EQUILIBRIUM ELECTROCHEMISTRY

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Electrochemical Cells

- **Electrochemical cell** - two electrodes in contact with an electrolyte
  - **Electrolyte** is an ionic conductor (solution, liquid, or solid)
  - **Electrode compartment** = electrode + electrolyte
  - If electrolytes are different compartments may be connect with salt bridge
  - Electrolyte solution in agar

- **Galvanic cell** - an electrochemical cell that produces electricity
- **Electrolytic cell -** an electrochemical cell in which a non-spontaneous reaction is driven by an external source of current

Types of Electrodes

`1. Metal/metal ion
   - Designation:$M(s)|M^+(aq)$
   - Redox couple: M^+ /M
   - Half reaction: $M^+(aq) + 1e^- \rightarrow M(s)$

2. Hidrogen (SHE)
   - Designation*:

     $Pt(s)|X_2(g)|X^+(aq)$ or $Pt(s)|X_2(g)|X^-(aq)$
   - Redox couple:

     X^+ /X_2 or X_2 / X^-
   - Half reaction:

     $X^+(aq) + 1e^- \rightarrow 1/2X_2(g)$ or $1/2X_2(g) + 1e^- \rightarrow X^-(aq)$

3. Metal/insoluble salt
   - Designation:$M(s)|MX(s)|X^-(aq)$
   - Redox couple: $MX /M,X^-$
   - Half reaction: $MX(s) + 1e^- \rightarrow M(s) + X^-(aq)$

4. Redoxs
   - Designation*: $Pt(s)| M^+(aq), M^{2+}(aq)$
   - Redox couple: M^+/M^{2+}
   - Half reaction: $M^{2+}(aq) + 1e^- \rightarrow M^+(aq)$

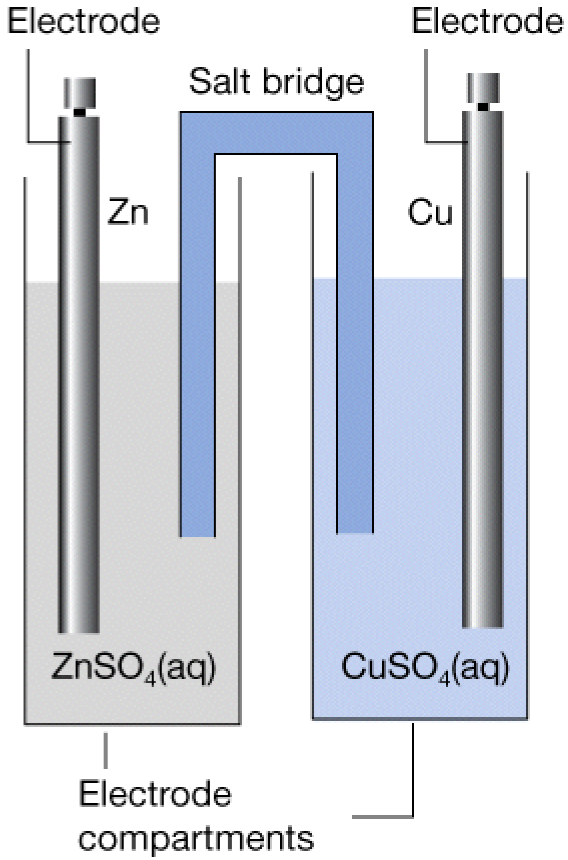
*Inert metal (Pt) source or sink of e^-

Electrochemical cells

- Liquid junction potential: due to the difference in the concentrations of electrolytes.

- The right-hand side electrochemical cell is often expressed as follows:
  $Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$

- The cathode reaction (copper ions being reduced to copper metal) is shown on the right. The double bar (||) represents the salt bridge that separates the two beakers, and the anode reaction is shown on the left: zinc metal is oxidized into zinc ions



Standard Potentials

- Since you can't measure the potential of a single electrode, one pair has been assigned, by convention a potential of 0
  - Standard hydrogen electrode (SHE):

$$\boxed{Pt(s)\,|\,H_2(g)\,|\,H^+(aq) \qquad E^{\emptyset} = 0}$$

- Other potentials determined by constructing cells in which SHE is left hand electrode:
  - Silver Chloride|Silver

$Pt(s)|H_2(g)|H^+(aq)||Cl^-(aq)|AgCl(s)|Ag \qquad E^{\emptyset}(AgCl, Ag, Cl^-)=+0.22V$

