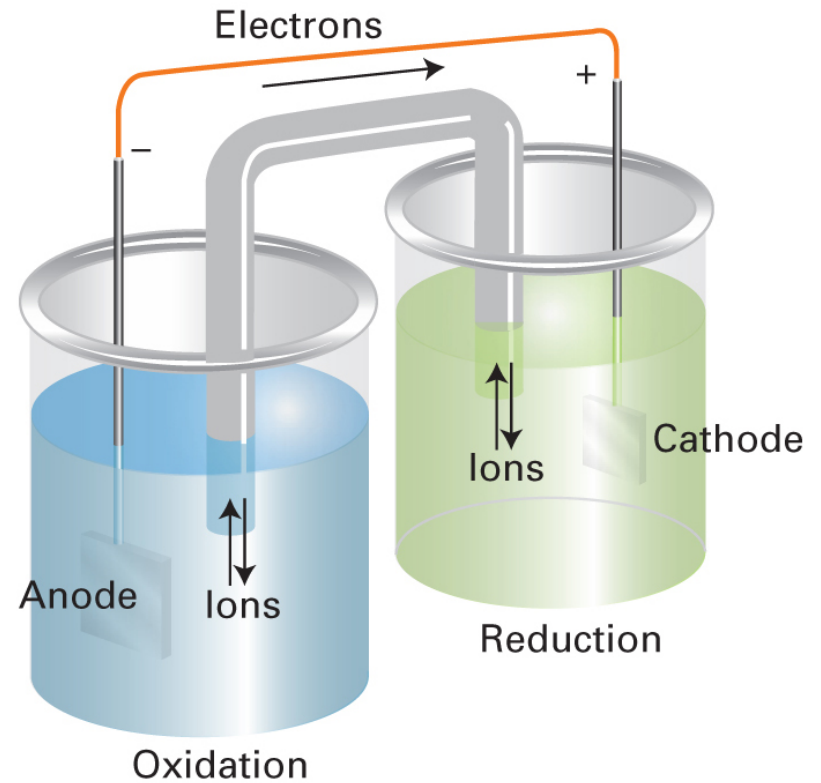
2) When the oxidizing agent & reducing agent are **physically separated**, e transfer through an external wire.

⇒ generates electricity.

3) salt bridge: connect two solns

4) electrodes; where the redox rxn occur

{ anode: oxidation occur
cathode: reduction occur



5) Cell potential ($\mathcal{E}_{\text{cell}}$)

a) The voltage difference between the electrodes.

\Rightarrow electromotive force (emf)

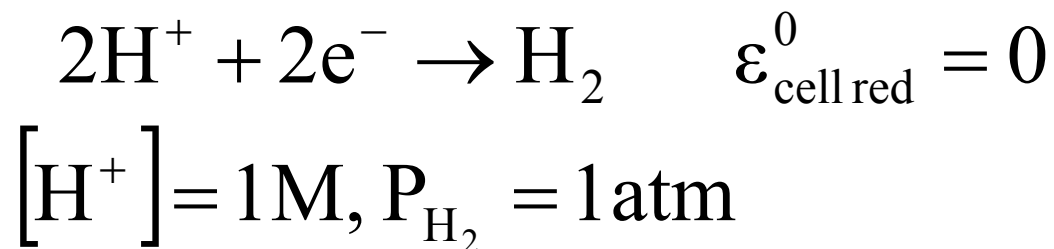
b) can be measured by voltmeter.

c) emf of a cell depends on

{ The nature of the electrodes
[ions]
Temp.

6) It is impossible to measure E_{cell} of a half-rxn directly,
∴ need a reference rxn \Rightarrow SHE

standard hydrogen electrode:



7) Standard reduction potential

$$E_{\text{red}}^0$$

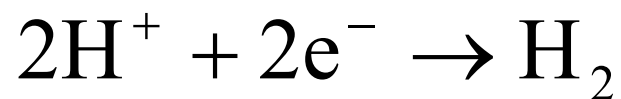


Table 9.3

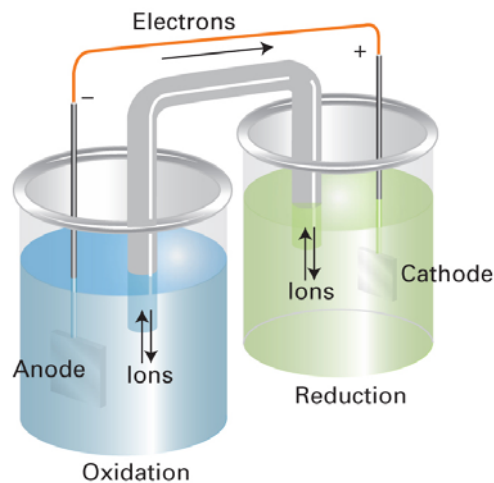
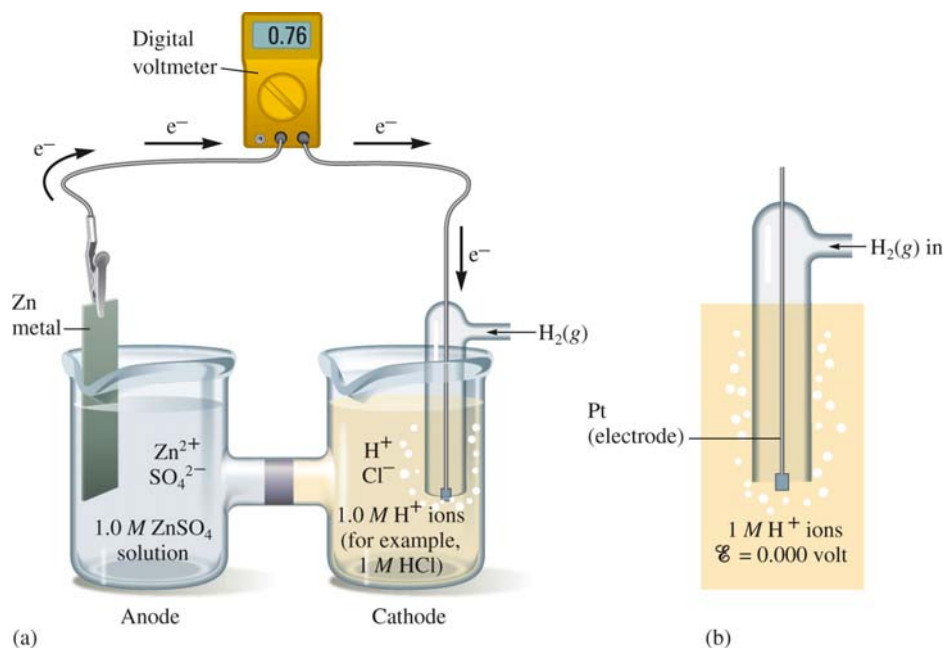


