

# EQUILIBRIUM ELECTROCHEMISTRY

**NANIK DWI NURHAYATI, S.SI,M.SI**

- <http://nanikdn.staff.uns.ac.id>
- E-mail : nanikdn@uns.ac.id

# 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. Hydrogen (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:  $MX(s) + 1e^- \rightarrow M(s) + X^-(aq)$

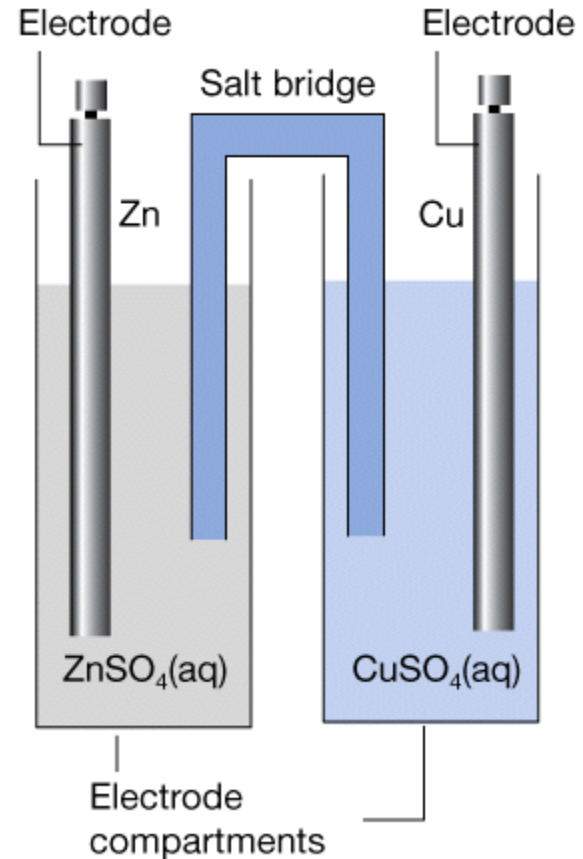
## 4. Redox

- 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  $e^-$

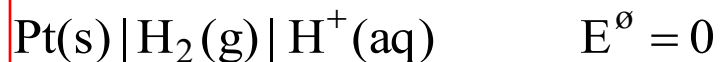
# Electrochemical cells

- Liquid junction potential: due to the difference in the concentrations of electrolytes.
- The right-hand side electrochemical cell is often expressed as follows:  
$$\text{Zn(s)}|\text{ZnSO}_4(\text{aq})||\text{CuSO}_4(\text{aq})|\text{Cu(s)}$$
- 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



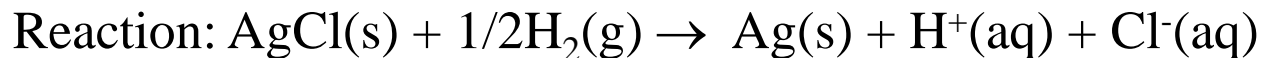
# Standard Potentials

- 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):



