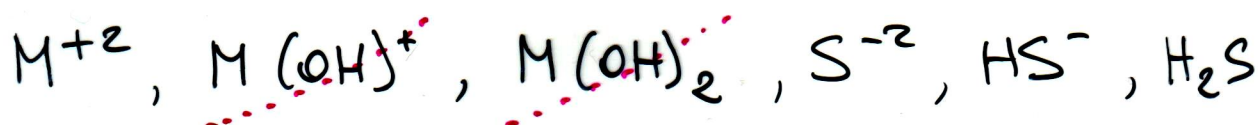
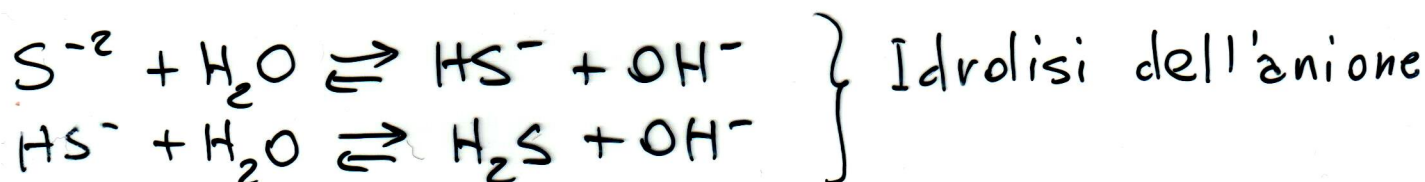
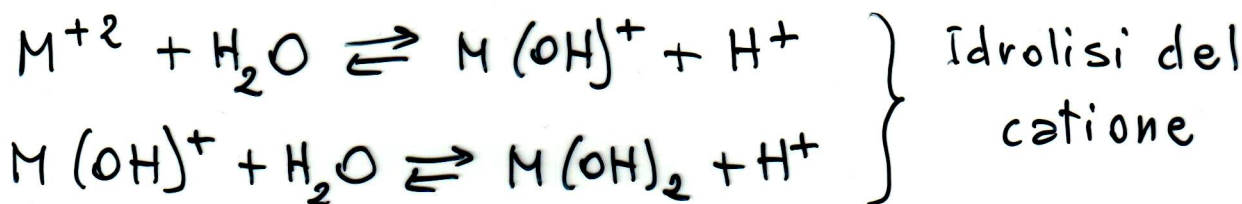


10. PRECIPITAZIONE E IDROLISI

ESEMPIO 1 \equiv CASO DEI SOLFURI

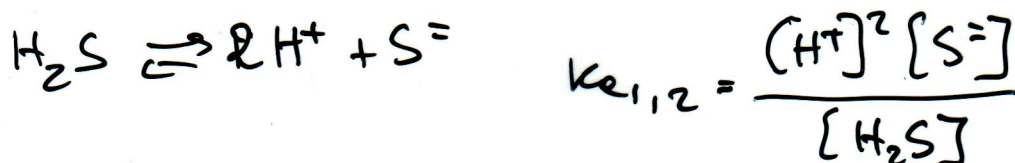
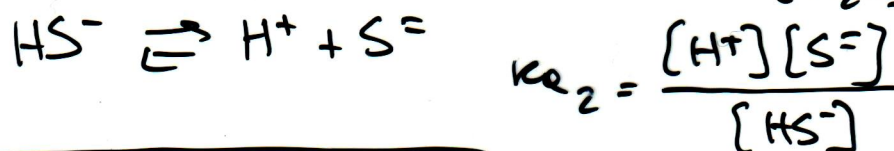
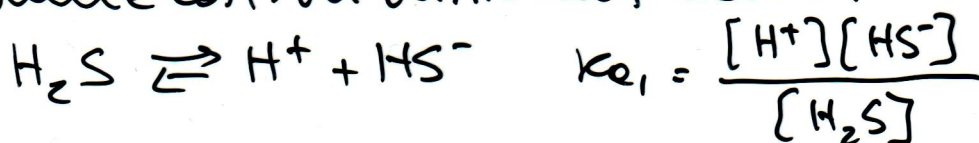


$$K_{ps,MS} = [M^{+2}][S^{-2}]$$



$$\Delta = [M^{+2}] = [S^{-2}] + [HS^-] + [H_2S] \quad (\text{conservazione delle specie})$$

esprimiamo $[HS^-]$ e $[H_2S]$ in funzione di $[S^{-2}]$ dalle cost. di dissociazione acide:



$$[HS^-] = \frac{[H^+][S^{=2}]}{K_{a2}} \quad ; \quad [H_2S] = \frac{[H^+]^2[S^{=2}]}{K_{a1,2}}$$

$$\Delta = [M^{+2}] = [S^{=}] + [HS^{-}] + [H_2S]$$

$$\Delta = [M^{+2}] = [S^{=}] + \frac{[H^{+}][S^{=}]}{K_{a2}} + \frac{[H^{+}]^2[S^{=}]}{K_{a1,2}}$$

$$\Delta = [M^{+2}] = [S^{=}] \left(1 + \frac{[H^{+}]}{K_{a2}} + \frac{[H^{+}]^2}{K_{a1,2}} \right)$$

$$\text{ma } [S^{=}] = \frac{K_{ps}}{[M^{+2}]} = \frac{K_{ps}}{\Delta}$$

$$\Delta = \frac{K_{ps}}{\Delta} \cdot \left(1 + \frac{[H^{+}]}{K_{a2}} + \frac{[H^{+}]^2}{K_{a1,2}} \right)$$

$$\Delta = \sqrt{K_{ps} \left(1 + \frac{[H^{+}]}{K_{a2}} + \frac{[H^{+}]^2}{K_{a1,2}} \right)}$$

quando la solubilità di MS non è influenzata dall'idrolisi di $S^{=}$? (cioè quando $\Delta = \sqrt{K_{ps}}$?)

$$[H^{+}] \ll K_{a2} \quad pH > pK_{a2} > 13 \quad \text{più limitante}$$

$$[H^{+}]^2 \ll K_{a1,2} \quad 2pH > pK_{a1,2} > 20$$

$$pH > 10$$

quindi solo a $pH > 13$ $\Delta_{MS} = \sqrt{K_{ps,MS}}$, in tutti gli altri valori di pH bisognerà tener conto dell'idrolisi.

Es.: HgS e SnS

$$K_{ps} = 10^{-52}$$

$$K_{ps} = 10^{-27}$$

calcoliamo le solubilità dei due solfuri a $\text{pH} = 0$

$$S = \sqrt{K_{ps} \left(1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1,2}} \right)} \quad S = \sqrt{K_{ps} \cdot \frac{K_{a1,2} K_{a2} + [H^+] K_{a1,2} + [H^+]^2 K_{a2}}{K_{a1,2} K_{a2}}}$$

$$\Delta_{\text{HgS}} = \sqrt{10^{-52} \left(\frac{10^{-33} + 10^{-20} + 10^{-13}}{10^{-33}} \right)}$$

$$\Delta_{\text{HgS}} = \sqrt{10^{-52} \cdot 10^{20}} = \sqrt{10^{-32}} = 10^{-16} \text{ M} \text{ a } \text{pH} = 0$$

la sua Δ ricavabile dal K_{ps} senza considerare l'idrolisi sarebbe $= \sqrt{10^{-52}} = 10^{-26} \text{ M}$

$$\Delta_{\text{SnS}} = \sqrt{10^{-27} \cdot \frac{10^{-33} + 10^{-20} + 10^{-13}}{10^{-33}}} = \sqrt{10^{-27} \cdot 10^{20}} = 10^{-8} \text{ M} \text{ a } \text{pH} = 0$$

non considerando l'idrolisi $\Delta = \sqrt{K_{ps}} = 10^{-13} \text{ M}$

calcoliamone ora le solubilità a $\text{pH} = 7$

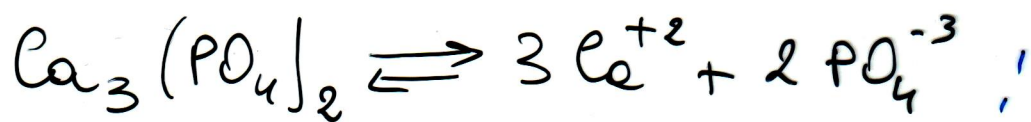
$$[H^+] = 10^{-7} \text{ M}$$

$$\Delta_{\text{HgS}} = \sqrt{K_{ps} \cdot \frac{10^{-33} + 10^{-20} \cdot 10^{-7} + 10^{-13} \cdot 10^{-14}}{10^{-33}}} = \sqrt{K_{ps} \cdot \frac{10^{-33} + 10^{-27} + 10^{-27}}{10^{-33}}}$$

$$\Delta_{\text{HgS}} = \sqrt{10^{-52} \cdot 2 \cdot 10^6} = 10^{-23} \text{ M} \text{ a } \text{pH} = 7$$

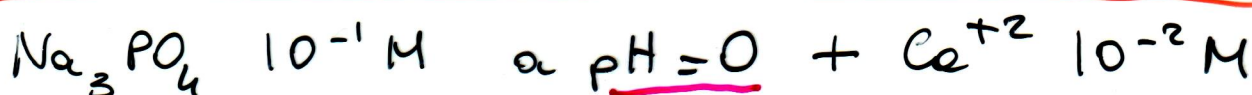
$$\Delta_{\text{SnS}} = \sqrt{10^{-27} \cdot 2 \cdot 10^6} = 10^{-10} \text{ M} \text{ a } \text{pH} = 7$$