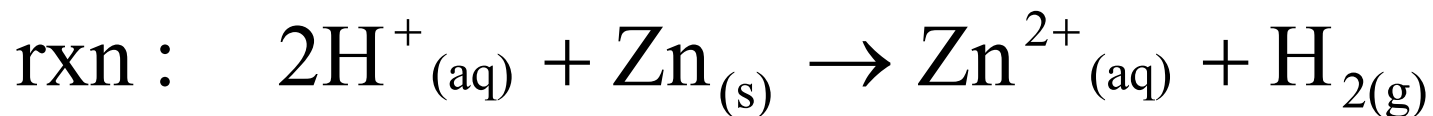
Table 9.3
Standard potentials at 25 °C

Reduction half-reaction			E°/V
Oxidizing agent		Reducing agent	
<i>Strongly oxidizing</i>			
F_2	$+ 2 e^- \rightarrow$	$2 F^-$	+2.87
$S_2O_8^{2-}$	$+ 2 e^- \rightarrow$	$2 SO_4^{2-}$	+2.05
Au^+	$+ e^- \rightarrow$	Au	+1.69
Pb^{4+}	$+ 2 e^- \rightarrow$	Pb^{2+}	+1.67
Ce^{4+}	$+ e^- \rightarrow$	Ce^{3+}	+1.61
$MnO_4^- + 8 H^+$	$+ 5 e^- \rightarrow$	$Mn^{2+} + 4 H_2O$	+1.51
Cl_2	$+ 2 e^- \rightarrow$	$2 Cl^-$	+1.36
$Cr_2O_7^{2-} + 14 H^+$	$+ 6 e^- \rightarrow$	$2 Cr^{3+} + 7 H_2O$	+1.33
$O_2 + 4 H^+$	$+ 4 e^- \rightarrow$	$2 H_2O$	+1.23, +0.81 at pH = 7
Br_2	$+ 2 e^- \rightarrow$	$2 Br^-$	+1.09
Ag^+	$+ e^- \rightarrow$	Ag	+0.80
Hg_2^{2+}	$+ 2 e^- \rightarrow$	$2 Hg$	+0.79
Fe^{3+}	$+ e^- \rightarrow$	Fe^{2+}	+0.77
I_2	$+ e^- \rightarrow$	$2 I^-$	+0.54
$O_2 + 2 H_2O$	$+ 4 e^- \rightarrow$	$4 OH^-$	+0.40, +0.81 at pH = 7
Cu^{2+}	$+ 2e^- \rightarrow$	Cu	+0.34
$AgCl$	$+ e^- \rightarrow$	$Ag + Cl^-$	+0.22
$2 H^+$	$+ 2 e^- \rightarrow$	H_2	0, by definition
Fe^{3+}	$+ 3 e^- \rightarrow$	Fe	-0.04
$O_2 + H_2O$	$+ 2 e^- \rightarrow$	$HO_2^- + OH^-$	-0.08
Pb^{2+}	$+ 2 e^- \rightarrow$	Pb	-0.13
Sn^{2+}	$+ 2 e^- \rightarrow$	Sn	-0.14
Fe^{2+}	$+ 2 e^- \rightarrow$	Fe	-0.44
Zn^{2+}	$+ 2 e^- \rightarrow$	Zn	-0.76
$2 H_2O$	$+ 2 e^- \rightarrow$	$H_2 + 2 OH^-$	-0.83, -0.42 at pH = 7
Al^{3+}	$+ 3 e^- \rightarrow$	Al	-1.66
Mg^{2+}	$+ 2 e^- \rightarrow$	Mg	-2.36
Na^+	$+ e^- \rightarrow$	Na	-2.71
Ca^{2+}	$+ 2 e^- \rightarrow$	Ca	-2.87
K^+	$+ e^- \rightarrow$	K	-2.93
Li^+	$+ e^- \rightarrow$	Li	-3.05
<i>Strongly reducing</i>			

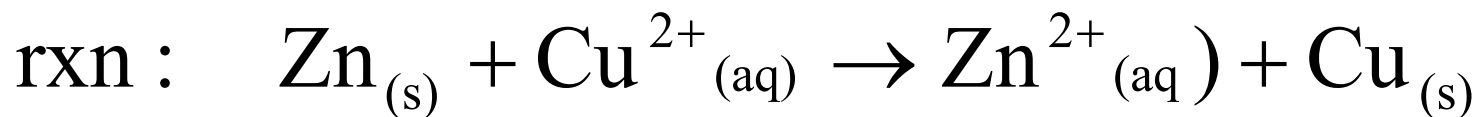
For a more extensive table, see the *Data section*.