Reaction: $AgCl(s) + 1/2H_2(g) \rightarrow Ag(s) + H^+(aq) + Cl^-(aq)$

- Because all potentials are relative to the hydrogen electrode, the reaction is listed without the contribution of the SHE,

$$\mathbf{AgCl(s) \rightarrow Ag(s) + Cl^-(aq)}$$

Standard Reduction Potentials

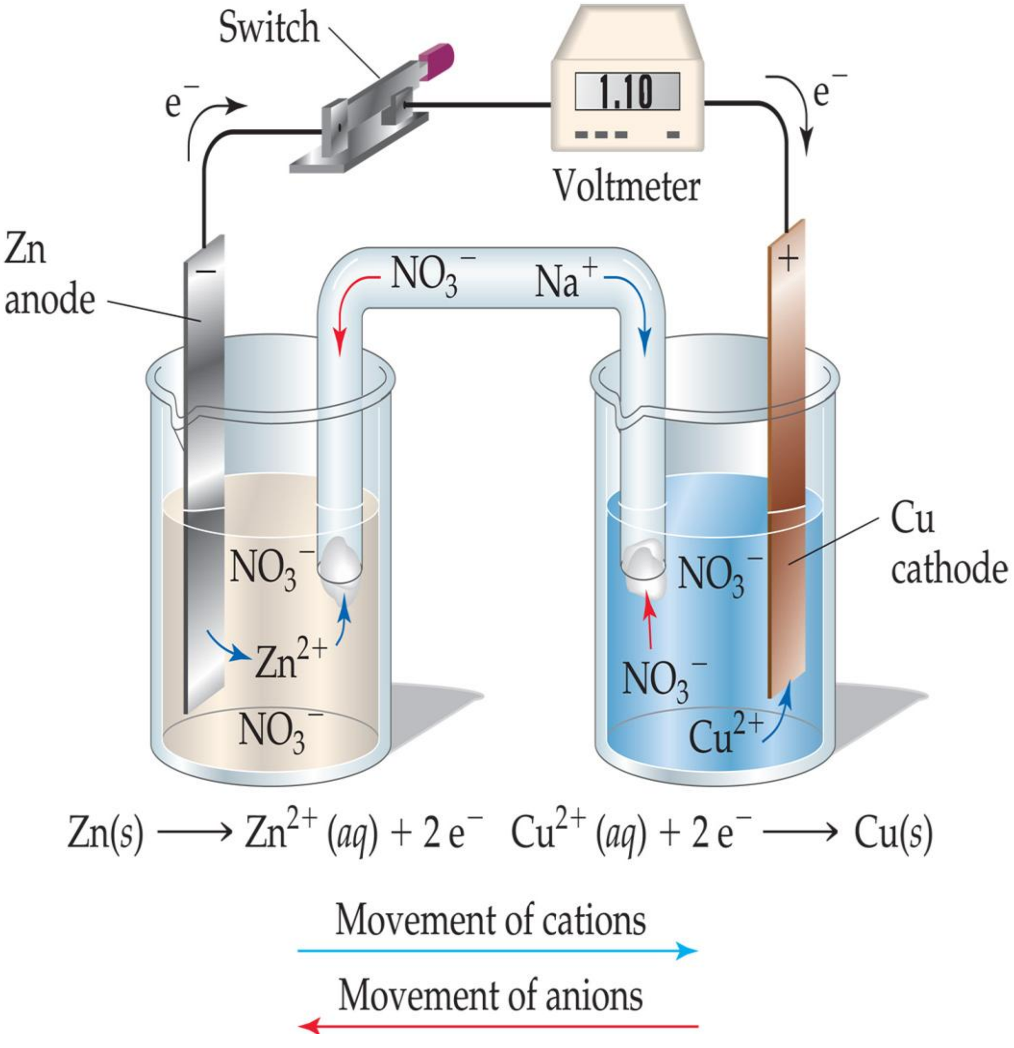
Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0 [defined]	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Reduction potentials for many electrodes have been measured and tabulated.

Voltaic Cells

- We can use that energy to do work if we make the electrons flow through an external device.
- We call such a setup a voltaic cell.

Voltaic Cells



- A typical cell looks like this.
- The oxidation occurs at the anode.
- The reduction occurs at the cathode.

Cell Potential and Free Energy

ΔG for a redox reaction can be found by using the equation

$$\Delta G = -nFE$$

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

where n is the number of moles of electrons transferred, and F is a constant, the Faraday.

