

## **3. Potentials and thermodynamics**

### **Learning subject**

1. Electrochemical reaction
2. Thermodynamics and potential
3. Nernst equation

### **Learning objective**

1. To set up electrochemical reaction
2. Understanding relation between thermodynamics and potential
3. Understanding the Nernst equation

# 1. Electrochemical reaction

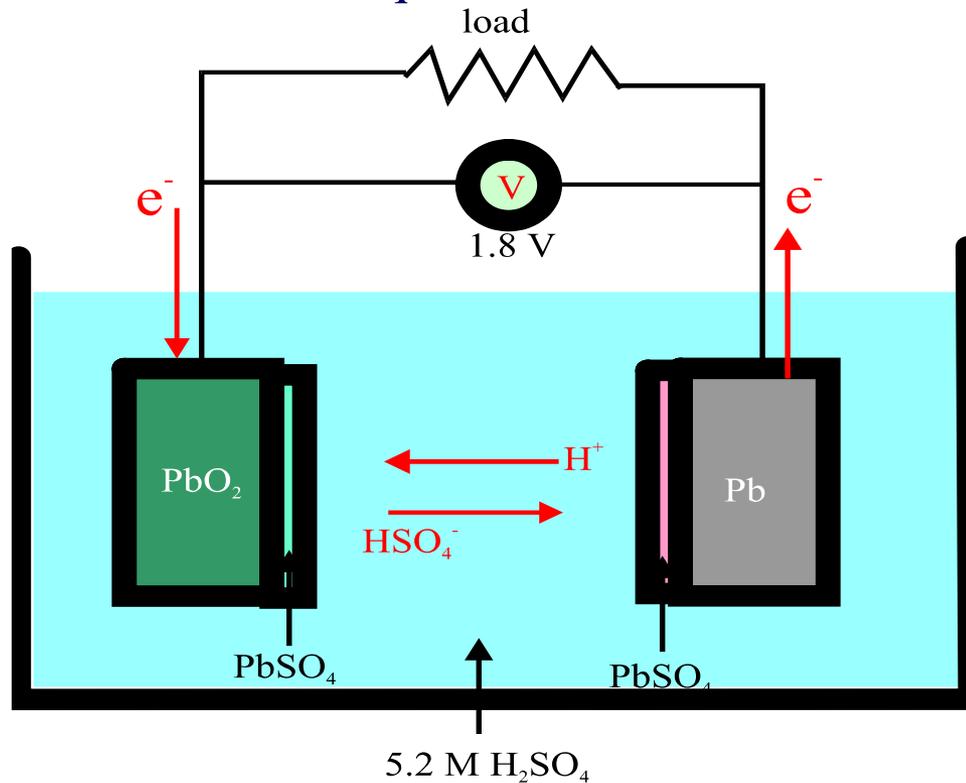
**Cell voltage (E):** electric potential difference between the two electronic conductors

**Measurement of E:** voltmeter

e.g., lead/acid cell (car battery)

**Electronic conductors:**  $\text{PbO}_2$ ,  $\text{Pb}$

**Ionic conductor:** concentrated aqueous solution of sulfuric acid



## Electrochemical reaction



Right-hand electrode: electrons produced: oxidation, “anode”

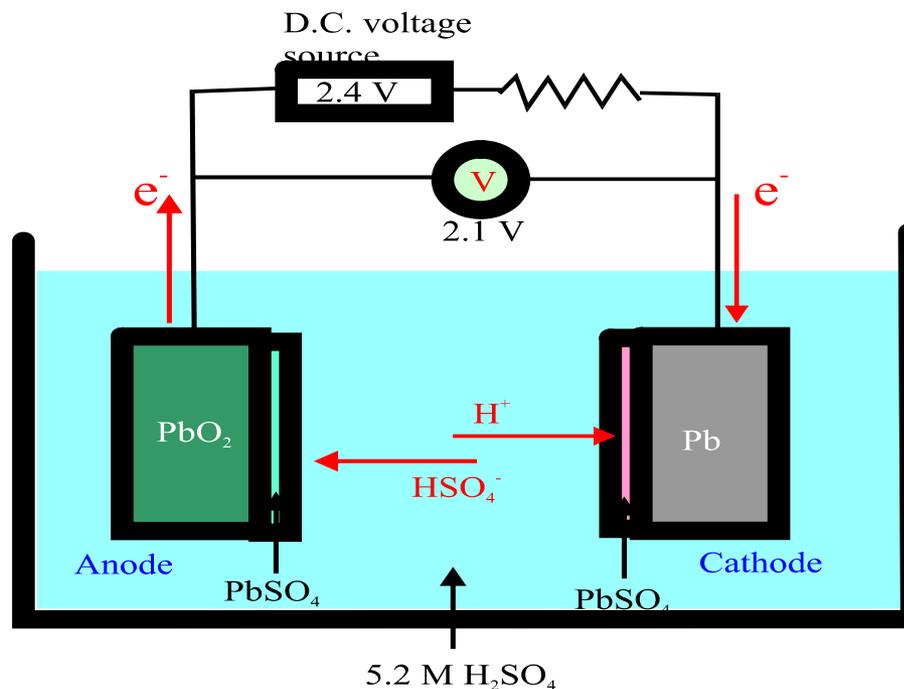
Left-hand electrode: electrons consumed; reduction, “cathode”

