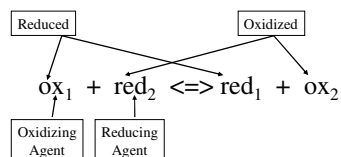


Ch. 14 & 16 An Introduction to Electrochemistry & Redox Titrations

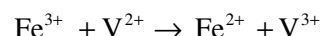
Redox Reaction - the basics



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

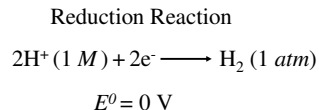
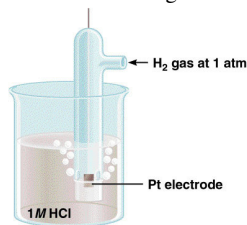
Oxidizing agent (oxidant): takes electrons

Reducing agent (reductant): gives electrons



Standard Electrode Potentials

Standard reduction potential (E°) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 M and all gases are at 1 atm.



Standard hydrogen electrode (S.H.E.)

Standard Reduction (Half-Cell) Potentials

- The S.H.E. is the cathode. It consists of a Pt electrode in a tube placed in 1 M H^+ solution. H_2 is bubbled through the tube.
- For the S.H.E., we assign

$$2\text{H}^+(aq, 1M) + 2\text{e}^- \rightarrow \text{H}_2(g, 1\text{ atm})$$
- E°_{red} of zero.
- The potential of a cell can be calculated from standard reduction potentials:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode})$$

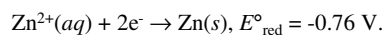
Standard Reduction (Half-Cell) Potentials

- Consider $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2\text{e}^-$. We measure E_{cell} relative to the S.H.E. (cathode):

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode})$$

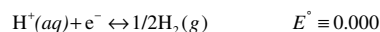
$$0.76\text{ V} = 0\text{ V} - E^\circ_{\text{red}}(\text{anode}).$$

- Therefore, $E^\circ_{\text{red}}(\text{anode}) = -0.76\text{ V}$.
- Standard reduction potentials must be written as reduction reactions:

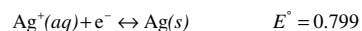


Standard Potentials

We use hydrogen (S.H.E.)



We can measure E° for other half-reactions, relative to the hydrogen reaction, e.g. for silver:



Standard reduction potentials are listed in Ap. H in your book. E° for the H_2 reaction is for the reaction at 25° C

Table 14-1 Ordered redox potentials

Oxidizing agent	Reducing agent	E° (V)
$F_2(g) + 2e^-$	$\rightleftharpoons 2F^-$	2.890
$O_3(g) + 2H^+ + 2e^-$	$\rightleftharpoons O_2(g) + H_2O$	2.075
$MnO_4^- + 8H^+ + 5e^-$	$\rightleftharpoons Mn^{2+} + 4H_2O$	1.507
$Ag^+ + e^-$	$\rightleftharpoons Ag(s)$	0.799
$Cu^{2+} + 2e^-$	$\rightleftharpoons Cu(s)$	0.339
$2H^+ + 2e^-$	$\rightleftharpoons H_2(g)$	0.000
$Cd^{2+} + 2e^-$	$\rightleftharpoons Cd(s)$	-0.402
$K^+ + e^-$	$\rightleftharpoons K(s)$	-2.936
$Li^+ + e^-$	$\rightleftharpoons Li(s)$	-3.040

Oxidizing power increases (upward arrow)
Reducing power increases (downward arrow)

Table 14-1
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Nernst Equation for a Half-Reaction

- The Nernst Equation relates the potential of the half reaction to equilibrium conditions

- For the half-reaction:

$$aA + ne^- \leftrightarrow bB \quad E^\circ \quad E = E^\circ - \frac{RT}{nF} \ln \frac{[B]^b}{[A]^a}$$

$$aA + bB + ne^- \leftrightarrow cC + dD \quad E^\circ \quad E = E^\circ - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