ESEMPIO 2 \equiv CASO DEI FOSFATI



$$K_{ps} = 10^{-29}$$

solubilità
idrolisi



$$[\text{Ca}^{+2}] = 10^{-2} \text{ M}$$

$$[\text{PO}_4^{-3}] + [\text{HPO}_4^{-2}] + [\text{H}_2\text{PO}_4^{-}] + [\text{H}_3\text{PO}_4] = 10^{-1} \text{ M}$$

$$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^{-}; \quad K_{e1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^{-}]}{[\text{H}_3\text{PO}_4]}; \quad \frac{[\text{H}_2\text{PO}_4^{-}]}{[\text{H}_3\text{PO}_4]} = \frac{K_{e1}}{[\text{H}^+]}$$

$$\text{H}_2\text{PO}_4^{-} \rightleftharpoons \text{H}^+ + \text{HPO}_4^{-2}; \quad K_{e2} = \frac{[\text{H}^+][\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^{-}]}; \quad \frac{[\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^{-}]} = \frac{K_{e2}}{[\text{H}^+]}$$

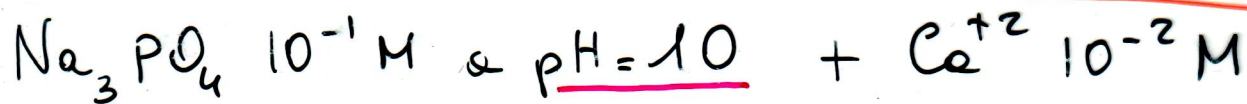
$$\text{HPO}_4^{-2} \rightleftharpoons \text{H}^+ + \text{PO}_4^{-3}; \quad K_{e3} = \frac{[\text{H}^+][\text{PO}_4^{-3}]}{[\text{HPO}_4^{-2}]}; \quad \frac{[\text{PO}_4^{-3}]}{[\text{HPO}_4^{-2}]} = \frac{K_{e3}}{[\text{H}^+]}$$

$$\frac{[\text{H}_2\text{PO}_4^{-}]}{[\text{H}_3\text{PO}_4]} = \frac{10^{-3}}{1} = 10^{-3}; \quad \frac{[\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^{-}]} = 10^{-8}; \quad \frac{[\text{PO}_4^{-3}]}{[\text{HPO}_4^{-2}]} = 10^{-12}$$

$$[\text{H}_3\text{PO}_4] \approx 10^{-1} \text{ M} \quad K_{e1,2,3} = \frac{[\text{H}^+]^3 [\text{PO}_4^{-3}]}{[\text{H}_3\text{PO}_4]} = 10^{-23}$$

$$[\text{PO}_4^{-3}] = \frac{10^{-23} \cdot 10^{-1}}{1} = 10^{-24} \text{ M}$$

$$[\text{Ca}^{+2}]^3 \cdot [\text{PO}_4^{-3}]^2 = (10^{-2})^3 \cdot (10^{-24})^2 = 10^{-54} \ll K_{ps_{\text{Ca}_3(\text{PO}_4)_2}}$$



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

$$[\text{PO}_4^{-3}] + [\text{HPO}_4^{-2}] + [\text{H}_2\text{PO}_4^{-}] + [\text{H}_3\text{PO}_4] = 10^{-1} \text{ M}$$

$$\frac{[\text{H}_2\text{PO}_4^{-}]}{[\text{H}_3\text{PO}_4]} = \frac{k_{a1}}{[\text{H}^+]} = \frac{10^{-3}}{10^{-10}} = 10^7$$

$$\frac{[\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^{-}]} = \frac{k_{a2}}{[\text{H}^+]} = \frac{10^{-8}}{10^{-10}} = 10^2$$

$$\frac{[\text{PO}_4^{-3}]}{[\text{HPO}_4^{-2}]} = \frac{k_{a3}}{[\text{H}^+]} = \frac{10^{-12}}{10^{-10}} = 10^{-2}$$

$$[\text{HPO}_4^{-2}] = 10^{-1} \text{ M}$$

$$[\text{PO}_4^{-3}] = 10^{-2} \cdot [\text{HPO}_4^{-2}] = 10^{-3} \text{ M}$$

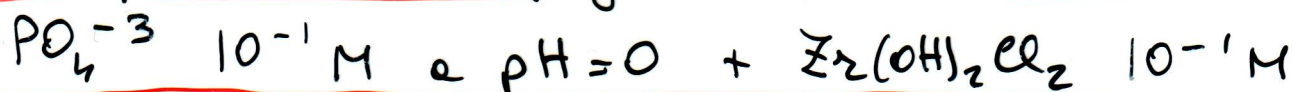
$$[\text{Ce}^{+2}]^3 [\text{PO}_4^{-3}]^2 = (10^{-2})^3 \cdot (10^{-3})^2 = 10^{-12} \gg K_{ps} \text{Ce}_3(\text{PO}_4)_2$$



$$K_{ps} \text{Zr}_3(\text{PO}_4)_4 = 10^{-132}$$

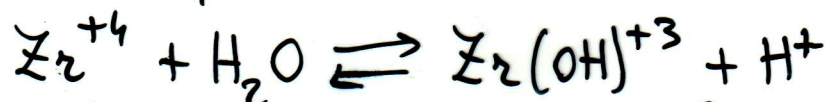
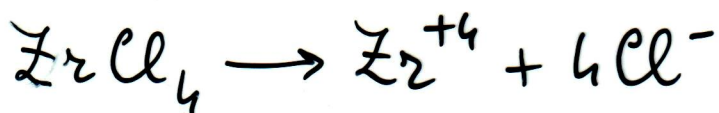
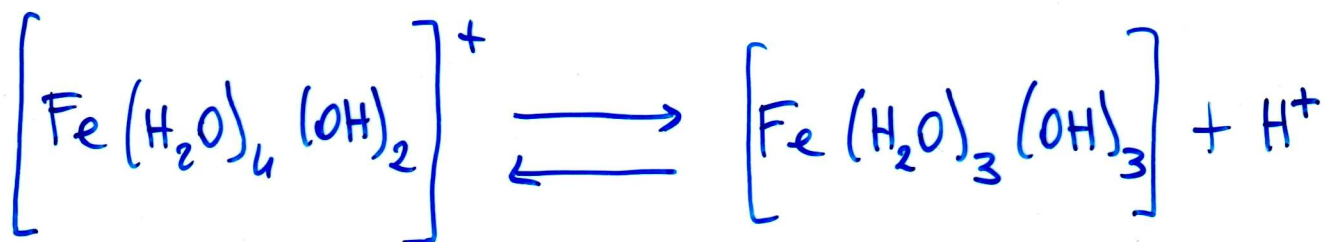
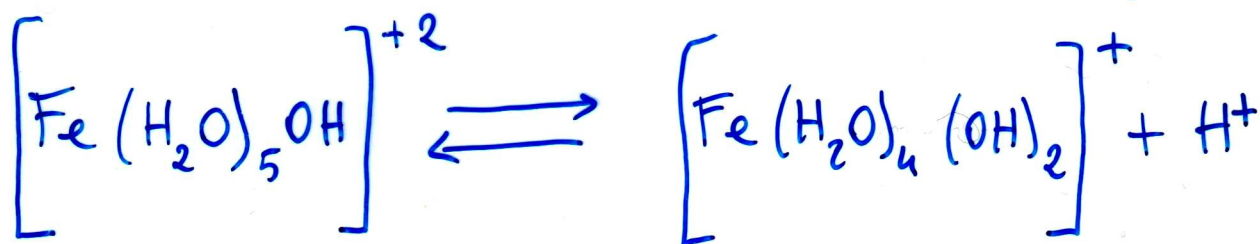
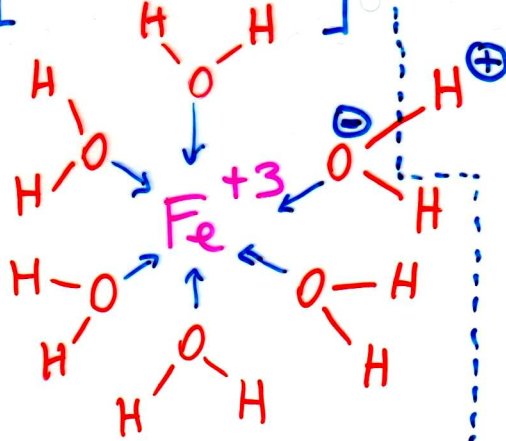
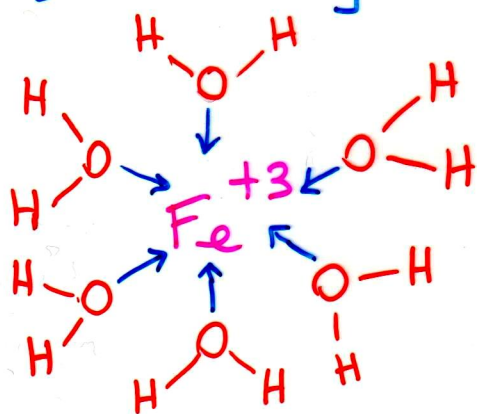
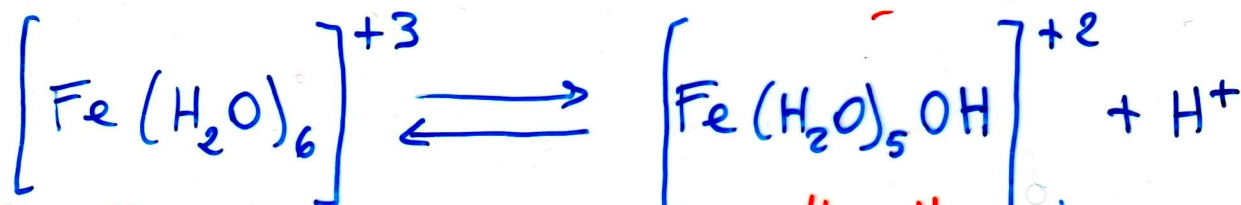
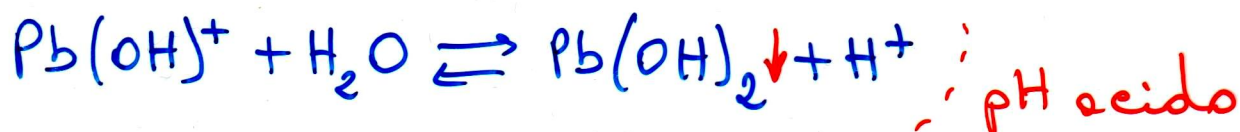