Energy is delivered by the cell into the load; ex) car: starting engine, lighting lamps

Galvanic cell: a cell which provides energy in this way, “discharge”

2.0 V without current flow, 1.8 V with current flow (load); “polarization”; voltages decrease in magnitude when energy is taken from them. the effect becomes greater if the current is increased.

“**charge**”: current flow in the opposite direction by using an external source (ex. Battery); Electrolytic cell; opposite direction to its spontaneous motion  
PbO<sub>2</sub> : anode, Pb: cathode



2.0 V; perfect balance between the applied and cell voltages, no current flow → equilibrium cell voltage or reversible cell voltage or null voltage or rest voltage or “open-circuit voltage”(since no current flows, it makes no difference if the circuit is interrupted, as by opening the switch)

## Types of electrochemical cells

(i) Galvanic cell: reactions occur spontaneously at the electrodes when they are connected externally by a conductor. Converting chemical energy into electrical energy. e.g., primary battery, secondary battery (discharging), fuel cell

(ii) Electrolytic cell: reactions are effected by an external voltage. Electrical energy to chemical reactions. e.g., electrolytic syntheses, electrorefining (e.g., copper), electroplating, secondary battery (charging)

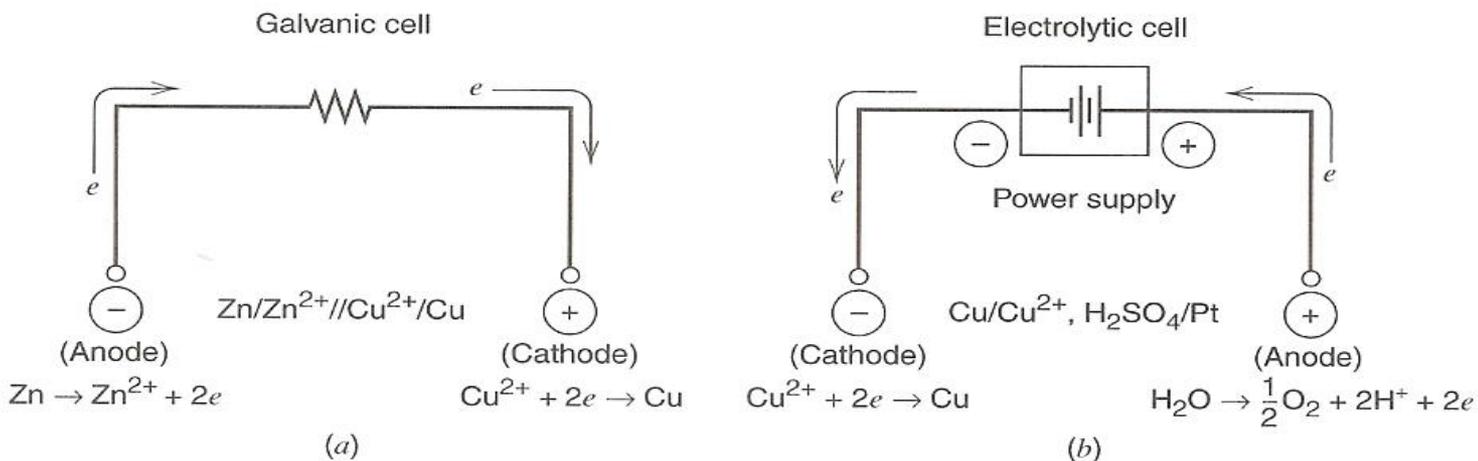
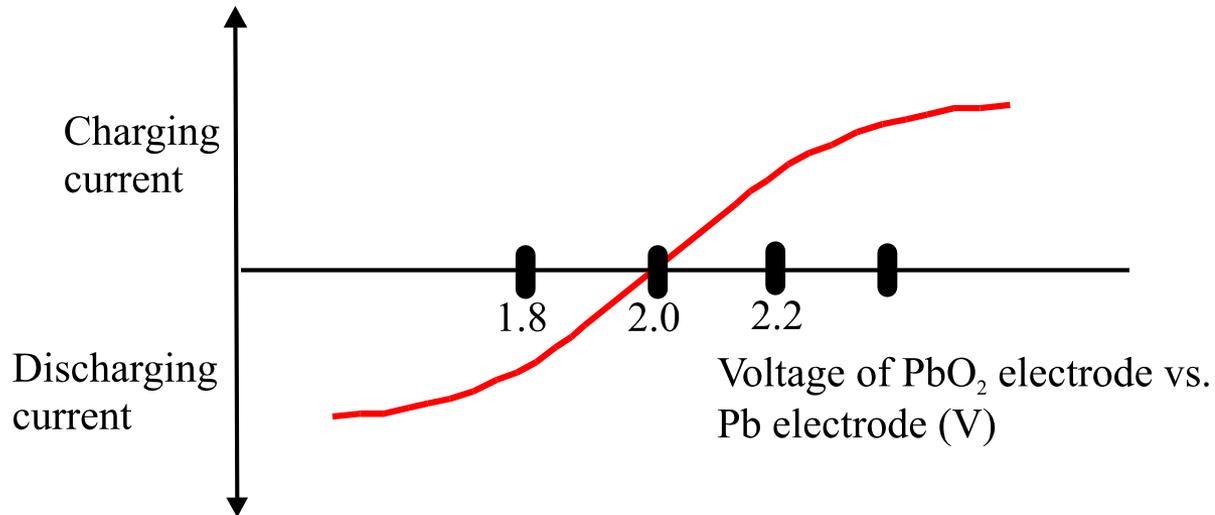


Figure 1.3.1 (a) Galvanic and (b) electrolytic cells.

## Voltammogram

Plot of cell currents versus the cell voltages (volt + am(pere) + mogram)



Not linear → electrochemical cells do not obey Ohm's law

Notation of the structure of cells



/: phase boundary, “,” or : two components in the same phase,

//: liquid junction (a salt bridge)

left: oxidation (anode), right: reduction(cathode)

