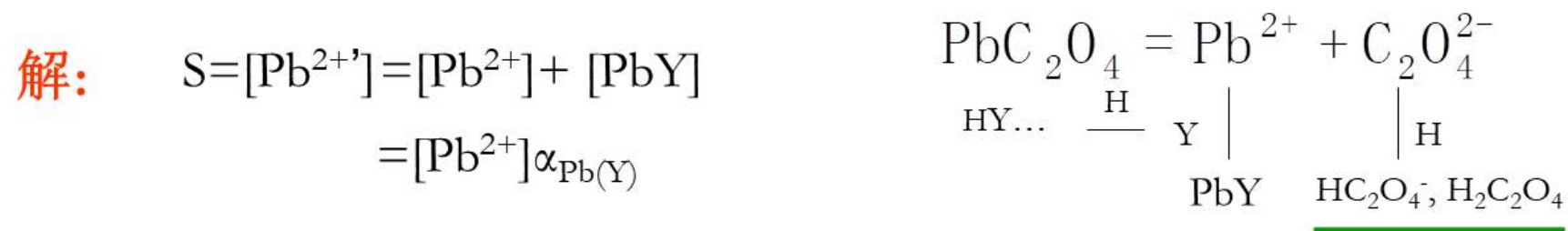


例： 计算 PbC_2O_4 在如下情况时的溶解度：沉淀与溶液达到平衡后pH为4.0，溶液中过量草酸为0.10mol/L，未与 Pb^{2+} 络合的EDTA的总浓度为0.010mol/L。

已知： $K_{\text{sp}}(\text{PbC}_2\text{O}_4)=10^{-9.7}$ ； $\lg K_{\text{PbY}}=18.0$ ； $\text{H}_2\text{C}_2\text{O}_4$: $\text{p}K_{\text{a1}}=1.1$, $\text{p}K_{\text{a2}}=4.0$



pH=4.0 $\lg \alpha_{\text{Y}(\text{H})}=8.6$

$$\alpha_{\text{Pb}(\text{Y})} = 1 + K_{\text{PbY}}[\text{Y}] = 1 + K_{\text{PbY}} \frac{[\text{Y}']}{\alpha_{\text{Y}(\text{H})}} \approx 10^{18.0} \times \frac{0.01}{10^{8.6}} = 10^{7.4}$$

$$[\text{C}_2\text{O}_4^{2-}]' = \mathbf{0.1} + S = [\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4] = [\text{C}_2\text{O}_4^{2-}] \alpha_{\text{C}_2\text{O}_4(\text{H})}$$

$$\alpha_{\text{C}_2\text{O}_4(\text{H})} = 1 + \frac{[\text{H}^+]}{K_{\text{a2}}} + \frac{[\text{H}^+]^2}{K_{\text{a2}}K_{\text{a1}}} = 1 + 10^{-4.0+4.0} + 10^{-8.0+4.0+1.1} = 2$$

设: $[\text{C}_2\text{O}_4^{2-}] = 0.1 + S$, 不略去S

$$s(0.1 + s) = [\text{Pb}^{2+}] [\text{C}_2\text{O}_4^{2-}] \alpha_{\text{Pb}(\text{Y})} \alpha_{\text{C}_2\text{O}_4^{2-}(\text{H})} = K_{\text{sp}} \alpha_{\text{Pb}(\text{Y})} \alpha_{\text{C}_2\text{O}_4^{2-}(\text{H})}$$

$$S = 0.062 \text{ mol/L}$$

若设: $[\text{C}_2\text{O}_4^{2-}] \approx 0.1$, 略去S

$$s \times 0.1 = K_{\text{sp}} \alpha_{\text{Pb}(\text{Y})} \alpha_{\text{C}_2\text{O}_4^{2-}(\text{H})}$$

$$S = 0.1 \text{ mol/L}$$

溶解度很大, 已不能形成沉淀, 且因S大, $[\text{C}_2\text{O}_4^{2-}]_{\text{总}}$ 中的S已不可忽略