Precipitat $\text{Zr}_3(\text{PO}_4)_4$ gie a $\text{pH} = 0$:



$$[\text{Zr}^{+4}] = 10^{-1} \text{ M} ; [\text{PO}_4^{-3}] = 10^{-24} \text{ M}$$

$$[\text{Zr}^{+4}]^3 [\text{PO}_4^{-3}]^4 = (10^{-1})^3 \cdot (10^{-24})^4 = 10^{-99} \gg K_{ps}$$



ESEMPIO 3 \equiv CASO DEGLI IDROSSIDI ANFOTERI

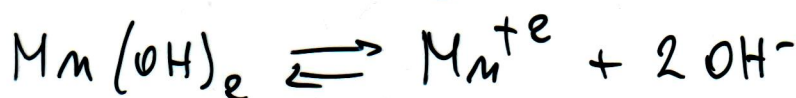
Anche per la precipitazione di elementi come idrossidi metallici si può fare una precipitazione frazionata.

Es. Fe^{+3} e Mn^{+2} 10^{-2} M

calcolare a che pH iniziano le precipitazioni dei rispettivi idrossidi:



$$K_{ps} \text{Fe}(\text{OH})_3 = 10^{-38}$$



$$K_{ps} \text{Mn}(\text{OH})_2 = 10^{-14}$$

pH di inizio precipitazione $\text{Fe}(\text{OH})_3$:

$$[\text{Fe}^{+3}][\text{OH}^-]^3 = 10^{-38} ; [\text{OH}^-] = \sqrt[3]{\frac{10^{-38}}{[\text{Fe}^{+3}]}} = \sqrt[3]{\frac{10^{-38}}{10^{-2}}} = 10^{-12} \text{ M}$$

$$\text{pOH} = 12 ; \text{pH} = 2$$

pH di inizio precipitazione $\text{Mn}(\text{OH})_2$:

$$[\text{Mn}^{+2}][\text{OH}^-]^2 = 10^{-14} ; [\text{OH}^-] = \sqrt{\frac{10^{-14}}{[\text{Mn}^{+2}]}} = \sqrt{\frac{10^{-14}}{10^{-2}}} = 10^{-6} \text{ M}$$

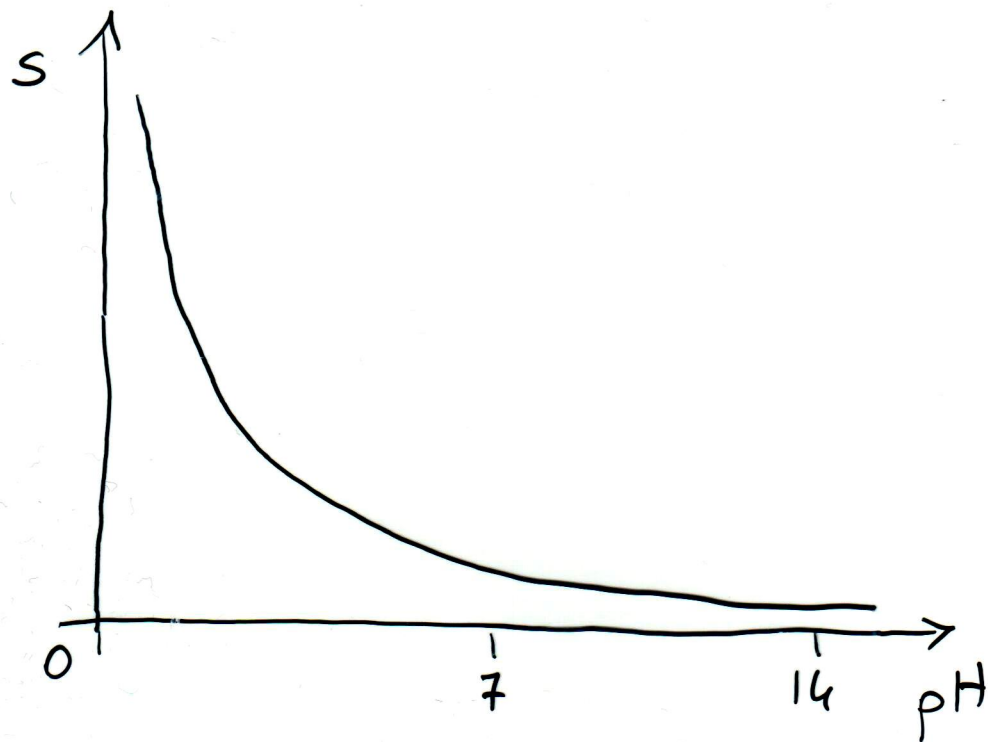
$$\text{pOH} = 6 \quad \text{pH} = 8$$

Ma a pH = 8 è quantitativa ($[] < 10^{-7} \text{ M}$) la precipitazione di $\text{Fe}(\text{OH})_3$?

$$[Fe^{+3}][OH^{-}]^3 = 10^{-38}$$

$$[OH^{-}] = 10^{-6} M$$

$$[Fe^{+3}] = \frac{10^{-38}}{[OH^{-}]^3} = \frac{10^{-38}}{(10^{-6})^3} = 10^{-20} M \ll 10^{-7} M$$



A quale valore di pH si ha la precipitazione quantitativa di $Fe(OH)_3$?

$$[Fe^{+3}][OH^{-}]^3 = 10^{-38}$$

$$[OH^{-}] = \sqrt[3]{\frac{10^{-38}}{10^{-7}}} = 10^{-10} M$$

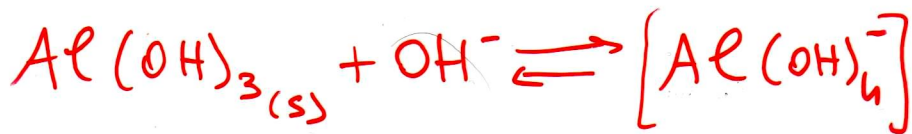
$$[Fe^{+3}] = 10^{-7} M$$

precipitazione quantitativa

$$pOH = 10 ; \underline{\underline{pH = 4}}$$



$$K_{ps} = [\text{Al}^{+3}][\text{OH}^-]^3 = 10^{-32}$$



$$K_{\text{inst. 4}} = \frac{[\text{OH}^-][\text{Al}(\text{OH})_3]}{[\text{Al}(\text{OH})_4^-]} = 10^{-2}$$

considerando
 $[\text{Al}(\text{OH})_3] = 1 \text{ M}$

$$\Delta = [\text{Al}^{+3}] + [\text{Al}(\text{OH})_4^-] = \frac{K_{ps}}{[\text{OH}^-]^3} + \frac{[\text{OH}^-]}{K_{\text{inst. 4}}}$$

$$\Delta = \frac{(K_{ps} \cdot K_{\text{inst. 4}}) + [\text{OH}^-]^4}{K_{\text{inst. 4}} \cdot [\text{OH}^-]^3}$$

e $\text{pH} = 0$

$$\Delta = \frac{(10^{-32} \cdot 10^{-2}) + (10^{-14})^4}{10^{-2} \cdot (10^{-14})^3} = \frac{10^{-34} + 10^{-56}}{10^{-2} \cdot 10^{-42}} = 10^{10} \text{ M}$$

e $\text{pH} = 4$

$$\Delta = \frac{10^{-34} + (10^{-10})^4}{10^{-2} \cdot (10^{-10})^3} = \frac{10^{-34} + 10^{-40}}{10^{-2} \cdot 10^{-30}} = 10^{-2} \text{ M}$$

e $\text{pH} = 5$

$$\Delta = \frac{10^{-34} + (10^{-9})^4}{10^{-2} \cdot (10^{-9})^3} = \frac{10^{-34} + 10^{-36}}{10^{-2} \cdot 10^{-27}} = 10^{-5} \text{ M}$$

e $\text{pH} = 7$

$$\Delta = \frac{10^{-34} + (10^{-7})^4}{10^{-2} \cdot (10^{-7})^3} = \frac{10^{-34} + 10^{-28}}{10^{-2} \cdot 10^{-21}} = 10^{-5} \text{ M}$$