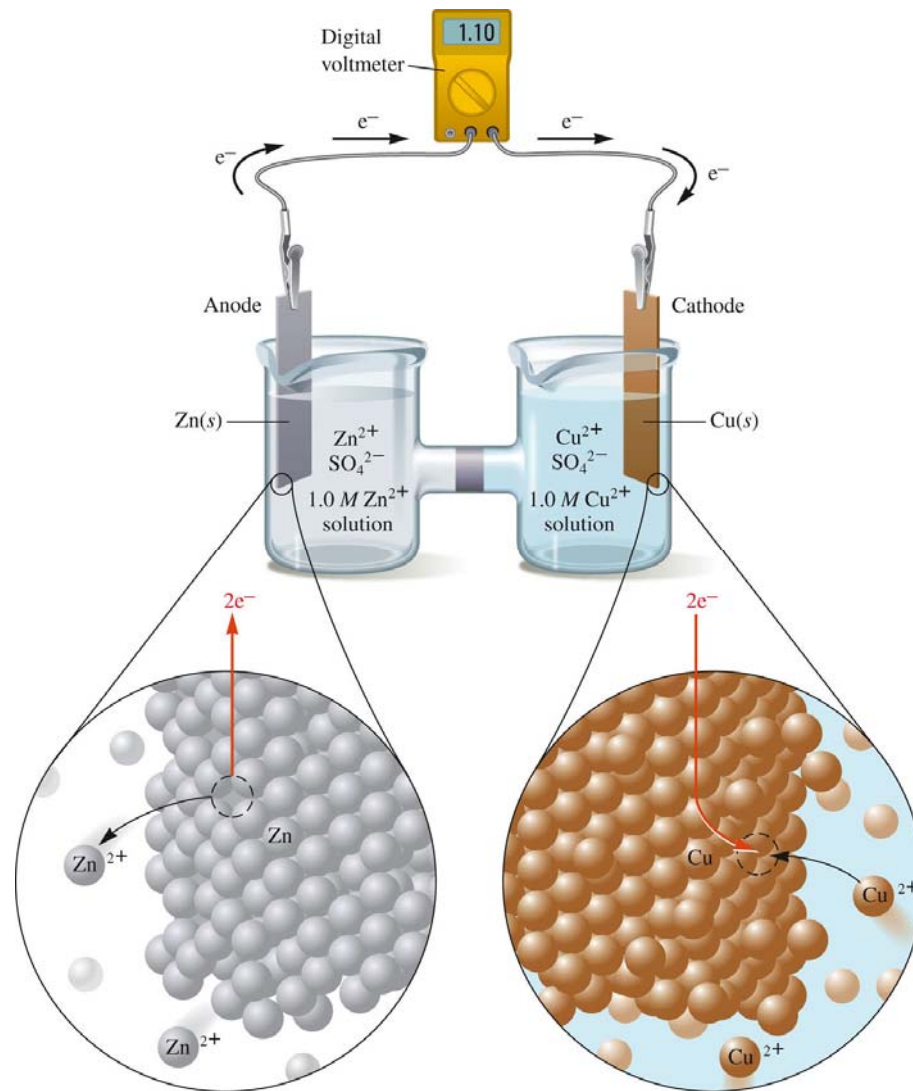
$$E_{\text{cell}}^0 = E_{\text{red}}^0 - E_{\text{ox}}^0 = E_{\text{R}}^0 - E_{\text{L}}^0$$



$$\underbrace{E_{\text{cell}}^0}_{0.76\text{V}} = \underbrace{E_{\text{H}^+ \rightarrow \text{H}_2}^0}_0 - \underbrace{E_{\text{Zn}^{2+} \rightarrow \text{Zn}}^0}_{-0.76\text{V}}$$



$$\underbrace{E_{\text{cell}}^0}_{1.10\text{V}} = \underbrace{E_{\text{Cu}^{2+} \rightarrow \text{Cu}}^0}_{0.34\text{V}} - \underbrace{E_{\text{Zn}^{2+} \rightarrow \text{Zn}}^0}_{-0.76\text{V}}$$



Ex: p222



Concept Check

Sketch a cell using the following solutions and electrodes. Include:

- The potential of the cell
- The direction of electron flow
- Labels on the anode and the cathode

a) Ag electrode in $1.0\text{ M Ag}^+(aq)$ and Cu electrode in $1.0\text{ M Cu}^{2+}(aq)$

Work

- Work is never the maximum possible if any current is flowing.
- In any real, spontaneous process some energy is always wasted – the actual work realized is always less than the calculated maximum.

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

$$E = \frac{-w}{q}$$

$$w = -qE \quad \& \quad q = nF \quad \leftarrow 96485 \text{ C/mol e}^- \quad \& \quad w_{\text{max}} = \Delta G$$

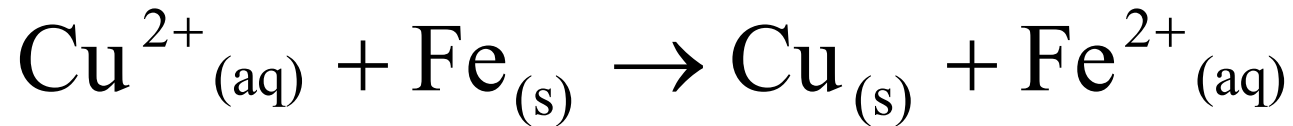
$$\therefore \Delta G = -nFE$$

standard condition :

