Chapters 19 & 20

Applications of Standard Electrode Potentials & Redox Titrations

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- Part 1: Calculating Potentials of Electrochemical Cells (Examples 19-1~10)--Nernst equation for half-cells and chemical cells

(1) For an half cell: Ox + ne = Red

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{Red}} = E^0 + \frac{0.0592}{n}\log\frac{a_{ox}}{a_{Red}} \quad (@298\ K)$$

(2) For an electrochemical cell:

$E_{cell} = E_{cathode(+,\,right)} - E_{anode(-,left)}$; $\Delta G = -nF\Delta E_{cell}$

$$\Delta E = \Delta E^0 - \frac{RT}{nF}\ln Q = \Delta E^0 - \frac{0.0592}{n}\log Q \text{ at 298 K (25 °C)}$$

(3) At chemical equilibrium:

$E_{cell} = E_{cathode(+,\,right)} - E_{anode(-,left)} = 0$

When the reaction reaches equalibrium

$$\ln K_{eq} = \frac{nF\Delta E^0}{RT}, \text{ or } \log K_{eq} = \frac{n\Delta E^0}{0.0592} \text{ (at 298K)}$$

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Example 19-1

Calculate the thermodynamic potential of the following cell and the free energy change associated with the cell reaction:

$$Cu|Cu^{2+}\ (0.0200\ M)||Ag^{+}(0.0200\ M)|Ag$$

Solution

The two half-reactions and standard potentials are

$$Ag^{+} + e^{-} \rightleftharpoons Ag(s) \qquad E^0 = 0.799\ V$$
$$Cu^{2+} + 2e^{-} \rightleftharpoons Cu(s) \qquad E^0 = 0.337\ V$$

The electrode potentials are

$$E_{Ag^{+}/Ag} = 0.799 - 0.0592 \log\frac{1}{0.0200} = 0.6984\ V$$

$$E_{Cu^{2+}/Cu} = 0.337 - \frac{0.0592}{2}\log\frac{1}{0.0200} = 0.2867\ V$$

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$$E_{cell} = E_{right} - E_{left} = E_{Ag^+/Ag} - E_{Cu^{2+}/Cu} = 0.6984 - 0.2867 = +0.412\ V$$

The free energy change ΔG for the reaction $Cu(s) + 2Ag^+ \rightleftharpoons Cu^{2+} + Ag(s)$ is found from

(1 calorie = 4.18 Joules)

$$\Delta G = -nFE_{cell} = -2 \times 96485\ C \times 0.412\ V = -79{,}503\ J\ (18.99\ kcal)$$

EXAMPLE 19-2

Calculate the potential for the cell

$$Ag|Ag^+(0.0200\ M) \parallel Cu^{2+}(0.0200\ M)|Cu$$

$$E_{Ag^+/Ag} = 0.6984\ V \quad \text{and} \quad E_{Cu^{2+}/Cu} = 0.2867\ V$$

$$E_{cell} = E_{right} - E_{left} = E_{Cu^{2+}/Cu} - E_{Ag^+/Ag} = 0.2867 - 0.6984 = -0.412\ V$$

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EXAMPLE 19-3

Calculate the potential of the following cell and indicate the reaction that would occur spontaneously if the cell were short-circuited (see Figure 19-1).

$$Pt|U^{4+}(0.200\ M), UO_2^{2+}(0.0150\ M), H^+(0.0300\ M) \parallel Fe^{2+}(0.0100\ M), Fe^{3+}(0.0250\ M)|Pt$$

