



5.2.8 沉淀和弱电解质的 生成对电极电势的影响

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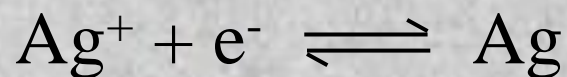
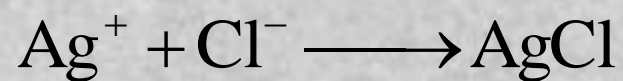
邱海霞



沉淀的生成对电极电势的影响

已知 $E^{\ominus}(\text{Ag}^+/\text{Ag}) = 0.799\text{V}$,若在该电极中加入 KCl 溶液 , 当 $c(\text{Cl}^-) = 1.0\text{mol}\cdot\text{L}^{-1}$ 时, $E(\text{Ag}^+/\text{Ag}) = ?$

$$K_{\text{sp}}^{\ominus}(\text{AgCl}) = 1.77 \times 10^{-10}$$



$$c(\text{Ag}^+) = \frac{K_{\text{sp}}^{\ominus}(\text{AgCl})}{c(\text{Cl}^-)} = 1.77 \times 10^{-10} \text{mol}\cdot\text{L}^{-1}$$

$$E(\text{Ag}^+/\text{Ag}) = E^{\ominus}(\text{Ag}^+/\text{Ag}) + 0.0592\text{V} \lg c(\text{Ag}^+)$$

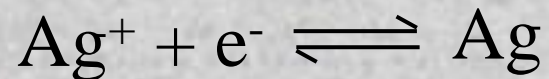
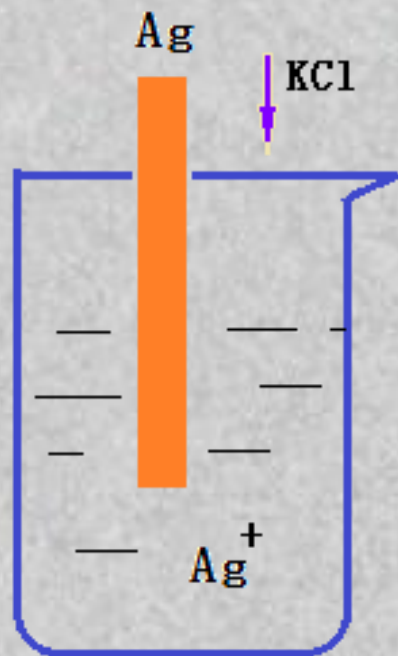
$$= 0.799\text{V} + 0.0592\text{V} \lg(1.77 \times 10^{-10})$$

$$= 0.222\text{V}$$

改变量 0.577V

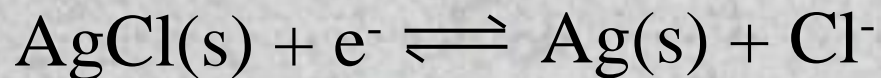


沉淀的生成对电极电势的影响



当 $c(\text{Cl}^-) = 1.0 \text{ mol} \cdot \text{L}^{-1}$ 时 ,

$$E(\text{Ag}^+/\text{Ag}) = 0.222 \text{ V}$$



当 $c(\text{Cl}^-) = 1.0 \text{ mol} \cdot \text{L}^{-1}$ 时 ,

AgCl/Ag 电对是否处于标准状态 ?

$$E^\ominus(\text{AgCl}/\text{Ag}) = E(\text{Ag}^+/\text{Ag})$$

$$E^\ominus(\text{AgCl}/\text{Ag}) = 0.222 \text{ V}$$



沉淀的生成对电极电势的影响

		电对	E^{\ominus} / V
$c(\text{Ag})^{+}$	K_{sp}^{\ominus}	$\text{Ag}^{+} + \text{e}^{-} \rightleftharpoons \text{Ag}$	0.799
减小	减小	$\text{AgCl(s)} + \text{e}^{-} \rightleftharpoons \text{Ag} + \text{Cl}^{-}$	0.222
		$\text{AgBr(s)} + \text{e}^{-} \rightleftharpoons \text{Ag} + \text{Br}^{-}$	0.071
		$\text{AgI(s)} + \text{e}^{-} \rightleftharpoons \text{Ag} + \text{I}^{-}$	-0.152

氧化态形成沉淀 E^{\ominus} 减小

还原态形成沉淀 E^{\ominus} 增加

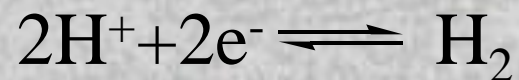


弱电解质的生成对电极电势的影响

在氢电极的半电池中，加入NaOAc溶液，
平衡时 $p(\text{H}_2) = p^\ominus, c(\text{HOAc}) = c(\text{OAc}^-) = 1.0 \text{ mol} \cdot \text{L}^{-1}$
求此时 $E(\text{H}^+/\text{H}_2) = ?$ $K_a^\ominus(\text{HOAc}) = 1.8 \times 10^{-5}$



$$\frac{c(\text{H}^+) \cdot c(\text{OAc}^-)}{c(\text{HOAc})} = K_a^\ominus(\text{HOAc}) \quad c(\text{H}^+) = K_a^\ominus(\text{HOAc}) = 1.8 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$



$$\begin{aligned} E(\text{H}^+/\text{H}_2) &= E^\ominus(\text{H}^+/\text{H}_2) + \frac{0.0592}{2} \lg \frac{c^2(\text{H}^+)}{p(\text{H}_2)/p^\ominus} \\ &= \frac{0.0592 \text{ V}}{2} \lg(1.8 \times 10^{-5})^2 = -0.281 \text{ V} \end{aligned}$$

改变量 **0.281V**