$$\Delta G^\circ = -nFE^\circ$$

examples

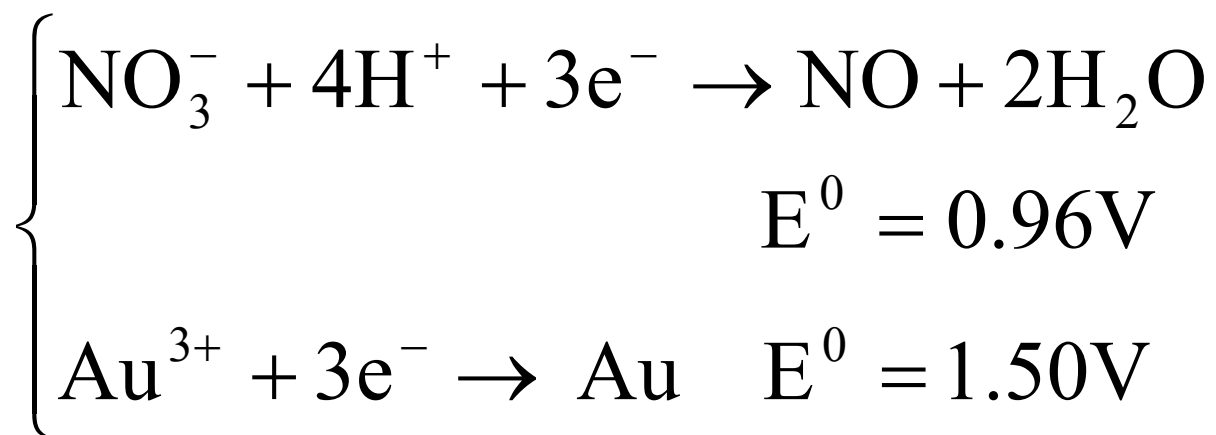
(1) Calculate ΔG°



$$E^\circ_{\text{rxn}} = E^\circ_{\text{re}} - E^\circ_{\text{ox}}$$

$$\Delta G^\circ = -nFE^\circ$$

(2) Predict whether 1M HNO₃ will dissolve gold metal to form 1M Au³⁺?



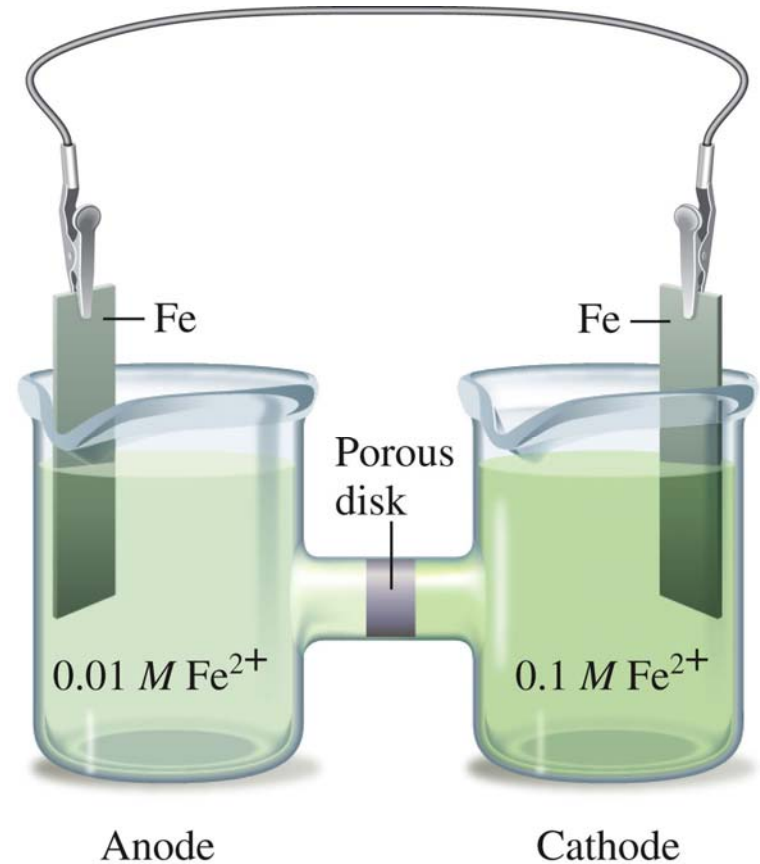
$$E_{\text{cell}}^0 = E_{\text{re}}^0 - E_{\text{ox}}^0 = -0.54\text{V}$$