## 2. Thermodynamics and potential

Why is it that chemical reactions in electrochemical cells proceed spontaneously in one direction and furnish current?

(thermodynamics: equilibrium, kinetics: reaction rate)

:

**Cell potential** of an electrochemical cell

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

or  $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

Gibbs free energy,  $\Delta G = -nFE_{\text{cell}}$

$\Delta G < 0 \rightarrow$  spontaneous

$$E^0: \text{standard electrode potential} = E_{\text{right}}^0 - E_{\text{left}}^0$$

$E_{\text{right}}^0, E_{\text{left}}^0$ ,: standard electrode potential of half reactions expresses as reductions vs. NHE(normal hydrogen electrode) with all species at unit activity ( $a_i = 1$ )

(see the Table of Standard Potentials)

## Basic electrochemical thermodynamics

**Reversibility:** thermodynamically important

(a) Chemical reversibility

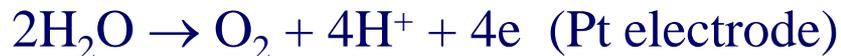


Reversing the cell  $\rightarrow$  reversed cell reaction “chemically reversible”



Discharging the cell:  $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2$  (hydrogen evolution)

Reversing the cell:



$\rightarrow$  “chemically irreversible”

(b) Thermodynamic reversibility: an infinitesimal reversal

Chemically reversible  $\rightarrow$  thermodynamically reversible or not

(c) Practical reversibility

- Actual process at finite rate → depends on the time domain
- In electrochemistry, following **Nernst equation (linkage E and concentrations)**



$$E = E^{0'} + (RT/nF)\ln(C_O/C_R)$$

→ electrochemically (or nernstian) reversible

## Reversibility & Gibbs free energy

Reversible: net work from the cell =  $\Delta G$

Irreversible: net work from the cell <  $\Delta G$

## Free energy & cell potential



Discharge the cell through  $R = \infty$  (zero current)  $\rightarrow$  reversible