Solution

The two half-reactions are

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^0 = +0.771\ V$$

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \qquad E^0 = +0.334\ V$$

The electrode potential for the right-hand electrode is

$$E_{right} = 0.771 - 0.0592 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$= 0.771 - 0.0592 \log \frac{0.0100}{0.0250} = 0.771 - (-0.0236)$$

$$= 0.7946\ V$$

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The electrode potential for the left-hand electrode is

$$E_{left} = 0.334 - \frac{0.0592}{2} \log \frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}$$

$$= 0.334 - \frac{0.0592}{2} \log \frac{0.200}{(0.0150)(0.0300)^4}$$

$$= 0.334 - 0.2136 = 0.1204\ V$$

and

$$E_{cell} = E_{right} - E_{left} = 0.7946 - 0.1204 = 0.6742\ V$$

The positive sign means that the spontaneous reaction is the oxidation of U^{4+} on the left and the reduction of Fe^{3+} on the right, or

$$U^{4+} + 2Fe^{3+} + 2H_2O \rightarrow UO_2^{2+} + 2Fe^{2+} + 4H^+$$

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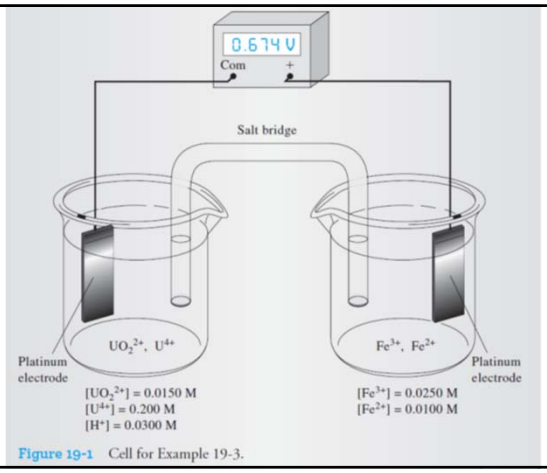

Figure 19-1 Cell for Example 19-3.

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EXAMPLE 19-4

Calculate the cell potential for

$$Ag|AgCl(sat'd), HCl(0.0200\ M)|H_2(0.800\ atm), Pt$$

Solution

The two half-reactions and their corresponding standard electrode potentials are (see Table 18-1).

$$2H^+ + 2e^- \rightleftharpoons H_2(g) \qquad E^0_{H^+/H_2} = 0.000\ V$$

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^- \qquad E^0_{AgCl/Ag} = 0.222\ V$$

$$E_{right} = 0.000 - \frac{0.0592}{2}\log\frac{P_{H_2}}{[H^+]^2} = -\frac{0.0592}{2}\log\frac{0.800}{(0.0200)^2}$$

$$= -0.0977\ V$$

$$E_{left} = 0.222 - 0.0592\log[Cl^-] = 0.222 - 0.0592\log 0.0200$$

$$= 0.3226\ V$$

$$E_{cell} = E_{right} - E_{left} = -0.0977 - 0.3226 = -0.420\ V$$

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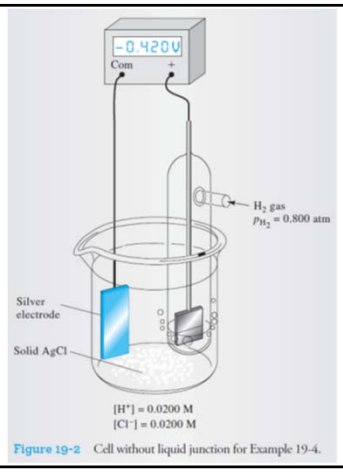

Figure 19-2 Cell without liquid junction for Example 19-4.

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EXAMPLE 19-10

Calculate the equilibrium constant for the reaction

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightleftharpoons 5MnO_2(s) + 4H^+$$

Comproportionation vs Disproportionation

Solution

In Appendix 5, we find

$$2MnO_4^- + 8H^+ + 6e^- \rightleftharpoons 2MnO_2(s) + 4H_2O \qquad E^0 = +1.695\ V$$
$$3MnO_2(s) + 12H^+ + 6e^- \rightleftharpoons 3Mn^{2+} + 6H_2O \qquad E^0 = +1.23\ V$$

$$\frac{6(1.695 - 1.23)}{0.0592} = \log \frac{[H^+]^{12}}{[MnO_4^-]^2[Mn^{2+}]^3[H^+]^8}$$

