

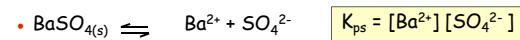
CEN 5774
Fundamentos de Química Analítica

Equilíbrios heterogêneos

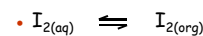
Fábio R. P. Rocha
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Equilíbrios heterogêneos

✓ Solubilidade

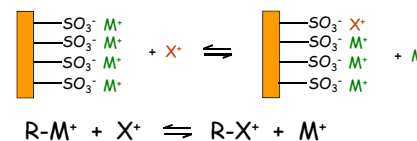


✓ Partição



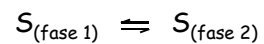
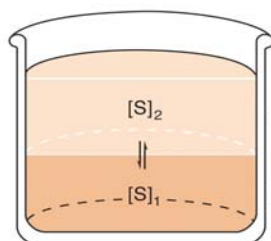
$$K_d = \frac{[\text{I}_2]_{org}}{[\text{I}_2]_{aq}}$$

✓ Troca iônica



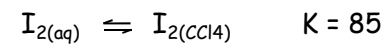
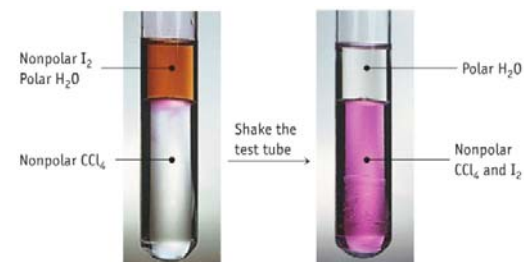
$$K = \frac{[\text{R-X}^+][\text{M}^+]}{[\text{R-M}^+][\text{X}^+]}$$

Equilíbrio de partição

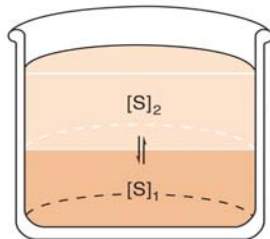


$$K = \frac{[S]_2}{[S]_1}$$

Equilíbrio de partição



Equilíbrio de partição



$$S_{(fase\ 1)} \rightleftharpoons S_{(fase\ 2)}$$

$$K = \frac{[S]_2}{[S]_1}$$

$$q = \frac{V_1}{V_1 + KV_2} \quad q = \text{fração remanescente na fase 1}$$

$$q^n = \left(\frac{V_1}{V_1 + KV_2} \right)^n$$

Eficiência de extração

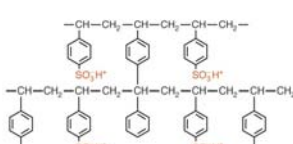
$$q^n = \left(\frac{V_1}{V_1 + KV_2} \right)^n \quad \rightarrow \quad \text{A eficiência de extração aumenta com o número de extrações}$$

✓ Exemplo:
Um soluto é 3 vezes mais solúvel em tolueno que em água. Calcule a fração de soluto remanescente em 100 mL de solução aquosa após:

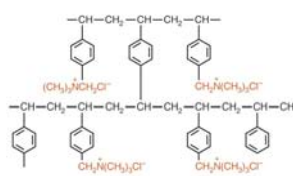
- (a) 1 extração com 500 mL de tolueno;
- (b) 5 extrações com 100 mL de tolueno.

Troca iônica

$$R-M^+ + X^- \rightleftharpoons R-X^- + M^+ \quad K = \frac{[R-X^-][M^+]}{[R-M^+][X^-]}$$



Strongly acidic cation-exchange resin



Strongly basic anion-exchange resin

Troca iônica

$$R-M^+ + X^- \rightleftharpoons R-X^- + M^+ \quad K = \frac{[R-X^-][M^+]}{[R-M^+][X^-]}$$

