EFFETTO MASCHERANTE DEI COMPLESSI

$$\left.\begin{matrix} Al^{+3} \\ Fe^{+3} \\ Ni^{+2} \\ Co^{+2} \end{matrix}\right| \xrightarrow{+NH_4OH} \begin{matrix} Al(OH)_3 \downarrow \\ Fe(OH)_3 \downarrow \\ [Ni(NH_3)_4]^{+2} \\ [Co(NH_3)_4]^{+2} \end{matrix}$$

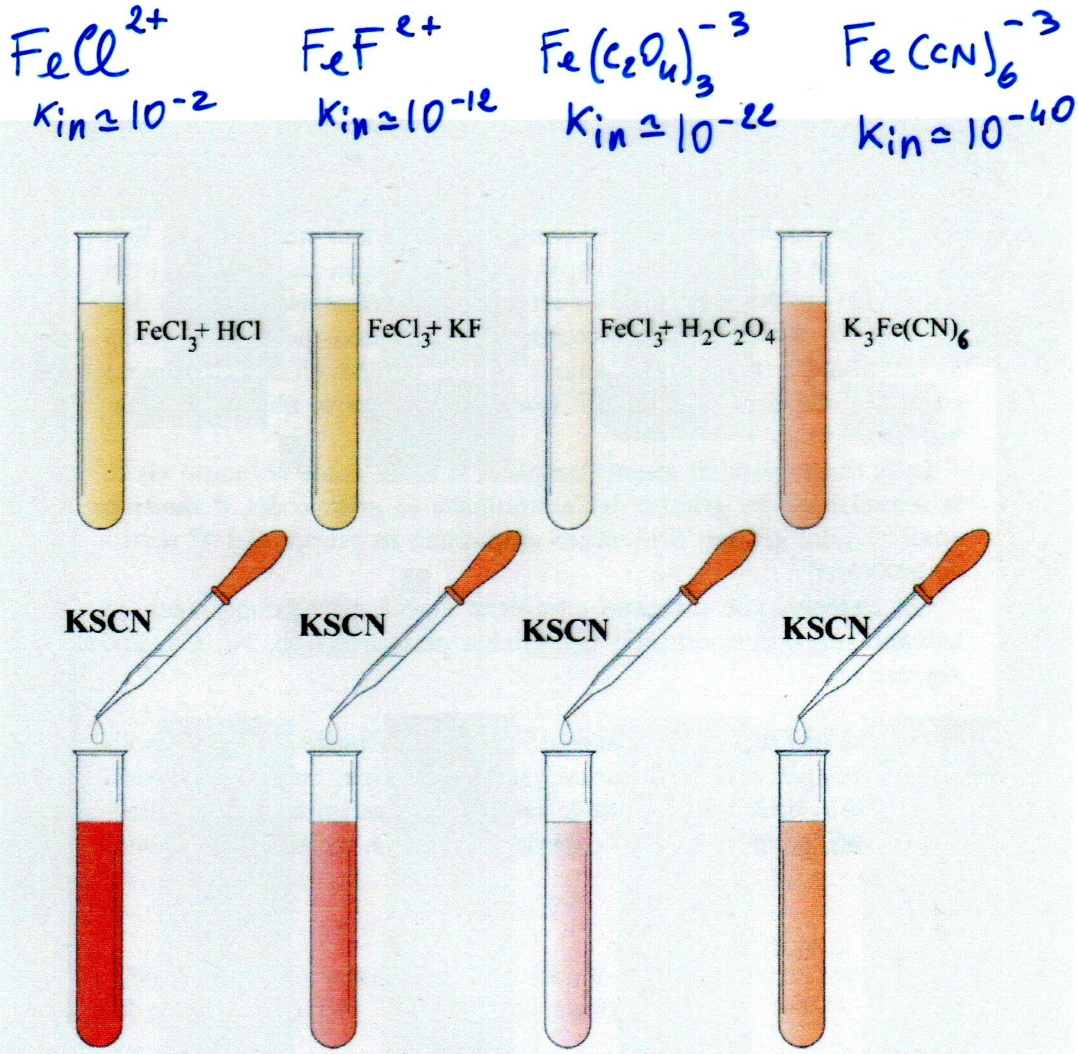
$$\left.\begin{matrix} Fe^{+3} \\ Co^{+2} \end{matrix}\right| \xrightarrow{+KSCN} \begin{matrix} Fe^{+3} + 6\,SCN^- \rightleftarrows Fe(SCN)_6^{-3} \quad k_{in} = 10^{-6} \\ Co^{+2} + 4\,SCN^- \rightleftarrows Co(SCN)_4^{-2} \quad k_{in} = 10^{-2} \end{matrix}$$