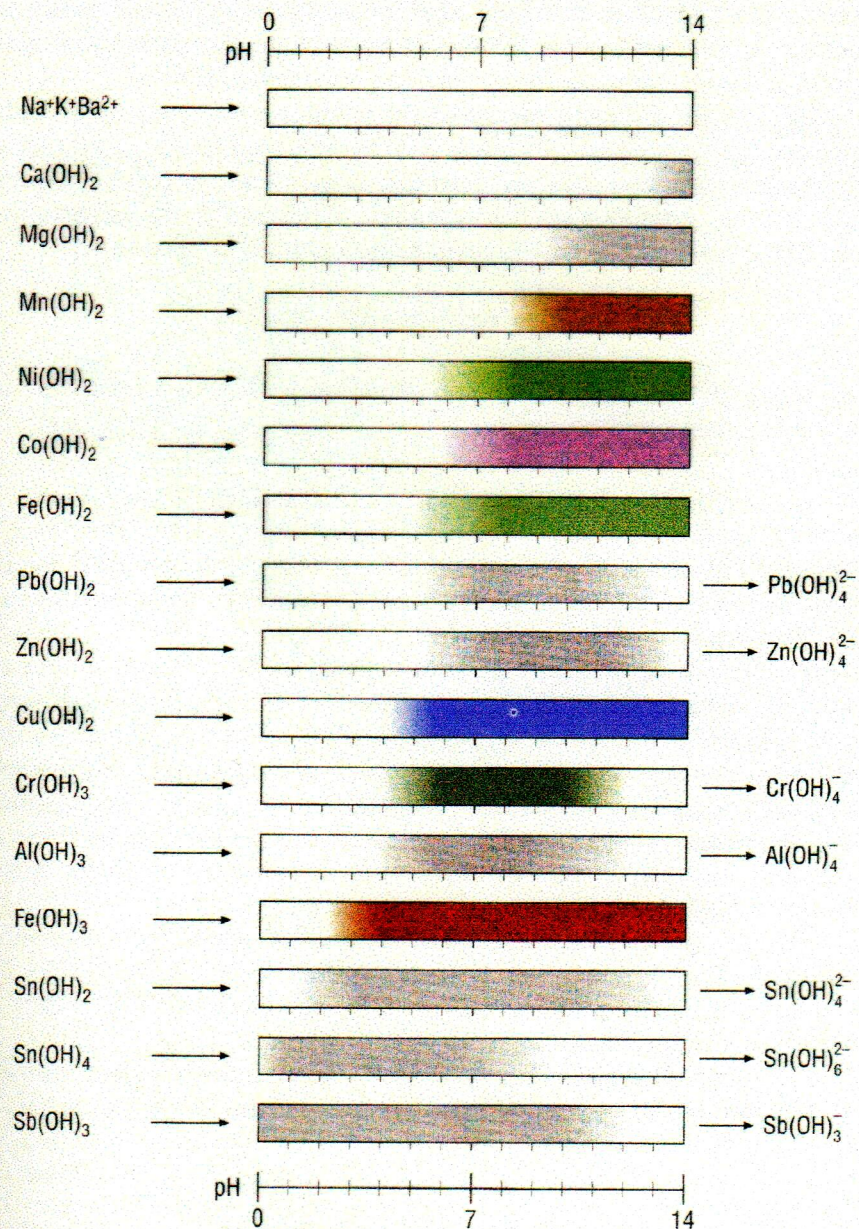
e $\text{pH} = 10$

$$\Delta = \frac{10^{-34} + (10^{-4})^4}{10^{-2} \cdot (10^{-4})^3} = \frac{10^{-34} + 10^{-16}}{10^{-2} \cdot 10^{-12}} = 10^{-2} \text{ M}$$

$$\text{e } \text{pH} = 12$$

$$\Delta = \frac{10^{-34} + (10^{-2})^4}{10^{-2} \cdot (10^{-2})^3} = \frac{10^{-34} + 10^{-8}}{10^{-2} \cdot 10^{-6}} = 1$$

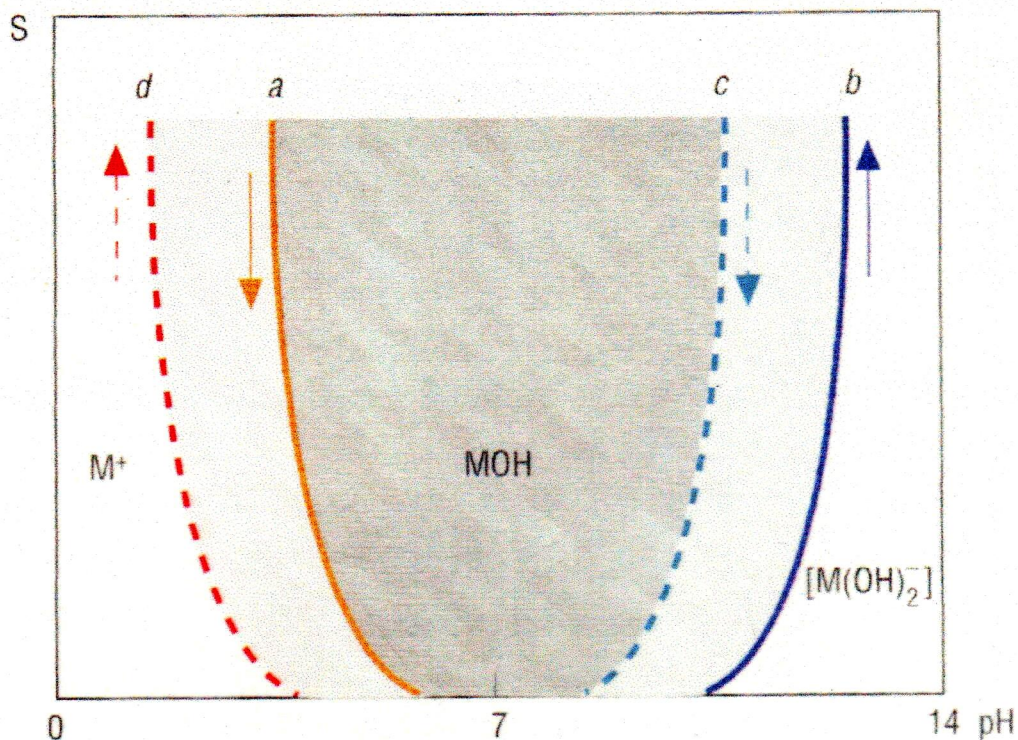
TABELLA 9-6 pH di precipitazione degli idrossidi.



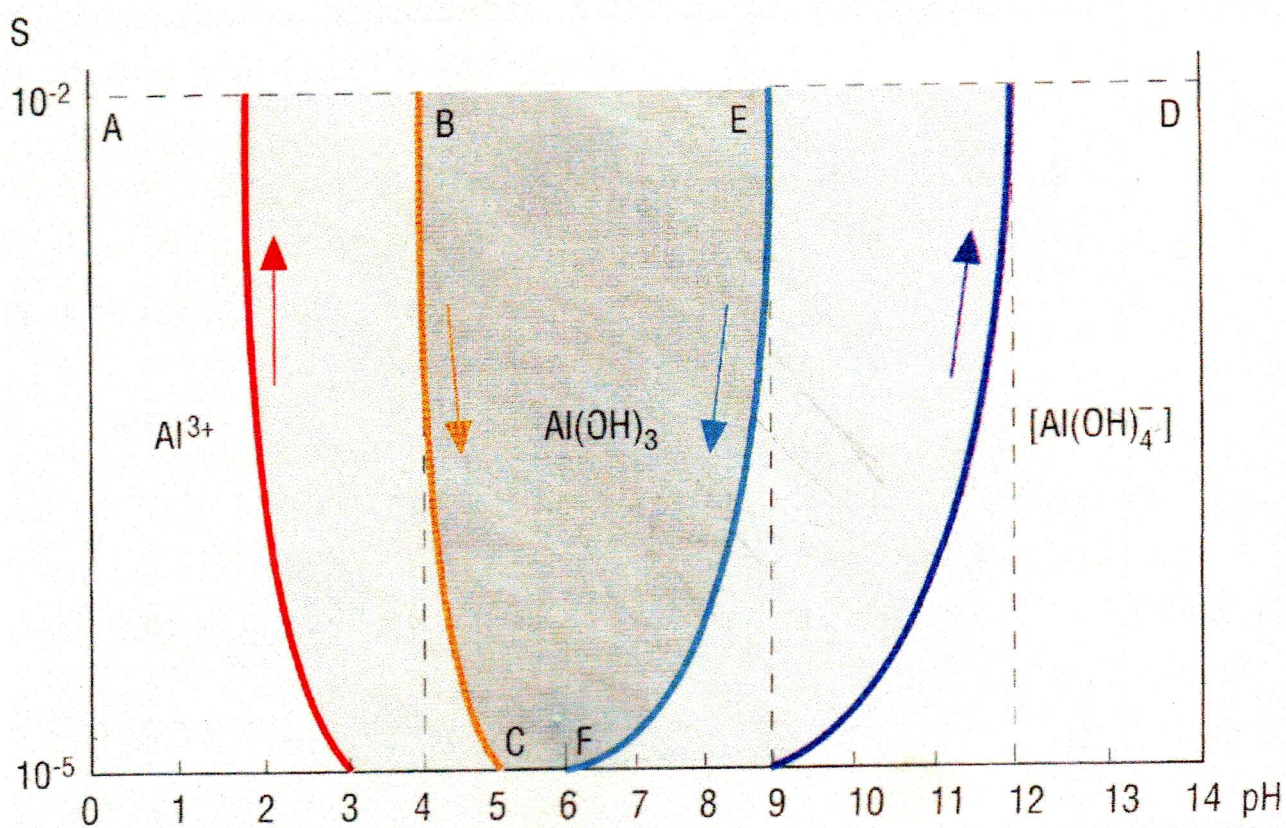
▬ = precipitazione parziale

▬ = precipitazione completa

Nota La temperatura, la forza ionica e la concentrazione della soluzione possono modificare i valori indicati. Spesso il precipitato non è un idrossido, bensì un ossido idrato.