(3) Concentration Cells

Determine

- a) e flow direction?
- b) anode? cathode?
- c) $E = ?$ at 25°C



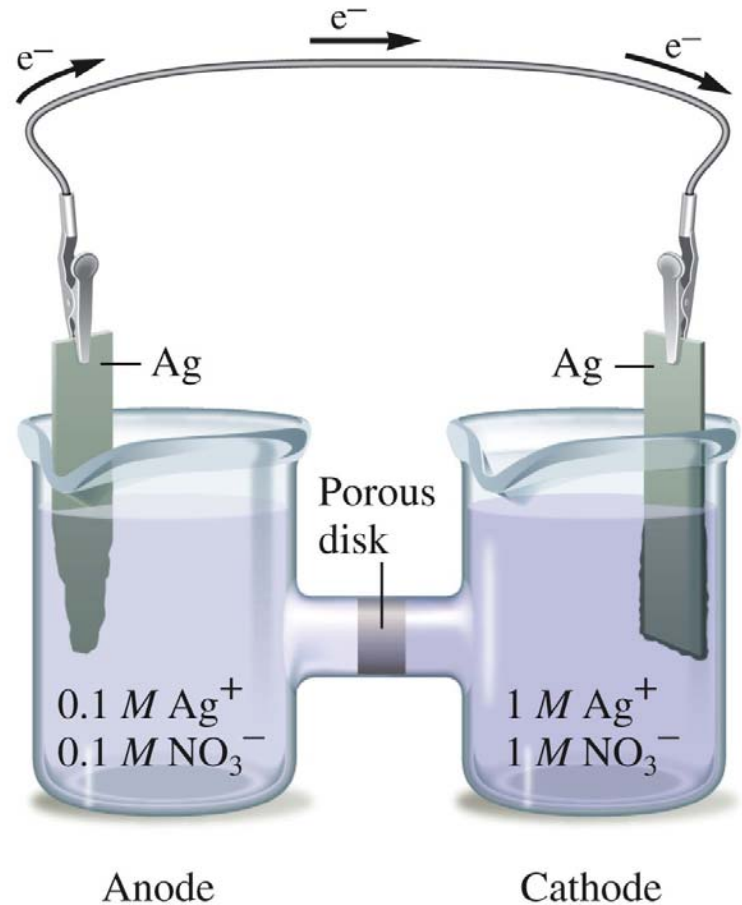
The Nernst eqn

$$\Delta G = \Delta G^\circ + RT \ln Q$$

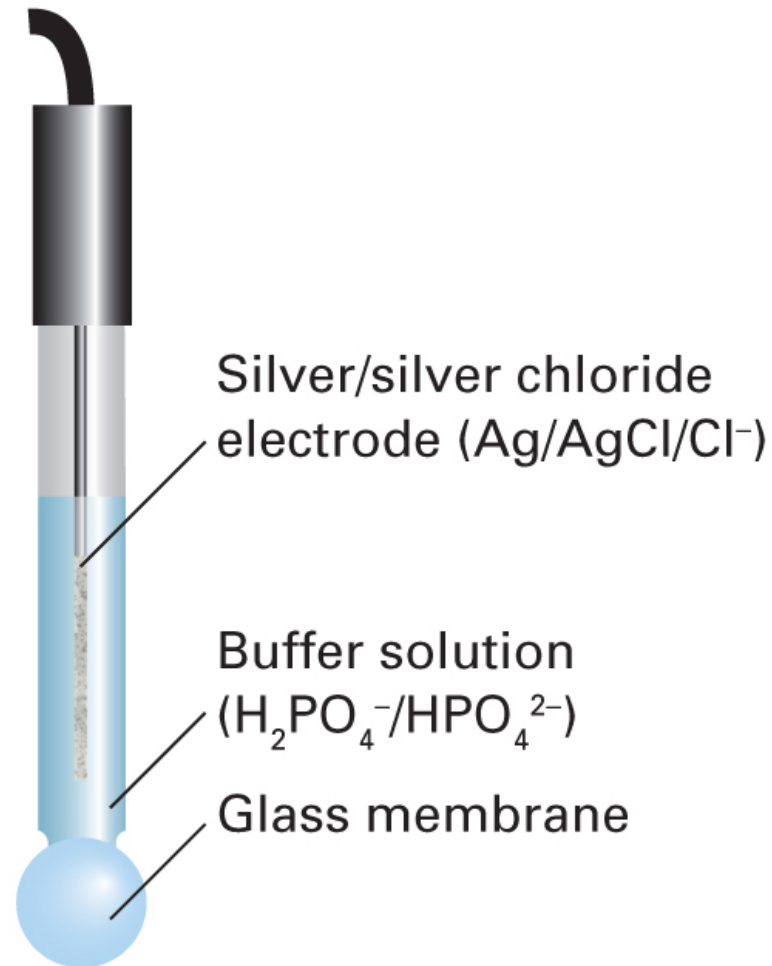
$$-nFE = -nFE^\circ + RT \ln Q$$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = E^\circ - \frac{0.0592}{n} \log Q$$



Ion-Selective Electrodes: pH meter



at equilibrium: $\Delta G=0$, $E_{\text{cell}}=0$, $Q=K$

$$\Delta G^{\circ} = -RT \ln K$$

$$E^{\circ} = \frac{RT}{nF} \ln K = \frac{0.0592}{n} \log K$$

(ex) Calculate K_{sp} for AgCl at 25°C

$$E = 0.58\text{V}$$

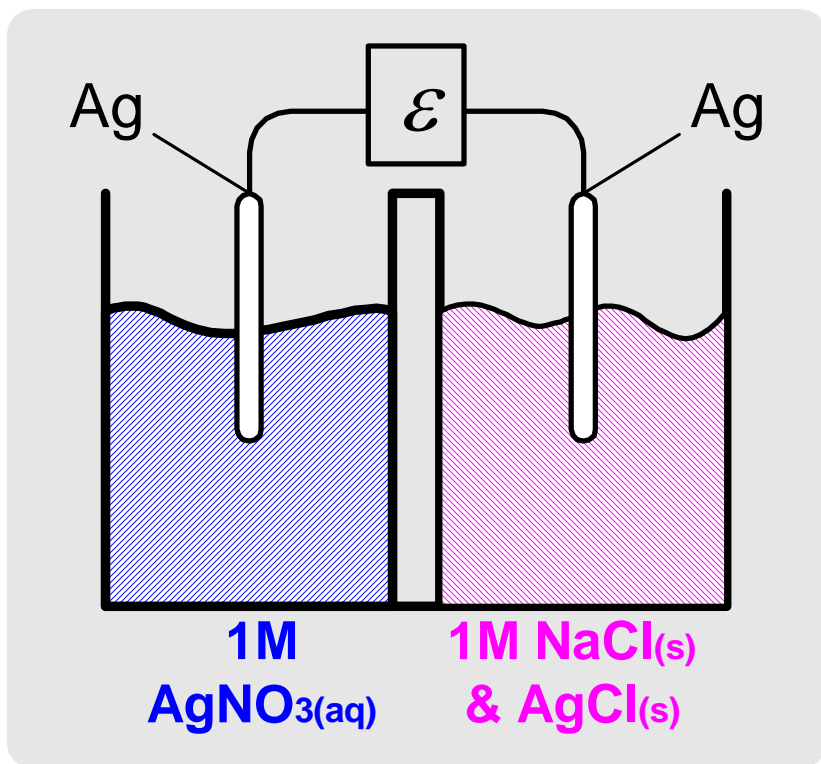
soln:

$$E^0 = 0?$$

$$E = 0.58\text{V}$$

$$= 0 - \frac{0.0592}{1} \log\left(\frac{[\text{Ag}^+]}{1.0}\right)$$

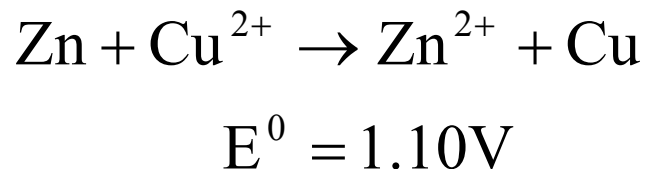
$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]_{\leftarrow 1.0\text{M}}$$