Table 26-3 Relative selectivity coefficients of ion-exchange resins

Cation	Sulfonic acid cation-exchange resin			Quarternary ammonium anion-exchange resin	
	Relative selectivity for divinylbenzene content			Anion	Relative selectivity
	4%	8%	10%		
Li ⁺	1.00	1.00	1.00	F ⁻	0.09
H ⁺	1.30	1.26	1.45	OH ⁻	0.09
Na ⁺	1.49	1.88	2.23	Cl ⁻	1.0
NH ₄ ⁺	1.75	2.22	3.07	Br ⁻	2.8
K ⁺	2.09	2.63	4.15	NO ₃ ⁻	3.8
Rb ⁺	2.22	2.89	4.19	I ⁻	8.7
Cs ⁺	2.37	2.91	4.15	ClO ₄ ⁻	10.0
Ag ⁺	4.00	7.36	19.4		
Tl ⁺	5.20	9.66	22.2		

SOURCE: Amberlite Ion Exchange Resins—Laboratory Guide (Rohm & Haas Co., 1979).

Equilíbrio de solubilidade



Lead iodide ($K_{sp} = 9.8 \times 10^{-9}$) is a bright yellow solid.

Constante do produto de solubilidade (Kps*)



$$K_{ps}^* = A_M^m A_X^n = q_M^m [M]^m q_X^n [X]^n$$

$$K_{ps}^* = q_M^m q_X^n K_{ps}$$

✓ Sólidos e líquidos puros $\Rightarrow A = 1$

Produto de solubilidade

- $BaSO_{4(s)} \rightleftharpoons Ba^{2+} + SO_4^{2-}$ $K_{ps} = [Ba^{2+}][SO_4^{2-}]$
- $Al(OH)_{3(s)} \rightleftharpoons Al^{3+} + 3 OH^-$ $K_{ps} = [Al^{3+}][OH^-]^3$
- $Hg_2Cl_{2(s)} \rightleftharpoons Hg_2^{2+} + 2Cl^-$ $K_{ps} = [Hg_2^{2+}][Cl^-]^2$
- $Ag_2CO_{3(s)} \rightleftharpoons 2Ag^+ + CO_3^{2-}$ $K_{ps} = [Ag^+]^2 [CO_3^{2-}]$

Constantes de produtos de solubilidade a 25 °C

Composto	Fórmula	K_{ps}	Notas
Hidróxido de alumínio	$Al(OH)_3$	3×10^{-34}	
Carbonato de bário	$BaCO_3$	$5,0 \times 10^{-9}$	
Cromato de bário	$BaCrO_4$	$2,1 \times 10^{-10}$	
Hidróxido de bário	$Ba(OH)_2 \cdot 8H_2O$	3×10^{-4}	
Iodato de bário	$Ba(IO_3)_2$	$1,57 \times 10^{-9}$	
Oxalato de bário	BaC_2O_4	1×10^{-6}	
Sulfato de bário	$BaSO_4$	$1,1 \times 10^{-10}$	
Carbonato de cádmio	$CdCO_3$	$1,8 \times 10^{-14}$	
Hidróxido de cádmio	$Cd(OH)_2$	$4,5 \times 10^{-15}$	
Oxalato de cádmio	CdC_2O_4	9×10^{-8}	
Sulfeto de cádmio	CdS	1×10^{-27}	
Carbonato de cálcio	$CaCO_3$	$4,5 \times 10^{-9}$	Calcita
	$CaCO_3$	$6,0 \times 10^{-9}$	Aragonita
Fluoreto de cálcio	CaF_2	$3,9 \times 10^{-11}$	
Hidróxido de cálcio	$Ca(OH)_2$	$6,5 \times 10^{-6}$	
Oxalato de cálcio	$CaC_2O_4 \cdot H_2O$	$1,7 \times 10^{-9}$	
Sulfato de cálcio	$CaSO_4$	$2,4 \times 10^{-5}$	
Carbonato de cobalto(II)	$CoCO_3$	$1,0 \times 10^{-10}$	
Hidróxido de cobalto(II)	$Co(OH)_2$	$1,3 \times 10^{-15}$	
sulfeto de cobalto(II)	CoS	5×10^{-22}	α
	CoS	3×10^{-26}	β

