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
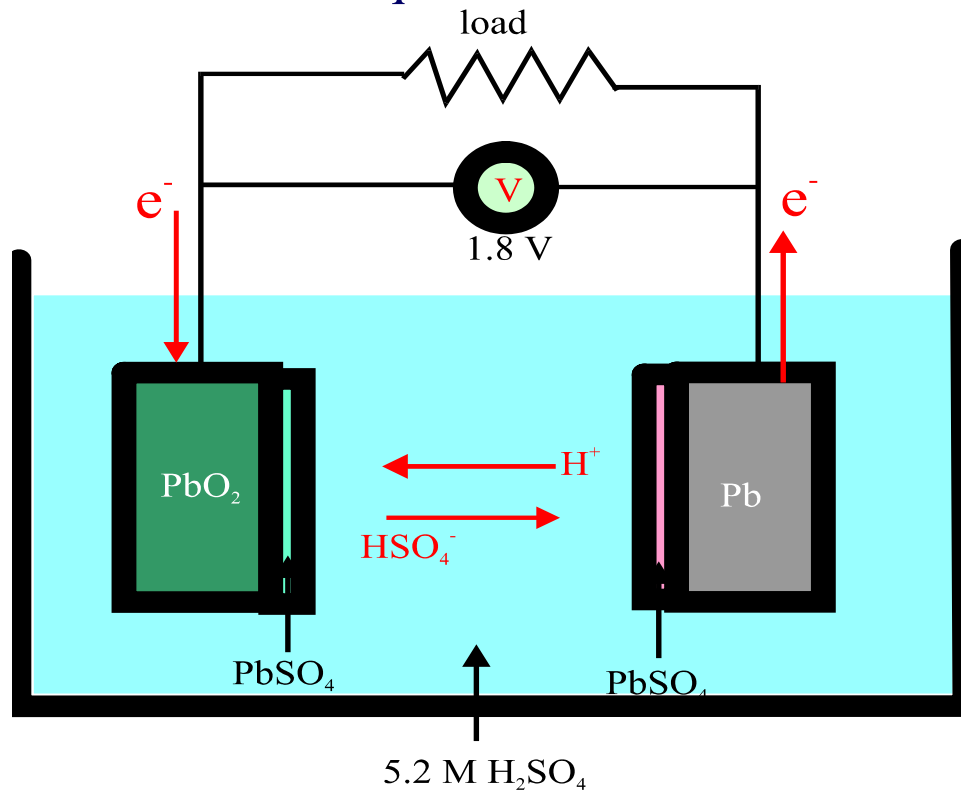
1. Electrochemical reaction

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

Measurement of E: voltameter

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

Electronic conductors: PbO_2, Pb

Ionic conductor: concentrated aqueous solution of sulfuric acid

load

e^-

V

1.8 V

e^-

PbO_2

H^+

HSO_4^-

Pb

$PbSO_4$

$PbSO_4$

5.2 M H_2SO_4

Electrochemical reaction

Anode: $Pb(s) + HSO_4^-(aq) \rightarrow 2e^- + PbSO_4(s) + H^+(aq)$
Cathode: $PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$
Cell: $PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

