

配位滴定法

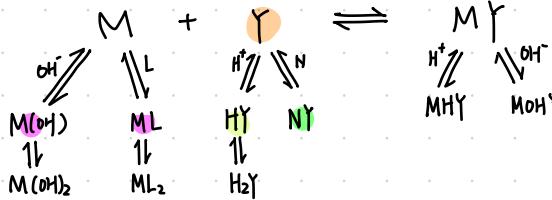
$$\text{稳定常数 } K_{\text{稳}} = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]}$$

$$\text{逐级稳定常数 } \beta_n = \prod_{i=1}^n K_{\text{稳}i}$$

$$\text{分布系数 } C_M = [\text{M}](1 + \sum_{i=1}^n \beta_i [\text{L}]^i)$$

$$\delta_{\text{ML}_n} = \frac{[\text{ML}_n]}{C_M} = \frac{\beta_n [\text{L}]^n}{1 + \sum_{i=1}^n \beta_i [\text{L}]^i}$$

副反应系数



$$\alpha_{M(L)} = 1 + \sum_{i=1}^n \beta_i [\text{L}]^i$$

$$\alpha_{Y(H)} = 1 + \sum_{i=1}^n \beta_i [\text{H}^+]^i \quad (\text{直表})$$

$$\alpha_{Y(N)} = 1 + K_{\text{MY}} [\text{N}]$$

$$(\alpha_{Y(N)} \text{ 总} = \sum_i \alpha_{Y(N_i)} - n + 1)$$

$$\alpha_Y = \alpha_{Y(H)} + \alpha_{Y(N)} - 1$$

条件稳定常数

$$K'_{\text{MY}} = K_{\text{MY}} \cdot \frac{\alpha_{\text{MY}}}{\alpha_{M(L)} \alpha_Y} \Leftrightarrow \lg K'_{\text{MY}} = \lg K_{\text{MY}} - \lg \alpha_M - \lg \alpha_Y$$

化学计量点

$$[\text{M}]_{\text{sp}} = \sqrt{\frac{C_M^{\text{sp}}}{K'_{\text{MY}}}} \Leftrightarrow pM_{\text{sp}} = \frac{1}{2}(pC_M^{\text{sp}} + \lg K'_{\text{MY}})$$

$$\text{滴定终点 } pM_{\text{ep}} = pM_{\text{sp}} - \lg \alpha_M$$

$$\begin{cases} \text{SP 前 } PM' = \lg K'_{\text{MY}} - 3.0 \\ \text{SP 后 } PM' = pC_M^{\text{sp}} + 3.0 \end{cases}$$

理论变色点

$$PM = \lg K'_{\text{MY}}$$

$$\Delta PM' = pM_{\text{ep}} - pM'_{\text{sp}} E_t = \frac{10^{-\Delta PM'} - 10^{-\Delta PM'}}{\sqrt{K'_{\text{MY}} \cdot C_M^{\text{sp}}}}$$

准确滴定

$$\lg(C_M^{\text{sp}} \cdot K'_{\text{MY}}) \geq 6$$

$$\lg(K'_{\text{MY}} C_M^{\text{sp}}) - \lg(K_{\text{MY}} C_N^{\text{sp}}) \geq 5$$

$$\log(\alpha_{Y(H)}) \leq \lg K'_{\text{MY}} - 8 \quad C = 0.01 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{酸度控制} \quad \text{最佳 } pM_{\text{ep}} = pM'_{\text{sp}} \quad [\text{OH}^-] \leq \left(\frac{K'_{\text{sp}}}{[\text{M}]} \right)^{\frac{1}{n}}$$

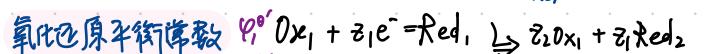
氧化还原滴定法

$$\text{Nernst 方程 } E_{\text{Ox}/\text{Red}} = E^\circ + \frac{0.059}{n} \lg \frac{a_{\text{ox}}}{a_{\text{red}}}$$

$$= E^\circ + \frac{0.059}{n} \lg \frac{[\text{Ox}]/[\text{Red}]}{[\text{Red}]/[\text{Ox}]} + \frac{0.059}{n} \lg \frac{C_{\text{Ox}}}{C_{\text{Red}}}$$

$$\text{条件电极电位 } E' = E^\circ + \frac{0.059}{n} \lg \frac{[\text{Ox}]/[\text{Red}]}{[\text{Red}]/[\text{Ox}]}$$

$$E_{\text{Ox}/\text{Red}} = E' + \frac{0.059}{n} \lg \frac{C_{\text{Ox}}}{C_{\text{Red}}}$$



$$\lg K' = \frac{(\varphi_1^\circ - \varphi_2^\circ)z}{0.059V} = \lg \frac{C_{\text{Red}_1}^{z_1} C_{\text{Ox}_2}^{z_2}}{C_{\text{Ox}_1}^{z_1} C_{\text{Red}_2}^{z_2}}$$

(z 为 z_1 与 z_2 的最小公倍数)

