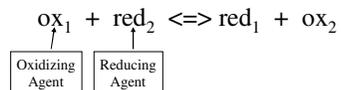


Ch.14 & 15 Electrochemistry

Redox Reaction



Redox reactions: involve transfer of electrons from one species to another.

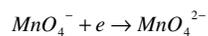
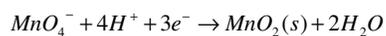
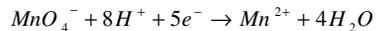
Oxidizing agent (oxidant): takes electrons

Reducing agent (reductant): gives electrons

Important Redox Titrants and the Reactions

Oxidizing Reagents (Oxidants)

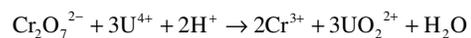
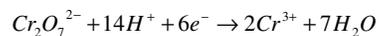
(1) Potassium Permanganate



Important Redox Titrants and the Reactions

Oxidizing Reagents (Oxidants)

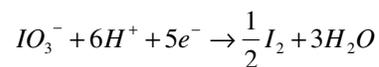
(2) Potassium Dichromate



Important Redox Titrants and the Reactions

Oxidizing Reagents (Oxidants)

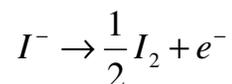
(3) Potassium Iodate



Important Redox Titrants and the Reactions

Reducing Reagent (Reductants)

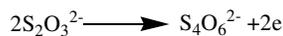
(1) Potassium Iodide



Important Redox Titrants and the Reactions

Reducing Reagent (Reductants)

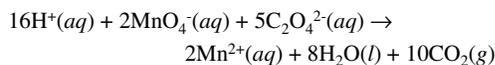
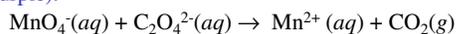
(2) Sodium Thiosulfate



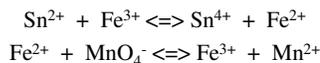
Balance Redox Reactions (Half Reactions)

1. Write down the (two half) reactions.
2. Balance the (half) reactions (Mass and Charge):
 - a. Start with elements other than H and O.
 - b. Balance O by adding water.
 - c. balance H by adding H⁺.
 - d. Balancing charge by adding electrons.
- (3. Multiply each half reaction to make the number of electrons equal.
4. Add the reactions and simplify.)

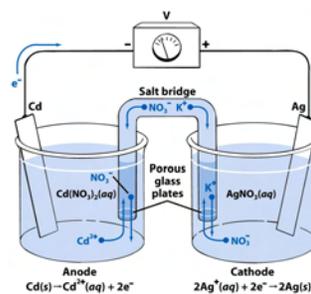
Example: Balance the two half reactions and redox reaction equation of the titration of an acidic solution of Na₂C₂O₄ (sodium oxalate, colorless) with KMnO₄ (deep purple).



Example: Balance



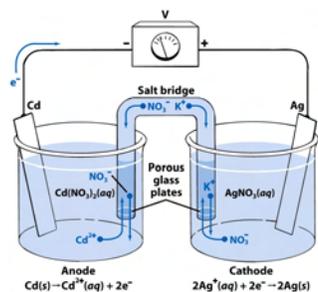
Galvanic Cells - Components



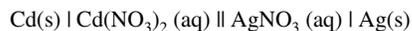
A galvanic (voltaic) cell uses a spontaneous chemical reaction to generate electricity.

- Electrodes (cathode and anode).
- Salt bridge: cations move from anode to cathode, anions move from cathode to anode.

Galvanic Cells - Line Notation



Line notation



Phase boundary Salt bridge Phase boundary

Free Energy and Electrochemical Reaction

- The free energy change, ΔG , for a chemical reaction at constant T, P equals the maximum possible electrical work that can be done by the reaction on its surroundings.

$$\text{Work} = -\Delta G = E \times q$$

$$\Delta G = -nFE$$

- A spontaneous reaction ($\Delta G < 0$) \rightarrow $E > 0$
- Think: how the equilibrium constant can be related to free energy?