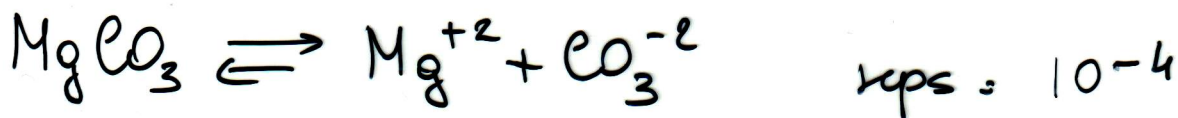
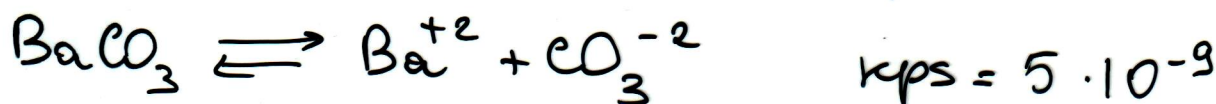
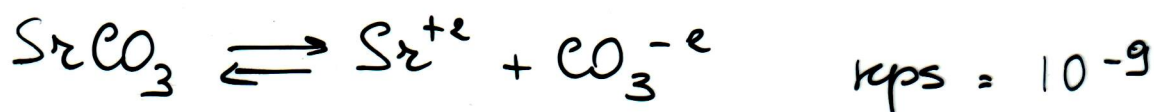
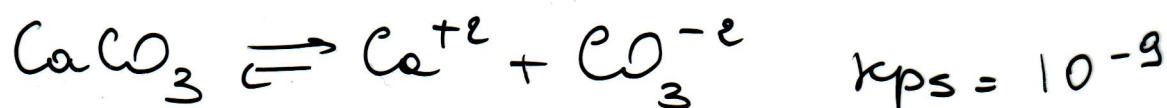


Solubilità di un idrossido anfotero MOH in funzione del pH.



Solubilità dell'idrossido di alluminio in funzione del pH (valori approssimati).

ESEMPIO 4 \equiv CASO DEI CARBONATI DEI METALLI ALCALINO-TERROSI

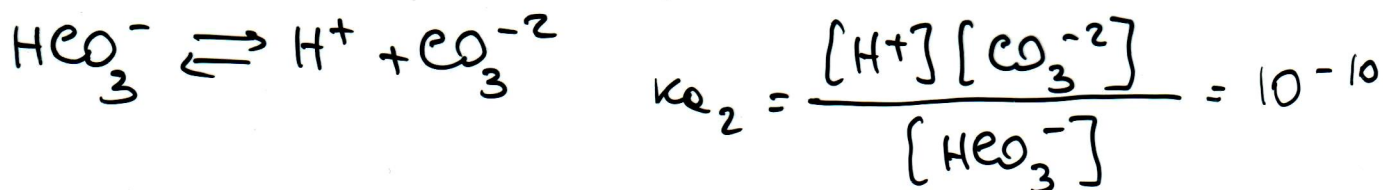


La precipitazione dei carbonati si effettua con $(\text{NH}_4)_2\text{CO}_3$ in tampone $\text{NH}_3 / \text{NH}_4\text{Cl}$ ($= \text{pH } 9$)

A $\text{pH} = 9$ precipiteranno solo i primi tre carbonati:



$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{K_{a1}}{[\text{H}^+]}$$

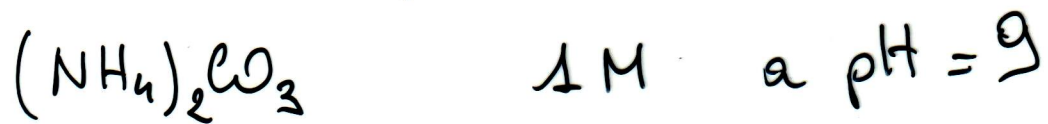
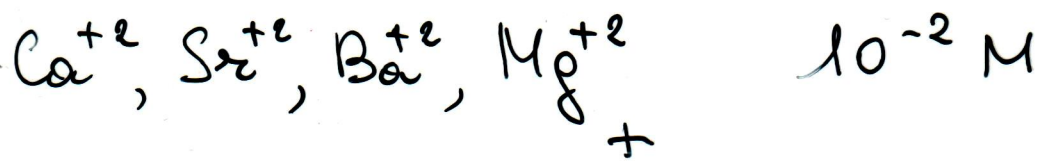


$$\frac{[\text{CO}_3^{-2}]}{[\text{HCO}_3^-]} = \frac{K_{a2}}{[\text{H}^+]}$$

a $\text{pH} = 9$:

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{K_{a1}}{[\text{H}^+]} = \frac{10^{-7}}{10^{-9}} = 10^2; \quad \frac{[\text{CO}_3^{-2}]}{[\text{HCO}_3^-]} = \frac{K_{a2}}{[\text{H}^+]} = \frac{10^{-10}}{10^{-9}} = 10^{-1}$$

quindi a $\text{pH} = 9$ la specie prevalente sarà
 HCO_3^-



$$[\text{HCO}_3^-] = 1 \text{ M} \quad (\text{specie prevalente})$$

$$\frac{[\text{CO}_3^{-2}]}{[\text{HCO}_3^-]} = 10^{-1} ; [\text{CO}_3^{-2}] = 10^{-1} \text{ M}$$

$$\downarrow \begin{cases} [\text{Ca}^{+2}][\text{CO}_3^{-2}] = 10^{-2} \cdot 10^{-1} = 10^{-3} \gg K_{\text{ps}} (10^{-9}) \\ [\text{Sr}^{+2}][\text{CO}_3^{-2}] = 10^{-2} \cdot 10^{-1} = 10^{-3} \gg K_{\text{ps}} (10^{-9}) \\ [\text{Ba}^{+2}][\text{CO}_3^{-2}] = 10^{-2} \cdot 10^{-1} = 10^{-3} \gg K_{\text{ps}} (5 \cdot 10^{-9}) \end{cases}$$
$$\uparrow [\text{Mg}^{+2}][\text{CO}_3^{-2}] = 10^{-2} \cdot 10^{-1} = 10^{-3} > K_{\text{ps}} (10^{-4})$$

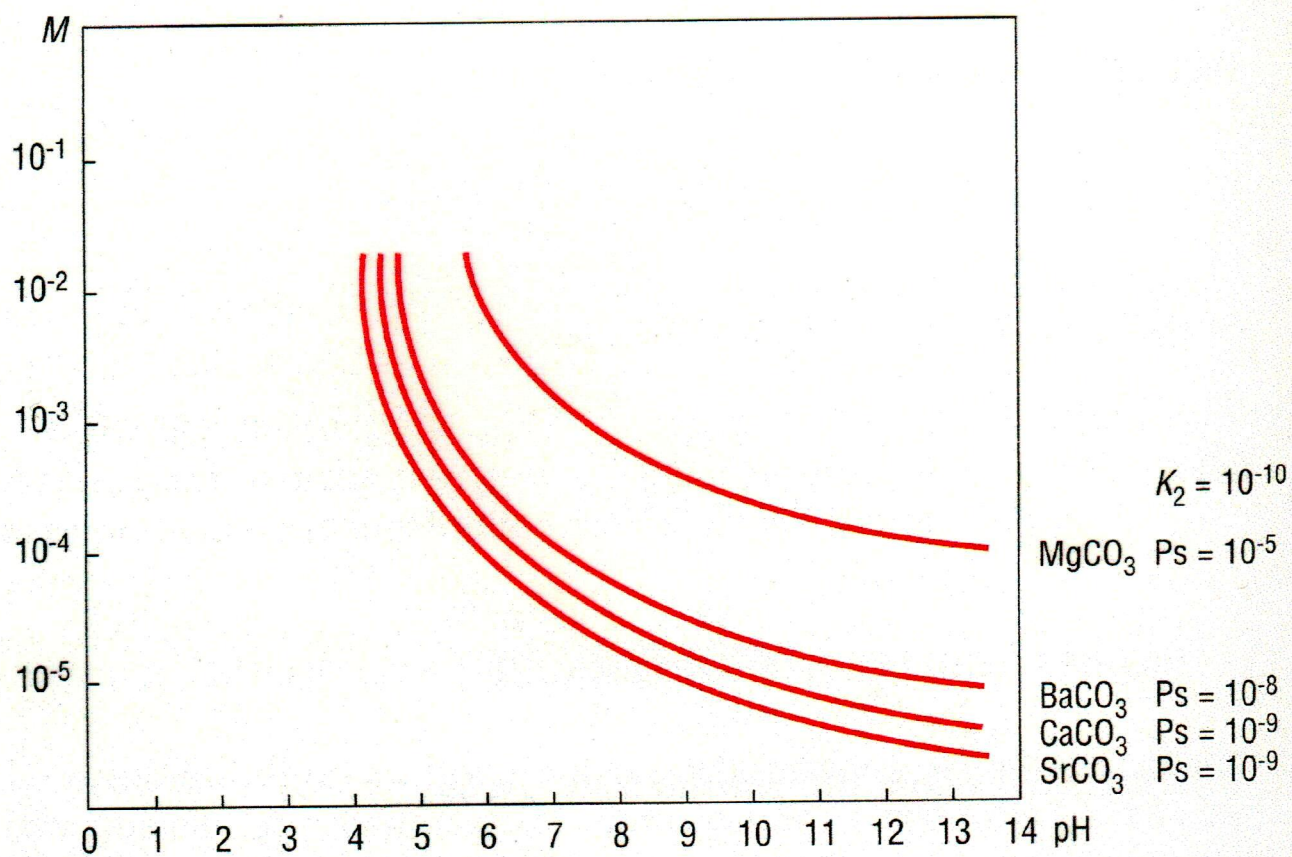


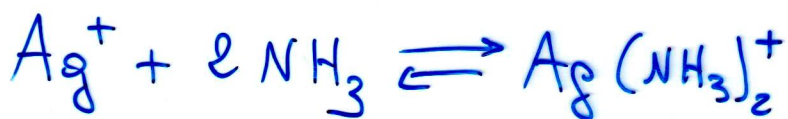
FIGURA 9-2 Solubilità dei carbonati alcalino-terrosi in funzione del pH (valori approssimati).