1 F = 96,485 C/mol = 96,485 J/V-mol

Nernst Equation

Dividing both sides by $-nF$, we get the Nernst equation:

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

or, using base-10 logarithms,

$$E = E^{\circ} - \frac{2.303\,RT}{nF} \ln Q$$

Nernst Equation

At room temperature (298 K),

$$\frac{2.303\,RT}{F} = 0.0592\text{ V}$$

Thus the equation becomes

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

$$E_{sel} = E^{o}_{sel} - \frac{0,059}{n}\,\text{Log}\,\frac{(C)c\quad(D)d}{(A)a\quad(B)b}$$

Reaction Equilibrium

$\Delta G = 0, E = 0$

$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{(C)^c\ (D)^d}{(A)^a\ (B)^b}$$

$$\underset{\longleftarrow}{\longrightarrow}$$

$$\frac{PCL_5}{(PCL_3)(Cl_2)} = K_C$$

$$PCl_{3(g)} + Cl_{2(g)} \Leftrightarrow PCl_{5(g)}$$

$$K = \frac{[a_{oksidasi}]}{[a_{reduksi}]}$$

$$E_{sel} = E^o_{sel} - \frac{RT}{nF}\ln K$$

$$K = e^{\frac{nFE^o_{sel}}{RT}}$$

$$E^o_{sel} = \frac{RT}{nF}\ln K$$

$$E_{sel} = E^o_{sel} - \frac{0{,}059}{n}\ \text{Log}\ \frac{(C)^c\ (D)^d}{(A)^a\ (B)^b}$$

$$E^o_{sel} = \frac{0{,}059}{n}\ \text{Log}\ K$$

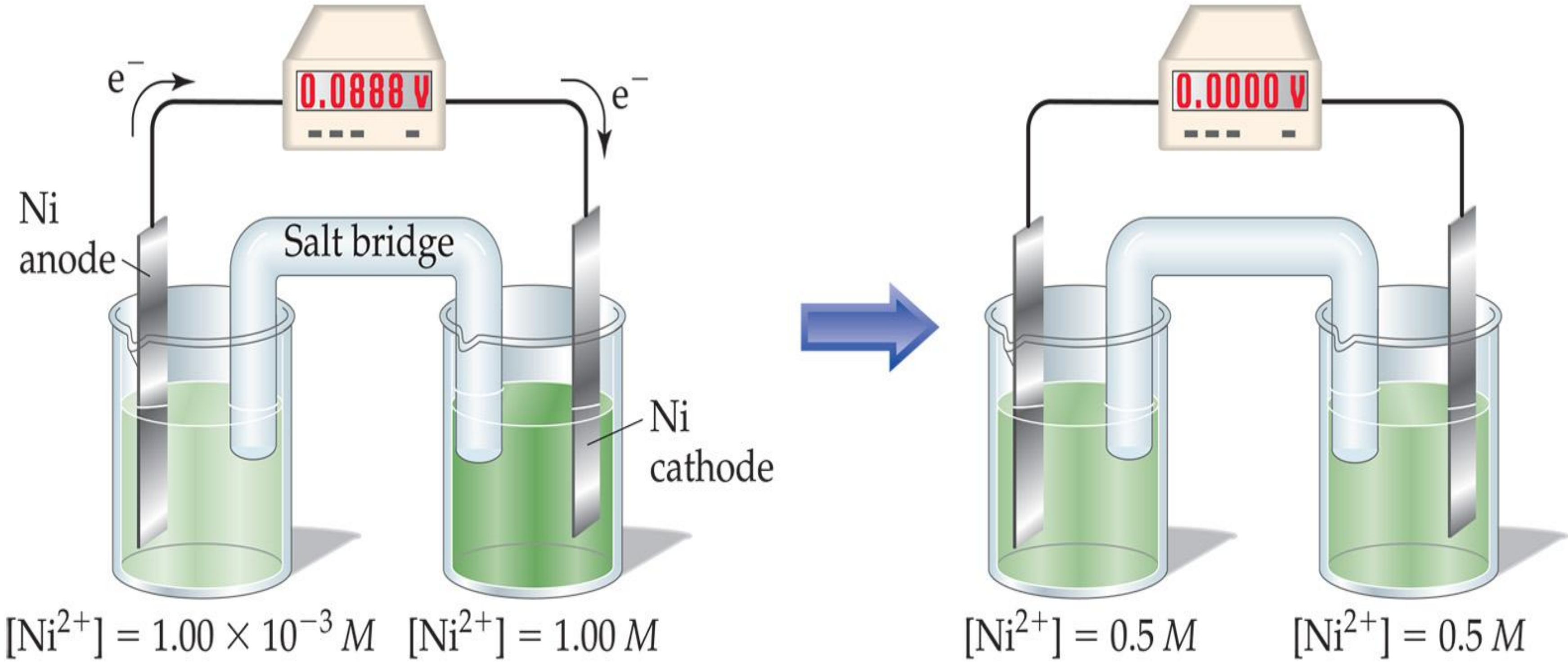
- At equilibrium, $\Delta G_{rxn} = 0$

$$\underbrace{\cancel{\Delta G_{rxn}}}_{0} = \Delta G^{o}_{rxn} + RT\ln(\underbrace{\cancel{Q}}_{K})$$

$$0 = \Delta G°_{rxn} + RT\ln(K)$$

$$\boxed{\Delta G°_{rxn} = -RT\ln(K)}$$

Concentration Cells



- Notice that the Nernst equation implies that a cell could be created that has the same substance at both electrodes.