E and Equilibrium Constants

- A galvanic cell produces electricity because the cell reaction is not at equilibrium; E for the net reaction can thus be related to K

$$aA + ne^- \leftrightarrow cC \quad E_+^{\circ}$$

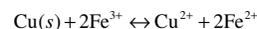
$$dD + ne^- \leftrightarrow fF \quad E_-^{\circ}$$

$$E = E_+ - E_- = E_+^{\circ} - \frac{0.05916}{n} \log \frac{[C]^c}{[A]^a} - \left(E_-^{\circ} - \frac{0.05916}{n} \log \frac{[F]^f}{[D]^d} \right)$$

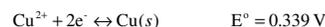
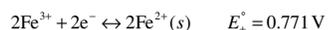
$$E = E^{\circ} - \frac{0.05916}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} = E^{\circ} - \frac{0.05916}{n} \log Q \quad \text{at } 25^{\circ}\text{C}$$

$$E = 0 \rightarrow E^{\circ} = \frac{0.05916}{n} \log K \quad \text{at } 25^{\circ}\text{C} \quad K = 10^{\left(\frac{nE^{\circ}}{0.05916} \right)} \text{ at } 25^{\circ}\text{C}$$

Example: Find the equilibrium constant



This can be divided into two half reactions:



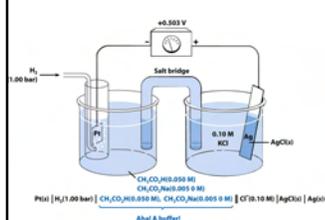
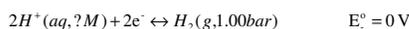
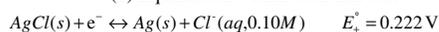
$$E^{\circ} = E_+^{\circ} - E_-^{\circ} = 0.771 - 0.339 = 0.432 \text{ V}$$

$$K = 10^{\left(\frac{nE^{\circ}}{0.05916} \right)} = 10^{\left(\frac{(2)(0.432)}{0.05916} \right)} = 4 \times 10^{14}$$

Cells as Chemical Probes

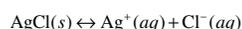
Two Equilibria: (1) Equilibrium between two half-cells

(2) Equilibrium within each half-cell



- The half-reaction that you write must involve species that appear in two oxidation states in the cell.

- The reaction is in equilibrium in the right cell is not the net cell reaction:



Survival Tips

Electrochemistry, chemical equilibrium, solubility, complex formation, and acid-base chemistry

- Write half-reactions and their standard potentials
- Write Nernst equation for the net reaction and put in all the known quantities.
- Solve for the unknown concentration and use that concentration in the chemical equilibrium equation to solve the problems.

Ex. p.286-287

Important Biochemical Reactions

- Formal potential, E° , meant to define potentials under conditions of biochemistry

Table 14-2 Reduction potentials of biological interest

Reaction	E° (V)	E° (V)
$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	+1.229	+0.816
$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	+0.771	+0.771
$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+0.535	+0.535
Cytochrome a (Fe^{3+}) + $e^- \rightarrow$ cytochrome a (Fe^{2+})	+0.290	+0.290
$\text{O}_2(g) + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2$	+0.695	+0.281
Cytochrome c (Fe^{3+}) + $e^- \rightarrow$ cytochrome c (Fe^{2+})	—	+0.254
2,6-Dichlorophenolindophenol + $2\text{H}^+ + 2e^- \rightarrow$ reduced 2,6-dichlorophenolindophenol	—	+0.22
Dehydroascorbate + $2\text{H}^+ + 2e^- \rightarrow$ ascorbate + H_2O	+0.390	+0.058
Fumarate + $2\text{H}^+ + 2e^- \rightarrow$ succinate	+0.433	+0.031
Methylene blue + $2\text{H}^+ + 2e^- \rightarrow$ reduced product	+0.532	+0.011
Glyoxylate + $2\text{H}^+ + 2e^- \rightarrow$ glyoxylate	—	-0.090
Oxaloacetate + $2\text{H}^+ + 2e^- \rightarrow$ malate	+0.330	-0.102
Pyruvate + $2\text{H}^+ + 2e^- \rightarrow$ lactate	+0.224	-0.190
Riboflavin + $2\text{H}^+ + 2e^- \rightarrow$ reduced riboflavin	—	-0.208
$\text{FAD} + 2\text{H}^+ + 2e^- \rightarrow \text{FADH}_2$	—	-0.219
(Glutathione-S) $_2$ + $2\text{H}^+ + 2e^- \rightarrow 2$ glutathione-SH	—	-0.23
Safranine T + $2e^- \rightarrow$ leuco-safranine T	-0.235	-0.289
(C $_6$ H $_5$ S) $_2$ + $2\text{H}^+ + 2e^- \rightarrow 2$ C $_6$ H $_5$ SH	—	-0.30
$\text{NAD}^+ + \text{H}^+ + 2e^- \rightarrow \text{NADH}$	-0.105	-0.320
$\text{NADP}^+ + \text{H}^+ + 2e^- \rightarrow \text{NADPH}$	—	-0.324
Cysteine + $2\text{H}^+ + 2e^- \rightarrow 2$ cysteine	—	-0.340
Acetoacetate + $2\text{H}^+ + 2e^- \rightarrow$ β -hydroxybutyrate	—	-0.346
Naniline + $2\text{H}^+ + 2e^- \rightarrow$ hypoxaniline + H_2O	—	-0.371
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.000	-0.414
Glucosate + $2\text{H}^+ + 2e^- \rightarrow$ glucose + H_2O	—	-0.44
$\text{SO}_4^{2-} + 2e^- + 2\text{H}^+ \rightarrow \text{SO}_3^{2-} + \text{H}_2\text{O}$	—	-0.454
$2\text{SO}_4^{2-} + 2e^- + 4\text{H}^+ \rightarrow \text{S}_2\text{O}_4^{2-} + 2\text{H}_2\text{O}$	—	-0.527