11. PRECIPITAZIONE E COMPLESSAZIONE

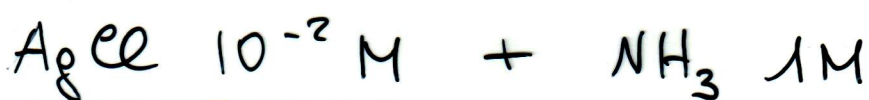
ESEMPIO 1 \equiv ALOGENURI D'ARGENTO ED AMMONIACA



$$K_{ps} = [\text{Ag}^+][\text{Cl}^-] = 10^{-10}$$



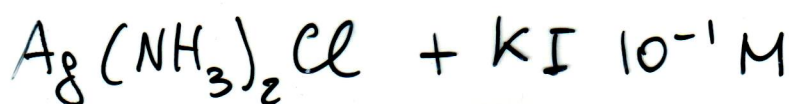
$$K_{\text{inst.}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = 10^{-8}$$



$$\frac{[\text{Ag}^+]}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{10^{-8}}{[\text{NH}_3]^2} = 10^{-8} \text{ quindi } \text{Ag}^+ \text{ è tutto complessato!}$$

$$[\text{Ag}(\text{NH}_3)_2^+] = 10^{-2} \text{ M} ; [\text{Ag}^+] = 10^{-10} \text{ M} ; [\text{Cl}^-] = 10^{-2} \text{ M}$$

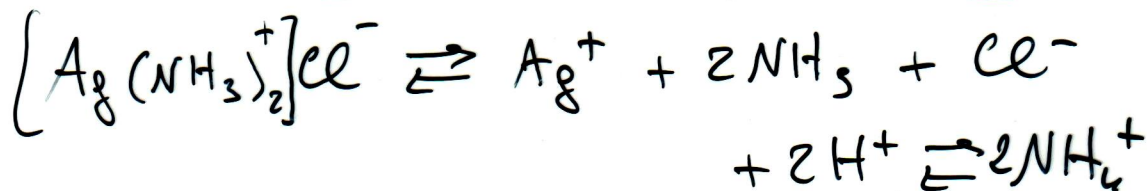
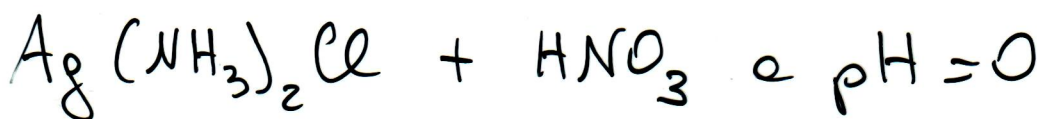
$$[\text{Ag}^+][\text{Cl}^-] = 10^{-10} \cdot 10^{-2} = 10^{-12} < K_{ps} \text{AgCl}$$



$$K_{ps} \text{AgI} = 10^{-16}$$

$$[Ag^+] = 10^{-10} M \quad [I^-] = 10^{-1} M$$

$$[Ag^+][I^-] = 10^{-10} \cdot 10^{-1} = 10^{-11} > K_{ps} AgI$$



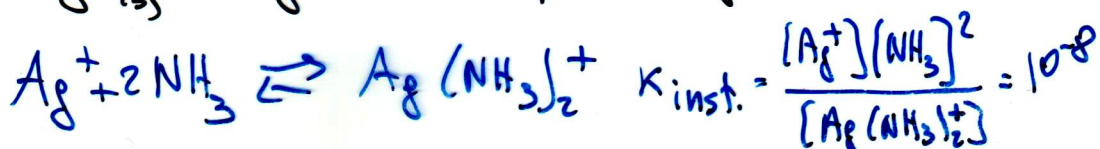
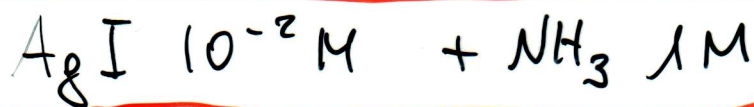
$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 10^{-5}$$

$$\frac{[NH_4^+]}{[NH_3]} = \frac{K_b}{[OH^-]} = \frac{10^{-5}}{10^{-14}} = 10^9, \quad [NH_4^+] = 1M$$

$$[NH_3] = 10^{-3} M; \quad \frac{[Ag^+]}{[Ag(NH_3)_2^+]} = \frac{10^{-8}}{[NH_3]^2} = 10^{10}$$

$$[Ag^+] = 10^{-2} M; \quad [Cl^-] = 10^{-2} M$$

$$[Ag^+][Cl^-] = 10^{-2} \cdot 10^{-2} = 10^{-4} \gg K_{ps} AgCl$$



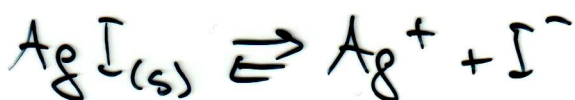
$$\frac{[Ag^+]}{[Ag(NH_3)_2^+]} = 10^{-8} \quad [Ag(NH_3)_2^+] = 10^{-2} M \quad [I^-] = 10^{-2} M$$

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

$$[Ag^+][I^-] = 10^{-10} \cdot 10^{-2} = 10^{-12} \gg K_{ps} AgI$$

Tuttavia la solubilità s di AgI in solut. di NH_3 1M è comunque aumentata:

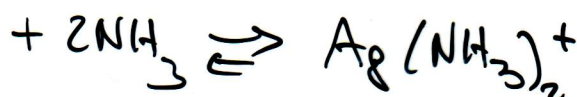
in acqua
semplice:



$$K_{ps} = [Ag^+][I^-] = 10^{-16}$$

$$s = [Ag^+] = [I^-] = \sqrt{K_{ps}} = 10^{-8} M$$

in NH_3 1M:



$$s = [Ag(NH_3)_2^+] = [I^-] = ?$$

$$\frac{[Ag^+]}{[Ag(NH_3)_2^+]} = K_{inst.}$$

$$[Ag^+][I^-] = K_{ps}$$

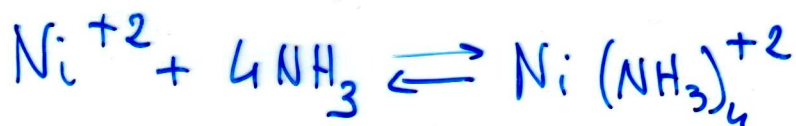
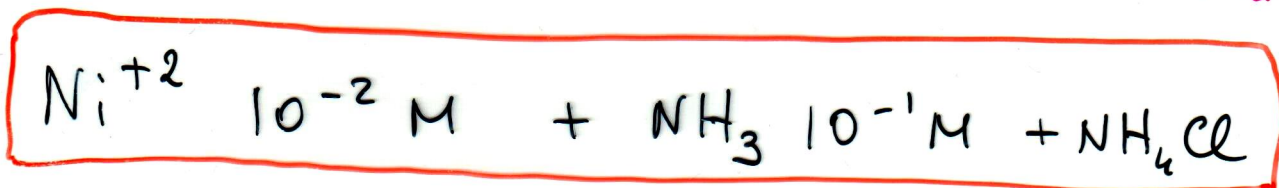
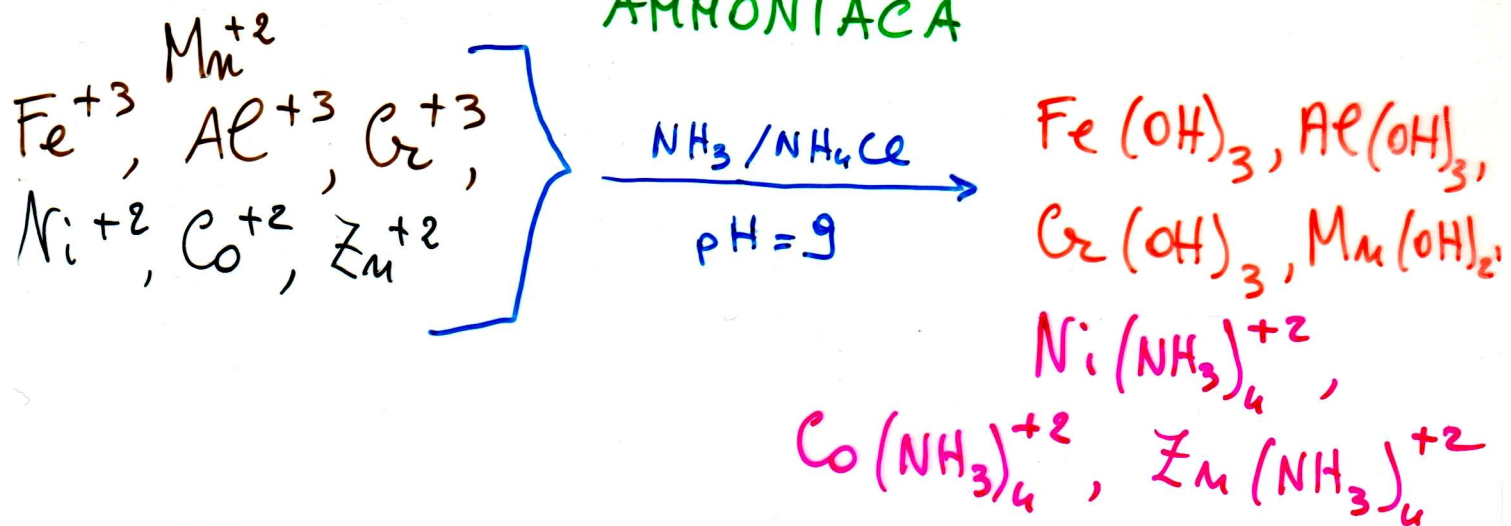
$$[Ag^+] = K_{inst.} \cdot s$$