$$\xrightarrow{+F^-} \begin{matrix} Fe^{+3} + 6\,F^- \rightleftarrows FeF_6^{-3} \quad k_{in} = 10^{-16} \\ Co^{+2} \end{matrix}$$

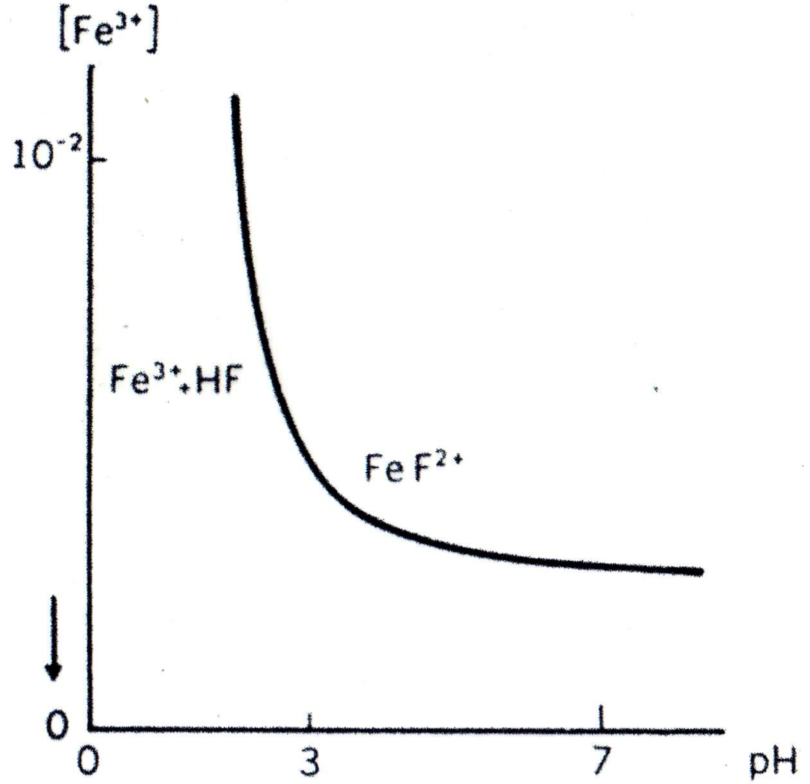
$$\downarrow + KSCN$$

$$Co^{+2} + 4\,SCN^- \rightleftarrows Co(SCN)_4^{-2} \quad k_{in} = 10^{-2}$$

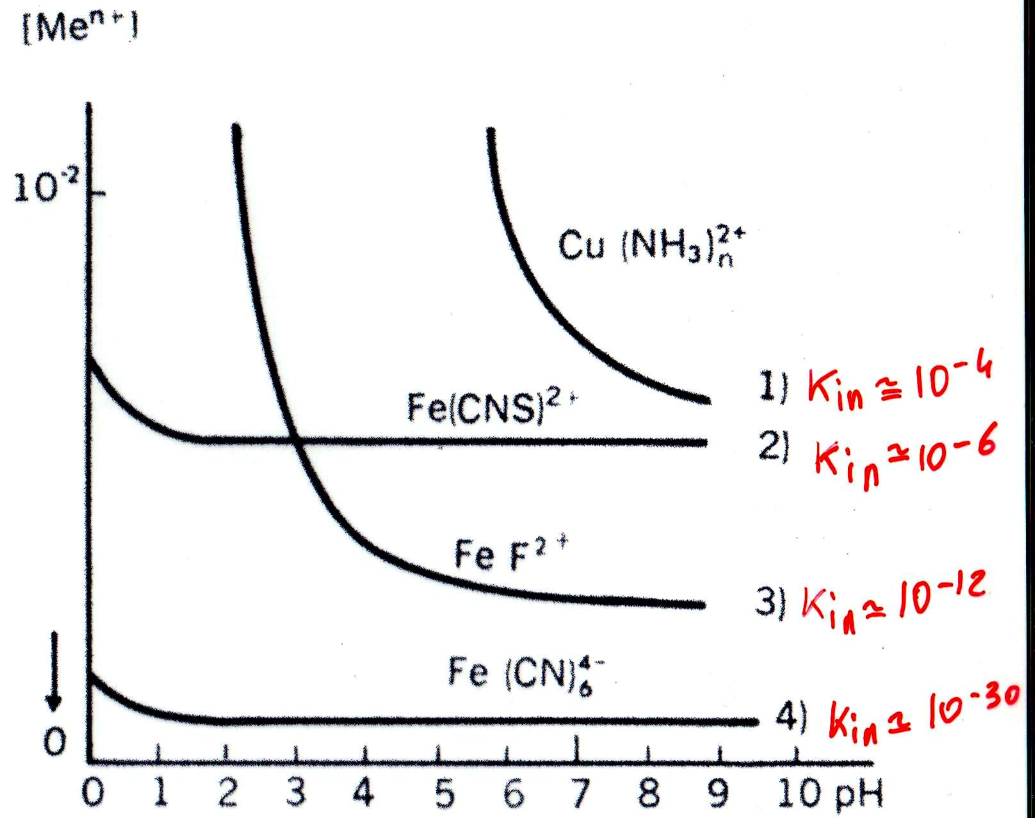
$$FeF_6^{-3}$$



L'effetto mascherante dei complessi . Soluzioni di ioni Fe^{3+} contenenti vari complessanti vengono trattate con KSCN; il composto $Fe(SCN)_3$ di colore rosso vivo si forma piu' facilmente nella soluzione cloridrica.



a). - Dissociazione del complesso FeF^{2+} al variare del pH.



b). - Dissociazione di vari complessi al variare del pH (valori approssimati).

EFFETTO DEL pH SUGLI EQUILIBRI DI COMPLESSAZIONE

1. IDROLISI DEL METALLO

Consideriamo una soluzione di Hg^{+2} 10^{-4} M
e Cl^- 1 M

equilibrio di complessazione:

$$Hg^{+2} + 4Cl^- \rightleftarrows HgCl_4^{-2}$$

$$K_{in} = \frac{[Hg^{+2}][Cl^-]^4}{[HgCl_4^{-2}]} = 10^{-16}$$