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); <u>Electrolytic cell</u>; opposite direction to its spontaneous motion
PbO$_2$: anode, Pb: cathode
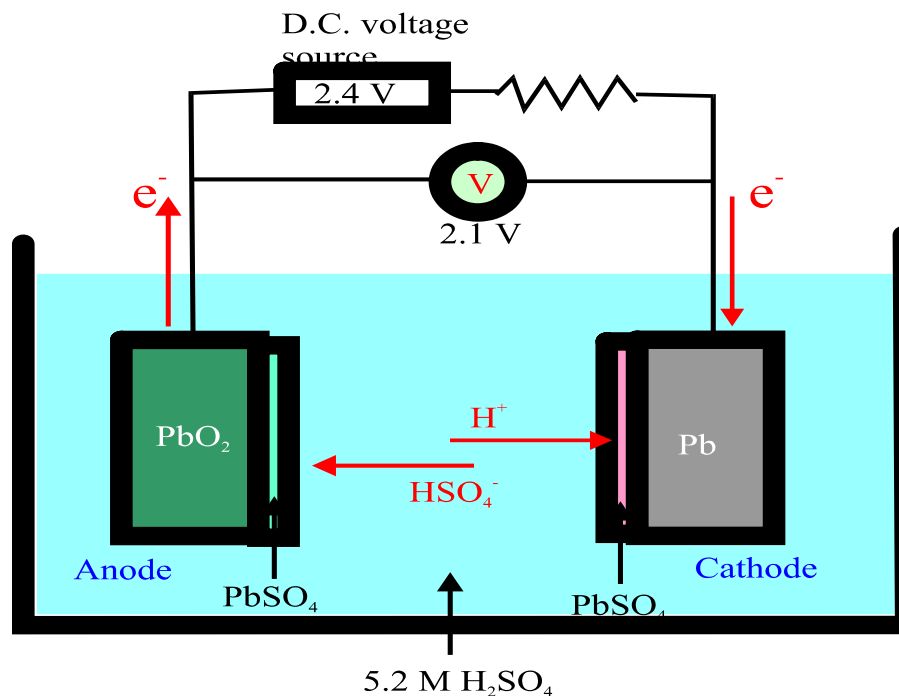
2.0 V; perfect balance between the applied and cell voltages, no current flow → <u>equilibrium cell voltage</u> or <u>reversible cell voltage</u> or <u>null voltage</u> or <u>rest voltage</u> or "<u>open-circuit voltage</u>"(since no current flows, it makes no difference if the circuit is interrupted, as by opening the switch)

Types of electrochemical cells

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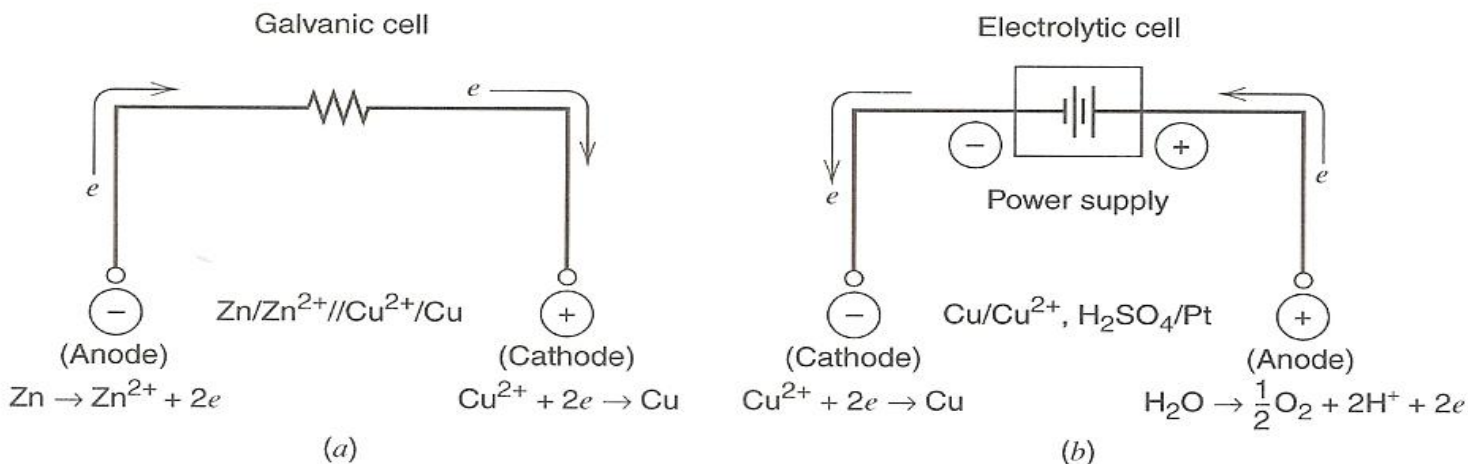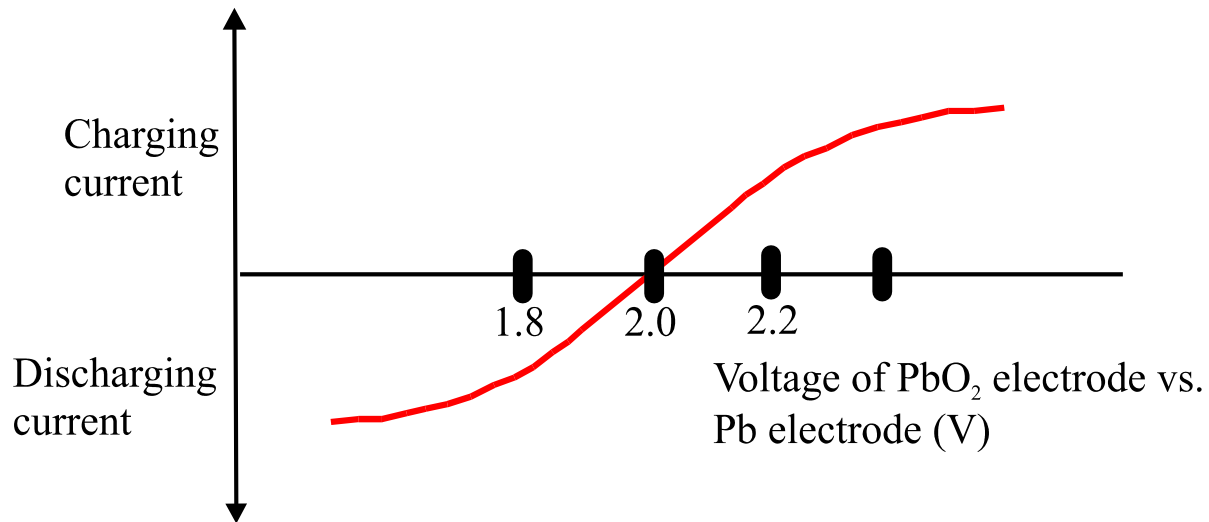
Galvanic cell