1) galvanic cell

① chemical E →
electrical E

② Fig 18.19(a)

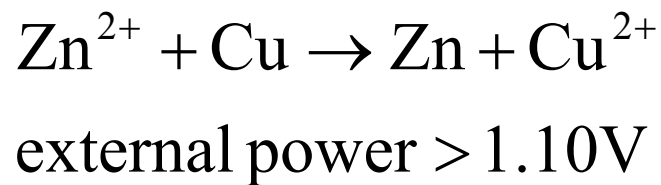


③ redox rxn:
spontaneous

electrolytic cell

electrical E →
chemical E

Fig 18.19(b)



nonspontaneous

Homework (4/07/2014)

- 9.14, 9.19, 9.20, 9.29, 9.35,9.37

Formal potential

- $\text{AgCl (s)} + \text{e}^- \leftrightarrow \text{Ag (s)} + \text{Cl}^-$
0.222 V
0.197 V in saturated KCl (formal potential)

$E^0 = 0.222\text{V}$:

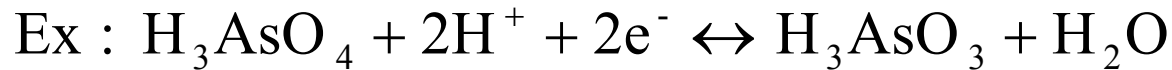
S.H.E. || Cl^- (aq, 1M) | AgCl (s) | Ag(s)

E^0' (formal potential) = 0.197 V (in saturated KCl)

S.H.E. || KCl (aq, saturated) | AgCl (s) | Ag(s)

Dependence of potential on pH

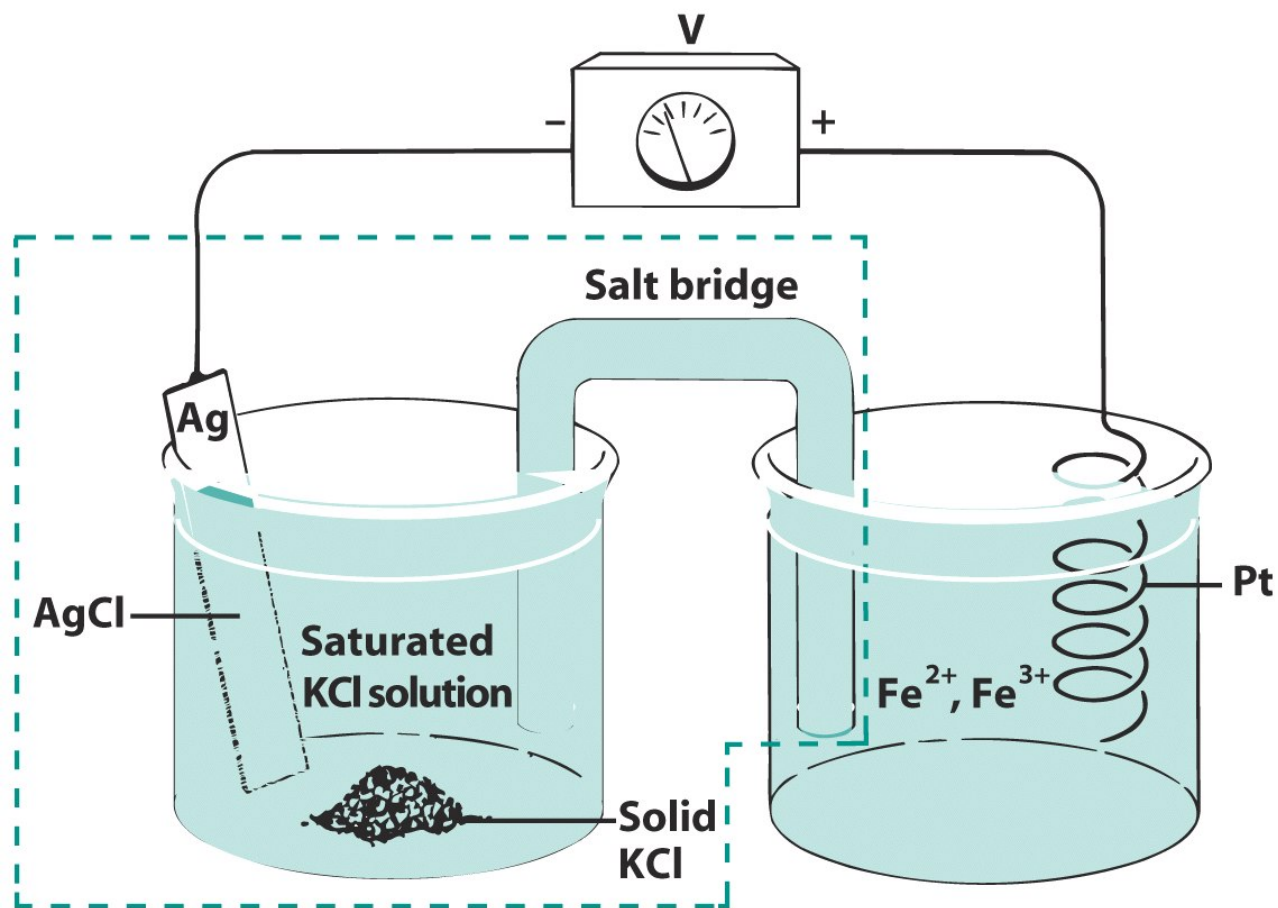
Many redox reactions involved protons, and their potentials are influenced greatly by pH.