Solubilidade e Kps

sal	Kps	S (mol L ⁻¹)
AgCl	$1,8 \times 10^{-10}$	$1,3 \times 10^{-5}$
AgBr	$3,3 \times 10^{-13}$	$5,7 \times 10^{-7}$
AgI	$1,5 \times 10^{-16}$	$1,2 \times 10^{-8}$

Solubilidade e Kps

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AgCl	$1,8 \times 10^{-10}$	$1,3 \times 10^{-5}$
AgBr	$3,3 \times 10^{-13}$	$5,7 \times 10^{-7}$
AgI	$1,5 \times 10^{-16}$	$1,2 \times 10^{-8}$
Ag ₂ CrO ₄	$9,0 \times 10^{-12}$	$1,3 \times 10^{-4}$

Exercício

- ✓ Calcule a solubilidade molar do AgCl e Ag₂CrO₄ em H₂O

$$K_{ps} [\text{AgCl}] = 1,8 \times 10^{-10}$$

$$K_{ps} [\text{Ag}_2\text{CrO}_4] = 9,0 \times 10^{-12}$$

Quociente de reação



$$Q_i = [\text{Ag}^+]_i [\text{Cl}^-]_i$$

- ✓ $Q = K_{ps} \Rightarrow$ sistema em equilíbrio
- ✓ $Q < K_{ps} \Rightarrow$ solução insaturada
- ✓ $Q > K_{ps} \Rightarrow$ solução supersaturada

Exercícios

- ✓ Haverá formação de precipitado com a mistura de 100 mL de solução $5,0 \times 10^{-6} \text{ mol L}^{-1} \text{ Ni}^{2+}$ e 300 mL de solução $1,2 \times 10^{-3} \text{ Na}_2\text{CO}_3 \text{ mol L}^{-1}$?
- ✓ Qual a menor concentração de Na_2CO_3 para que a precipitação seja quantitativa?

$$K_{ps}(\text{NiCO}_3) = 6,6 \times 10^{-9}$$

Exercício

- ✓ Verifique se é possível a separação de $1,0 \times 10^{-2} \text{ mol L}^{-1} \text{ Cl}^-$ de $1,0 \times 10^{-3} \text{ mol L}^{-1} \text{ CrO}_4^{2-}$ por precipitação dos sais insolúveis com Ag^+ .

$$K_{ps}(\text{AgCl}) = 1,8 \times 10^{-10}$$

$$K_{ps}(\text{Ag}_2\text{CrO}_4) = 9,0 \times 10^{-12}$$

Fatores que afetam a solubilidade

- $\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$
- $\text{AgCH}_3\text{COO}_{(s)} \rightleftharpoons \text{Ag}^+ + \text{CH}_3\text{COO}^-$
- $\text{Ag}_2\text{CO}_{3(s)} \rightleftharpoons 2\text{Ag}^+ + \text{CO}_3^{2-}$

Fatores que afetam a solubilidade

- $\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$
- $\text{AgCH}_3\text{COO}_{(s)} \rightleftharpoons \text{Ag}^+ + \text{CH}_3\text{COO}^-$
- $\text{Ag}_2\text{CO}_{3(s)} \rightleftharpoons 2\text{Ag}^+ + \text{CO}_3^{2-}$
- ✓ Temperatura
- ✓ Presença de eletrólitos
- ✓ Presença de íon comum
- ✓ Formação de complexos
- ✓ Acidez
 - $\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{CH}_3\text{COOH} + \text{H}_2\text{O}$

Efeito de eletrólitos



$C(\text{KNO}_3)$ (mol L ⁻¹)	Solubilidade (mol L ⁻¹)
0,000	$1,28 \times 10^{-5}$
0,001	$1,32 \times 10^{-5}$
0,010	$1,43 \times 10^{-5}$