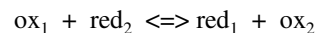
of moles of electrons

Nernst Equation for a Half-Reaction

At 298K (25°C)

$$E = E^\circ - \frac{0.05916V}{n} \log Q$$

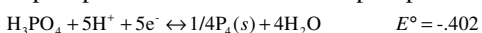
Nernst Equation for a Complete Reaction



$$E = E_+ - E_-$$

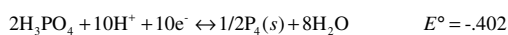
Example (Nernst)

- Write the Nernst equation for the reduction of phosphoric acid to solid white phosphorous:



$$E = -0.402 - \frac{0.05916}{5} \log \frac{1}{[H_3PO_4][H^+]^5}$$

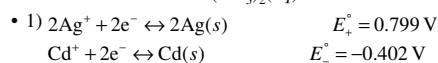
- Note that multiplying the reaction by any factor does not affect E° or the calculated E :



$$E = -0.402 - \frac{0.05916}{10} \log \frac{1}{[H_3PO_4]^2 [H^+]^{10}}$$

Example (Net Reaction)

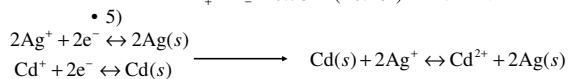
- Find the voltage for the Ag-Cd cell and state if the reaction is spontaneous if the right cell contained 0.50 M $AgNO_3(aq)$ and the left contained 0.010 M $Cd(NO_3)_2(aq)$



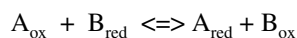
$$2) E_+ = 0.799 - \frac{0.05916}{2} \log \frac{1}{[0.50]^2} = 0.781 \text{ V}$$

$$3) E_- = -0.402 - \frac{0.05916}{2} \log \frac{1}{[0.010]} = -0.461 \text{ V}$$

$$4) E = E_+ - E_- = 0.781 - (-0.461) = +1.242 \text{ V}$$



Determination of the Equivalence Point



At equivalence point, $E_{cell}=0$:

$$E_A^\circ - \frac{0.0592}{n_A} \log \frac{[A_{red}]}{[A_{ox}]} = E_B^\circ - \frac{0.0592}{n_B} \log \frac{[B_{red}]}{[B_{ox}]}$$

$A_{red} = B_{ox}$ and $B_{red} = A_{ox}$ at the equivalence point

$$E = \frac{n_A E_A^\circ + n_B E_B^\circ}{n_A + n_B} \quad \text{Valid for simple Redox expressions}$$

Redox Titration Curve

EXAMPLE: Derive the titration curve for 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0 M in $HClO_4$. Potential of saturated calomel electrode is 0.241 V.

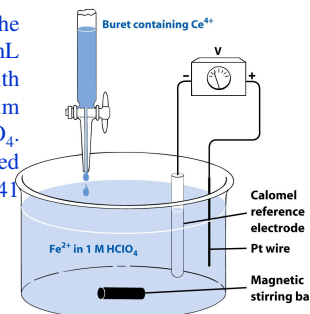
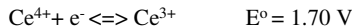


Figure 18-1 Quantitative Chemical Analysis, Seventh Edition © 2003 W. H. Freeman and Company

EXAMPLE: Derive the titration curve for 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0 M in $HClO_4$. Potential of saturated calomel electrode is 0.241 V.

Titration reaction: $Fe^{2+} + Ce^{4+} \rightleftharpoons Ce^{3+} + Fe^{3+}$

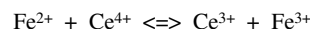


At 0.00 mL of Ce^{4+} added, initial point no Ce^{4+} present; minimal, unknown $[Fe^{3+}]$; thus, insufficient information to calculate E

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.241$$

$$= 0.767 - \frac{0.0592}{1} \log \frac{1.54 \times 10^{-2}}{2.038 \times 10^{-2}} - 0.241 = 0.533 \text{ V}$$

EXAMPLE: Derive the titration curve for 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0 M in $HClO_4$. Potential of saturated calomel electrode is 0.241 V.