Table 14-2
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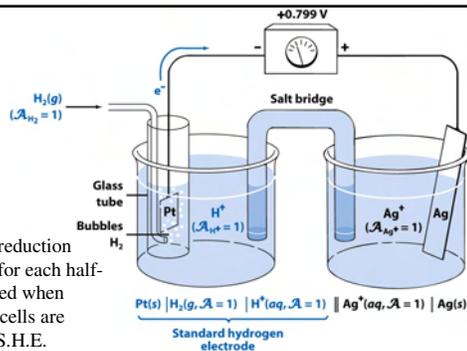
Potentiometry

- Potentiometry:** the use of electrodes to measure voltages from chemical reactions.
- Electroactive species:** can donate or accept electrons at an electrode; can be measured as the part of a galvanic cell (analyte)
- Reference electrode:** we then connect the analyte half-reaction to a second cell with a fixed composition (known potential), the 2nd half-cell is called reference electrode.
- Indicator electrode:** responds to analyte
 - Metal electrodes: inert metals, e.g., Pt, Au
 - Ion-selective electrodes: respond to specific analytes

S.H.E. (again)

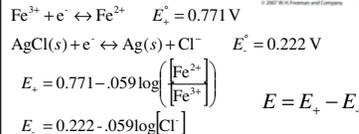
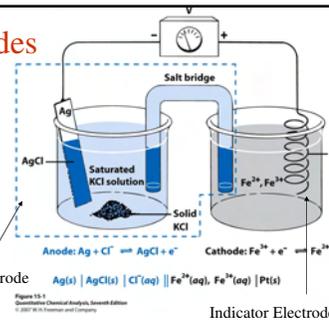
The standard reduction potential, E° , for each half-cell is measured when different half-cells are connected to S.H.E.

S.H.E. || Ag^+ (aq, $\alpha=1$) | $\text{Ag}(s)$
Standard means that the activities of all species are unity.
 Not practical for regular use due to the hydrogen gas



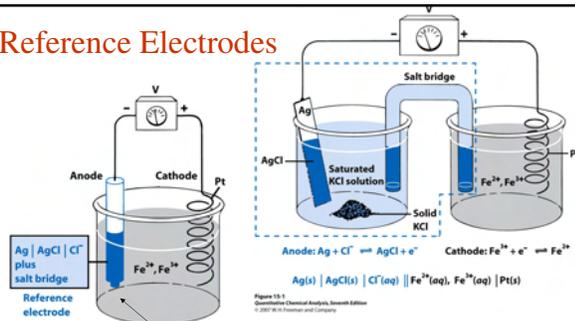
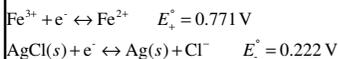
Reference Electrodes

Detect $\text{Fe}^{2+}/\text{Fe}^{3+}$ in solution: a Pt wire (indicator electrode) in the half-cell and connect this half cell to a 2nd half-cell at a constant potential.