Efeito do íon comum

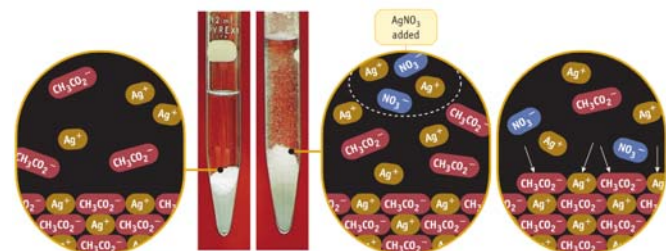


FIGURE 18.13 The common ion effect. The tube at the left contains a saturated solution of silver acetate, AgCH_3CO_2 . When 1.0 M AgNO_3 is added to the tube (right), more solid silver acetate forms.

Exercício

- ✓ Calcule a solubilidade molar do $\text{Ba}(\text{IO}_3)_2$ em:
- H_2O
 - $0,0200 \text{ mol L}^{-1} \text{ Ba}(\text{NO}_3)_2$
 - $0,0200 \text{ mol L}^{-1} \text{ NaIO}_3$

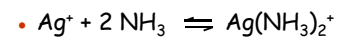
$$K_{ps} [\text{Ba}(\text{IO}_3)_2] = 1,57 \times 10^{-9}$$

Formação de complexos solúveis



$\text{AgCl}(s)$ in water

After adding $\text{NH}_3(aq)$



Formação de complexos solúveis

$\text{AgCl}(s)$, $K_{sp} = 1,8 \times 10^{-10}$
(a) AgCl precipitates on adding NaCl(aq) to $\text{AgNO}_3(\text{aq})$ (see Figure 3.7).

$[\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$
(b) The precipitate of AgCl dissolves on adding aqueous NH_3 to give water-soluble $[\text{Ag}(\text{NH}_3)_2]^+$.

$\text{AgBr}(s)$, $K_{sp} = 5,4 \times 10^{-13}$
(c) The silver-ammonia complex ion is changed to insoluble AgBr on adding NaBr(aq).

$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}(\text{aq})$
(d) Solid AgBr is dissolved on adding $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$. The product is the water-soluble complex ion $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$.

Efeito da acidez

$\text{AgCl} + \text{Ag}_3\text{PO}_4$

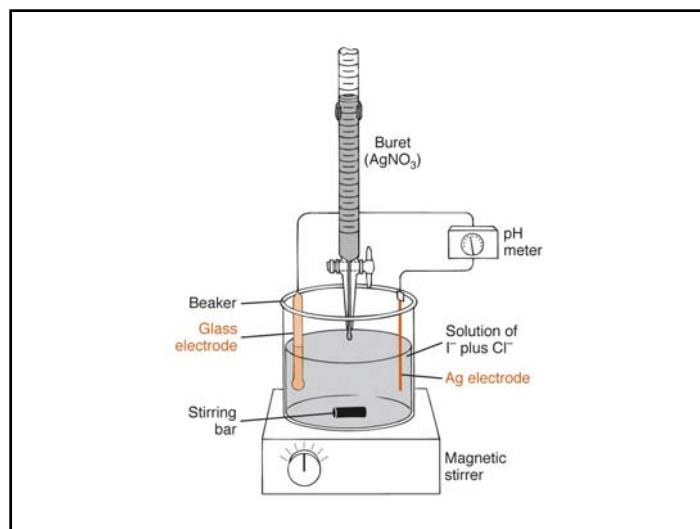
$\xrightarrow{\text{HNO}_3}$

AgCl

Solubilidade do BaCO_3

- $\text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$ $K_{ps} = 1,1 \times 10^{-10}$
 $S = (K_{ps})^{1/2} = 1,0 \times 10^{-5} \text{ mol L}^{-1}$
- $\text{BaCO}_3 \rightleftharpoons \text{Ba}^{2+} + \text{CO}_3^{2-}$ $K_{ps} = 9,3 \times 10^{-10}$
 $S_1 = (K_{ps})^{1/2} = 3,0 \times 10^{-5} \text{ mol L}^{-1}$
- Hidrólise:** $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$
 $S_2 = 1,0 \times 10^{-4} \text{ mol L}^{-1}$
- $\text{BaCO}_3 + \text{H}^+ \rightleftharpoons \text{Ba}^{2+} + \text{HCO}_3^-$
 $\text{pH } 2 \rightarrow S_3 = 1,1 \times 10^{-2} \text{ mol L}^{-1}$
 $S_3/S = 1100$