$Zn/Zn^{2+}//Cu^{2+}/Cu$

(Anode)
$Zn \rightarrow Zn^{2+} + 2e$

(Cathode)
$Cu^{2+} + 2e \rightarrow Cu$

(a)

Electrolytic cell

Power supply

$Cu/Cu^{2+}, H_2SO_4/Pt$

(Cathode)
$Cu^{2+} + 2e \rightarrow Cu$

(Anode)
$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e$

(b)

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

Figure) A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

Voltammogram

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

Not linear $\rightarrow$ electrochemical cells do not obey Ohm's law

Notation of the structure of cells

$$Zn/Zn^{2+}, Cl^-/AgCl/Ag$$
$$Hg/Hg_2Cl_2/Cl^-(aq)//Zn^{2+}(aq)/Zn$$

/: 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

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

Gibbs free energy, $\mathbf{\Delta G = -nFE_{cell}}$
$\Delta G < 0 \rightarrow$ spontaneous

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

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

(see the Table of Standard Potentials)

Basic electrochemical thermodynamics

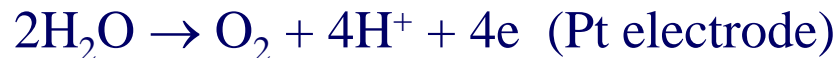**Reversibility**: thermodynamically important

(a) <u>Chemical reversibility</u>

$$Pt/H_2/H^+, Cl^-/AgCl/Ag \quad 0.222 \text{ V}$$

$H_2 + 2AgCl \rightarrow 2Ag + 2Cl^- + 2H^+$

Reversing the cell $\rightarrow$ reversed cell reaction "<u>chemically reversible</u>"

$$Zn/ H^+, SO_4^{2-}/Pt$$

Discharging the cell: $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ (hydrogen evolution)

Reversing the cell:

$\quad\quad 2H^+ + 2e \rightarrow H_2 \quad\quad\quad$ (Zn electrode)

$\quad\quad 2H_2O \rightarrow O_2 + 4H^+ + 4e$ (Pt electrode)

$\quad\quad 2H_2O \rightarrow 2H_2 + O_2 \quad\quad$ (Net)

$\rightarrow$ "<u>chemically irreversible</u>"

(b) <u>Thermodynamic reversibility</u>: an infinitesimal reversal

$\quad\quad$ Chemically reversible $\rightarrow$ thermodynamically reversible or not

    (c) <u>Practical reversibility</u>

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

$$O + ne = R$$

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

→ <u>electrochemically (or nernstian) reversible</u>

Reversibility & Gibbs free energy

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

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

Free energy & cell potential

$$Zn/Zn^{2+} \ (a=1), \ Cl^- \ (a=1)/AgCl/Ag$$

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

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

$Zn + 2AgCl \rightarrow Zn^{2+} + 2Ag + 2Cl^- \qquad E_{rxn} = 0.985$ V (spontaneous)