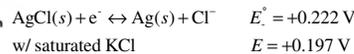
Reference Electrodes

The entire left half-cell containing appropriate solutions and a salt bridge.

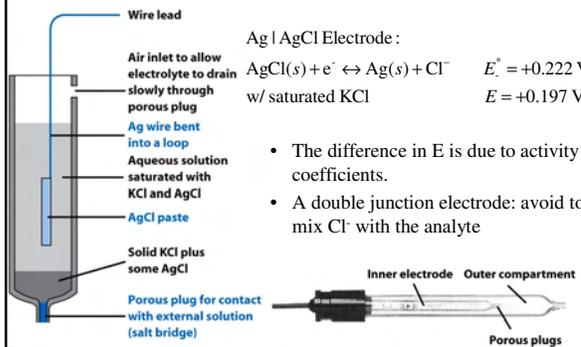


Silver-Silver Chloride Electrode

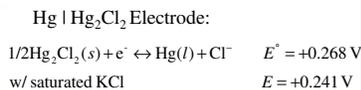
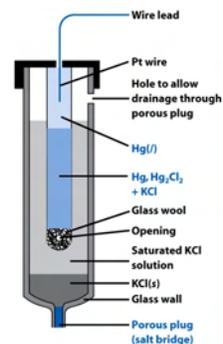
$\text{Ag} | \text{AgCl}$ Electrode:



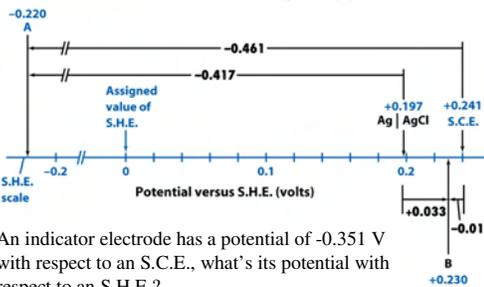
- The difference in E is due to activity coefficients.
- A double junction electrode: avoid to mix Cl^- with the analyte



Saturated Calomel Electrode (S.C.E.)



Voltage Conversions between Different Reference Scales



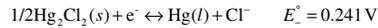
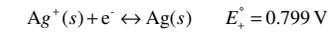
An indicator electrode has a potential of -0.351 V with respect to an S.C.E., what's its potential with respect to an S.H.E.?
 $-0.351 \text{ V} + 0.241 \text{ V} = -0.110 \text{ V}$

Indicator Electrodes - Metal Electrodes

- Metal electrodes: develop potential in response to a redox reaction on their surface
- Pt is mostly inert, not participating in reactions
 - It simply allows electron transfer to/from solution
- Platinum is the most common metal indicator electrode
Gold is also an inert metal indicator electrode
- Carbon electrodes are often used because many redox reactions are very fast on a carbon surface

Indicator Electrodes-Metal electrodes

- Metal electrodes: develop potential in response to a redox reaction on their surface
- Inert metal indicator electrode: allows electron transfer to/from the solution but not participating in reactions, e.g., Pt (the most common one), Au.
- Silver Indicator Electrode



$$E = E_+ - E_- = 0.799 - 0.059 \log \left(\frac{1}{[\text{Ag}^+]} \right) - 0.241$$

$$E = 0.558 + 0.059 \log [\text{Ag}^+]$$

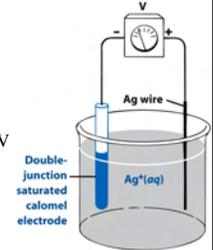
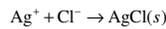


Figure 15-6
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Example: 100.0 mL solution containing 0.100 M NaCl was titrated with 0.100 M AgNO₃ and monitored with a S.C.E. What voltage reading would be observed after 65.0 mL?



$$V_e = 100.0 \text{ mL}$$

$$E = 0.558 + 0.05916 \log [\text{Ag}^+]$$

$$[\text{Cl}^-] = (0.350)(0.100 \text{ M}) \left(\frac{100.0}{165.0} \right) = 0.021 \text{ M}$$