$$[Ag^+] = \frac{K_{ps}}{s}$$

$$K_{inst.} \cdot s = \frac{K_{ps}}{s} ; 10^{-8} \cdot s = \frac{10^{-16}}{s} ; s^2 = 10^{-8}$$

$$s = 10^{-4} M$$

ESEMPIO 2 \equiv IONI Ni^{+2} , Co^{+2} e Zn^{+2} E AMMONIACA



$$K_{inst} = \frac{[Ni^{+2}][NH_3]^4}{[Ni(NH_3)_4^{+2}]} = 10^{-8}$$



$$K_{ps} = [Ni^{+2}][OH^-]^2 = 10^{-16}$$

$$\frac{[Ni^{+2}]}{[Ni(NH_3)_4^{+2}]} = \frac{K_{inst}}{[NH_3]^4} = \frac{10^{-8}}{10^{-4}} = 10^{-4}$$

$$[Ni(NH_3)_4^{+2}] \approx 10^{-2} M \quad [Ni^{+2}] = 10^{-6} M$$

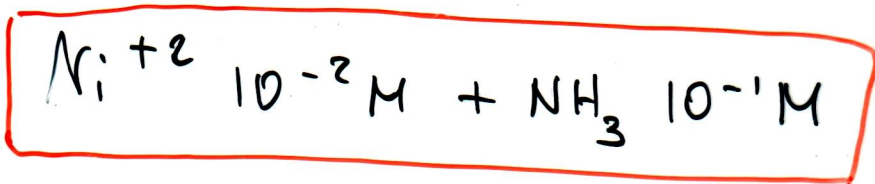
a pH = 9, $[OH^-] = 10^{-5} M$:

$$[Ni^{+2}][OH^-]^2 = 10^{-6} \cdot (10^{-5})^2 = 10^{-16} = K_{ps}$$

in realtà, senza approssimazioni

$$[Ni^{+2}][OH^-]^2 = 9,6 \cdot 10^{-18} \approx 10^{-17} < K_{ps}$$

E se non avessimo tamponato a $\text{pH} = 9$ con NH_4Cl ?



$$\frac{[\text{Ni}^{+2}]}{[\text{Ni}(\text{NH}_3)_6^{+2}]} = \frac{K_{\text{inst}}}{[\text{NH}_3]^4} = \frac{10^{-8}}{(10^{-1})^4} = 10^{-4}$$

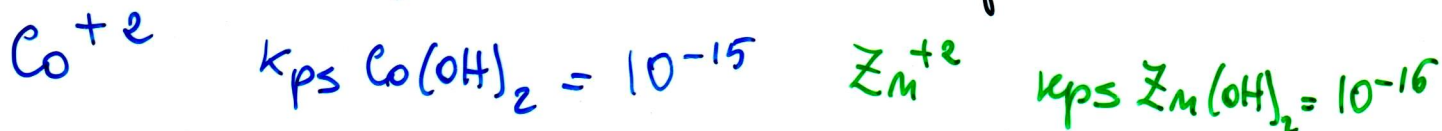
$$[\text{Ni}(\text{NH}_3)_6^{+2}] = 10^{-2} \text{M} \quad [\text{Ni}^{+2}] = 10^{-6} \text{M}$$

$$[\text{OH}^-] = \sqrt{K_b C_b} = \sqrt{10^{-5} \cdot 10^{-1}} = 10^{-3} \text{M}$$

$$[\text{Ni}^{+2}] [\text{OH}^-]^2 = 10^{-6} \cdot (10^{-3})^2 = 10^{-12} \gg K_{\text{ps}} (10^{-16})$$

Si avrebbe quindi precipitato di $\text{Ni}(\text{OH})_2$

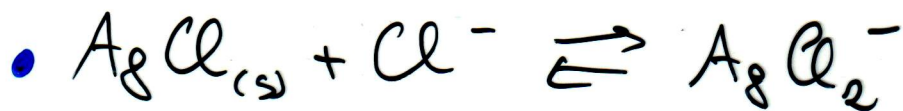
Lo stesso comportamento varrebbe per



non viene complessato il Mn^{+2} , la cui precipitazione al 3° gruppo non è quantitativa, ma il suo idrossido resta comunque in soluzione (è più solubile dei precedenti)



Caso particolare: Un reattivo precipitante, se usato in eccesso, può comportarsi da complessante.

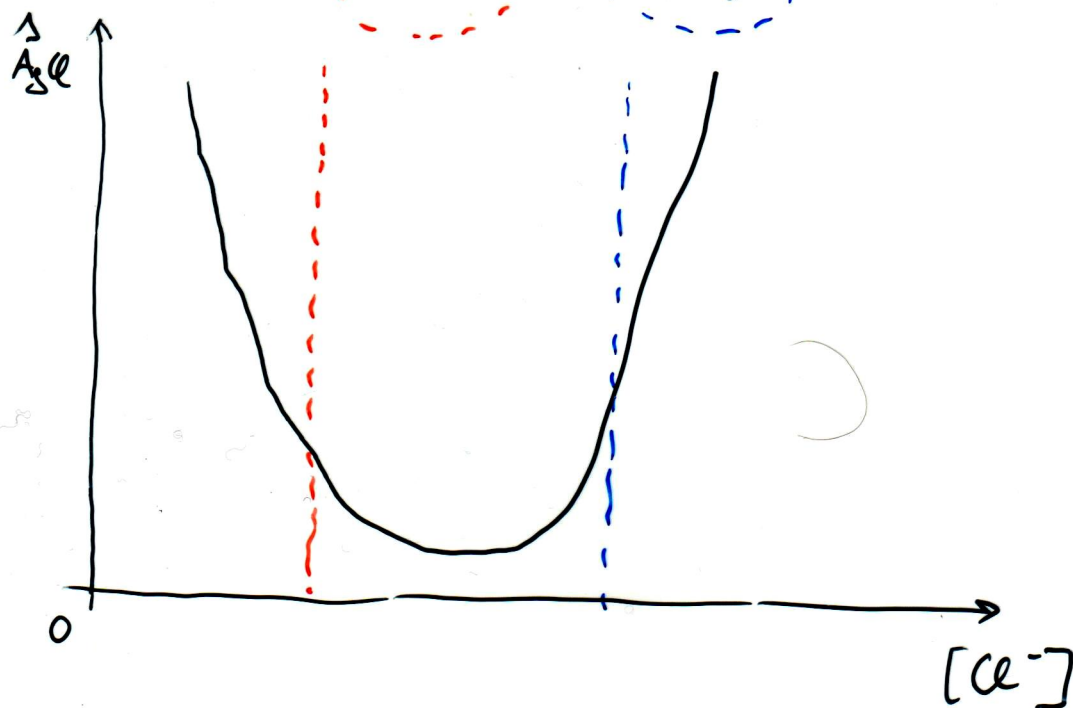


$$\Delta_{\text{AgCl}} = [\text{Ag}^+] + [\text{AgCl}_2^-]$$

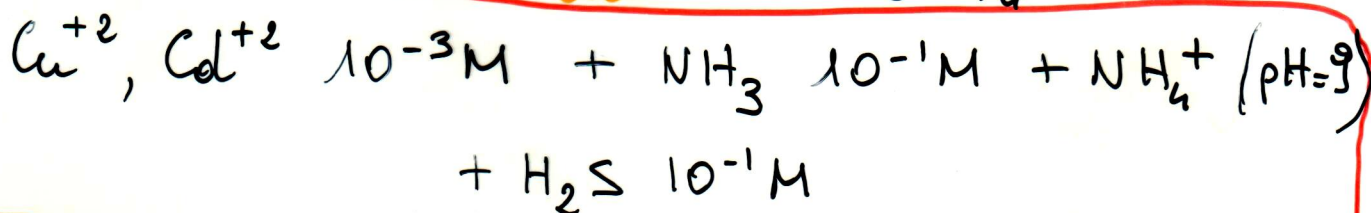
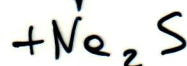
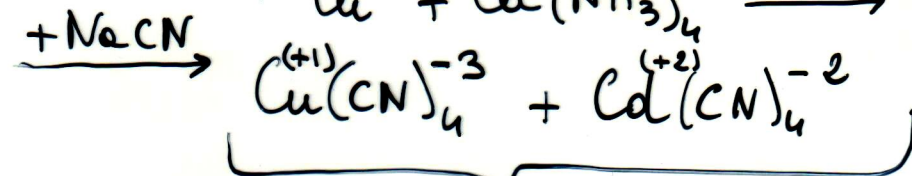
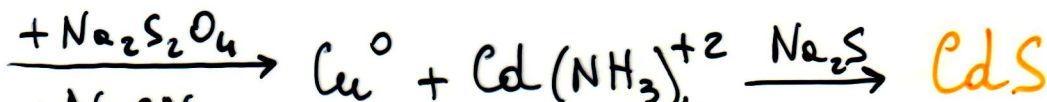
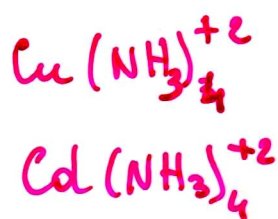
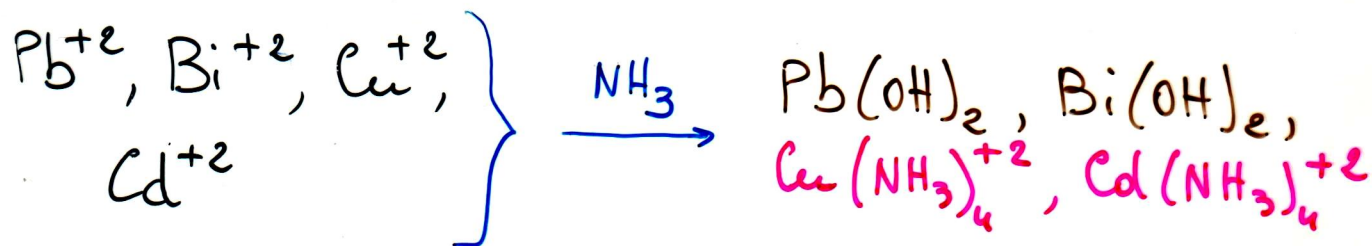
- $K_{ps_{\text{AgCl}}} = [\text{Ag}^+][\text{Cl}^-] = 10^{-10}$; $[\text{Ag}^+] = \frac{K_{ps}}{[\text{Cl}^-]}$