Reversed cell: -0.985 V (nonspontaneous)

Positive E_{rxn} (spontaneous reaction))

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

When all substances are at unit activity, $\Delta G^0 = -nFE_{rxn}^0$
E_{rxn}^0: standard potential of the cell reaction

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

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

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

Half-reactions & reduction potentials
Half-reaction potential to a standard reference electrode
- NHE (normal hydrogen electrode) or SHE (standard)

$Pt/H_2(a=)/H^+(a=1)$ $\qquad$ E = 0 V at all temperatures

Reaction: $2H^+ + 2e = H_2$

See standard electrode potentials for the reduction in any book!

3. Nernst equation

E obtained from the Nernst equation

$oO + \ldots + \mathbf{ne^-} = rR + \ldots$ \qquad (reduction)

$pP + \ldots = qQ + \ldots + \mathbf{ne^-}$ \qquad (oxidation)

$oO + pP + \ldots = qQ + rR + \ldots$ \quad E_{cell} \quad (cell reaction)

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

a: activity

activity term: minor contribution to the cell voltage

activity (a) $\rightarrow$ concentration (c); $a = \gamma c$, γ; activity coefficient

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

Example:

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \qquad E^0 = +1.23 \text{ V}$$

$$E = E^0 - (RT/2F)\ln[(a_{H^+}{}^4)/a_{Mn2+}], \qquad a_{MnO2}, a_{H2O} = \text{unity}$$

$$\Delta G = -nFE$$

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 $\nu H_2 + \nu_O O \rightarrow \nu_R R + \nu H^+$

$\Delta G = \Delta G^0 + RT\ln(a_R^{\nu R} a_{H+}^{\nu H+}/a_O^{\nu O} a_{H2}^{\nu H2})$
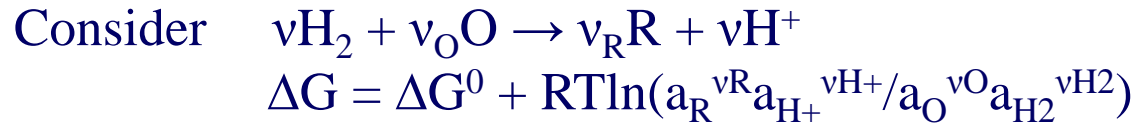
a: activity ($a_{H+} = a_{H2} = 1$), $\Delta G = -nFE$ & $\Delta G^0 = -nFE^0$

<u>Nernst equation</u>

$E = E^0 - (RT/nF)\ln(a_R^{\nu R} a_{H+}^{\nu H+}/a_O^{\nu O} a_{H2}^{\nu H2}) = E^0 + (RT/nF)\ln(a_O^{\nu O}/a_R^{\nu R})$

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

Formal potential

Activity a = γ[A], γ: activity coefficient → unconvenient to use activity due to unknown activity

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

$E^{0'}$: formal potential

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

Selected Standard Electrode Potentials in Aqueous Solutions at 25° in V *vs.* NHE[a]

Reaction	Potential, V
$Ag^+ + e = Ag$	0.7996
$AgBr + e = Ag + Br^-$	0.0713
$AgCl + e = Ag + Cl^-$	0.2223
$AgI + e = Ag + I^-$	−0.1519
$Ag_2O + H_2O + 2e = 2Ag + 2OH^-$	0.342
$Al^{3+} + 3e = Al(0.1\ M\ NaOH)$	−1.706
$Au^+ + e = Au$	1.68
$Au^{3+} + 2e = Au^+$	1.29
p-benzoquinone $+ 2H^+ + 2e =$ hydroquinone	0.6992
$Br_2(aq) + 2e = 2Br^-$	1.087
$Ca^{2+} + 2e = Ca$	−2.76
$Cd^{2+} + 2e = Cd$	−0.4026
$Cd^{2+} + 2e = Cd(Hg)$	−0.3521
$Ce^{4+} + e = Ce^{3+}(1\ M\ H_2SO_4)$	1.44
$Cl_2(g) + 2e = 2Cl^-$	1.3583
$HClO + H^+ + e = \frac{1}{2}Cl_2 + H_2O$	1.63

Table C.1—(continued)