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1.8 \times 10^{-10}}{0.021} = 8.5 \times 10^{-9}$$

$$E = 0.558 + 0.05916 \log (8.5 \times 10^{-9}) = 0.081 \text{ V}$$

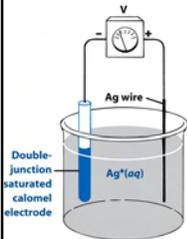


Figure 15-6
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Junction Potential

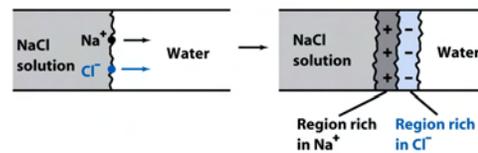


Figure 15-7
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- Junction potential: A voltage difference develops whenever dissimilar electrolyte solutions are in contact.
- Happens at the salt bridge/solution interface since different ions have different mobilities in water.
- A major (fundamental) source of error in a potential measurement.

Ion Mobilities and Liquid Junction Potentials

Table 15-1 Mobilities of ions in water at 25°C

Ion	Mobility (m ² /(s + V)) ^a
H ⁺	36.30 × 10 ⁻⁸
Rb ⁺	7.92 × 10 ⁻⁸
K ⁺	7.62 × 10 ⁻⁸
NH ₄ ⁺	7.61 × 10 ⁻⁸
La ³⁺	7.21 × 10 ⁻⁸
Ba ²⁺	6.59 × 10 ⁻⁸
Ag ⁺	6.42 × 10 ⁻⁸
Ca ²⁺	6.12 × 10 ⁻⁸
Cu ²⁺	5.56 × 10 ⁻⁸
Na ⁺	5.19 × 10 ⁻⁸
Li ⁺	4.01 × 10 ⁻⁸
OH ⁻	20.50 × 10 ⁻⁸
Fe(CN) ₆ ⁴⁻	11.45 × 10 ⁻⁸
Fe(CN) ₆ ³⁻	10.47 × 10 ⁻⁸
SO ₄ ²⁻	8.27 × 10 ⁻⁸
Br ⁻	8.13 × 10 ⁻⁸
I ⁻	7.96 × 10 ⁻⁸
Cl ⁻	7.91 × 10 ⁻⁸
NO ₃ ⁻	7.40 × 10 ⁻⁸
ClO ₄ ⁻	7.05 × 10 ⁻⁸
F ⁻	5.70 × 10 ⁻⁸
HCO ₃ ⁻	4.61 × 10 ⁻⁸
CH ₃ CO ₂ ⁻	4.24 × 10 ⁻⁸

^a The mobility of an ion is the terminal velocity that the particle achieves in an electric field of 1 V/cm. Mobility = velocity/field. The units of mobility are therefore (m/s)/(V/cm) = m²/(s + V).

Table 15-1
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Table 15-2 Liquid junction potentials at 25°C

Junction	Potential (mV)
0.1 M NaCl 0.1 M KCl	-6.4
0.1 M NaCl 3.5 M KCl	-0.2
1 M NaCl 3.5 M KCl	-1.9
0.1 M HCl 0.1 M KCl	+27
0.1 M HCl 3.5 M KCl	+3.1

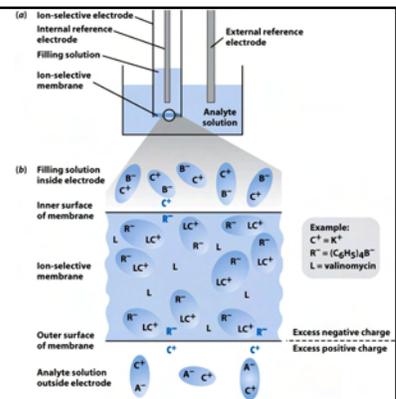
NOTE: A positive sign means that the right side of the junction becomes positive with respect to the left side.

Table 15-2
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Ion-Selective Electrodes (ISE)

- Responds selectively to one ion using an ion-selective membrane
- Do not involve redox reactions
- The electric potential across the membrane depends on [analyte]
- E is measured by two reference electrodes

$$E = \text{constant} + \frac{0.05916}{n} \log [C^+]_{\text{out}} \quad \text{at } 25^\circ\text{C} \quad n = \text{charge of analyte}$$



Glass Electrode (pH Combination Electrode)

- The most common ISE
- A glass membrane selectively binds H^+
- Two Ag|AgCl reference electrodes measure the potential difference across the glass membrane
- An ion-exchange equilibrium is on the surface of the glass membrane

Figure 15-9
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$Ag(s) | AgCl(s) | Cl^-(aq) || H^+(a_{out}) | H^+(a_{in}), Cl^-(aq) | AgCl(s) | Ag(s)$

The Glass Membrane of a pH Electrode

- Cross section of the glass membrane of a pH electrode.
- H^+ can diffuse into the membrane to replace the metal ions through binding to oxygen in glass (ion-exchange equilibrium).