- $K_{\text{inst.}} = \frac{[\text{Cl}^-]}{[\text{AgCl}_2^-]} = 10^5$; $[\text{AgCl}_2^-] = \frac{[\text{Cl}^-]}{K_{\text{inst}}}$

$$\Delta_{\text{AgCl}} = \frac{K_{ps}}{[\text{Cl}^-]} + \frac{[\text{Cl}^-]}{K_{\text{inst}}}$$



ESEMPIO 3 \equiv SEPARAZIONE $\text{Cu}^{+2} / \text{Cd}^{+2}$



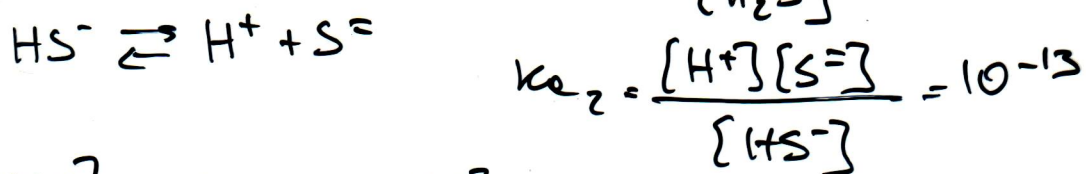
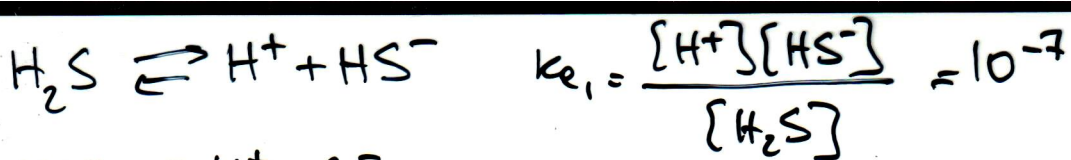
$$K_{\text{inst.}} \text{Cu(NH}_3)_4^{+2} = \frac{[\text{Cu}^{+2}][\text{NH}_3]^4}{[\text{Cu(NH}_3)_4^{+2}]} = 10^{-12}$$



$$K_{\text{inst.}} \text{Cd(NH}_3)_4^{+2} = \frac{[\text{Cd}^{+2}][\text{NH}_3]^4}{[\text{Cd(NH}_3)_4^{+2}]} = 10^{-7}$$

$$\frac{[\text{Cu}^{+2}]}{[\text{Cu(NH}_3)_4^{+2}]} = \frac{K_{\text{inst.}}}{[\text{NH}_3]^4} = \frac{10^{-12}}{10^{-4}} = 10^{-8}; \quad \underline{[\text{Cu}^{+2}] = 10^{-8} \cdot 10^{-3} = 10^{-11}\text{M}}$$

$$\frac{[\text{Cd}^{+2}]}{[\text{Cd(NH}_3)_4^{+2}]} = \frac{K_{\text{inst.}}}{[\text{NH}_3]^4} = \frac{10^{-7}}{10^{-4}} = 10^{-3}; \quad \underline{[\text{Cd}^{+2}] = 10^{-3} \cdot 10^{-3} = 10^{-6}\text{M}}$$



$$\frac{[\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{K_{a1}}{[\text{H}^+]} = \frac{10^{-7}}{10^{-9}} = 10^2; \quad \frac{[\text{S}^{2-}]}{[\text{HS}^-]} = \frac{K_{a2}}{[\text{H}^+]} = \frac{10^{-13}}{10^{-9}} = 10^{-4}$$

à $\text{pH} = 9$ prevale la specie HS^-

$$[\text{HS}^-] \approx 10^{-1} \text{ M}; \quad [\text{S}^{2-}] = 10^{-4} \cdot [\text{HS}^-] = 10^{-5} \text{ M}$$



$$K_{ps} = [\text{Cu}^{+2}][\text{S}^{2-}] = 10^{-36}$$

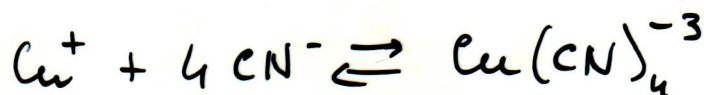
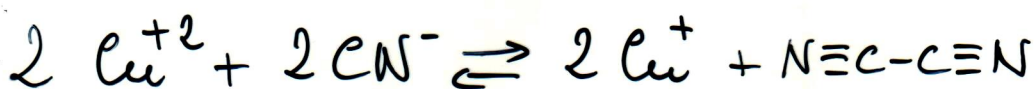
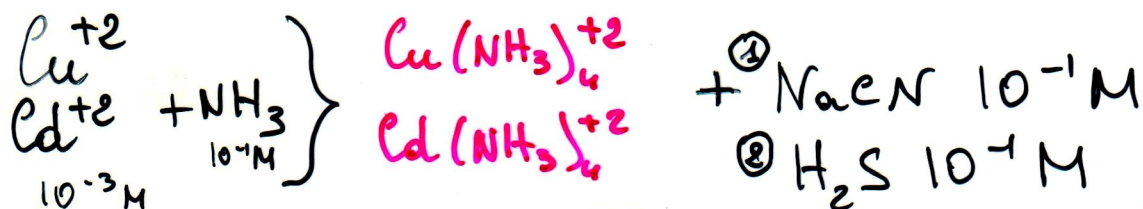
$$[\text{Cu}^{+2}] = 10^{-11} \text{ M}; \quad [\text{S}^{2-}] = 10^{-5} \text{ M}$$

$$[\text{Cu}^{+2}][\text{S}^{2-}] = 10^{-11} \cdot 10^{-5} = 10^{-16} \gg K_{ps}$$



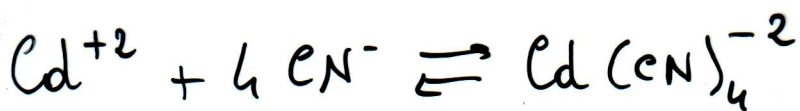
$$K_{ps} = [\text{Cd}^{+2}][\text{S}^{2-}] = 10^{-28}$$

$$[\text{Cd}^{+2}] = 10^{-6} \text{ M}; \quad [\text{S}^{2-}] = 10^{-5} \text{ M}; \quad [\text{Cd}^{+2}][\text{S}^{2-}] = 10^{-11} \gg K_{ps}$$



$$K_{\text{inst.}} \text{Cu}(\text{CN})_4^{-3} = \frac{[\text{Cu}^+][\text{CN}^-]^4}{[\text{Cu}(\text{CN})_4^{-3}]} = 10^{-30}$$

$$K_{\text{inst.}} \text{Cu}(\text{NH}_3)_4^{+2} = 10^{-12}$$

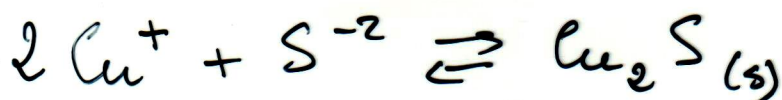


$$K_{\text{inst.}} = \frac{[\text{Cd}^{+2}][\text{CN}^-]^4}{[\text{Cd}(\text{CN})_4^{-2}]} = 10^{-17}$$

$$K_{\text{inst.}} \text{Cd}(\text{NH}_3)_4^{+2} = 10^{-7}$$

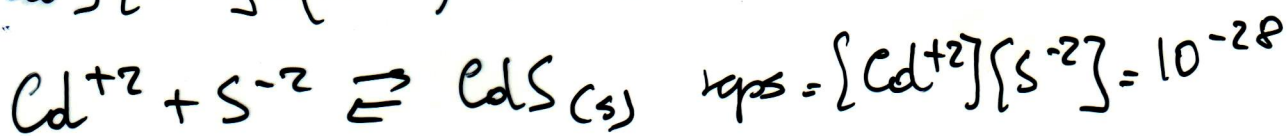
$$[\text{Cu}^+] = \frac{K_{\text{inst.}} \text{Cu}(\text{CN})_4^{-3} \cdot [\text{Cu}(\text{CN})_4^{-3}]}{[\text{CN}^-]^4} = \frac{10^{-30} \cdot 10^{-3}}{(10^{-1})^4} = 10^{-29} \text{ M}$$

$$[\text{Cd}^{+2}] = \frac{K_{\text{inst.}} \text{Cd}(\text{CN})_4^{-2} \cdot [\text{Cd}(\text{CN})_4^{-2}]}{[\text{CN}^-]^4} = \frac{10^{-17} \cdot 10^{-3}}{(10^{-1})^4} = 10^{-16} \text{ M}$$



$$K_{\text{ps}} = [\text{Cu}^+]^2 [\text{S}^{-2}] = 10^{-49}$$

$$[\text{Cu}^+]^2 [\text{S}^{-2}] = (10^{-29})^2 \cdot 10^{-5} = 10^{-63} \ll K_{\text{ps}}$$



$$[\text{Cd}^{+2}][\text{S}^{-2}] = 10^{-16} \cdot 10^{-5} = 10^{-21} > K_{\text{ps}}$$