Volumetria de precipitação

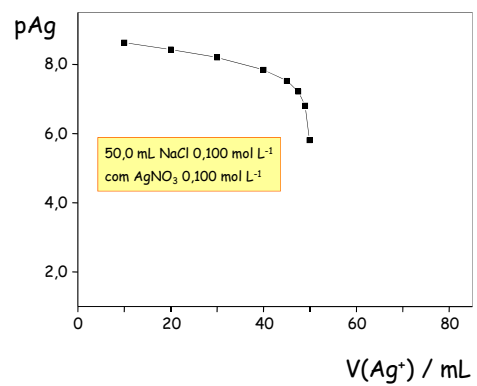


Curvas de titulação

$V(\text{Ag}^+) / \text{mL}$	pAg
0	—
10,00	8,57
20,00	8,38
30,00	8,14
45,00	7,47
49,90	5,75

50,0 mL NaCl 0,100 mol L^{-1}
com AgNO_3 0,100 mol L^{-1}

Curvas de titulação



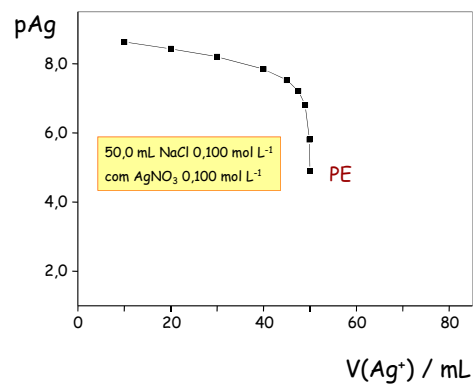
50,0 mL NaCl 0,100 mol L^{-1}
com AgNO_3 0,100 mol L^{-1}

Curvas de titulação

$V(\text{Ag}^+) / \text{mL}$	pAg
0	—
10,00	8,57
20,00	8,38
30,00	8,14
45,00	7,47
49,90	5,75
50,00	4,87

50,0 mL NaCl 0,100 mol L^{-1}
com AgNO_3 0,100 mol L^{-1}

Curvas de titulação

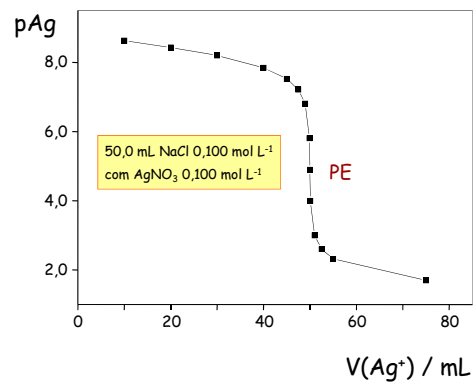


Curvas de titulação

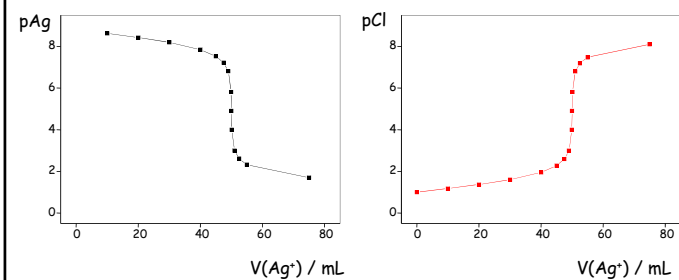
V(Ag ⁺) / mL	pAg
0	—
10,00	8,57
20,00	8,38
30,00	8,14
45,00	7,47
49,90	5,75
50,00	4,87
50,10	4,00
51,00	3,00
75,00	1,70