Temperature Dependence of K

- We now have two definitions for $\Delta G°$

$$\Delta G°_{rxn} = -RT\ln(K) = \Delta H° - T\Delta S°$$

- Rearranging (dividing by -RT)

$$\ln(K) = \frac{-\Delta H°}{R}\left(\frac{1}{T}\right) + \frac{\Delta S°}{R}$$

$$y \quad = \quad m \quad x \quad + \quad b$$

- Plot of ln(K) vs 1/T is a straight line

T Dependence of K (cont.)

- we know the T dependence of K, we can predict K at another temperature:

$$\ln(K_2) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_2}\right) + \frac{\Delta S^\circ}{R} \quad - \quad \ln(K_1) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_1}\right) + \frac{\Delta S^\circ}{R}$$

$$\boxed{\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

the van't Hoff equation.

Determine pH

- Again concentration is replaced with activity

$$pH = -\log A_{H^+} = -\log [H^+]\gamma_{H^+}$$

pH = - log [H+] .

pH = - log aH+

$Pt \mid H_{2(g)} \mid H^{+}_{(H+)} \mid\mid H^{+}_{(std)} \mid H_{2(g)}$

$H^{+} + e^{-} = \frac{1}{2} H_{2(g)}$ $E^{o} = 0{,}0000$ V

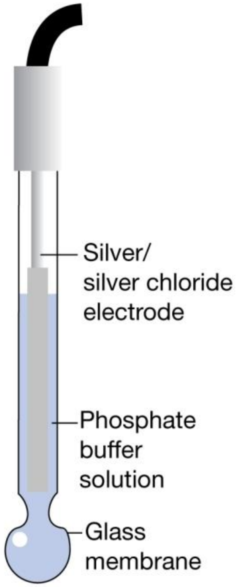
$$E_{sel} = E^{o}_{sel} - 0{,}0591 \log \frac{[oksidasi]}{[reduksi]}$$

$$E_{sel} = -0{,}059 \log \frac{(H^{+})}{(H^{+})_{std}}$$

pH and pKa

$$H^+(aq) + 1e^- \rightarrow \frac{1}{2} H_2(g) \qquad Q = \frac{\left(f_{H_2}/p^{\o}\right)^{0.5}}{a_{H^+}}$$

Glass Electrode



- For hydrogen electrode (1/2 reaction above), $E^{\o} = 0$
  - If $f_{H2} = p^{\o}$, $Q = 1/a_{H+}$ and $E = (RT/F)\ln(a_{H+})$
    - $E = E^{\o} - (RT/nF)\ln Q$
    - Converting ln to log (ln =2.303log), $E = (RT/F)\,2.303\log(a_{H+})$
    - Define $pH = -\log a_H$ so $E = -2.303(RT/F)pH$
      - At 25°C, E= -59.16mVpH
- Measurement
  - Direct method: hydrogen electrode + saturated calomel reference electrode (Hg_2Cl_2)
    - At 25°C, pH = (E + E(calomel))/ (-59.16mV)
  - Indirect method:
    - Replace hydrogen electrode with glass electrode sensitive to hydrogen activity (but not permeable to H^+
      - E(glass) α pH, E(glass) = 0 when pH = 7

pKa

- Since we learned pH = pKa when concentration of acid and conjugate base are equal pKa can be measured directly from pH measurement

- Ion-Selective electrodes - related to glass electrode except potentials sensitive to other species (see Box 10.2, p 278)

$Pb(s) \mid Pb^{2+}$ (jenuh, $PbCl_2$) $\mid\mid Pb^{2+}$ (0.05 M) $\mid Pb(s)$

Esel = 0.015 volt

oxsidation : $Pb(s) \rightarrow Pb^{2+}$ (jenuh, $PbCl_2$) + 2e E°sel = 0,13 V

Reduction : $Pb^{2+} + 2e \rightarrow Pb(s)$ E°sel = - 0,13 V

$$Esel = E°sel - \log \frac{(Pb^{2+} \text{ (jenuh, } PbCl_2))}{(Pb^{2+})}$$

$$0.015 = 0 - 0.0296 (\log a - \log 0.05)$$

$a = [Pb^{2+}] = 1.6 \times 10^{-2}$ M

$[Cl^-] = 2 [Pb^{2+}] = 3.2 \times 10^{-2}$ M

$Ksp = [Pb^{2+}][Cl^-]^2$

$= [1.6 \times 10^{-2}][3.2 \times 10^{-2}]^2$

$= 1.6 \times 10^{-5}$

THANK YOU