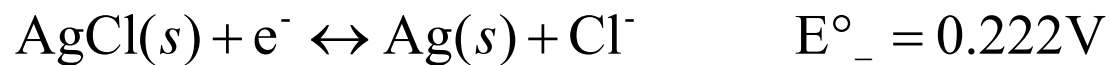
$$\begin{aligned} E &= E^\circ - \frac{0.0592}{2} \log \frac{[\text{H}_3\text{AsO}_3]}{[\text{H}_3\text{AsO}_4][\text{H}^+]^2} \\ &= E^\circ + 0.0592 \log[\text{H}^+] - \frac{0.0592}{2} \log \frac{[\text{H}_3\text{AsO}_3]}{[\text{H}_3\text{AsO}_4]} \\ &= E^\circ - 0.0592\text{pH} - \frac{0.0592}{2} \log \frac{[\text{H}_3\text{AsO}_3]}{[\text{H}_3\text{AsO}_4]} \end{aligned}$$

$$E' \approx E^\circ - 0.059\text{pH}$$

E^0 and the Equilibrium Constant



E° and the Equilibrium Constant



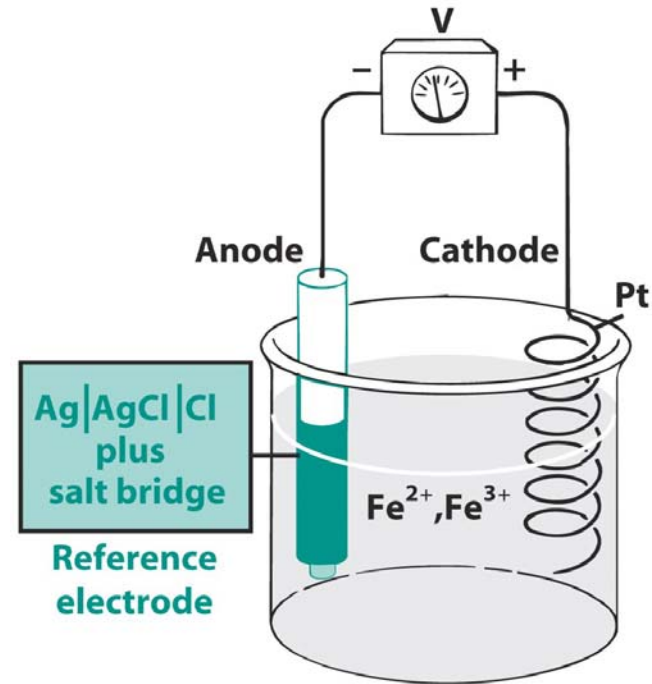
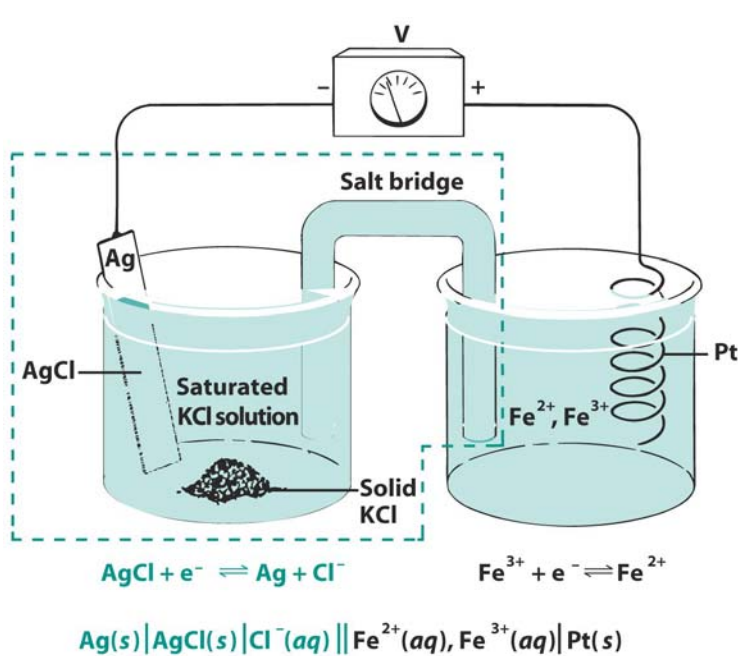
$$E_{\text{cell}} = E_+(E_{\text{Fe}^{3+}, \text{Fe}^{2+}}) - E_-(E_{\text{AgCl}, \text{Ag}}) > 0$$

$$\begin{aligned} &= \left(E^\circ_+ - \frac{0.059}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) \\ &\quad - \left(E^\circ_- - \frac{0.059}{n} \log [\text{Cl}^-] \right) \\ &= (E^\circ_+ - E^\circ_-) - \frac{0.059}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}][\text{Cl}^-]} \\ &= E^\circ - \frac{0.059}{n} \log Q \end{aligned}$$