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

- » Silver Chloride|Silver



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



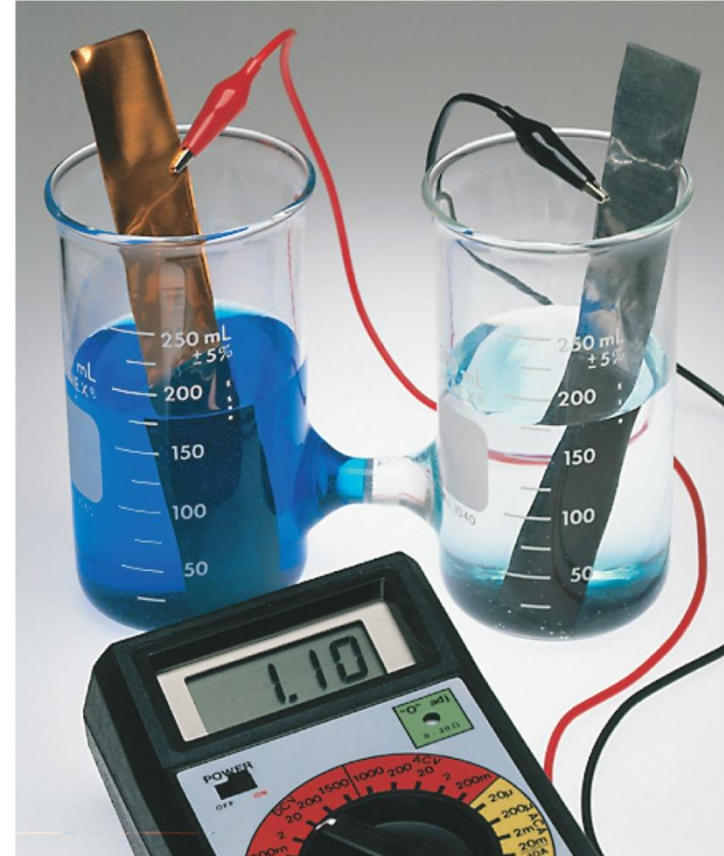
# Standard Reduction Potentials

Potential (V)	Reduction Half-Reaction
+2.87	$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$
+1.51	$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$
+1.36	$\text{Cl}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$
+1.23	$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$
+1.06	$\text{Br}_2(\text{l}) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(\text{aq})$
+0.96	$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \longrightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$
+0.80	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$
+0.77	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$
+0.68	$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$
+0.59	$\text{MnO}_4^-(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 3 \text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4 \text{OH}^-(\text{aq})$
+0.54	$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$
+0.40	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$
+0.34	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(\text{s})$
0 [defined]	$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$
-0.28	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ni}(\text{s})$
-0.44	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$
-0.76	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$
-0.83	$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$
-1.66	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$
-2.71	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$
-3.05	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$

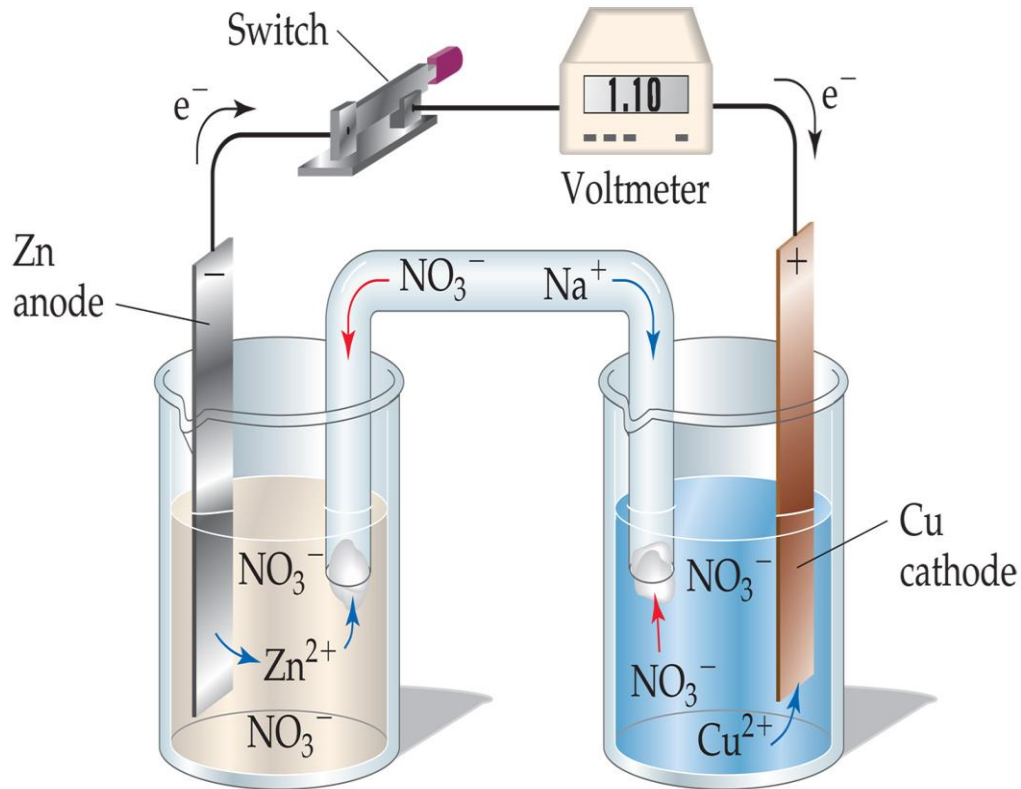
Reduction potentials for many electrodes have been measured and tabulated.

# Voltaic Cells

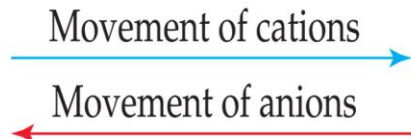
- We can use that energy to do work if we make the electrons flow through an external device.
- We call such a setup a **voltaic cell**.