$$47.1 = \log \frac{[H^+]^4}{[MnO_4^-]^2[Mn^{2+}]^3} = \log K_{eq}$$

$$K_{eq} = \text{antilog } 47.1 = 1 \times 10^{47}$$

$3\ Cl_2 + 6\ OH^- \rightarrow 5\ Cl^- + ClO_3^- + 3\ H_2O$

$2\ O_2^- + 2\ H^+ \rightarrow H_2O_2 + O_2$

$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

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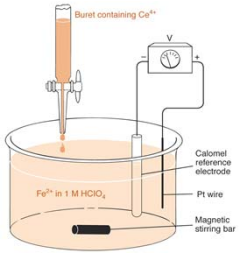
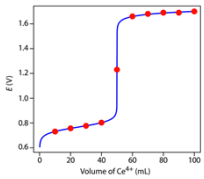
Part 2: Constructing Redox Titration Curves





Ref. E (SCE)||Fe^{3+}, Fe^{2+},Ce^{4+}, Ce^{3+} | Pt

$E_{cell} = E_{system} - E_{SCE}$

$E_{system} = E_{cell} + E_{SCE} = E_{Fe^{3+}/Fe^{2+}} = E_{Ce^{4+}/Ce^{3+}}$

Fe^{2+} (Analyte) + Ce^{4+} (Titrant) $\rightleftharpoons$ Fe^{3+} + Ce^{3+} (rapid and reversible)

Reaction is rapid and reversible, hence at equilibrium

$E_{Fe^{3+}/Fe^{2+}} = E_{Ce^{4+}/Ce^{3+}} = E_{system}$

(*During the entire titration process*)

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Calculation of Equivalence Potential

For $Ox_1 + n_{Ox_1} e \rightleftharpoons Red_1$

$Ox_2 + n_{Ox_2} e \rightleftharpoons Red_2$

$Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2$

$$E_{eq} = \frac{n_{Ox_1} E^0_{Ox_1/Red_1} + n_{Ox_2} E^0_{Ox_2/Red_2}}{n_{Ox_1} + n_{Ox_2}}$$

e.g., Fe^{2+} + Ce^{4+} $\Leftrightarrow$ Ce^{3+} + Fe^{3+}

$$E_{eq} = \frac{n_{Fe} E^0_{Fe} + n_{Ce} E^0_{Ce}}{n_{Fe} + n_{Ce}} = \frac{1 \cdot 1.44 + 1 \cdot 0.68}{2} = 1.06\ V$$

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However:

$U^{4+} + 2Ce^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 2Ce^{3+} + 4H^+$

in 1.0 M H_2SO_4

$UO_2^{2+} + 4H^+ + 2e \rightleftharpoons U^{4+} + 2H_2O \quad E^0 = 0.334$ V

$Ce^{4+} + e \rightleftharpoons Ce^{3+} \quad E^{0'} = 1.44$ V

$$E_{eq} = \frac{2E^0_{UO_2^{2+}/U^{4+}} + E^{0'}_{Ce^{4+}/Ce^{3+}}}{3} + \frac{0.0592}{3}\log[H^+]^4$$

$$= \frac{2\times 0.334 + 1.44}{3} + \frac{0.0592}{3}\log(1.0^*)^4 = 0.703 \text{ V}$$

E_{eq} is pH dependent. * with dilution effect.

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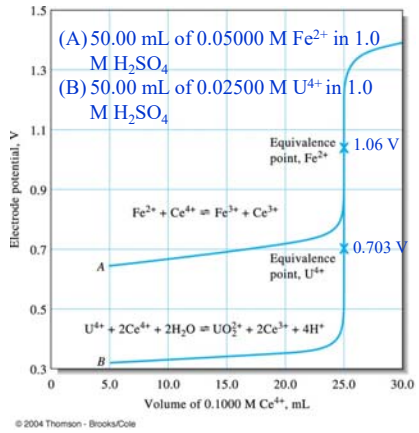

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Redox Titration Curve

EXAMPLE 1: 50.00 mL of 0.0500 M Fe^{2+} is titrated with 0.1000 M Ce^{4+} in a medium that is 1.0 M in H_2SO_4. How many mLs of Ce^{4+} are required to reach to the equivalence point,?