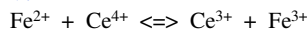


At 15.00 mL of Ce^{4+} added, $V_{Fe}M_{Fe} > V_{Ce}M_{Ce}$
"Buffer region"

$$[Fe^{3+}] = \frac{V_{Ce}M_{Ce}}{V_{Fe} + V_{Ce}}$$

$$= \frac{(15.00 \text{ mL})(0.1000 \text{ M})}{(50.00 + 15.00) \text{ mL}} = 2.308 \times 10^{-2} \text{ M}$$

EXAMPLE: Derive the titration curve for 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0 M in $HClO_4$. Potential of saturated calomel electrode is 0.241 V.



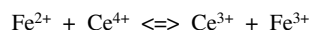
At 15.00 mL of Ce^{4+} added, $V_{Fe}M_{Fe} > V_{Ce}M_{Ce}$
"Buffer region"

$$[Fe^{3+}] = 2.308 \times 10^{-2} \text{ M}$$

$$[Fe^{2+}] = \frac{V_{Fe}M_{Fe} - V_{Ce}M_{Ce}}{V_{Fe} + V_{Ce}}$$

$$= \frac{(50.00 \text{ mL})(0.0500 \text{ M}) - (15.00 \text{ mL})(0.1000 \text{ M})}{(50.00 + 15.00) \text{ mL}} = 1.54 \times 10^{-2} \text{ M}$$

EXAMPLE: Derive the titration curve for 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0 M in $HClO_4$. Potential of saturated calomel electrode is 0.241 V.



At 15.00 mL of Ce^{4+} added, $V_{Fe}M_{Fe} > V_{Ce}M_{Ce}$
"Buffer region"

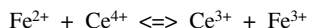
Half-reactions: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad E^\circ = 0.767 \text{ V}$

$$[Fe^{3+}] = 2.308 \times 10^{-2} \text{ M} \quad [Fe^{2+}] = 1.538 \times 10^{-2} \text{ M}$$

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.241$$

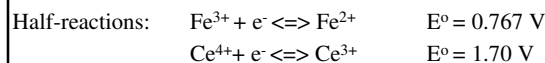
$$= 0.767 - \frac{0.0592}{1} \log \frac{1.54 \times 10^{-2}}{2.038 \times 10^{-2}} - 0.241 = 0.533 \text{ V}$$

EXAMPLE: Derive the titration curve for 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0 M in HClO_4 . Potential of saturated calomel electrode is 0.241 V.



At 25.00 mL of Ce^{4+} added, $V_{\text{Fe}}M_{\text{Fe}} = V_{\text{Ce}}M_{\text{Ce}}$,

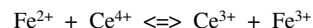
Equivalence point



$$E = \frac{n_{\text{Fe}}E_{\text{Fe}} + n_{\text{Ce}}E_{\text{Ce}}}{n_{\text{Fe}} + n_{\text{Ce}}} - 0.241$$

$$= \frac{0.767 + 1.70}{1+1} - 0.241 = 1.23 - 0.241 = 0.99 \text{ V}$$

EXAMPLE: Derive the titration curve for 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0 M in HClO_4 . Potential of saturated calomel electrode is 0.241 V.



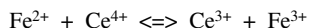
At 26.00 mL of Ce^{4+} added, $V_{\text{Fe}}M_{\text{Fe}} < V_{\text{Ce}}M_{\text{Ce}}$,

After equivalence point

$$[\text{Ce}^{3+}] = \frac{V_{\text{Fe}}M_{\text{Fe}}}{V_{\text{Fe}} + V_{\text{Ce}}}$$

$$= \frac{(50.00\text{mL})(0.0500\text{M})}{(50.00 + 26.00)\text{mL}} = 3.29 \times 10^{-2} \text{ M}$$

EXAMPLE: Derive the titration curve for 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0 M in HClO_4 . Potential of saturated calomel electrode is 0.241 V.