# 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

$\Delta G$  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.

$$1 F = 96,485 \text{ C/mol} = 96,485 \text{ J/V-mol}$$

# 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),

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

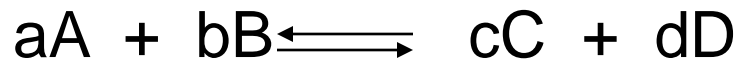
Thus the equation becomes

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

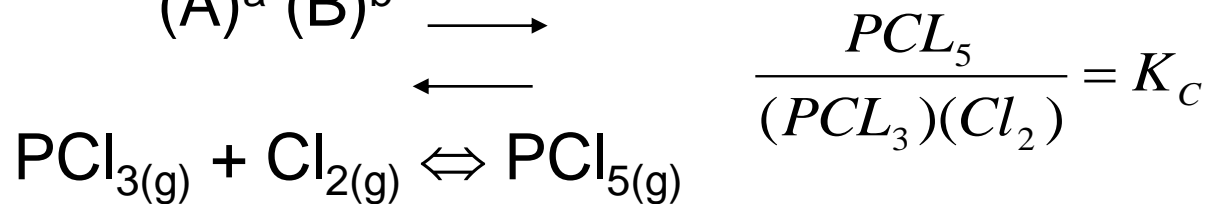
$$E_{\text{sel}} = E^{\circ}_{\text{sel}} - \frac{0,059}{n} \text{Log} \frac{(C)c}{(A)a} \frac{(D)d}{(B)b}$$

# Reaction Equilibrium

$$\Delta G = 0, E = 0$$



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



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

$$E_{sel}^o = \frac{RT}{nF} \ln K$$

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

$$K = e^{\frac{nFE_{sel}^o}{RT}}$$

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

$$E_{sel}^o = \frac{0,059}{n} \text{Log} K$$

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

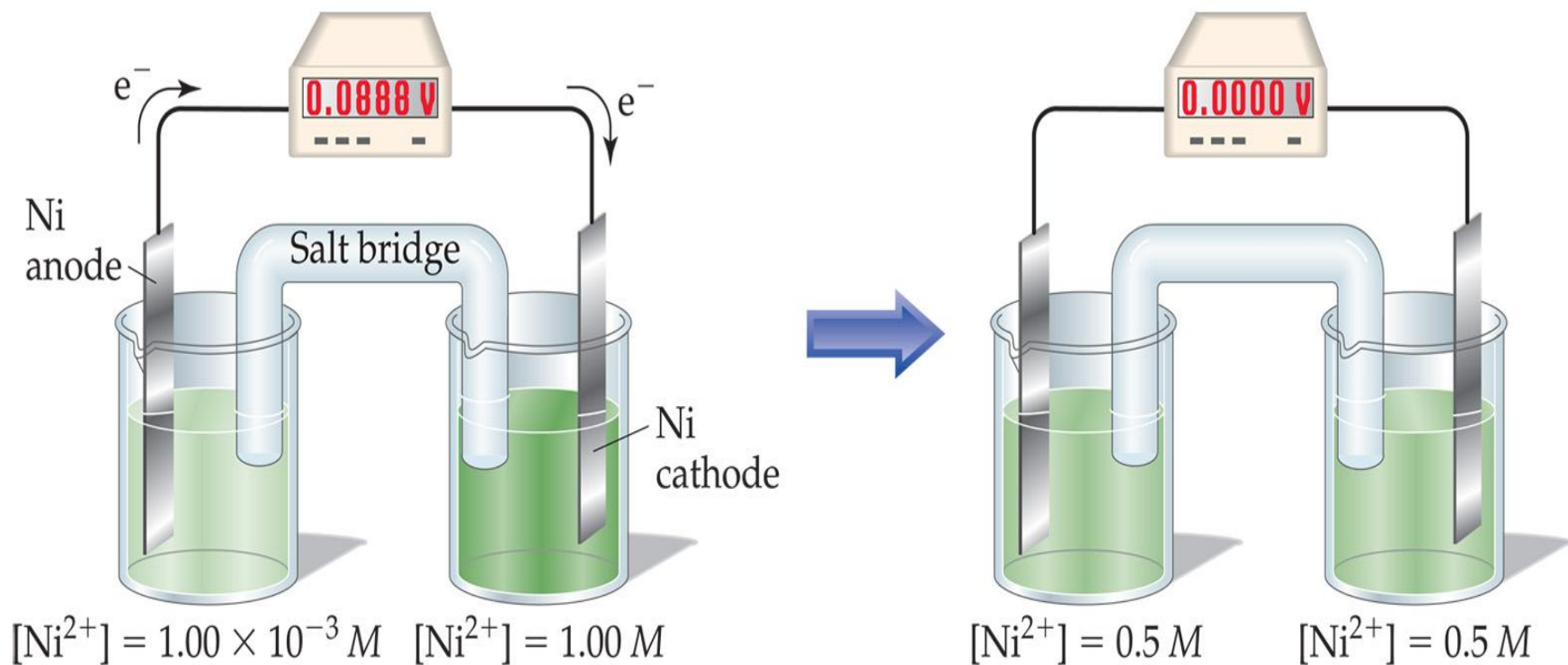
$$\cancel{0} \Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^{\circ} + RT \ln(\cancel{Q})$$