$Fe^{2+} + Ce^{4+} \Leftrightarrow Ce^{3+} + Fe^{3+}$

At equivalence point,

$$n_{Ce^{4+}} = n_{Fe^{2+}};\ (CV)_{Ce^{4+}} = (CV)_{Fe^{2+}}$$

$$0.1000 \bullet V_{Ce^{4+}} = (50.00 \bullet 0.0500)_{Fe^{2+}}$$

$$V_{Ce^{4+}} = 25.00\ mL$$

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Effect of Variables on Redox Titration Curves

- E_{system} is usually independent of dilution → Redox titration curves are usually independent of analyte and titrant concentrations--Different from neutralization, precipitation and complexation titrations.
- The larger the equilibrium constants or the standard ΔE^0 ($\log K_{eq} = n\Delta E^0/0.0592$), the greater the change in equivalence-point region—Similar to other types of titrations.

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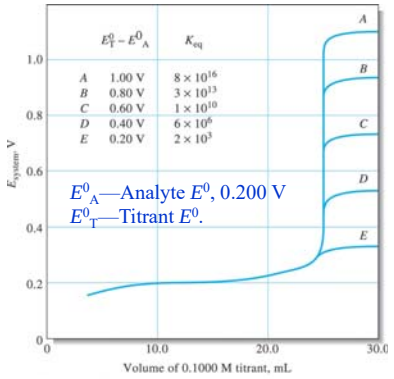

Effect of titrant electrode potential on reaction completeness.

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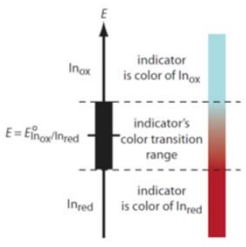
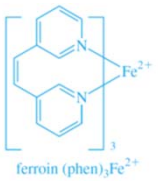
Oxidation/Reduction Indicators

- General redox indicators—substances change color upon redox reaction, which is dependent only on the potential of the titration system.





ferroin $(phen)_3Fe^{2+}$

$(phen)_3Fe^{3+} + e^- \rightleftharpoons (phen)_3Fe^{2+}$

pale blue red

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General Redox Indicators

$In_{ox} + ne \rightleftharpoons In_{red}$ $\quad E = E^0_{In_{ox}/In_{red}} + \frac{0.0592}{n} \log \frac{[In_{OX}]}{[In_{Red}]}$

The color change is seen when $\frac{[In_{OX}]}{[In_{Red}]} \leq \frac{1}{10}$

changes to $\frac{[In_{OX}]}{[In_{Red}]} \geq \frac{10}{1}$ (overall change 100 times)

$E = E^0_{In_{ox}/In_{red}} \pm \frac{0.0592}{n}$

$0.118/n$ V is needed for the E_{system} change.

Many indicators, $n = 2$, 59 mV E_{system} change sufficient.

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TABLE 19-3

Selected Oxidation/Reduction Indicators*

Indicator	Color		Transition Potential, V	Conditions
	Oxidized	Reduced		
5-Nitro-1,10-phenanthroline iron(II) complex	Pale blue	Red-violet	+1.25	1 M H_2SO_4
2,3'-Diphenylamine dicarboxylic acid	Blue-violet	Colorless	+1.12	7-10 M H_2SO_4
1,10- Phenanthroline iron(II) complex	Pale blue	Red	+1.11	1 M H_2SO_4
5-Methyl 1,10-phenanthroline iron(II) complex	Pale blue	Red	+1.02	1 M H_2SO_4
Erioglaucin A	Blue-red	Yellow-green	+0.98	0.5 M H_2SO_4
Diphenylamine sulfonic acid	Red-violet	Colorless	+0.85	Dilute acid
Diphenylamine	Violet	Colorless	+0.76	Dilute acid
p-Ethoxychrysoidine	Yellow	Red	+0.76	Dilute acid
Methylene blue	Blue	Colorless	+0.53	1 M acid
Indigo tetrasulfonate	Blue	Colorless	+0.36	1 M acid
Phenosafranine	Red	Colorless	+0.28	1 M acid

*Data in part from I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, 2nd ed., Vol. 1, p. 140.