50,0 mL NaCl 0,100 mol L⁻¹
com AgNO₃ 0,100 mol L⁻¹

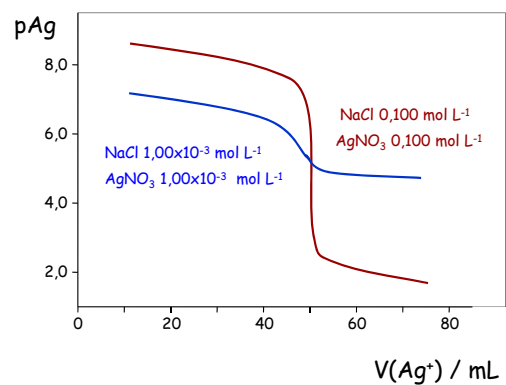
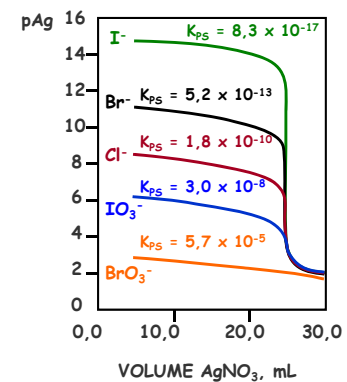
Curvas de titulação



Curvas de titulação



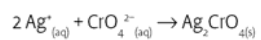
Efeito da concentração

Efeito da magnitude do K_{PS} 

Indicadores



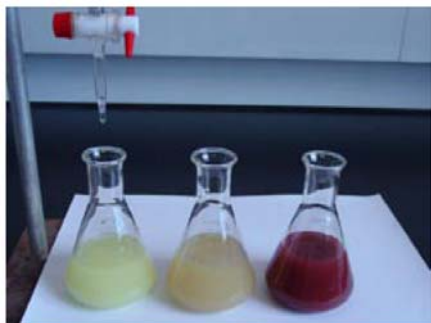
método de Mohr



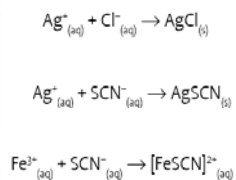
Solubilidade e Kps

sal	Kps	S (mol L ⁻¹)
AgCl	$1,8 \times 10^{-10}$	$1,3 \times 10^{-5}$
AgBr	$3,3 \times 10^{-13}$	$5,7 \times 10^{-7}$
AgI	$1,5 \times 10^{-16}$	$1,2 \times 10^{-8}$
Ag ₂ CrO ₄	$9,0 \times 10^{-12}$	$1,3 \times 10^{-4}$