K

$$0 = \Delta G_{\text{rxn}}^{\circ} + RT \ln(K)$$

$$\Delta G_{\text{rxn}}^{\circ} = -RT \ln(K)$$

# 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  $\Delta G^\circ$

$$\Delta G^\circ_{\text{rxn}} = -RT \ln(K) = \Delta H^\circ - T\Delta S^\circ$$

- Rearranging (dividing by  $-RT$ )

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

$$y = m x + b$$

- 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:

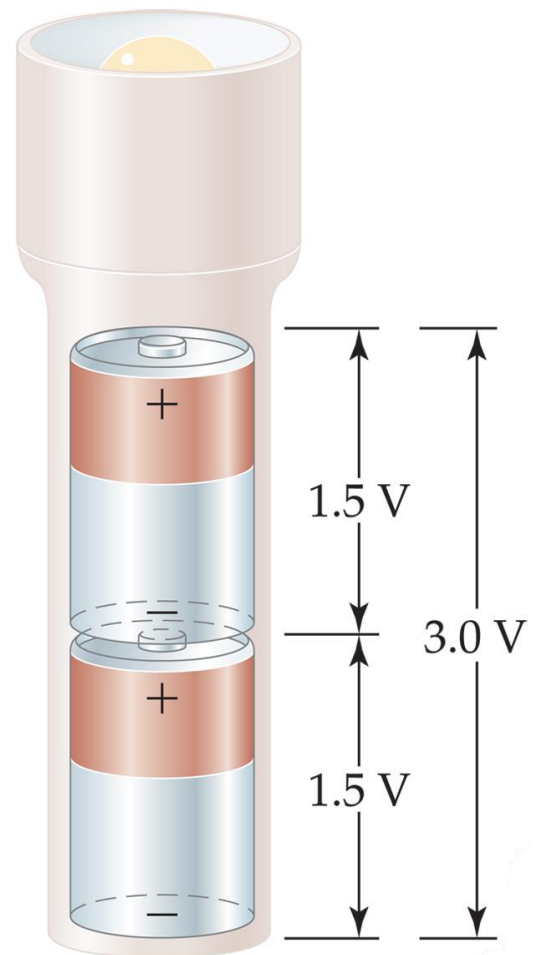
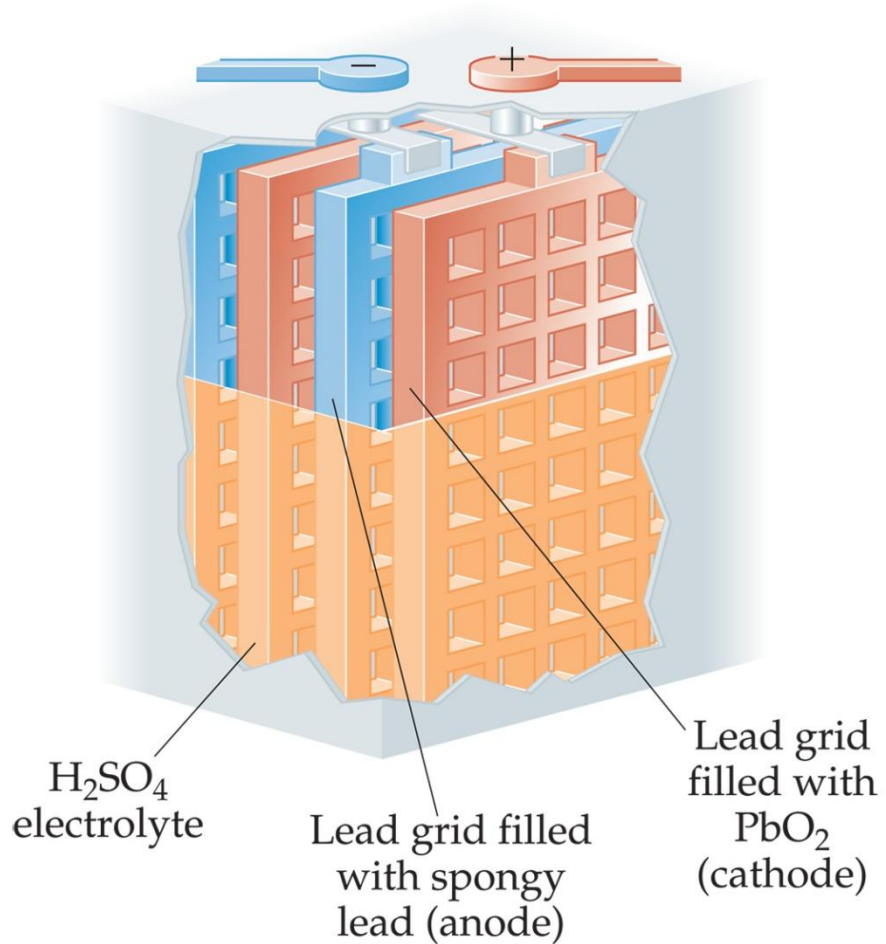
$$\ln(K_2) = \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} \right) + \frac{\Delta S^\circ}{R} \quad - \quad \ln(K_1) = \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_1} \right) + \frac{\Delta S^\circ}{R}$$