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Oxidation/Reduction Indicators

- Specific indicators: (1) Starch for I_3^-, (2) SCN^- (thiocyanate) for Fe(III)
- $I_2 + I^- = I_3^-$ (triiodide ion)

$$\text{Starch} + I_3^- \rightleftharpoons \text{Starch-}I_3^-\text{-complex} \overset{+e}{\rightleftharpoons} \text{Starch} + 3I^-$$

(red-brown) (blue) (colorless)

$$SCN^- + Fe^{3+} \rightleftharpoons Fe^{III}(SCN)^{2+} \overset{+e}{\rightleftharpoons} SCN^- + Fe^{2+}$$

(yellow-green) (Orange/Red) (colorless)

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The Strong Oxidants - Potassium Permanganate and Cerium (IV)

MnO_4^- (purple) + $8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$ $E^0 = 1.51$ V

$Ce^{4+} + e \rightleftharpoons Ce^{3+}$ $E^{0\prime} = 1.44$ V (1 M H_2SO_4)

Reactions are in strong acidic media.

MnO_4^- (purple) is a self-indicator.

Can be standardized with oxalate:

$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightleftharpoons 2Mn^{2+} + 10CO_2(g) + 8H_2O$

$Ce^{4+} + H_2C_2O_4 \rightleftharpoons 2Ce^{3+} + 2CO_2(g) + 2H^+$

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TABLE 20-3

Some Common Oxidants Used as Standard Solutions

Reagent and Formula	Reduction Product	Standard Potential, V	Standardized With	Indicator*	Stability†
Potassium permanganate, $KMnO_4$	Mn^{2+}	1.51‡	$Na_2C_2O_4$, Fe, As_2O_3	MnO_4^-	(b)
Potassium bromate, $KBrO_3$	Br^-	1.44‡	$KBrO_3$	(1)	(a)
Cerium(IV), Ce^{4+}	Ce^{3+}	1.44‡	$Na_2C_2O_4$, Fe, As_2O_3	(2)	(a)
Potassium dichromate, $K_2Cr_2O_7$	Cr^{3+}	1.33‡	$K_2Cr_2O_7$, Fe	(3)	(a)
Iodine, I_2	I^-	0.536‡	$BaS_2O_3 \cdot H_2O$, $Na_2S_2O_3$	starch	(c)

*(1) α-Napthoflavone; (2) 1,10-phenanthroline iron(II) complex (ferroin); and (3) diphenylamine sulfonic acid.

†(a) indefinitely stable; (b) moderately stable, requires periodic standardization; and (c) somewhat unstable, requires frequent standardization.

‡$E^{0\prime}$ in 1 M H_2SO_4.