At 26.00 mL of Ce^{4+} added, $V_{\text{Fe}}M_{\text{Fe}} < V_{\text{Ce}}M_{\text{Ce}}$,

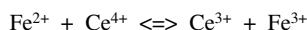
After equivalence point

$$[\text{Ce}^{3+}] = 3.29 \times 10^{-2} \text{ M}$$

$$[\text{Ce}^{4+}] = \frac{V_{\text{Ce}}M_{\text{Ce}} - V_{\text{Fe}}M_{\text{Fe}}}{V_{\text{Fe}} + V_{\text{Ce}}}$$

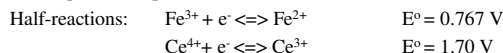
$$= \frac{(26.00\text{mL})(0.1000\text{M}) - (50.00\text{mL})(0.0500\text{M})}{(50.00 + 26.00)\text{mL}} = 1.32 \times 10^{-3} \text{ M}$$

EXAMPLE: Derive the titration curve for 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0 M in HClO_4 . Potential of saturated calomel electrode is 0.241 V.



At 26.00 mL of Ce^{4+} added, $V_{\text{Fe}}M_{\text{Fe}} > V_{\text{Ce}}M_{\text{Ce}}$

After equivalence point



$$[\text{Ce}^{3+}] = 3.29 \times 10^{-2} \text{ M} \quad [\text{Ce}^{4+}] = 1.32 \times 10^{-3} \text{ M}$$

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} - 0.241$$

$$= 1.70 - \frac{0.0592}{1} \log \frac{3.29 \times 10^{-2}}{1.32 \times 10^{-3}} - 0.241 = 0.63 \text{ V}$$

Theoretical curve for titration of 100.0 mL of 0.500 M Fe^{2+} with 0.100 M Ce^{4+} in 1 M HClO_4 . (p.330-331)

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} - 0.241$$

$$= 0.767 - \frac{0.0592}{1} \log 1 - 0.241 = 0.526 \text{ V}$$

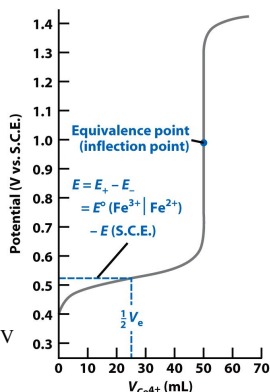


Figure 16-2
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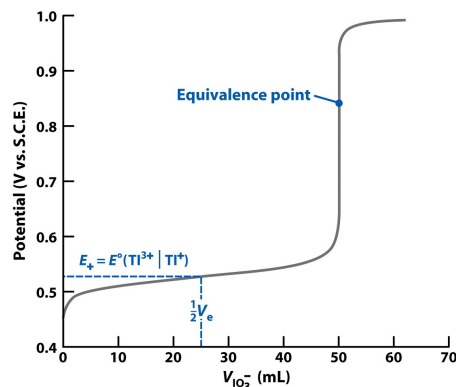


Figure 16-3
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Table 16-2 Redox indicators

Indicator	Color		E°
	Oxidized	Reduced	
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

Table 16-2
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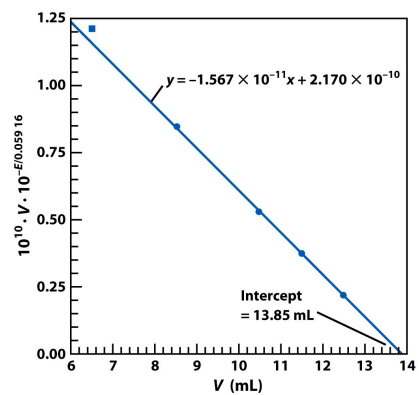


Figure 16-4
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