Indicadores

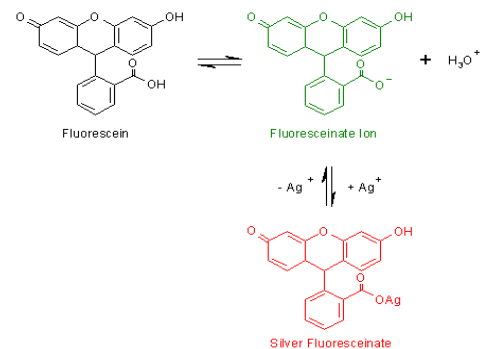


método de Volhard



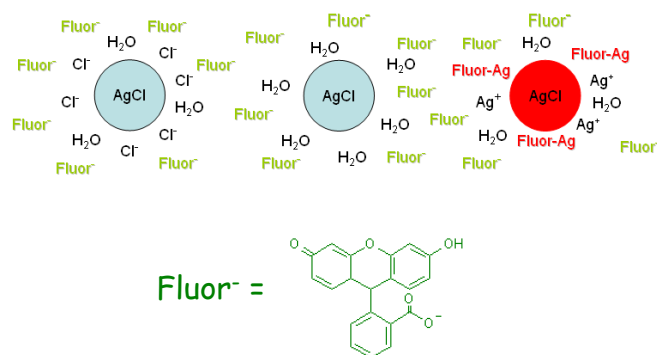
Indicadores de adsorção

método de Fajans



Indicadores de adsorção

método de Fajans



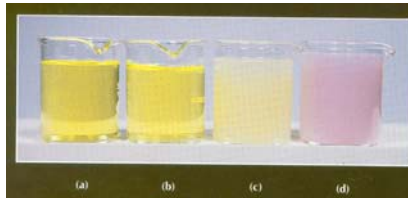
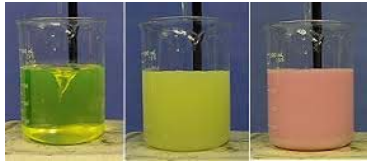
Indicadores de adsorção

método de Fajans



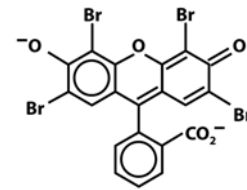
Indicadores de adsorção

método de Fajans

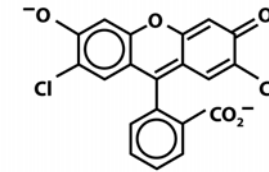


Argentometric determination of chloride: Fajans method (Section 9B-3). (a) aqueous 2', 7'-dichlorofluorescein; (b) same, plus 1 mL 0.10 M Ag⁺. Note the absence of a precipitate; (c) same, plus AgCl and an excess of Cl⁻; (d) same, plus AgCl and the first slight excess of Ag⁺.

Indicadores de adsorção



tetrabromofluoresceína
(eosina)



diclorofluoresceína

Aplicações de titulações de precipitação

Table 7-1 Applications of precipitation titrations

Species analyzed	Notes
	VOEGHARD METHOD
Br ⁻ , I ⁻ , SCN ⁻ , CNO ⁻ , AsO ₄ ³⁻	Precipitate removal is unnecessary.
Cl ⁻ , PO ₄ ³⁻ , CN ⁻ , C ₂ O ₄ ²⁻ , CO ₃ ²⁻ , S ²⁻ , CrO ₄ ²⁻	Precipitate removal required.
BH ₄ ⁻	Back titration of Ag ⁺ left after reaction with BH ₄ ⁻ : BH ₄ ⁻ + 8Ag ⁺ + 8OH ⁻ → 8Ag(s) + H ₂ BO ₃ ⁻ + 5H ₂ O
K ⁺	K ⁺ is first precipitated with a known excess of (C ₆ H ₄) ₂ B ⁻ . Remaining (C ₆ H ₄) ₂ B ⁻ is precipitated with a known excess of Ag ⁺ . Unreacted Ag ⁺ is then titrated with SCN ⁻ .
	FAJANS METHOD
Cl ⁻ , Br ⁻ , I ⁻ , SCN ⁻ , Fe(CN) ₆ ⁴⁻	Titration with Ag ⁺ . Detection with dyes such as fluorescein, dichlorofluorescein, eosin, bromophenol blue.
F ⁻	Titration with Th(NO ₃) ₃ to produce ThF ₃ . End point detected with alizarin red S.
Zn ²⁺	Titration with K ₂ Fe(CN) ₆ to produce K ₂ Zn ₃ [Fe(CN) ₆] ₂ . End-point detection with diphenylamine.
SO ₄ ²⁻	Titration with Ba(OH) ₂ in 50 vol % aqueous methanol using alizarin red S as indicator.
Hg ₂ ²⁺	Titration with NaCl to produce Hg ₂ Cl ₂ . End point detected with bromophenol blue.
PO ₄ ³⁻ , C ₂ O ₄ ²⁻	Titration with Pb(CH ₃ COO) ₂ to give Pb ₃ (PO ₄) ₂ or PbC ₂ O ₄ . End point detected with dibromofluorescein (PO ₄ ³⁻) or fluorescein (C ₂ O ₄ ²⁻).