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TABLE 20-5

Some Applications of Potassium Permanganate and Cerium(IV) Solutions

Substance Sought	Half-Reaction	Conditions
Sn	$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$	Prereduction with Zn
H_2O_2	$H_2O_2 \rightleftharpoons O_2(g) + 2H^+ + 2e^-$	
Fe	$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$	Prereduction with $SnCl_2$ or with Jones or Walden reductor
$Fe(CN)_6^{4-}$	$Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-} + e^-$	
V	$VO^{2+} + 3H_2O \rightleftharpoons V(OH)_4^+ + 2H^+ + e^-$	Prereduction with Bi amalgam or SO_2
Mo	$Mo^{3+} + 4H_2O \rightleftharpoons MoO_4^{2-} + 8H^+ + 3e^-$	Prereduction with Jones reductor
W	$W^{5+} + 4H_2O \rightleftharpoons WO_4^{2-} + 8H^+ + 3e^-$	Prereduction with Zn or Cd
U	$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$	Prereduction with Jones reductor
Ti	$Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e^-$	Prereduction with Jones reductor
$H_2C_2O_4$	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	
Mg, Ca, Zn, Co, Pb, Ag	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	Sparingly soluble metal oxalates filtered, washed, and dissolved in acid; liberated oxalic acid titrated
HNO_2	$HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-$	15-min reaction time; excess $KMnO_4$ back-titrated
K	$K_3NaCo(NO_2)_6 + 6H_2O \rightleftharpoons Co^{2+} + 6NO_3^- + 12H^+ + 2K^+ + Na^+ + 11e^-$	Precipitated as $K_3NaCo(NO_2)_6$; filtered and dissolved in $KMnO_4$; excess $KMnO_4$ back-titrated
Na	$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$	Precipitated as $NaZn(UO_2)_3(OAc)_9$; filtered, washed, dissolved; U determined as above

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Strong Reducing Agents—Fe(II) and thiosulfate

(1) $Fe^{2+} \rightleftharpoons Fe^{3+} + e$ (freshly prepared from stable agent)

(2) $2S_2O_3^{2-}$ (thiosulfate) $\rightleftharpoons S_4O_6^{2-}$ (tetrathionate) + 2e

Standardized with pottasium iodate:

https://www.youtube.com/watch?v=_tZYYZ9F7fM

IO_3^- + $5I^-$ (excess) + $6H^+$ $\rightleftharpoons$ $3I_2$ + $2H_2O$ (in flask)

$I_2 + 2S_2O_3^{2-}$ (Titrant, in burette) $\rightleftharpoons S_4O_6^{2-} + I^-$

1 mol IO_3^- = 3 mol I_2 = 6 mol $S_2O_3^{2-}$

Indicator: I_2-starch (blue)

I_2-starch + $2S_2O_3^{2-}$ (*excess*) $\rightleftharpoons S_4O_6^{2-} + I^-$ + *starch*

blue colorless

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EXAMPLE 20-1

A solution of sodium thiosulfate was standardized by dissolving 0.1210 g KIO_3 (214.00 g/mol) in water, adding a large excess of KI, and acidifying with HCl. The liberated iodine required 41.64 mL of the thiosulfate solution to decolorize the blue starch/iodine complex. Calculate the molar concentration of the $Na_2S_2O_3$.

Solution 1 mol IO_3^- = 6 mol $S_2O_3^{2-}$

$$\text{amount } Na_2S_2O_3 = 0.1210 \text{ g } KIO_3 \times \frac{1 \text{ mmol } KIO_3}{0.21400 \text{ g } KIO_3} \times \frac{6 \text{ mmol } Na_2S_2O_3}{\text{mmol } KIO_3}$$

$$= 3.3925 \text{ mmol } Na_2S_2O_3$$

$$c_{Na_2S_2O_3} = \frac{3.3925 \text{ mmol } Na_2S_2O_3}{41.64 \text{ mL } Na_2S_2O_3} = 0.08147 \text{ M}$$

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TABLE 20-2

Some Applications of Sodium Thiosulfate as a Reductant

Analyte	Half-Reaction	Special Conditions
IO_4^-	$IO_4^- + 8H^+ + 7e^- \rightleftharpoons \frac{1}{2}I_2 + 4H_2O$	Acidic solution
	$IO_4^- + 2H^+ + 2e^- \rightleftharpoons IO_3^- + H_2O$	Neutral solution
IO_3^-	$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$	Strong acid
BrO_3^-, ClO_3^-	$XO_3^- + 6H^+ + 6e^- \rightleftharpoons X^- + 3H_2O$	Strong acid
Br_2, Cl_2	$X_2 + 2I^- \rightleftharpoons I_2 + 2X^-$	
NO_2^-	$HNO_2 + H^+ + e^- \rightleftharpoons NO(g) + H_2O$	
Cu^{2+}	$Cu^{2+} + I^- + e^- \rightleftharpoons CuI(s)$	
O_2	$O_2 + 4Mn(OH)_2(s) + 2H_2O \rightleftharpoons 4Mn(OH)_3(s)$	Basic solution
	$Mn(OH)_3(s) + 3H^+ + e^- \rightleftharpoons Mn^{2+} + 3H_2O$	Acidic solution
O_3	$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$	
Organic peroxide	$ROOH + 2H^+ + 2e^- \rightleftharpoons ROH + H_2O$	

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Calculation Examples

1. Aqueous solutions containing approximately 3% (w/w) H_2O_2 are sold in drug stores as a disinfectant. A method for determining the peroxide content involves the use of 0.01145 M $KMnO_4$. Assume that you wish to use between 30 and 45 mL of the above $KMnO_4$ reagent for a titration. Calculate the amount of H_2O_2 needs to take.

$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$$

The amount of $KMnO_4$ in 35 to 45 mL of the reagent is between

$$\text{amount } KMnO_4 = 35 \text{ mL } KMnO_4 \times 0.01145 \frac{\text{mmol } KMnO_4}{\text{mL } KMnO_4}$$

$$= 0.401 \text{ mmol } KMnO_4$$

and

$$\text{amount } KMnO_4 = 45 \times 0.01145 = 0.515 \text{ mmol } KMnO_4$$

The amount of H_2O_2 consumed by 0.401 mmol of $KMnO_4$ is

$$\text{amount } H_2O_2 = 0.401 \text{ mmol } KMnO_4 \times \frac{5 \text{ mmol } H_2O_2}{2 \text{ mmol } KMnO_4} = 1.00 \text{ mmol } H_2O_2$$

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and

$$\text{amount } H_2O_2 = 0.515 \times \frac{5}{2} = 1.29 \text{ mmol } H_2O_2$$

We, therefore, need to take samples that contain from 1.00 to 1.29 mmol H_2O_2.

$$\text{mass sample} = 1.00 \text{ mmol } H_2O_2 \times 0.03401 \frac{\text{g } H_2O_2}{\text{mmol } H_2O_2} \times \frac{100 \text{ g sample}}{3 \text{ g } H_2O_2}$$

$$= 1.1 \text{ g sample}$$

to

$$\text{mass sample} = 1.29 \times 0.03401 \times \frac{100}{3} = 1.5 \text{ g sample}$$

Thus, our samples should weigh between 1.1 and 1.5 g. These should be diluted to perhaps 75 to 100 mL with water and made slightly acidic with dilute H_2SO_4 before titration.

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The purity of a sample of sodium oxalate, $Na_2C_2O_4$, is determined by titrating with a standard solution of $KMnO_4$. If a 0.5116-g sample requires 35.62 mL of 0.0400 M $KMnO_4$ to reach the titration's end point, what is the %w/w $Na_2C_2O_4$ in the sample.

2.

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightleftharpoons 2Mn^{2+} + 10CO_2(g) + 8H_2O$$

The moles of $KMnO_4$ used to reach the end point is

$$(0.0400 \text{ M } KMnO_4)(0.03562 \text{ L}) = 1.42 \times 10^{-3} \text{ mol } KMnO_4$$

which means the sample contains

$$1.42 \times 10^{-3} \text{ mol } KMnO_4 \times \frac{5 \text{ mol } Na_2C_2O_4}{2 \text{ mol } KMnO_4} = 3.55 \times 10^{-3} \text{ mol } Na_2C_2O_4$$

Thus, the %w/w $Na_2C_2O_4$ in the sample of ore is

$$3.55 \times 10^{-3} \text{ mol } Na_2C_2O_4 \times \frac{134.00 \text{ g } Na_2C_2O_4}{\text{mol } Na_2C_2O_4} = 0.476 \text{ g } Na_2C_2O_4$$

$$\frac{0.476 \text{ g } Na_2C_2O_4}{0.5116 \text{ g sample}} \times 100 = 93.0\% \text{ w/w } Na_2C_2O_4$$

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