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

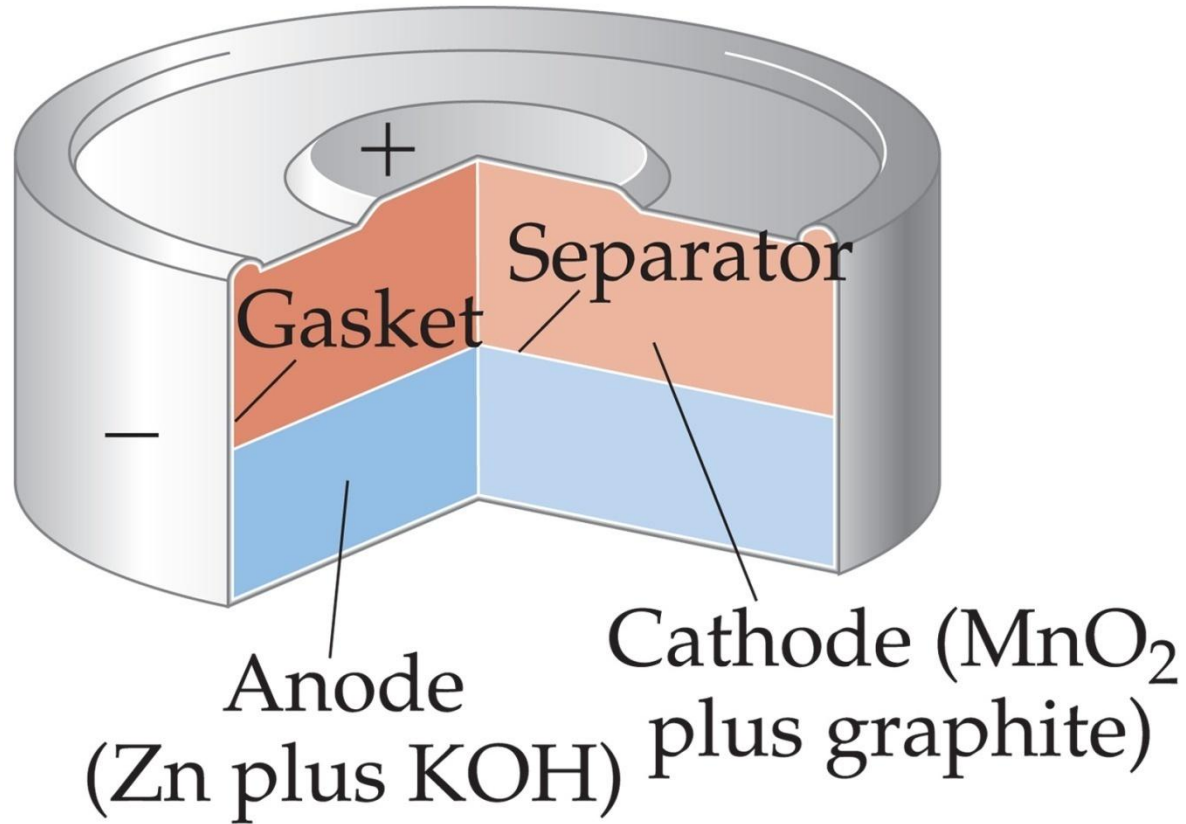
the van't Hoff equation.