$\rightarrow \Delta E$  (potential difference) is the equilibrium value (open-circuit)



Positive  $E_{\text{rxn}}$  (spontaneous reaction))

$$\Delta G = -nFE_{\text{rxn}}$$

When all substances are at unit activity,  $\Delta G^0 = -nFE_{\text{rxn}}^0$

$E_{\text{rxn}}^0$ : standard potential of the cell reaction

$$\Delta S = -(\partial\Delta G/\partial T)_p = nF(\partial E_{\text{rxn}}/\partial T)_p$$

$$\Delta H = \Delta G + T\Delta S = nF[T(\partial E_{\text{rxn}}/\partial T)_p - E_{\text{rxn}}]$$

$$RT\ln K_{\text{rxn}} = -\Delta G^0 = nFE_{\text{rxn}}^0$$

## Half-reactions & reduction potentials

Half-reaction potential to a standard reference electrode

- NHE (normal hydrogen electrode) or SHE (standard)



$E = 0 \text{ V}$  at all temperatures



See standard electrode potentials for the reduction in any book!

### 3. Nernst equation

#### E obtained from the Nernst equation



$$E_{\text{cell}} = E^0 - (RT/nF)\ln[(a_Q^q a_R^r \dots)/(a_O^o a_P^p \dots)]$$

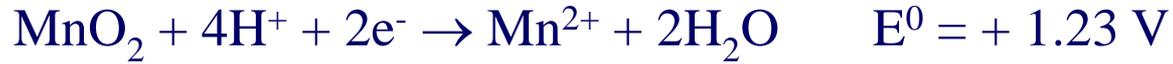
a: activity

activity term: minor contribution to the cell voltage

**activity (a)** → concentration (c);  $a = \gamma c$ ,  $\gamma$ ; activity coefficient

$a_i \cong 1$  (solvent, pure solid, ideal solution)

Example:



$$E = E^0 - (RT/2F)\ln[(a_{\text{H}^+})^4/a_{\text{Mn}^{2+}}], \quad a_{\text{MnO}_2}, a_{\text{H}_2\text{O}} = \text{unity}$$

$$\Delta G = -nFE$$

$$\text{cf. } RT/2F = [(8.314 \text{ JK}^{-1}\text{mol}^{-1})(298 \text{ K})/2(96485 \text{ JV}^{-1}\text{mol}^{-1})] = 0.01285 \text{ V}$$

## Cell potential & concentration

Consider  $v_{\text{H}_2} + v_{\text{O}}\text{O} \rightarrow v_{\text{R}}\text{R} + v_{\text{H}^+}\text{H}^+$

$$\Delta G = \Delta G^0 + RT \ln(a_{\text{R}}^{v_{\text{R}}} a_{\text{H}^+}^{v_{\text{H}^+}} / a_{\text{O}}^{v_{\text{O}}} a_{\text{H}_2}^{v_{\text{H}_2}})$$

a: activity ( $a_{\text{H}^+} = a_{\text{H}_2} = 1$ ),  $\Delta G = -nFE$  &  $\Delta G^0 = -nFE^0$

### Nernst equation

$$E = E^0 - (RT/nF) \ln(a_{\text{R}}^{v_{\text{R}}} a_{\text{H}^+}^{v_{\text{H}^+}} / a_{\text{O}}^{v_{\text{O}}} a_{\text{H}_2}^{v_{\text{H}_2}}) = E^0 + (RT/nF) \ln(a_{\text{O}}^{v_{\text{O}}} / a_{\text{R}}^{v_{\text{R}}})$$

$$E_{\text{rxn}} = E_{\text{right}} - E_{\text{left}} > 0 \text{ (spontaneous reaction)}$$

## Formal potential

Activity  $a = \gamma[A]$ ,  $\gamma$ : activity coefficient  $\rightarrow$  inconvenient to use activity due to unknown activity

$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} - \frac{RT}{nF} \ln \frac{[R]}{[O]}$$

$$E = E^{0'} - \frac{RT}{nF} \ln \frac{[R]}{[O]}$$

$E^{0'}$  : formal potential

- Ionic strength  $\rightarrow$  effect on activity coefficient  $\rightarrow$  formal potential is different from that in each medium  $\rightarrow$  standard potential: from ionic strength to extrapolate to zero ionic strength