Reaction	Potential, V
$Sn^{4+} + 2e = Sn^{2+}$	0.15
$Tl^+ + e = Tl$	-0.3363
$Tl^+ + e = Tl(Hg)$	-0.3338
$Tl^{3+} + 2e = Tl^+$	1.247
$U^{3+} + 3e = U$	-1.8
$U^{4+} + e = U^{3+}$	-0.61
$UO_2^+ + 4H^+ + e = U^{4+} + 2H_2O$	0.62
$UO_2^{2+} + e = UO_2^+$	0.062
$V^{2+} + 2e = V$	-1.2
$V^{3+} + e = V^{2+}$	-0.255
$VO^{2+} + 2H^+ + e = V^{3+} + H_2O$	0.337
$VO_2^+ + 2H^+ + e = VO^{2+} + H_2O$	1.00
$Zn^{2+} + 2e = Zn$	-0.7628
$ZnO_2^{2-} + 2H_2O + 2e^- = Zn + 4OH^-$	-1.216

Table C.1—(*continued*)

Reaction	Potential, V
$Co^{2+} + 2e = Co$	-0.28
$Co^{3+} + e = Co^{2+}(3\ M\ HNO_3)$	1.842
$Cr^{2+} + 2e = Cr$	-0.557
$Cr^{3+} + e = Cr^{2+}$	-0.41
$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$	1.33
$Cu^+ + e = Cu$	0.522
$Cu^{2+} + 2CN^- + e = Cu(CN)_2^-$	1.12
$Cu^{2+} + e = Cu^+$	0.158
$Cu^{2+} + 2e = Cu$	0.3402
$Cu^{2+} + 2e = Cu(Hg)$	0.345
$Eu^{3+} + e = Eu^{2+}$	-0.43
$\frac{1}{2}F_2 + H^+ + e = HF$	3.03
$Fe^{2+} + 2e = Fe$	-0.409
$Fe^{3+} + e = Fe^{2+}(1\ M\ HCl)$	0.770
$Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}(1\ M\ H_2SO_4)$	0.69
$2H^+ + 2e = H_2$	0.0000
$2H_2O + 2e = H_2 + 2OH^-$	-0.8277
$H_2O_2 + 2H^+ + 2e = 2H_2O$	1.776
$2Hg^{2+} + 2e = Hg_2^{2+}$	0.905
$Hg_2^{2+} + 2e = 2Hg$	0.7961
$Hg_2Cl_2 + 2e = 2Hg + 2Cl^-$	0.2682
$Hg_2Cl_2 + 2e = 2Hg + 2Cl^-(sat'd.\ KCl)$	0.2415
$HgO + H_2O + 2e = Hg + 2OH^-$	0.0984
$Hg_2SO_4 + 2e = 2Hg + SO_4^{2-}$	0.6158
$I_2 + 2e = 2I^-$	0.535
$I_3^- + 2e^- = 3I^-$	0.5338
$K^+ + e = K$	-2.924
$Li^+ + e = Li$	-3.045
$Mg^{2+} + 2e = Mg$	-2.375
$Mn^{2+} + 2e = Mn$	-1.029
$Mn^{3+} + e = Mn^{2+}$	1.51
$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$	1.208
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	1.491
$Na^+ + e = Na$	-2.7109
$Ni^{2+} + 2e = Ni$	-0.23
$Ni(OH)_2 + 2e = Ni + 2OH^-$	-0.66
$O_2 + 2H^+ + 2e = H_2O_2$	0.682
$O_2 + 4H^+ + 4e = 2H_2O$	1.229
$O_2 + 2H_2O + 4e = 4OH^-$	0.401
$O_3 + 2H^+ + 2e = O_2 + H_2O$	2.07
$Pb^{2+} + 2e = Pb$	-0.1263
$Pb^{2+} + 2e = Pb(Hg)$	-0.1205
$PbO_2 + 4H^+ + 2e = Pb^{2+} + 2H_2O$	1.46
$PbO_2 + SO_4^{2-} + 4H^+ + 2e = PbSO_4 + 2H_2O$	1.685
$PbSO_4 + 2e = Pb + SO_4^{2-}$	-0.356
$Pd^{2+} + 2e = Pd$	0.83
$Pt^{2+} + 2e = Pt$	~ 1.2
$PtCl_4^{2-} + 2e = Pt + 4Cl^-$	0.73
$PtCl_6^{2-} + 2e = PtCl_4^{2-} + 2Cl^-$	0.74
$S + 2e = S^{2-}$	-0.508
$Sn^{2+} + 2e = Sn$	-0.1364

