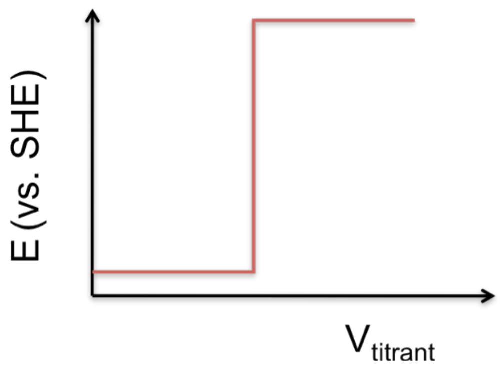
Redox Titration Curve

Regions of Redox titration curve



- **Initial point**
  - potential is undefined
- **Before equiv pt**
  - Analyte in excess
  - Analyte redox potential defines solution potential
- **At equiv pt**
  - equilibrium back rxn defines potential
  - Trick to get E_{cell}
- **After equiv pt**
  - Titrant in excess
  - Titrant redox potential defines solution potential

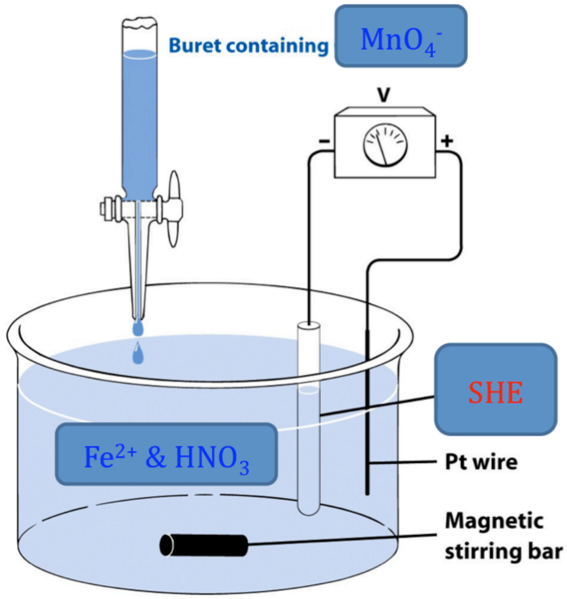


Figure 16-1
Quantitative Chemical Analysis, Seventh Edition
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Example: Calculate the titration curve for titration of 25.0 mL of 0.100 M Fe^{2+} in 1.00 M HNO_3 with 0.0200 M MnO_4^- in 1.00 M HNO_3.

Measure E_{cell} as a function of vol. MnO_4^- added.

Titration rxn:

$$MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \rightleftharpoons Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$$

$$V_{eq} = \frac{25\text{mL}(0.100\text{M})}{(0.0200\text{M})} \bullet \frac{1}{5} = 25\text{mL}$$

Region 1: 0 mL MnO_4^- added

Solution is 0.100 M Fe^{2+} plus 1.00 M HNO_3.

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^o = 0.771V$

$$E_{cell} = E_C - E_{SHE}, \quad E_{SHE} = 0$$

$$E_C = 0.771V - \frac{0.05916}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

- cannot calculate E_{cell}.

Region 2: 12.5 mL MnO_4^- added

	MnO_4^-	+ $5\ Fe^{2+}$	+ $8\ H^+$ ⇌	Mn^{2+}	+ $4\ H_2O$	+ $5\ Fe^{3+}$
Initial:	12.5mLx0.02M =0.250 mmol	25.0 mLx0.1M =2.50 mmol		0		0
Final:	0	2.50-**5**x0.250M =1.25 mmol		0.250mmol		**5**x0.250M = 1.25 mmol
		=0.0333M				= 0.0333M

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ E° = 0.771V

$$E_C = 0.771V - \frac{0.05916}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$= 0.771V - \frac{0.05916}{1}\log\frac{0.0333M}{0.0333M}$$

= 0.771V

Region 3: 25.0 mL MnO_4^- added

Equivalence point

$MnO_4^- + 5\ Fe^{2+} + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O + 5\ Fe^{3+}$

Analyte: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E°_{Fe3+/Fe2+} = 0.771$ V

Titrant: $MnO_4^- + 8\ H^+ + 5\ e^- \rightleftharpoons Mn^{2+} + 4\ H_2O$ $E°_{MnO4-/Mn2+} = 1.51$ V

- -

If the stoichiometry of the redox reaction were 1:1, E° at the equivalent point would have been **an average of the two E°s** (example in Harris, p. 343). However, when the ratio is not 1:1, a **weighted average** should be used.