**Selected Standard Electrode Potentials in Aqueous Solutions at 25° in V vs. NHE<sup>a</sup>**

Reaction	Potential, V
$\text{Ag}^+ + e = \text{Ag}$	0.7996
$\text{AgBr} + e = \text{Ag} + \text{Br}^-$	0.0713
$\text{AgCl} + e = \text{Ag} + \text{Cl}^-$	0.2223
$\text{AgI} + e = \text{Ag} + \text{I}^-$	-0.1519
$\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2e = 2\text{Ag} + 2\text{OH}^-$	0.342
$\text{Al}^{3+} + 3e = \text{Al}(0.1\text{ M NaOH})$	-1.706
$\text{Au}^+ + e = \text{Au}$	1.68
$\text{Au}^{3+} + 2e = \text{Au}^+$	1.29
$p\text{-benzoquinone} + 2\text{H}^+ + 2e = \text{hydroquinone}$	0.6992
$\text{Br}_2(aq) + 2e = 2\text{Br}^-$	1.087
$\text{Ca}^{2+} + 2e = \text{Ca}$	-2.76
$\text{Cd}^{2+} + 2e = \text{Cd}$	-0.4026
$\text{Cd}^{2+} + 2e = \text{Cd(Hg)}$	-0.3521
$\text{Ce}^{4+} + e = \text{Ce}^{3+}(1\text{ M H}_2\text{SO}_4)$	1.44
$\text{Cl}_2(g) + 2e = 2\text{Cl}^-$	1.3583
$\text{HClO} + \text{H}^+ + e = \frac{1}{2}\text{Cl}_2 + \text{H}_2\text{O}$	1.63

**Table C.1—(continued)**

Reaction	Potential, V
$\text{Sn}^{4+} + 2e = \text{Sn}^{2+}$	0.15
$\text{Tl}^+ + e = \text{Tl}$	-0.3363
$\text{Tl}^+ + e = \text{Tl}(\text{Hg})$	-0.3338
$\text{Tl}^{3+} + 2e = \text{Tl}^+$	1.247
$\text{U}^{3+} + 3e = \text{U}$	-1.8
$\text{U}^{4+} + e = \text{U}^{3+}$	-0.61
$\text{UO}_2^+ + 4\text{H}^+ + e = \text{U}^{4+} + 2\text{H}_2\text{O}$	0.62
$\text{UO}_2^{2+} + e = \text{UO}_2^+$	0.062
$\text{V}^{2+} + 2e = \text{V}$	-1.2
$\text{V}^{3+} + e = \text{V}^{2+}$	-0.255
$\text{VO}^{2+} + 2\text{H}^+ + e = \text{V}^{3+} + \text{H}_2\text{O}$	0.337
$\text{VO}_2^+ + 2\text{H}^+ + e = \text{VO}^{2+} + \text{H}_2\text{O}$	1.00
$\text{Zn}^{2+} + 2e = \text{Zn}$	-0.7628
$\text{ZnO}_2^{2-} + 2\text{H}_2\text{O} + 2e = \text{Zn} + 4\text{OH}^-$	-1.216

Table C.1—(continued)