Reference Electrodes

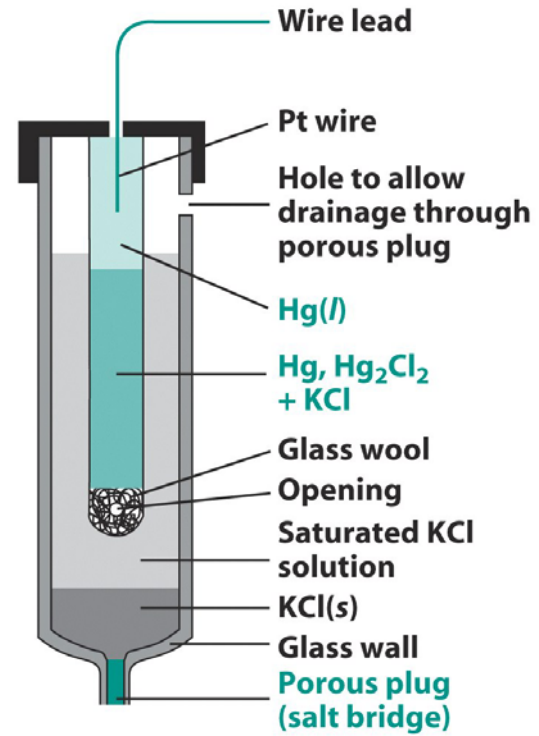
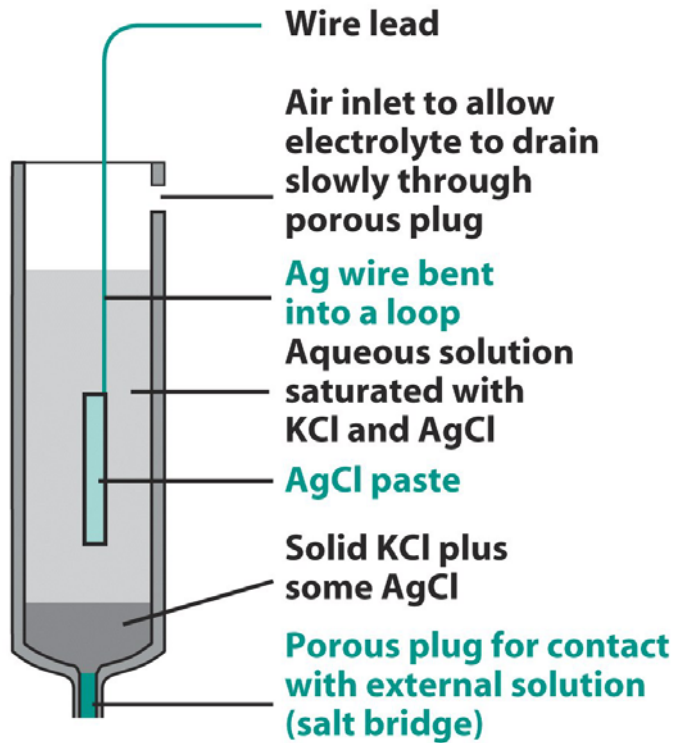
Indicator electrode: responds to analyte concentration

Reference electrode: maintains a fixed potential



$$E_{\text{cell}} = E_+ - E_- = \left(E^\circ_+ - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) - \left(E^\circ_- - 0.0592 \log [\text{Cl}^-] \right)$$

Reference Electrodes



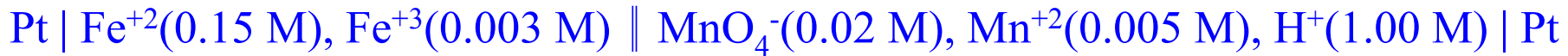
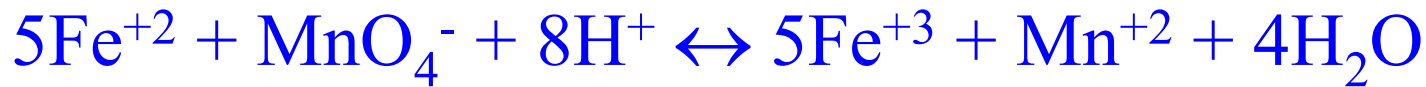
- Silver-Silver Chloride
- $\text{AgCl} + \text{e}^- \leftrightarrow \text{Ag(s)} + \text{Cl}^-$
 - $E^0 = 0.222 \text{ V}$
 - $E \text{ (saturated KCl)} = 0.197 \text{ V}$

- Calomel
 - $\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \leftrightarrow 2\text{Hg(l)} + 2\text{Cl}^-$
 - $E^0 = 0.268 \text{ V}$
 - $E \text{ (saturated KCl)} = 0.241 \text{ V}$
- saturated calomel electrode (S.C.E.)

Ex:

- One beaker contains a solution of 0.020 M KMnO_4 , 0.005 M MnSO_4 , and 0.500 M H_2SO_4 ; and a second beaker contains 0.150 M FeSO_4 and 0.0015 M $\text{Fe}_2(\text{SO}_4)_3$. The 2 beakers are connected by a salt bridge and Pt electrodes are placed one in each. The electrodes are connected via a wire with a voltmeter in between
- *What would be the potential of each half-cell (a) before reaction and (b) after reaction?*
- *What would be the measured cell voltage (c) at the start of the reaction and (d) after the reaction reaches eq.?*
- Assume H_2SO_4 to be completely ionized and equal volumes in each beaker.

Ans:



$$\begin{aligned} \text{(a)} \quad E_{\text{Fe}} &= E_{\text{Fe(III)/Fe(II)}}^{\circ} - (0.059/1) \log [\text{Fe}^{+2}]/[\text{Fe}^{+3}] \\ &= 0.771 - 0.059 \log (0.150)/(0.0015 \times 2) = 0.671 \text{ V} \end{aligned}$$

$$\begin{aligned} E_{\text{Mn}} &= E_{\text{MnO}_4^-/\text{Mn}^{+2}}^{\circ} - (0.059/5) \log [\text{Mn}^{+2}]/[\text{MnO}_4^-][\text{H}^+]^8 \\ &= 1.51 - 0.059/5 \log (0.005)/(0.02)(1.00)^8 = 1.52 \text{ V} \end{aligned}$$

(b) At eq., $E_{\text{Fe}} = E_{\text{Mn}}$, 可以含鐵之半反應來看，
先找出平衡時兩個鐵離子的濃度，得

$$E_{\text{Fe}} = 0.771 - 0.059 \log (0.05)/(0.103) = 0.790 \text{ V}$$

$$\text{(c)} \quad E_{\text{cell}} = E_{\text{Mn}} - E_{\text{Fe}} = 1.52 - 0.671 = 0.849 \text{ V}$$

(d) At eq., $E_{\text{Fe}} = E_{\text{Mn}}$, 所以 $E_{\text{cell}} = 0 \text{ V}$