- -

$$E_{eq} = \frac{n_1E_1^0 + n_2E_2^0}{n_1 + n_2}$$

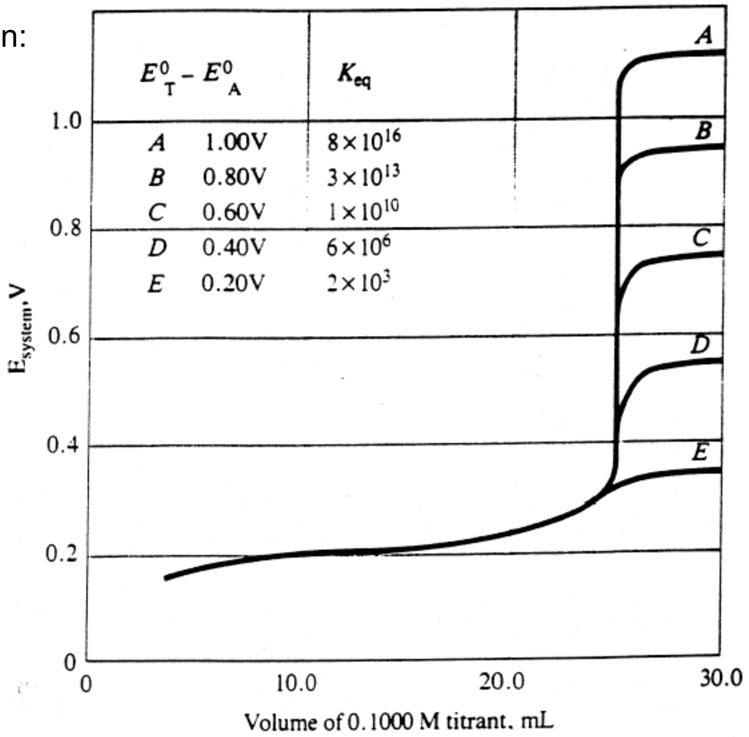
$$E_{eq} = \frac{(1 \times 0.771V) + (5 \times 1.51V)}{1+5} = 1.39V$$

Factors affecting the sharpness of the curve

1) Concentration of the analyte:
   - limit of detection (LOD) for redox titrations is ~1 mM.

2) Completeness of the titration rxn:

$$\log K_{eq} = \frac{n(E^0{}_A - E^0{}_B)}{0.0592}$$



Endpoint Detection

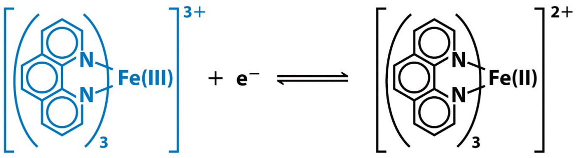
Potential:
electrode can detect $\Delta E^\circ_{rxn} \geq 0.2$ V

Visual redox endpoint indicators - need $\Delta E^\circ_{rxn} \geq 0.4$ V

a) self indicating,
   - e.g. MnO_4^- has a strong purple colour

b) Complexation indicators - form a complex with one of the species in the titration and change colour upon complexation.
   - e.g. when using I_2 (or actually I_3^-) or I^- as titrant
   - starch forms a deep blue complex with the I_3^-

c) Redox indicators - change colour when going from oxidized to reduced form.



Oxidized ferroin
(pale blue)
In(oxidized)

Reduced ferroin
(red)
In(reduced)