Reaction	Potential, V
$\text{Co}^{2+} + 2e = \text{Co}$	-0.28
$\text{Co}^{3+} + e = \text{Co}^{2+} (3 M \text{HNO}_3)$	1.842
$\text{Cr}^{2+} + 2e = \text{Cr}$	-0.557
$\text{Cr}^{3+} + e = \text{Cr}^{2+}$	-0.41
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$\text{Cu}^+ + e = \text{Cu}$	0.522
$\text{Cu}^{2+} + 2\text{CN}^- + e = \text{Cu}(\text{CN})_2^-$	1.12
$\text{Cu}^{2+} + e = \text{Cu}^+$	0.158
$\text{Cu}^{2+} + 2e = \text{Cu}$	0.3402
$\text{Cu}^{2+} + 2e = \text{Cu}(\text{Hg})$	0.345
$\text{Eu}^{3+} + e = \text{Eu}^{2+}$	-0.43
$\frac{1}{2}\text{F}_2 + \text{H}^+ + e = \text{HF}$	3.03
$\text{Fe}^{2+} + 2e = \text{Fe}$	-0.409
$\text{Fe}^{3+} + e = \text{Fe}^{2+} (1 M \text{HCl})$	0.770
$\text{Fe}(\text{CN})_6^{3-} + e = \text{Fe}(\text{CN})_6^{4-} (1 M \text{H}_2\text{SO}_4)$	0.69
$2\text{H}^+ + 2e = \text{H}_2$	0.0000
$2\text{H}_2\text{O} + 2e = \text{H}_2 + 2\text{OH}^-$	-0.8277
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e = 2\text{H}_2\text{O}$	1.776
$2\text{Hg}_2^{2+} + 2e = \text{Hg}_2^{2+}$	0.905
$\text{Hg}_2^{2+} + 2e = 2\text{Hg}$	0.7961
$\text{Hg}_2\text{Cl}_2 + 2e = 2\text{Hg} + 2\text{Cl}^-$	0.2682
$\text{Hg}_2\text{Cl}_2 + 2e = 2\text{Hg} + 2\text{Cl}^- (\text{sat'd. KCl})$	0.2415
$\text{HgO} + \text{H}_2\text{O} + 2e = \text{Hg} + 2\text{OH}^-$	0.0984
$\text{Hg}_2\text{SO}_4 + 2e = 2\text{Hg} + \text{SO}_4^{2-}$	0.6158
$\text{I}_2 + 2e = 2\text{I}^-$	0.535
$\text{I}_3^- + 2e = 3\text{I}^-$	0.5338
$\text{K}^+ + e = \text{K}$	-2.924
$\text{Li}^+ + e = \text{Li}$	-3.045
$\text{Mg}^{2+} + 2e = \text{Mg}$	-2.375
$\text{Mn}^{2+} + 2e = \text{Mn}$	-1.029
$\text{Mn}^{3+} + e = \text{Mn}^{2+}$	1.51
$\text{MnO}_2 + 4\text{H}^+ + 2e = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.208
$\text{MnO}_4^- + 8\text{H}^+ + 5e = \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.491
$\text{Na}^+ + e = \text{Na}$	-2.7109
$\text{Ni}^{2+} + 2e = \text{Ni}$	-0.23
$\text{Ni}(\text{OH})_2 + 2e = \text{Ni} + 2\text{OH}^-$	-0.66
$\text{O}_2 + 2\text{H}^+ + 2e = \text{H}_2\text{O}_2$	0.682
$\text{O}_2 + 4\text{H}^+ + 4e = 2\text{H}_2\text{O}$	1.229
$\text{O}_2 + 2\text{H}_2\text{O} + 4e = 4\text{OH}^-$	0.401
$\text{O}_3 + 2\text{H}^+ + 2e = \text{O}_2 + \text{H}_2\text{O}$	2.07
$\text{Pb}^{2+} + 2e = \text{Pb}$	-0.1263
$\text{Pb}^{2+} + 2e = \text{Pb}(\text{Hg})$	-0.1205
$\text{PbO}_2 + 4\text{H}^+ + 2e = \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.46
$\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e = \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.685
$\text{PbSO}_4 + 2e = \text{Pb} + \text{SO}_4^{2-}$	-0.356
$\text{Pd}^{2+} + 2e = \text{Pd}$	0.83
$\text{Pt}^{2+} + 2e = \text{Pt}$	~1.2
$\text{PtCl}_4^{2-} + 2e = \text{Pt} + 4\text{Cl}^-$	0.73
$\text{PtCl}_6^{2-} + 2e = \text{PtCl}_4^{2-} + 2\text{Cl}^-$	0.74
$\text{S} + 2e = \text{S}^{2-}$	-0.508
$\text{Sn}^{2+} + 2e = \text{Sn}$	-0.1364

## Example: Zn/Zn<sup>2+</sup>(aq), Cu<sup>2+</sup>(aq)/Cu



$$E_{\text{cell}}^0 = +0.34 - (-0.76) = +1.10 \text{ V}$$

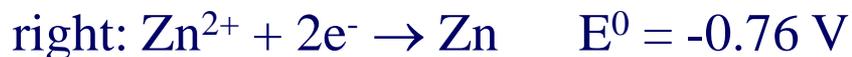
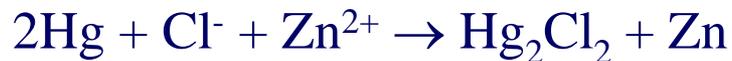
$$\Delta\Delta G^0 = -2 \times 1.10(\text{V}) \times 96485 (\text{JV}^{-1}\text{mol}^{-1}) = -212 \text{ kJmol}^{-1}$$

reaction  $\rightarrow$  spontaneous

$$E_{\text{cell}} = E^0 - (\text{RT}/2\text{F})\ln(a_{\text{Zn}^{2+}}/a_{\text{Cu}^{2+}})$$