# Applications of Oxidation-Reduction Reactions Batteries



# Alkaline Batteries



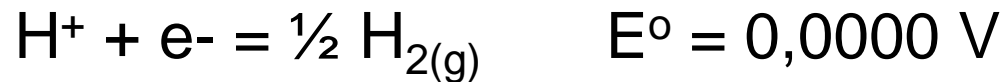
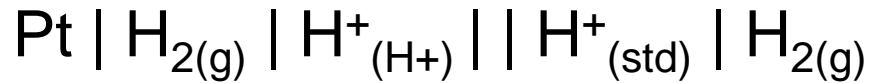
# Determine pH

- Again concentration is replaced with activity

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

$$\text{pH} = -\log [\text{H}^+] \quad .$$

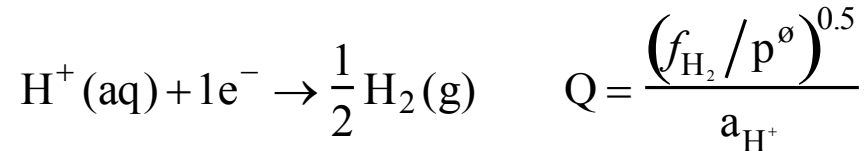
$$\text{pH} = -\log a_{\text{H}^+}$$



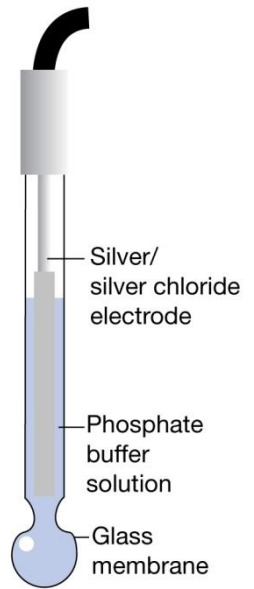
$$E_{\text{sel}} = E^\circ_{\text{sel}} - 0,0591 \log \frac{[\textit{oksidasi}]}{[\textit{reduksi}]}$$

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

# pH and pKa



*Glass Electrode*



- For hydrogen electrode (1/2 reaction above),  $E^\ominus = 0$

- If  $f_{\text{H}_2} = p^\ominus$ ,  $Q = 1/a_{\text{H}^+}$  and  $E = (RT/F) \ln(a_{\text{H}^+})$ 
  - $E = E^\ominus - (RT/nF) \ln Q$
  - Converting ln to log ( $\ln = 2.303 \log$ ),  $E = (RT/F) 2.303 \log(a_{\text{H}^+})$
  - Define  $\text{pH} = -\log a_{\text{H}^+}$  so  $E = -2.303(RT/F) \text{pH}$ 
    - At 25°C,  $E = -59.16 \text{mVpH}$

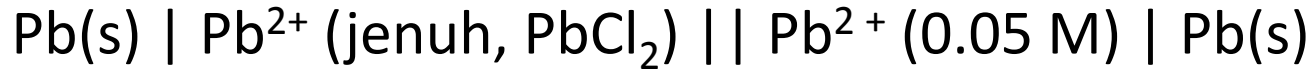
## Measurement

- Direct method: hydrogen electrode + saturated calomel reference electrode ( $\text{Hg}_2\text{Cl}_2$ )
  - At 25°C,  $\text{pH} = (E + E(\text{calomel})) / (-59.16 \text{mV})$
- Indirect method:
  - Replace hydrogen electrode with glass electrode sensitive to hydrogen activity (but not permeable to  $\text{H}^+$ )
    - $E(\text{glass}) \propto \text{pH}$ ,  $E(\text{glass}) = 0$  when  $\text{pH} = 7$

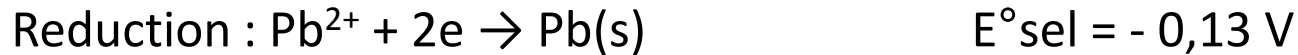
## pKa

- Since we learned  $\text{pH} = \text{pKa}$  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)



$$E_{\text{sel}} = 0.015 \text{ volt}$$



$$E_{\text{sel}} = E^{\circ}_{\text{sel}} - \frac{\log (\text{Pb}^{2+} (\text{jenuh, PbCl}_2) )}{(\text{Pb}^{2+})}$$

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

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

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

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

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

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

**THANK YOU**