equilibrio di idrolisi:

$$Hg^{+2} + 2H_2O \rightleftarrows Hg(OH)_2 + 2H^+$$

$$K_{i_{1,2}} = \frac{[Hg(OH)_2][H^+]^2}{[Hg^{+2}]} = 10^{-6}$$

Poiché gli equilibri sono simultanei:

$$K_{in} \cdot K_{i_{1,2}} = \frac{[Hg^{+2}][Cl^-]^4[Hg(OH)_2][H^+]^2}{[HgCl_4^{-2}]\;[Hg^{+2}]} = 10^{-22}$$

$$\frac{[Hg(OH)_2]}{[HgCl_4^{-2}]} = \frac{10^{-22}}{[H^+]^2 \cdot [Cl^-]^4}$$

A pH 2:

$[H^+] = 10^{-2}\,M \qquad [Cl^-] = 1M$

$$\frac{[Hg(OH)_2]}{[HgCl_4^{-2}]} = \frac{10^{-22}}{[H^+]^2[Cl^-]^4} \qquad \frac{[Hg(OH)_2]}{[HgCl_4^{-2}]} = \frac{10^{-22}}{10^{-4}} = 10^{-18}$$

la specie prevalente è quindi il complesso, per cui

$[HgCl_4^{-2}] = 10^{-4}\,M$; $[Hg(OH)_2] = 10^{-22}\,M$;

$$[Hg^{+2}] = \frac{K_{in} \cdot [HgCl_4^{-2}]}{[Cl^-]^4} = \frac{10^{-16} \cdot 10^{-4}}{1} = 10^{-20}\,M$$

A pH 7:

$[H^+] = 10^{-7}\,M \qquad [Cl^-] = 1M$

$$\frac{[Hg(OH)_2]}{[HgCl_4^{-2}]} = \frac{10^{-22}}{[H^+]^2[Cl^-]^4} = \frac{10^{-22}}{(10^{-7})^2} = \frac{10^{-22}}{10^{-14}} = 10^{-8}$$