Response of the electrode:
 $E = \text{constant} + \beta (0.0592) \log [H^+]_{out}$
 $E = \text{constant} - \beta (0.0592) \text{pH}_{out}$ at $25^\circ C$

$\beta \sim 1.00$, electromotive efficiency measured during calibration.

Errors in pH Measurement

1. Calibration standards (± 0.01 pH)
2. Junction potential (~ 0.01 pH)
3. Junction potential drift (recalibrate every 2 hrs)
4. Sodium error (when $[H^+]$ is low and $[Na^+]$ is high)
5. Acid error (strong acid, the glass surface is saturated with H^+)
6. Equilibration time (~ 30 s with adequate stirring)
7. Hydration of glass (A dry electrode requires several hours of soaking)
8. Temperature (calibrate at same T as measurement)
9. Cleaning (remove hydrophobic liquid)

Selectivity Coefficient

$k_{A,X} = \frac{\text{response to X}}{\text{response to A}}$

- The selectivity coefficient: the relative response of the electrode to different species
- The smaller k is, the less interference there is due to ion X

Response of ion - selective electrode:
 $E = \text{constant} \pm \beta \left(\frac{0.0592}{n} \right) \log \left[a_A + \sum_x (k_{A,x} a_x) \right]$ at $25^\circ C$

$k_{K^+, Na^+} = 1 \times 10^{-5}$
 $k_{K^+, Cs^+} = 0.44$
 $k_{K^+, Rb^+} = 2.8$

Specifications for Electrochemical Techniques

Advantages

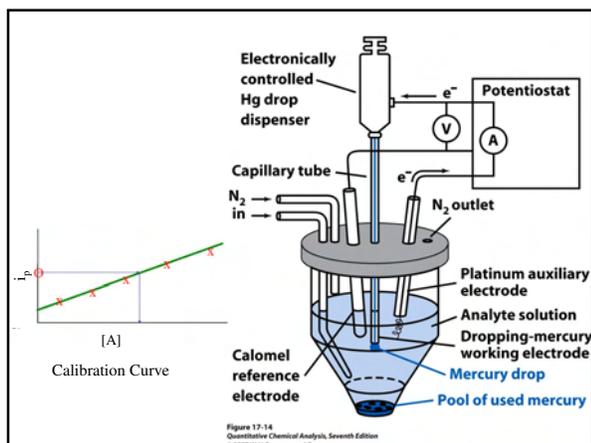
- Linear response to analyte over wide dynamic range
- Nondestructive
- Short response times
- Unaffected by color/turbidity (limited matrix effects)
- Cheap

Disadvantages

- Sensitivity (High detection limits)
- Not universal

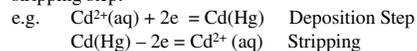
Voltammetry

- A collection of techniques in which the relation between current and voltage is observed during electrochemical process.
- Can be used to
 - (1) Study electroactivity of ions and molecules at the electrode/solution interface
 - (2) Probe coupled chemical reactions and measure electron transfer rates
 - (3) Examine electrode surfaces
- An electrochemical cell consists of a working (analyzing) electrode, an auxiliary (counter) electrode, and a reference electrode. The control device is a potentiostat.

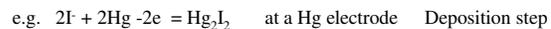


Stripping Analysis

Anodic stripping voltammetry (ASV): analytes are reduced and deposited onto an electrode. They are reoxidized during the stripping step.



Cathodic stripping voltammetry (CSV): typically anions are oxidized and deposited onto an electrode with subsequent stripping via a negative potential scan.



Trace analysis (enhanced sensitivity) can be realized since sample analytes are preconcentrated from a large-volume dilute solution into (onto) a small-volume electrode under forced convection.