Example: Zn/Zn^{2+}(aq), Cu^{2+}(aq)/Cu

Cell: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Right: $Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = +0.34$ V
 Left: $Zn^{2+} + 2e^- \rightarrow Zn$ $E^0 = -0.76$ V
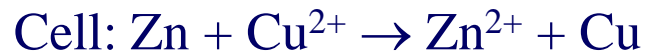
$E_{cell}^0 = +0.34 - (-0.76) = +1.10$ V

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

reaction $\rightarrow$ spontaneous

$$E_{cell} = E^0 - (RT/2F)\ln(a_{Zn2+}/(a_{Cu2+}))$$

If we assume $a_{Zn2+} = a_{Cu2+}$, $E_{cell} = $ 1.10 V

Example: $Hg/Hg_2Cl_2/Cl^-(aq)//Zn^{2+}(aq)/Zn$

$2Hg + Cl^- + Zn^{2+} \rightarrow Hg_2Cl_2 + Zn$

right: $Zn^{2+} + 2e^- \rightarrow Zn$ $E^0 = -0.76$ V

left: $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$ $E^0 = +0.27$ V
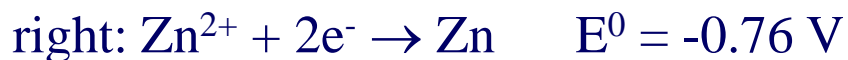
$E_{cell}{}^0 = -0.76 - 0.27 = -1.03$ V, $\Delta G^0 = +199$ kJmol^{-1}, <u>should be opposite direction</u>

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

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

Cell: $PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

From thermodynamics Table,

Standard Gibbs Energy (kJmol^{-1}): -813.76 ($PbSO_4(s)$), -237.13 ($H_2O(l)$), -218.96 ($PbO_2(s)$), -755.91 ($HSO_4^-(aq)$), cf) ΔG^0 for element ($Pb(s)$) and $H^+(aq) = 0$

$\Delta G^0 = 2\Delta G^0 (PbSO_4(s)) + 2\Delta G^0 (H_2O(l)) - [\Delta G^0 (PbO_2(s)) + 2\Delta G^0 (HSO_4^-(aq))]$

$= -371$ kJmol^{-1}

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

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

battery acid: 5.2 M

$$E_{cell} = 1.923 \text{ V} - (RT/2F)\ln[a_{H2O(l)}{}^2/(a_{H+(aq)}{}^2 a_{HSO4-(aq)}{}^2)]$$

$$= 1.923 \text{ V} - 0.01285\ln [1/(5.2)^2] = \textbf{2.008 V}$$

(Problems)

1. Indicate in the following reactions which are reductions and which are oxidations:
(1) $Fe^{2+} + 2e^- \rightarrow Fe$ (2) $Cl^- \rightarrow 1/2Cl_2 + e^-$ (3) $Fe^{2+} \rightarrow Fe^{3+} + e^-$
(4) $CrO_4^{2-} + 3e^- \rightarrow Cr^{3+}$ (5) $O_2 + 4e^- \rightarrow 2O^{2-}$ (6) $Br_2 + 2e^- \rightarrow 2Br^-$
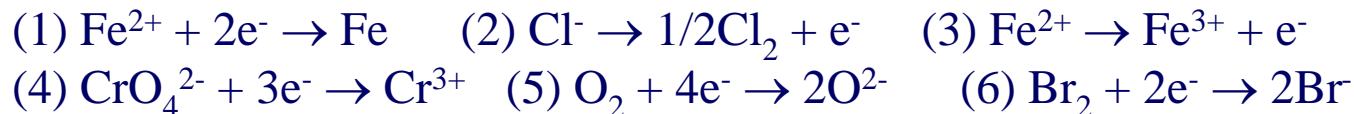
2. A Galvanic cell is constructed from a Cu^{2+}/Cu electrode and an Ag^+/Ag electrode.
(1) Make a schematic drawing of the cell

(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:
(1) $Cu + 2HCl = CuCl_2 + H_2$

(2) $Ag + FeCl_3 = FeCl_2 + AgCl$