$[HgCl_4^{-2}] = 10^{-4}\,M$; $[Hg(OH)_2] = 10^{-8} \cdot 10^{-4} = 10^{-12}\,M$

$$[Hg^{+2}] = K_{in} \cdot [HgCl_4^{-2}] = 10^{-16} \cdot 10^{-4} = 10^{-20}\,M$$

A pH 14:

$[H^+] = 10^{-14}\,M \qquad [Cl^-] = 1M$

$$\frac{[Hg(OH)_2]}{[HgCl_4^{-2}]} = \frac{10^{-22}}{[H^+]^2[Cl^-]^4} = \frac{10^{-22}}{10^{-28}} = 10^{6}$$

$[Hg(OH)_2] = 10^{-4}\,M$; $[HgCl_4^{-2}] = \frac{10^{-4}}{10^6} = 10^{-10}\,M$

$$[Hg^{+2}] = K_{in} \cdot [HgCl_4^{-2}] = 10^{-16} \cdot 10^{-10} = 10^{-26}\,M$$

2. IDROLISI DEL LIGANDO

Consideriamo una soluzione di Ag^+ 10^{-3} M
e NH_3 1 M

equilibri di complessazione:

1
$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+$$
$$K_{in_1} = \frac{[Ag^+][NH_3]}{[Ag(NH_3)^+]} = 5 \cdot 10^{-4}$$

2
$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+$$
$$K_{in_2} = \frac{[Ag(NH_3)^+][NH_3]}{[Ag(NH_3)_2^+]} = 10^{-4}$$

equilibri di idrolisi:

$$NH_4^+ OH^- \rightleftharpoons NH_3 + H^+ + OH^-$$
$$K_i = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-5}} \simeq 10^{-9}$$

da cui:
$$\frac{[NH_3]}{[NH_4^+]} = \frac{K_i}{[H^+]} = \frac{10^{-9}}{[H^+]}$$

mentre dagli equilibri di complessazione ovvero:

1) $$\frac{[Ag^+]}{[Ag(NH_3)^+]} = \frac{K_{in1}}{[NH_3]} = \frac{5 \cdot 10^{-4}}{[NH_3]}$$

2) $$\frac{[Ag(NH_3)^+]}{[Ag(NH_3)_2^+]} = \frac{K_{in2}}{[NH_3]} = \frac{10^{-4}}{[NH_3]}$$

A pH 14:

$[H^+] = 10^{-14}$ M $\qquad \frac{[NH_3]}{[NH_4^+]} = \frac{K_i}{[H^+]} = \frac{10^{-9}}{10^{-14}} = 10^5$

$[NH_3] = 1$ M $\qquad \frac{[Ag^+]}{[Ag(NH_3)^+]} = \frac{5\cdot10^{-4}}{[NH_3]} = 5\cdot10^{-4}$

$$\frac{[Ag(NH_3)^+]}{[Ag(NH_3)_2^+]} = \frac{10^{-4}}{[NH_3]} = 10^{-4} \Rightarrow [Ag(NH_3)_2^+] = 10^{-3}\ M$$

$[Ag(NH_3)^+] = 10^{-7}$ M

$[Ag^+] = 5\cdot10^{-11}$ M

A pH 9:

$[H^+] = 10^{-9}$ M $\qquad \frac{[NH_3]}{[NH_4^+]} = \frac{K_i}{[H^+]} = \frac{10^{-9}}{10^{-9}} = 1$

legge conservaz. delle specie NH_3 ← $[NH_3] + [NH_4^+] = 1$

$[NH_3] = [NH_4^+] = 5\cdot10^{-1}$ M

$$\frac{[Ag^+]}{[Ag(NH_3)^+]} = \frac{5\cdot10^{-4}}{[NH_3]} = \frac{5\cdot10^{-4}}{5\cdot10^{-1}} = 10^{-3}$$

$$\frac{[Ag(NH_3)^+]}{[Ag(NH_3)_2^+]} = \frac{10^{-4}}{[NH_3]} = \frac{10^{-4}}{5\cdot10^{-1}} = 2\cdot10^{-4}$$