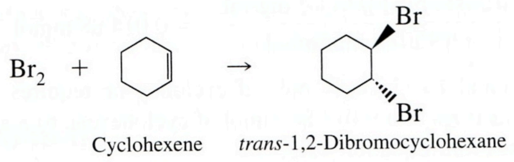
Table 15-2 Redox Indicators

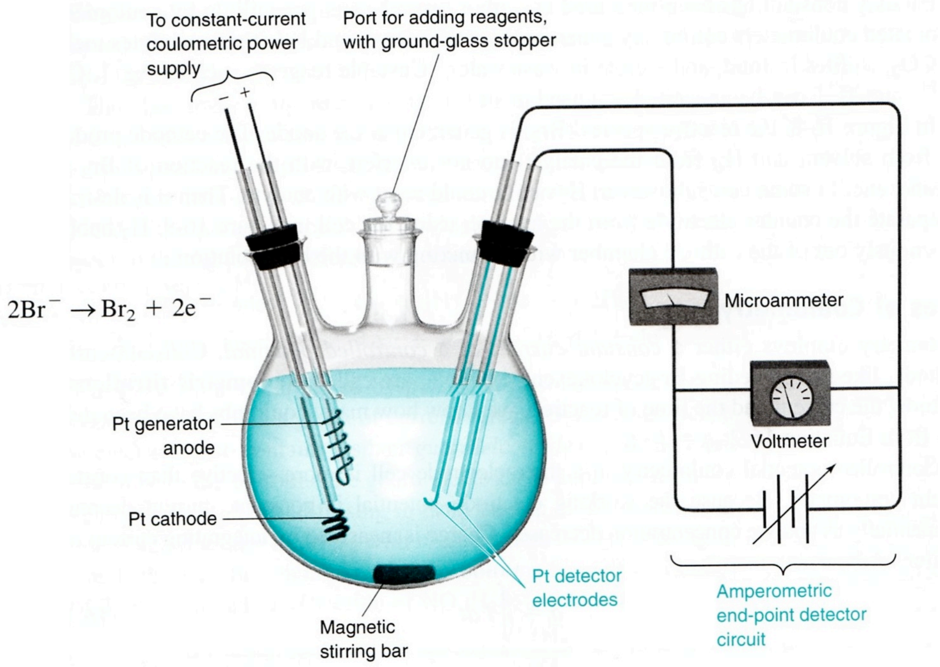
	Color		
Indicator	**Oxidized**	**Reduced**	**$E°$**
Phenosafranine	Red	Colorless	0.28
Indigo tetrasulfonate	Blue	Colorless	0.36
Methylene blue	Blue	Colorless	0.53
Diphenylamine	Violet	Colorless	0.75
4′-Ethoxy-2,4-diaminoazobenzene	Yellow	Red	0.76
Diphenylamine sulfonic acid	Red-violet	Colorless	0.85
Diphenylbenzidine sulfonic acid	Violet	Colorless	0.87
Tris(2,2′-bipyridine)iron	Pale blue	Red	1.120
Tris(1,10-phenanthroline)iron (ferroin)	Pale blue	Red	1.147
Tris(5-nitro-1,10-phenanthroline)iron	Pale blue	Red-violet	1.25
Tris(2,2′-bipyridine)ruthenium	Pale blue	Yellow	1.29

Coulometric Titration (Sec. 16-3)

Titration to quantify the titrant (or analyte) during an electrolysis reaction by measuring the amount of electricity (in coulombs) consumed: constant current x time

Example from Harris:





Two pairs of electrodes are used: one pair electrolytically generates the titrant (e.g., Br_2, I_2) and the other pair monitors the redox potential of the solution to detect the end point.

To determine the # of moles from current applied:

Moles of $e^- = \frac{I \cdot t}{F}$, where I is current (in A = C/s), t is time, and F is 96 485 C/mol)
(see example on p. 370)

Karl-Fischer Titration (p. 385)
- performed 1/2 million times per day; determine traces of water in organic environment.
- titration can be volumetric (larger vol of water) or coulometric (trace amt).

Reagents:

$$ROH + SO_2 + B \rightarrow BH^+ + ROSO_2^-$$

Coulometry:

$$2\,I^- \rightarrow I_2 + 2e^-$$

Titration:

$$H_2O + I_2 + ROSO_2^- + 2B \rightarrow ROSO_3^- + 2BH^+I^-$$

- the net reaction is oxidation of SO_2 by I_2, forming $ROSO_3^-$ while consuming one mole of H_2O for each mole of I_2

American Society for Testing and Materials (ASTM) – develops international standards for material, products, systems and materials used in construction, transportation and manufacturing:

D4377 – KF water in crude oil
D5530 – KF water in hazardous waste
D1123 – KF water in engine coolant

E203 – water by vol. KF

Amperometry (Sec 16-4)
- measurement of electrical current for analytical purposes
- a pair of electrodes are dring an electrolysis reaction (involving an analyte)
- the current, proportional to the analyte concentration, is measured

Analyte (electrode surface) + $ne^- \rightleftharpoons$ product

$\downarrow\uparrow$ mass transfer - slow

Analyte (bulk soln)

▪ potential is set to faciliate fast electrolysis

Transport of analyte to the electrode surface becomes the rate determining step

Current $\propto$ Rate of diffusion $\propto$ $[\text{Analyte}]_{\text{bulk}} - [\text{Analyte}]_{\text{surf}}$
If the electrode reaction is fast, $[\text{Analyte}]_{\text{surf}} = 0$
Limiting Current $\propto$ Rate of diffusion $\propto$ $[\text{Analyte}]_{\text{bulk}}$

Limiting current (diffusion current)
- current observed when electrolysis is performed under concentration polarization
- proportional to the concentration of analyte

Clark electrode (Box 16-1)
- amperometric electrode for the measurement of dissolved O_2

Cathode (Pt electrode): $O_2 + 4H^+ + 4e^- \rightleftharpoons 2\,H_2O$
Anode (Ag | AgCl electrode): $4\,Ag + 4\,Cl^- \rightleftharpoons 4\,AgCl + 4\,e^-$

Amperometry: -0.6 V vs. Ag/AgCl reference applied to drive reaction
fixed $[H^+]$, fixed $[Cl^-]$