If we assume  $a_{\text{Zn}^{2+}} = a_{\text{Cu}^{2+}}$ ,  $E_{\text{cell}} = 1.10 \text{ V}$

**Example: Hg/Hg<sub>2</sub>Cl<sub>2</sub>/Cl<sup>-</sup>(aq)//Zn<sup>2+</sup>(aq)/Zn**



$E_{\text{cell}}^0 = -0.76 - 0.27 = -1.03 \text{ V}$ ,  $\Delta G^0 = +199 \text{ kJmol}^{-1}$ , should be opposite direction

## Measurement of $E^0$

(i) experiment

(ii)  $E^0 = (RT/nF)\ln K$ ,  $K$ ; equilibrium constant of cell  $\leftarrow K = \exp(-\Delta G^0/RT)$

(iii)  $E^0 = E_{\text{right}}^0 - E_{\text{left}}^0$  or  $E^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$  (from Table)

(iv)  $E^0 = -\Delta G^0/nF$



From thermodynamics Table,

Standard Gibbs Energy ( $\text{kJmol}^{-1}$ ): -813.76 ( $\text{PbSO}_4(\text{s})$ ), -237.13 ( $\text{H}_2\text{O}(\text{l})$ ), -218.96 ( $\text{PbO}_2(\text{s})$ ), -755.91 ( $\text{HSO}_4^-(\text{aq})$ ), cf)  $\Delta G^0$  for element ( $\text{Pb}(\text{s})$ ) and  $\text{H}^+(\text{aq}) = 0$

$$\begin{aligned}\Delta G^0 &= 2\Delta G^0 (\text{PbSO}_4(\text{s})) + 2\Delta G^0 (\text{H}_2\text{O}(\text{l})) - [\Delta G^0 (\text{PbO}_2(\text{s})) + 2\Delta G^0 (\text{HSO}_4^-(\text{aq}))] \\ &= -371 \text{ kJmol}^{-1}\end{aligned}$$

$$\rightarrow \Delta G^0 = -nFE^0$$

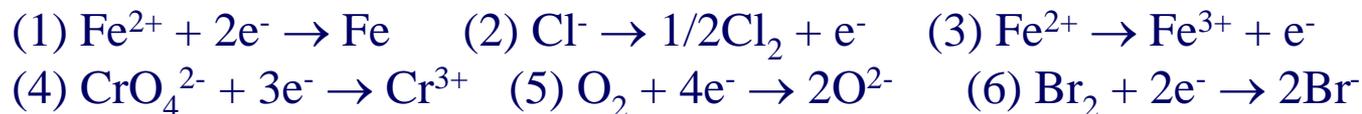
$$\rightarrow E^0 = 371000(\text{Jmol}^{-1})/[2 \times 96485 (\text{JV}^{-1}\text{mol}^{-1})] = 1.923 \text{ V}$$

battery acid: 5.2 M

$$\begin{aligned}E_{\text{cell}} &= 1.923 \text{ V} - (RT/2F)\ln[a_{\text{H}_2\text{O}(\text{l})}^2/(a_{\text{H}^+(\text{aq})}^2 a_{\text{HSO}_4^-(\text{aq})}^2)] \\ &= 1.923 \text{ V} - 0.01285\ln [1/(5.2)^2] = \mathbf{2.008 \text{ V}}\end{aligned}$$

(Problems)

1. Indicate in the following reactions which are reductions and which are oxidations:



2. A Galvanic cell is constructed from a  $\text{Cu}^{2+}/\text{Cu}$  electrode and an  $\text{Ag}^+/\text{Ag}$  electrode.

(1) Make a schematic drawing of the cell

(2) Write the reactions at the electrode

(3) Indicate the anode and the cathode

3. Assuming standard states for all reactants and products, determine the spontaneous direction of the following reactions by calculating the cell potential:

