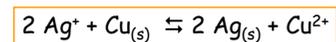
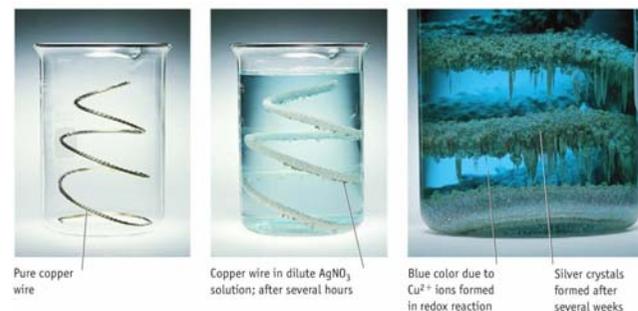


CEN 5774
Fundamentos de Química Analítica

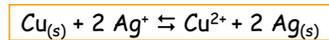
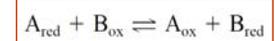
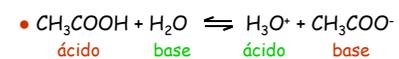
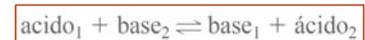
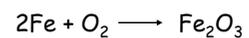
Equilíbrio redox

Fábio R. P. Rocha
(frprocha@cena.usp.br)

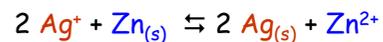
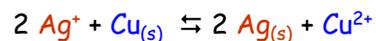
Reações redox



Reações redox



Reações redox



Oxidantes: $\text{Ag}^+ > \text{Cu}^{2+} > \text{Zn}^{2+}$

Redutores: $\text{Zn} > \text{Cu} > \text{Ag}$

Número de oxidação

5. Hidrogênio \Rightarrow nox = +1; Oxigênio \Rightarrow nox = -2

• Ex.: OH^- , H_2O , CaO , CaCO_3

• Exceção:

- hidretos (CaH_2) e peróxidos (O_2^{2-} , H_2O_2) \Rightarrow nox = -1

6. Halogênios (Cl, Br, I) \Rightarrow nox = -1

• Ex.: NaCl , CaBr_2 , HI

• Exceção: compostos com oxigênio e fluor: ClO^- , BrO_3^-

Número de oxidação

1. Átomos em um elemento puro \Rightarrow nox = 0

• Ex.: Cu , I_2 , S_8 , F_2

2. Íons monoatômicos \Rightarrow nox = carga do íon

• Ex.: Ca^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+}

3. Composto neutro $\Rightarrow \sum \text{nox} = 0$

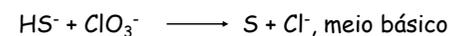
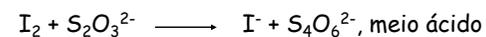
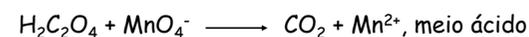
Íon poliatômico $\Rightarrow \sum \text{nox} =$ carga do íon

4. Fluor \Rightarrow nox = -1

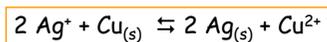
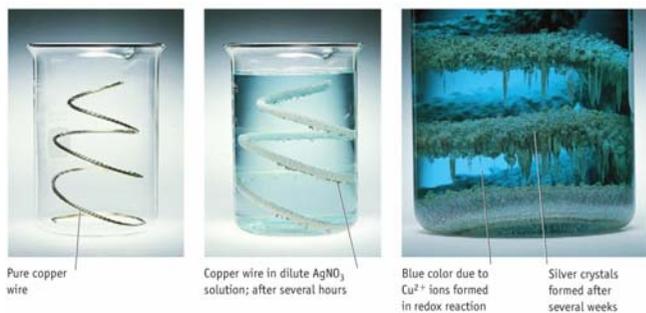
• Ex.: NaF , CaF_2

Balanceamento de equações

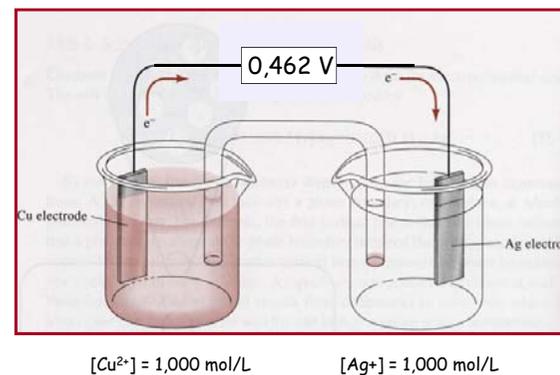
✓ Exemplos



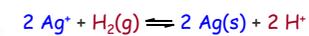
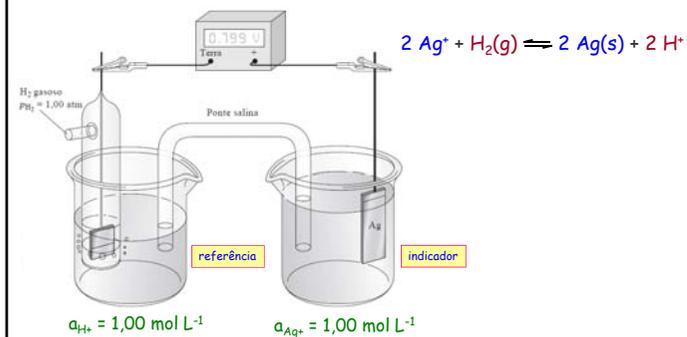
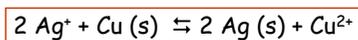
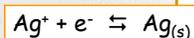
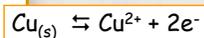
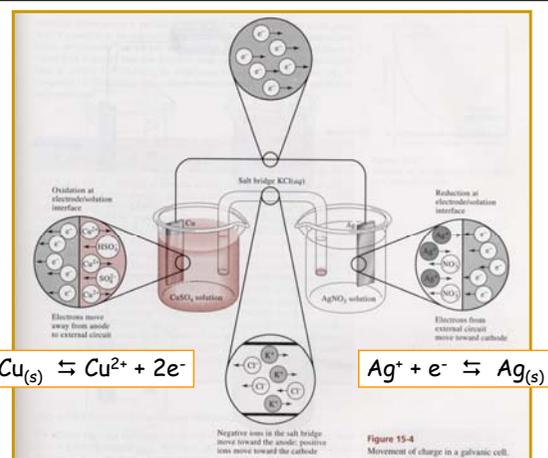
Reações redox



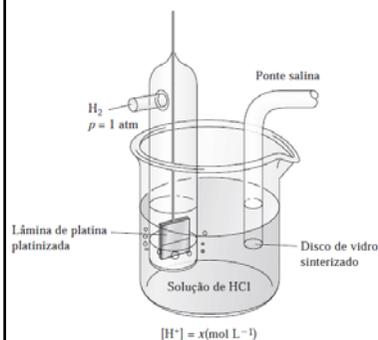
Cela galvânica



Potencial padrão de eletrodo (E⁰)

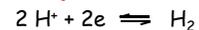


Eletrodo padrão de hidrogênio

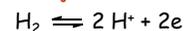


✓ eletrodo reversível;

• reação catódica:

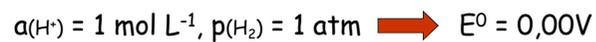


• reação anódica:

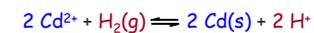
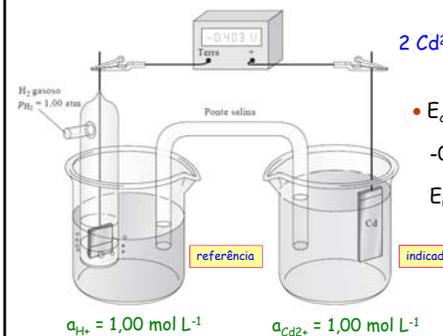


✓ $E = f(T, a_{\text{H}^+}, p_{\text{H}_2})$

Convenção



Potencial padrão de eletrodo (E^0)



$$E_{\text{cela}} = E_{\text{indicador}} - E_{\text{referência}}$$

$$-0,403 = E_{\text{indicador}} - 0$$

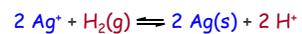
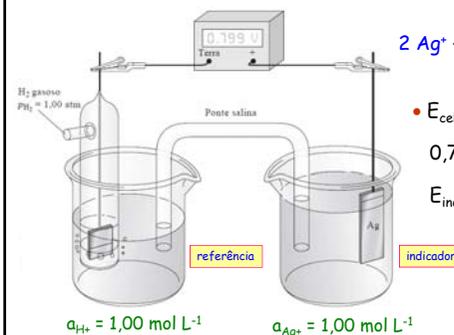
$$E_{\text{indicador}} = -0,403 \text{ V}$$

$$a_{\text{H}^+} = 1,00 \text{ mol L}^{-1}$$

$$a_{\text{Cd}^{2+}} = 1,00 \text{ mol L}^{-1}$$



Potencial padrão de eletrodo (E^0)



$$E_{\text{cela}} = E_{\text{indicador}} - E_{\text{referência}}$$

$$0,799 = E_{\text{indicador}} - 0$$

$$E_{\text{indicador}} = +0,799 \text{ V}$$

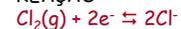
$$a_{\text{H}^+} = 1,00 \text{ mol L}^{-1}$$

$$a_{\text{Ag}^+} = 1,00 \text{ mol L}^{-1}$$



Tabela de potenciais padrão (relativos)

REAÇÃO

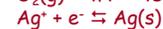


E^0 a 25 °C (V)

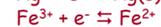
+1,359



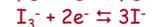
+1,229



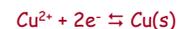
+0,799



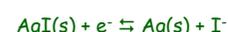
+0,771



+0,536



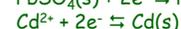
+0,337



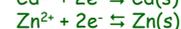
-0,151



-0,350



-0,403



-0,763

Potencial padrão de eletrodo (E^0)

- ✓ Potencial de eletrodo quando produtos e reagentes apresentam $a = 1$
- ✓ IUPAC \Rightarrow Potenciais de redução
- ✓ $E^0 = f(T)$
- ✓ Independe do número de mols de reagentes

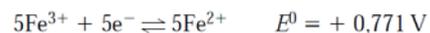


Tabela de potenciais padrão (relativos)

REAÇÃO	E^0 a 25 °C (V)	
OXIDANTES		
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-$	+1,359	↑ • espécies mais efetivas como receptores de e^- , agentes oxidantes
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O}$	+1,229	
$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}(\text{s})$	+0,799	
$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$	+0,771	
$\text{I}_3^- + 2e^- \rightleftharpoons 3\text{I}^-$	+0,536	
$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}(\text{s})$	+0,337	
	0,000	
REDUTORES		
$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(\text{g})$	0,000	↓ • espécies mais efetivas como doadores de e^- , agentes redutores
$\text{AgI}(\text{s}) + e^- \rightleftharpoons \text{Ag}(\text{s}) + \text{I}^-$	-0,151	
$\text{PbSO}_4(\text{s}) + 2e^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}$	-0,350	
$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}(\text{s})$	-0,403	
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}(\text{s})$	-0,763	

Potencial padrão de eletrodo (E^0)

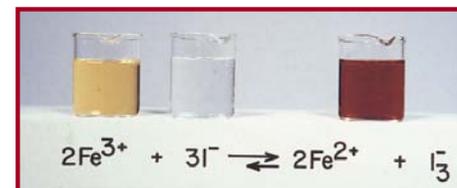
- ✓ Potencial positivo \Rightarrow reação espontânea em relação ao H_2/H^+

$$\ln K_{\text{eq}} = \frac{nFE_{\text{célula}}^0}{RT} \quad \Rightarrow \quad \log K_{\text{eq}} = \frac{nE_{\text{cél}}^0}{0,0592} \quad 25 \text{ °C}$$

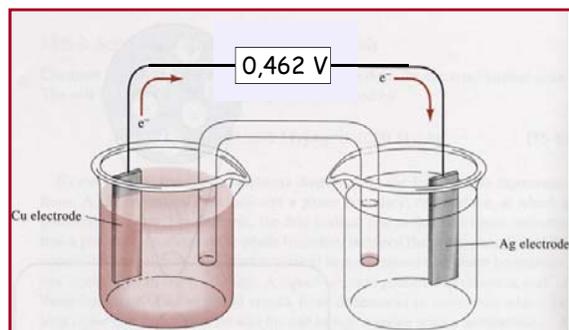
Potenciais Padrão de Eletrodos*	
Reação	E^0 a 25 °C, V
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-$	+1,359
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O}$	+1,229
$\text{Br}_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{Br}^-$	+1,087
$\text{Br}_2(\text{l}) + 2e^- \rightleftharpoons 2\text{Br}^-$	+1,065
$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}(\text{s})$	+0,799
$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(\text{g})$	0,000
$\text{AgI}(\text{s}) + e^- \rightleftharpoons \text{Ag}(\text{s}) + \text{I}^-$	-0,151
$\text{PbSO}_4 + 2e^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}$	-0,350
$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}(\text{s})$	-0,403
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}(\text{s})$	-0,763

Aplicação de potenciais de eletrodo

- ✓ Com base na tabela de potenciais padrão de eletrodo, quais espécies predominam em uma mistura de Fe^{3+} com I^- ?



Cela galvânica



$[Cu^{2+}] = 1,000 \text{ mol/L}$

$[Ag^+] = 1,000 \text{ mol/L}$

Equação de Nernst



$$E = E^0 - \frac{RT}{nF} \ln \frac{A_C^c A_D^d}{A_A^a A_B^b}$$

E^0 = potencial padrão do eletrodo

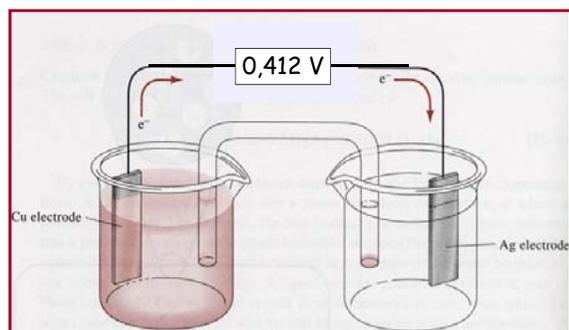
R = constante dos gases = $8,314 \text{ J K}^{-1} \text{ mol}^{-1}$

T = temperatura (Kelvin)

n = número de mols de elétrons

F = constante de Faraday = 96485 C mol^{-1}

Cela galvânica



$[Cu^{2+}] = 0,0200 \text{ mol/L}$

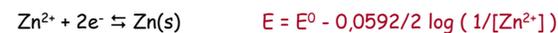
$[Ag^+] = 0,0200 \text{ mol/L}$

Equação de Nernst



$$E = E^0 - \frac{0,0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad 25^\circ\text{C}$$

EXEMPLOS:

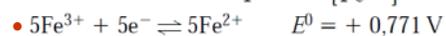


Potencial padrão de eletrodo (E^0)

- ✓ Potencial de eletrodo quando produtos e reagentes apresentam $a = 1$
- ✓ IUPAC \Rightarrow Potenciais de redução
- ✓ $E^0 = f(T)$
- ✓ Independe do número de mols de reagentes



$$E = 0,771 - \frac{0,0592}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$



$$E = 0,771 - \frac{0,0592}{5} \log \left(\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right)^5$$

Sistemas que envolvem precipitados e complexos

- $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}_{(s)} \quad E^0 = +0,799 \text{ V}$
- $\text{AgCl}_{(s)} + \text{e}^- \rightleftharpoons \text{Ag}_{(s)} + \text{Cl}^- \quad E^0 = +0,222 \text{ V}$
- $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-} + \text{e}^- \rightleftharpoons \text{Ag}_{(s)} + 2 \text{S}_2\text{O}_3^{2-} \quad E^0 = +0,017 \text{ V}$

EXEMPLO 18-3

Calcule o potencial de eletrodo para um eletrodo de prata imerso em uma solução $0,0500 \text{ mol L}^{-1}$ de NaCl utilizando (a) $E_{\text{Ag}^+/\text{Ag}}^0 = 0,799 \text{ V}$ e (b) $E_{\text{AgCl}/\text{Ag}}^0 = 0,222 \text{ V}$.



A concentração de Ag^+ nessa solução é dada por

$$[\text{Ag}^+] = \frac{K_{\text{ps}}}{[\text{Cl}^-]} = \frac{1,82 \times 10^{-10}}{0,0500} = 3,64 \times 10^{-9} \text{ mol L}^{-1}$$

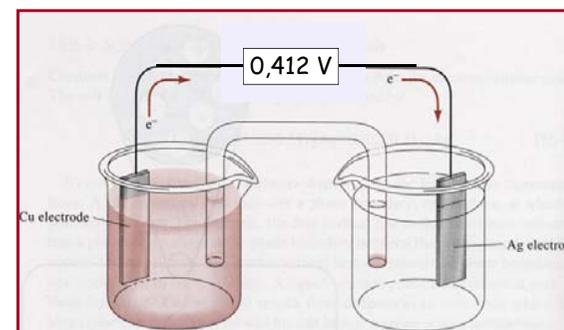
Substituindo-se esses valores na expressão de Nernst, temos

$$E = 0,799 - 0,0592 \log \frac{1}{3,64 \times 10^{-9}} = 0,299 \text{ V}$$

(b) Aqui podemos escrever

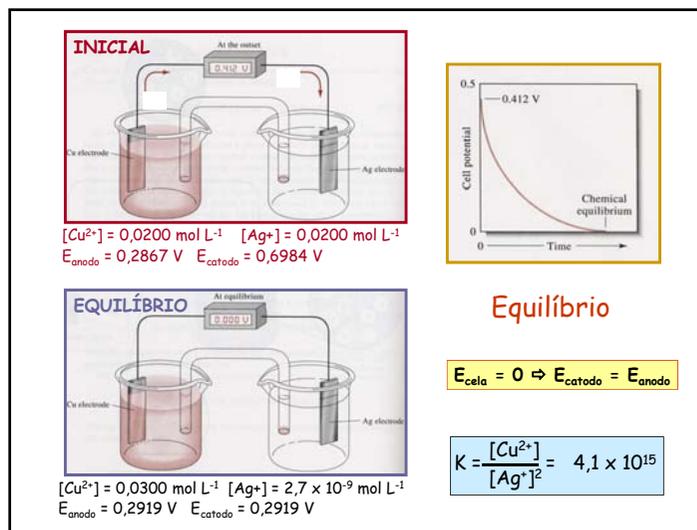
$$E = 0,222 - 0,0592 \log [\text{Cl}^-] = 0,222 - 0,0592 \log 0,0500 = 0,299 \text{ V}$$

Cela galvânica

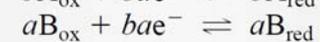
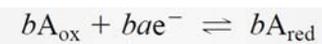
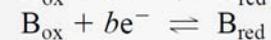


$[\text{Cu}^{2+}] = 0,0200 \text{ mol/L}$

$[\text{Ag}^+] = 0,0200 \text{ mol/L}$



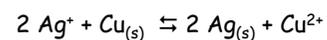
Potenciais x Constantes de equilíbrio



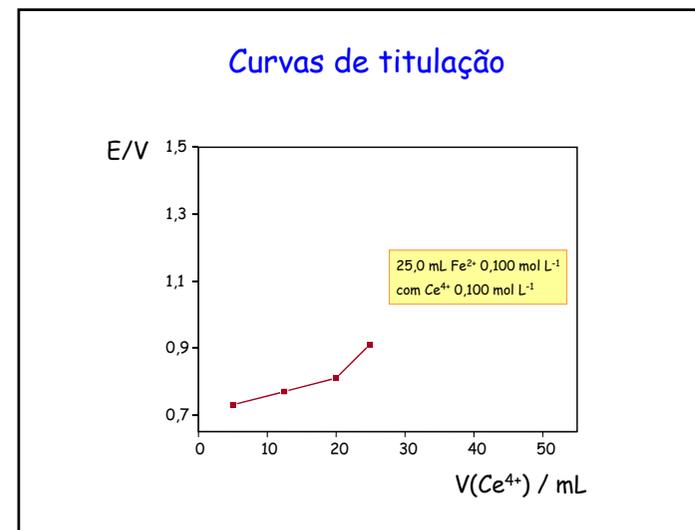
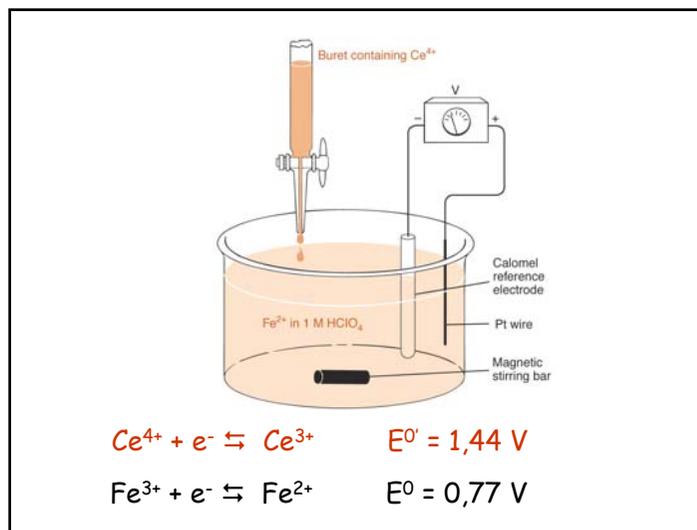
$$\log K_{\text{eq}} = \frac{ab(E_{\text{B}}^0 - E_{\text{A}}^0)}{0,0592}$$

Potenciais x Constantes de equilíbrio

✓ Com base nos valores de E⁰, calcule a constante de equilíbrio para a reação:



Volumetria redox



Curvas de titulação

V(Ce ⁴⁺) / mL	E/V
0	—
5,00	0,73
12,50	0,77
20,00	0,81
24,90	0,91

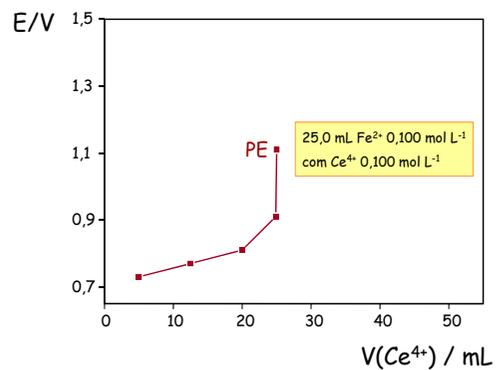
25,0 mL Fe^{2+} 0,100 mol L⁻¹
 com Ce^{4+} 0,100 mol L⁻¹

Curvas de titulação

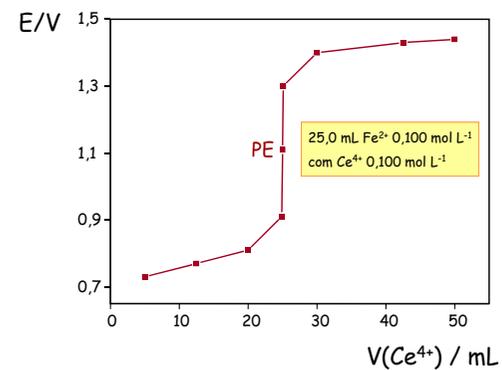
V(Ce ⁴⁺) / mL	E/V
0	—
5,00	0,73
12,50	0,77
20,00	0,81
24,90	0,91
25,00	1,11

25,0 mL Fe^{2+} 0,100 mol L⁻¹
 com Ce^{4+} 0,100 mol L⁻¹

Curvas de titulação



Curvas de titulação



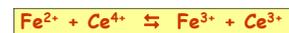
Curvas de titulação

V(Ce ⁴⁺) / mL	E/V
0	—
5,00	0,73
12,50	0,77
20,00	0,81
24,90	0,91
25,00	1,11
25,10	1,30
30,00	1,40
42,50	1,43
50,00	1,44

25,0 mL Fe²⁺ 0,100 mol L⁻¹
com Ce⁴⁺ 0,100 mol L⁻¹

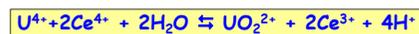
Curvas de titulação

50,00 mL Fe²⁺ 0,0500 mol/L



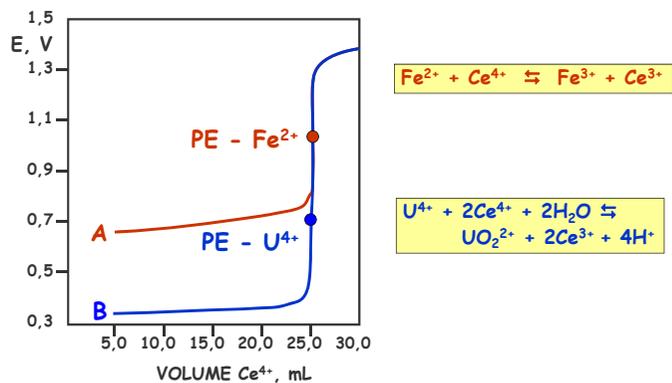
0,1000 mol/L Ce⁴⁺

50,00 mL U⁴⁺ 0,0250 mol/L

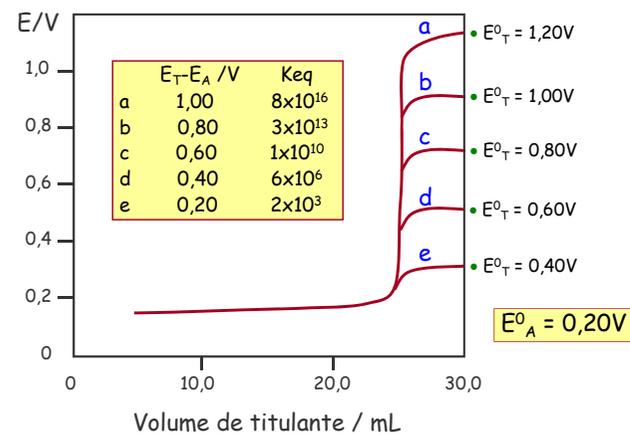


$$E_{\text{eq}} = \frac{(2E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\text{eq}} + E_{\text{UO}_2^{2+}/\text{U}^{4+}}^{\text{eq}})}{3} - \frac{0,0592}{3} \log \frac{1}{[\text{H}^+]^4}$$

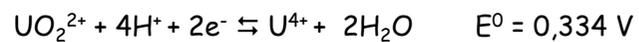
Curvas de titulação



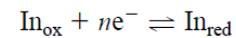
Efeito da extensão da reação



Potenciais de eletrodo



Indicadores redox



$$E = E^0_{\text{In}_{\text{ox}}/\text{In}_{\text{red}}} - \frac{0,0592}{n} \log \frac{[\text{In}_{\text{red}}]}{[\text{In}_{\text{ox}}]}$$

$$\frac{[\text{In}_{\text{red}}]}{[\text{In}_{\text{ox}}]} = \frac{1}{10}$$

$$\frac{[\text{In}_{\text{red}}]}{[\text{In}_{\text{ox}}]} = 10$$

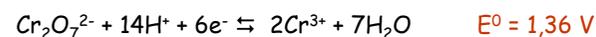
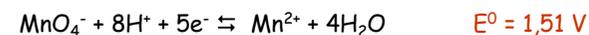
$$E = E^0_{\text{In}} \pm \frac{0,0592}{n}$$

Indicadores redox

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

Titulações redox

✓ oxidantes



✓ redutores



Escolha do indicador

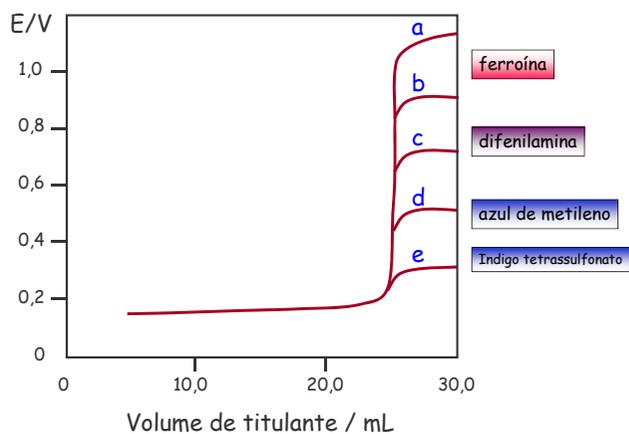


Table 16-4 Titrations with standard triiodide (iodimetric titrations)

Species analyzed	Oxidation reaction	Notes
As^{3+}	$\text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^-$	Titrate directly in NaHCO_3 solution with I_2^- .
Sn^{2+}	$\text{SnCl}_2^- + 2\text{Cl}^- \rightleftharpoons \text{SnCl}_4^- + 2\text{e}^-$	Sn(IV) is reduced to Sn(II) with granular Fe or Ni in 1 M HCl and titrated in the absence of oxygen.
N_2H_4 SO_2	$\text{N}_2\text{H}_4 \rightleftharpoons \text{N}_2 + 4\text{H}^+ + 4\text{e}^-$ $\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$ $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{SO}_3^{2-} + 4\text{H}^+ + 2\text{e}^-$	Titrate in NaHCO_3 solution. Add SO_2 (or H_2SO_3 or HSO_3^- or SO_3^{2-}) to excess standard I_2^- in dilute acid and back-titrate unreacted I_2^- with standard thiosulfate.
H_2S	$\text{H}_2\text{S} \rightleftharpoons \text{S(s)} + 2\text{H}^+ + 2\text{e}^-$	Add H_2S to excess I_2^- in 1 M HCl and back-titrate with thiosulfate.
Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+}	$\text{M}^{2+} + \text{H}_2\text{S} \rightleftharpoons \text{MS(s)} + 2\text{H}^+$ $\text{MS(s)} \rightleftharpoons \text{M}^{2+} + \text{S} + 2\text{e}^-$	Precipitate and wash metal sulfide. Dissolve in 3 M HCl with excess standard I_2^- and back-titrate with thiosulfate.
Cysteine, glutathione, thioylsulfonic acid, mercaptosulfonamide	$2\text{RSH} \rightleftharpoons \text{RSSR} + 2\text{H}^+ + 2\text{e}^-$	Titrate the sulphydryl compound at pH 4-5 with I_2^- .
HCN	$\text{I}_2 + \text{HCN} \rightleftharpoons \text{ICN} + \text{I}^- + \text{H}^+$	Titrate in carbonate-bicarbonate buffer, using <i>p</i> -xylene as an extraction indicator.
$\text{H}_2\text{C=O}$	$\text{H}_2\text{C=O} + 3\text{OH}^- \rightleftharpoons \text{HCO}_2^- + 2\text{H}_2\text{O} + 2\text{e}^-$	Add excess I_2^- plus NaOH to the unknown. After 5 min, add HCl and back-titrate with thiosulfate.
Glucose (and other reducing sugars)	$\text{RCH=O} + 3\text{OH}^- \rightleftharpoons \text{RCO}_2^- + 2\text{H}_2\text{O} + 2\text{e}^-$	Add excess I_2^- plus NaOH to the sample. After 5 min, add HCl and back-titrate with thiosulfate.
Ascorbic acid (vitamin C)	Ascorbate + $\text{H}_2\text{O} \rightleftharpoons$ dehydroascorbate + $2\text{H}^+ + 2\text{e}^-$	Titrate directly with I_2^- .
H_2PO_3	$\text{H}_2\text{PO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4 + 2\text{H}^+ + 2\text{e}^-$	Titrate in NaHCO_3 solution.

Table 16-5 Titration of I_2^- produced by analyte (iodometric titrations)

Species analyzed	Reaction	Notes
Cl_2	$Cl_2 + 3I^- \rightleftharpoons 2Cl^- + I_3^-$	Reaction in dilute acid.
$HOCl$	$HOCl + H^+ + 3I^- \rightleftharpoons Cl^- + I_3^- + H_2O$	Reaction in 0.5 M H_2SO_4 .
Br_2	$Br_2 + 3I^- \rightleftharpoons 2Br^- + I_3^-$	Reaction in dilute acid.
BrO_3^-	$BrO_3^- + 6H^+ + 9I^- \rightleftharpoons Br^- + 3I_2 + 3H_2O$	Reaction in 0.5 M H_2SO_4 .
IO_3^-	$2IO_3^- + 16I^- + 12H^+ \rightleftharpoons 6I_2 + 6H_2O$	Reaction in 0.5 M HCl.
IO_2^-	$2IO_2^- + 22I^- + 16H^+ \rightleftharpoons 8I_2 + 8H_2O$	Reaction in 0.5 M HCl.
O_2	$O_2 + 4Mn(OH)_2 + 2H_2O \rightleftharpoons 4Mn(OH)_3$ $2Mn(OH)_3 + 6H^+ + 6I^- \rightleftharpoons 2Mn^{2+} + 2I_3^- + 6H_2O$	The sample is treated with Mn^{2+} , NaOH, and KI. After 1 min, it is acidified with H_2SO_4 , and I_3^- is titrated.
H_2O_2	$H_2O_2 + 3I^- + 2H^+ \rightleftharpoons I_3^- + 2H_2O$	Reaction in 1 M H_2SO_4 with NH_4MoO_4 catalyst.
O_3^a	$O_3 + 3I^- + 2H^+ \rightleftharpoons O_2 + I_3^- + H_2O$	O_3 is passed through neutral 2 wt % KI solution. Add H_2SO_4 and titrate.
NO_2^-	$2HNO_2 + 2H^+ + 3I^- \rightleftharpoons 2NO + I_3^- + 2H_2O$	The nitric oxide is removed (by bubbling CO_2 generated in situ) prior to titration of I_3^- .
As^{5+}	$H_3AsO_4 + 2H^+ + 3I^- \rightleftharpoons H_3AsO_3 + I_3^- + H_2O$	Reaction in 5 M HCl.
$S_2O_8^{2-}$	$S_2O_8^{2-} + 3I^- \rightleftharpoons 2SO_4^{2-} + I_3^-$	Reaction in neutral solution. Then acidify and titrate.
Cu^{2+}	$2Cu^{2+} + 5I^- \rightleftharpoons 2CuI(s) + I_3^-$	NH_4HF_2 is used as a buffer.
$Fe(CN)_6^{4-}$	$2Fe(CN)_6^{4-} + 3I^- \rightleftharpoons 2Fe(CN)_6^{3-} + I_3^-$	Reaction in 1 M HCl.
MnO_2	$2MnO_2 + 16H^+ + 15I^- \rightleftharpoons 2Mn^{2+} + 5I_2 + 8H_2O$	Reaction in 0.1 M HCl.
MnO_2	$MnO_2(s) + 4H^+ + 3I^- \rightleftharpoons Mn^{2+} + I_3^- + 2H_2O$	Reaction in 0.5 M H_3PO_4 or HCl.
$Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 9I^- \rightleftharpoons 2Cr^{3+} + 3I_2 + 7H_2O$	Reaction in 0.4 M HCl requires 5 min for completion and is particularly sensitive to air oxidation.
Ce^{4+}	$2Ce^{4+} + 3I^- \rightleftharpoons 2Ce^{3+} + I_3^-$	Reaction in 1 M H_2SO_4 .

a. The pH must be ≥ 7 when O_3 is added to I^- . In acidic solution each O_3 produces 1.25 I_3^- , not 1 I_3^- .
[N. V. Klassen, D. Marchington, and H. C. E. McGowan, *Anal. Chem.* 1994, 66, 2921.]