进行程度 用 $\frac{C_{\text{Red}_1}}{C_{\text{Ox}_1}}$ 或 $\frac{C_{\text{Ox}_2}}{C_{\text{Red}_2}}$ 表示反应进行程度。

$$\text{反应进行 } 99.9\% \text{ 以上} \Rightarrow \frac{C_{\text{Red}_1}}{C_{\text{Ox}_1}} \geq 10^3, \frac{C_{\text{Ox}_2}}{C_{\text{Red}_2}} \geq 10^3$$

理论变色点 $\varphi_{\text{In}}^\circ(Y) = \varphi_{\text{ep}}$

理论变色范围 $\varphi_{\text{In}}^\circ \pm \frac{0.059}{z} (V)$

化学计量点电势 $\varphi_{\text{sp}} = \frac{z_1 \varphi_1^\circ + z_2 \varphi_2^\circ}{z_1 + z_2}$

滴定突跃 滴定剂: $\varphi_1^\circ z_1$ 待测物: $\varphi_2^\circ z_2$

$$(\varphi_2^\circ + \frac{0.059V}{z_2} \lg 10^3) \sim (\varphi_1^\circ + \frac{0.059V}{z_1} \lg 10^{-3})$$

终点误差 $\Delta \varphi = \varphi_{\text{ep}} - \varphi_{\text{sp}}$

条件 1° 对称电对

1° 电子转移数为 1
 $E_t = \frac{10^{-\Delta \varphi / 0.059V} - 10^{-\Delta \varphi / 0.059V}}{10^{-\Delta \varphi / 2 \times 0.059V}}$

重量分析法



溶解度

固有溶解度

$$S^\circ = \alpha_{\text{MA}(\text{固})}$$

$$S = S^\circ + [\text{M}^+] \approx [\text{M}^+] \approx [\text{A}^-]$$

溶解度积

$$K_{\text{sp}}^\circ = \alpha_{\text{M}^+} \cdot \alpha_{\text{A}^-}$$

$$K_{\text{sp}} = [\text{M}^+] \cdot [\text{A}^-] = \frac{K_{\text{sp}}^\circ}{\gamma_{\text{M}^+} \gamma_{\text{A}^-}}$$

多元酸滴定的误差

$$E_t = \frac{10^{-\Delta \text{PH}} - 10^{-\Delta \text{PH}}}{\sqrt{K_{\text{a}1}/K_{\text{a}2}}} \quad \text{H}_3\text{P}_4$$

$$E_t = \frac{10^{-\Delta \text{PH}} - 10^{-\Delta \text{PH}}}{2\sqrt{K_{\text{a}2}/K_{\text{a}3}}} \quad \text{SP}_1$$

$$E_t = \frac{10^{-\Delta \text{PH}} - 10^{-\Delta \text{PH}}}{\sqrt{K_{\text{a}3}/K_{\text{a}4}}} \quad \text{SP}_2$$

$$E_t = \frac{10^{-\Delta \text{PH}} - 10^{-\Delta \text{PH}}}{\sqrt{K_{\text{a}2} C_{\text{H}_3\text{P}_4}^{\text{sp}}/K_w}} \quad \text{SP}_3$$

$$E_t = \frac{10^{-\Delta \text{PH}} - 10^{-\Delta \text{PH}}}{\sqrt{K_{\text{a}1}/K_{\text{a}2}}} \quad \text{H}_2\text{A}$$

$$E_t = \frac{10^{-\Delta \text{PH}} - 10^{-\Delta \text{PH}}}{2\sqrt{K_{\text{a}2}/K_{\text{a}3}}} \quad \text{SP}_1$$

$$E_t = \frac{10^{-\Delta \text{PH}} - 10^{-\Delta \text{PH}}}{\sqrt{K_{\text{a}3}/C_{\text{H}_2\text{A}}^{\text{sp}}/K_w}} \quad \text{SP}_2$$

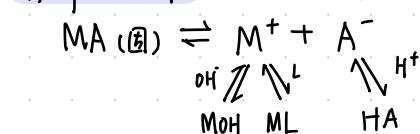
$$E_t = \frac{10^{-\Delta \text{px}} - 10^{-\Delta \text{px}}}{\sqrt{C_x^{\text{sp}}/K_{\text{sp}}}}$$

关系 $M_m A_n$

$$S = \left(\frac{K_{\text{sp}}}{m^m n^n} \right)^{\frac{1}{m+n}}$$

$$\alpha_{\text{A}(\text{H})} = 1 + \frac{1}{K_{\text{a}2}} [\text{H}^+] + \frac{1}{K_{\text{a}1} K_{\text{a}2}} [\text{H}^+]^2$$

$$\alpha_{\text{M}(\text{L})} = 1 + \beta_1 [\text{L}] + \beta_2 [\text{L}]^2$$



$$K_{\text{sp}}' = K_{\text{sp}} \cdot \alpha_{\text{M}(\text{L})} = \frac{K_{\text{sp}}}{\delta_{\text{M}} \cdot \delta_{\text{A}}}$$

$$S' = \left(\frac{K_{\text{sp}}'}{m^m n^n} \right)^{\frac{1}{m+n}}$$

$$K_{\text{sp}}' \geq K_{\text{sp}} \geq K_{\text{sp}}^\circ$$

同离子效应

$$S = \frac{1}{m} \left(\frac{K_{\text{sp}}}{C_A^n} \right)^{\frac{1}{m}}$$