$\Rightarrow [Ag(NH_3)_2^+] = 10^{-3}$ M

$[Ag(NH_3)^+] = 2\cdot10^{-7}$ M

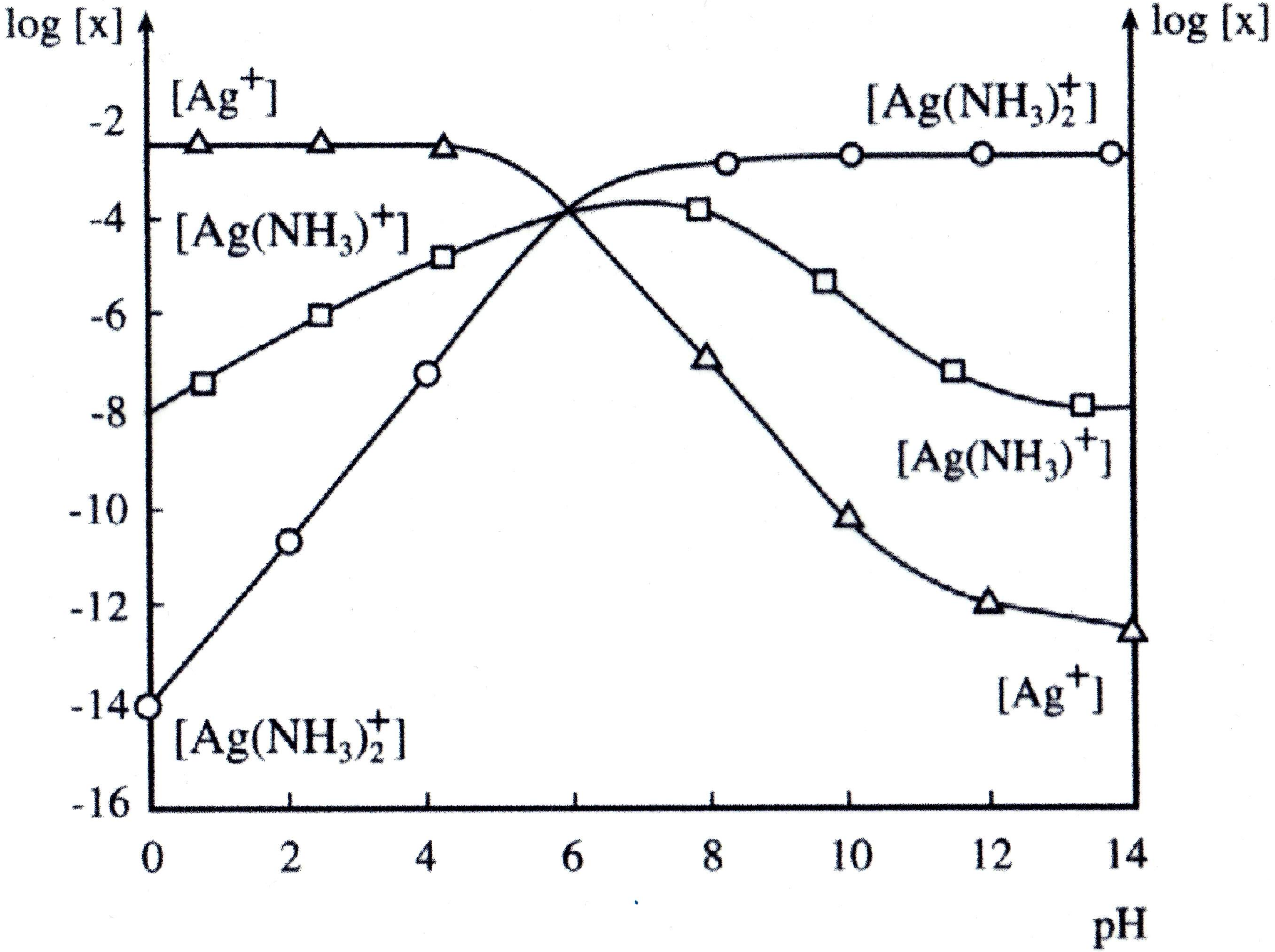
$[Ag^+] = 2\cdot10^{-10}$ M

A pH 5:

$[H^+] = 10^{-5}$ M $\qquad \frac{[NH_3]}{[NH_4^+]} = \frac{K_i}{[H^+]} = \frac{10^{-9}}{10^{-5}} = 10^{-4}$

$[NH_4^+] = 1$ M ; $[NH_3] = 10^{-4}$ M

$\frac{[Ag^+]}{[Ag(NH_3)^+]} = \frac{5\cdot10^{-4}}{[NH_3]} = 5 \quad ; \quad \frac{[Ag(NH_3)^+]}{[Ag(NH_3)_2^+]} = \frac{10^{-4}}{[NH_3]} = 1$


log [x]
log [x]
[Ag$^+$]
[Ag(NH$_3$)$_2^+$]
[Ag(NH$_3$)$^+$]
[Ag(NH$_3$)$^+$]
[Ag(NH$_3$)$_2^+$]
[Ag$^+$]
-2
-4
-6
-8
-10
-12
-14
-16
0
2
4
6
8
10
12
14
pH

legge di conservaz. delle specie Ag: $[Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+] = 10^{-3} M$

$$[Ag(NH_3)^+] = \frac{[Ag^+]}{5} = [Ag(NH_3)_2^+]$$

$$[Ag^+] + \frac{[Ag^+]}{5} + \frac{[Ag^+]}{5} = 10^{-3} M$$

$$[Ag^+]\left(1 + \frac{1}{5} + \frac{1}{5}\right) = 10^{-3} \quad [Ag^+] = 7 \cdot 10^{-4} M$$

$$[Ag(NH_3)_2^+] = [Ag(NH_3)^+] = 1.4 \cdot 10^{-4} M$$

A pH 0:

$$[H^+] = 1 M \quad \frac{[NH_3]}{[NH_4^+]} = \frac{k_i}{[H^+]} = 10^{-9}$$

$$[NH_4^+] = 1 M ; [NH_3] = 10^{-9} M$$

$$\frac{[Ag^+]}{[Ag(NH_3)^+]} = \frac{5 \cdot 10^{-4}}{[NH_3]} = \frac{5 \cdot 10^{-4}}{10^{-9}} = 5 \cdot 10^5$$

$$\frac{[Ag(NH_3)^+]}{[Ag(NH_3)_2^+]} = \frac{10^{-4}}{[NH_3]} = \frac{10^{-4}}{10^{-9}} = 10^5$$

$\Rightarrow$ $[Ag^+] = 10^{-3} M$

$[Ag(NH_3)^+] = 2 \cdot 10^{-9} M$

$[Ag(NH_3)_2^+] = 2 \cdot 10^{-14} M$

~ ~ ~ ~

$$Co^{+3} + 6\,CN^- \rightleftarrows Co(CN)_6^{-3}$$

$$k_{in} = \frac{[Co^{+3}][CN^-]^6}{[Co(CN)_6^{-3}]} = 10^{-64}$$

Supponiamo di avere una soluz. con Co^{+3} $10^{-3} M$

e CN^- $1 M$

equilibrio di idrolisi del ligando $CN^- + H_2O \rightleftarrows HCN + OH^-$

$$k_i = \frac{[HCN][OH^-]}{[CN^-]} = 10^{-5}$$

A pH = 0 $[H^+] = 1\,M$ $[OH^-] = 10^{-14}\,M$

$$\frac{[HCN]}{[CN^-]} = \frac{Ki}{[OH^-]} = \frac{10^{-5}}{10^{-14}} = 10^{9}$$

$[HCN] = 1\,M$; $[CN^-] = 10^{-9}\,M$

$$\frac{[Co^{+3}]}{[Co(CN)_6^{-3}]} = \frac{10^{-64}}{[CN^-]^6} = \frac{10^{-64}}{(10^{-9})^6} = 10^{-10}$$

anche a pH = 0 $[Co(CN)_6^{-3}] > [Co^{+3}]$ di un fattore 10^{10}, quindi il Co^{+3} è tutto complessato

VARIAZIONI DI pH IN SEGUITO A FORMAZIONE DI COMPLESSI

$Al(OH)_3\downarrow + 6F^- \rightleftarrows AlF_6^{-3} + 3OH^-$; - - - pH + basico

$Zn(OH)_2\downarrow + 4F^- \rightleftarrows$ ~~X~~ $Zn(OH)_2\downarrow$