



5.2.7 浓度对电极电势的影响

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浓度对电极电势的影响

$$E = E^{\ominus} + \frac{0.0592\text{V}}{z} \lg \frac{c^{\text{a}}(\text{氧化态})}{c^{\text{b}}(\text{还原态})}$$

1. $E^{\ominus}(\text{Cu}^{2+}/\text{Cu}) = 0.34\text{V}$

$c(\text{Cu}^{2+})=10^{-3}\text{mol L}^{-1}$, $E(\text{Cu}^{2+}/\text{Cu})=?$

2. $E^{\ominus}(\text{Cl}_2/\text{Cl}^-) = 1.3583\text{V}$, $c(\text{Cl}^-)=10^{-3}\text{mol L}^{-1}$,

$p(\text{Cl}_2)=100\text{kPa}$, $E(\text{Cl}_2/\text{Cl}^-)=?$

3. $E^{\ominus}(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = 1.36\text{V}$, $c(\text{H}^+)=10^{-3}\text{mol L}^{-1}$

$c(\text{Cr}_2\text{O}_7^{2-}) = c(\text{Cr}^{3+}) = 1.0\text{mol} \cdot \text{L}^{-1}$

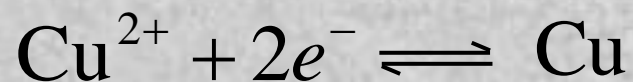
$E(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = ?$



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1. $E^{\ominus}(\text{Cu}^{2+}/\text{Cu}) = 0.34\text{V}$

$c(\text{Cu}^{2+}) = 10^{-3}\text{mol L}^{-1}$, $E(\text{Cu}^{2+}/\text{Cu}) = ?$



$$E(\text{Cu}^{2+}/\text{Cu}) = E^{\ominus}(\text{Cu}^{2+}/\text{Cu}) + \frac{0.0592\text{V}}{2} \lg c(\text{Cu}^{2+})$$

$$= 0.34\text{V} + \frac{0.0592\text{V}}{2} \lg 10^{-3}$$

$$= 0.25\text{V}$$

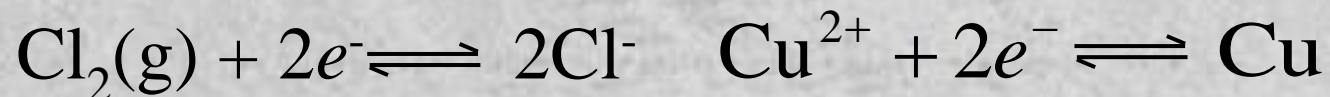
改变量 **0.09V**



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2. $E^{\ominus}(\text{Cl}_2/\text{Cl}^-) = 1.3583\text{V}$, $c(\text{Cl}^-) = 10^{-3}\text{mol L}^{-1}$,

$p(\text{Cl}_2) = 100\text{kPa}$, $E(\text{Cl}_2/\text{Cl}^-) = ?$



$$E(\text{Cl}_2/\text{Cl}^-) = E^{\ominus}(\text{Cl}_2/\text{Cl}^-) + \frac{0.0592\text{V}}{2} \lg \frac{p(\text{Cl}_2)/p^{\ominus}}{c^2(\text{Cl}^-)}$$

$$= 1.3583\text{V} + \frac{0.0592\text{V}}{2} \lg \frac{1}{(10^{-3})^2}$$

$$= 1.54\text{V}$$

改变量 **0.18V**

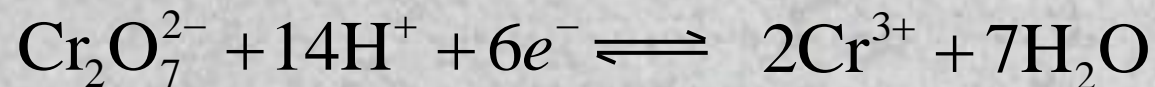


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$$3. \quad E^{\ominus}(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = 1.36\text{V}$$

$$c(\text{H}^+) = 10^{-3} \text{mol} \cdot \text{L}^{-1}, c(\text{Cr}_2\text{O}_7^{2-}) = c(\text{Cr}^{3+}) = 1.0 \text{mol} \cdot \text{L}^{-1},$$

$$E(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = ?$$



$$E(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = E^{\ominus}(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) + \frac{0.0592\text{V}}{6} \lg \frac{c(\text{Cr}_2\text{O}_7^{2-}) \cdot c^{14}(\text{H}^+)}{c^2(\text{Cr}^{3+})}$$

$$= 1.36\text{V} + \frac{0.0592\text{V}}{6} \lg(10^{-3})^{14}$$

$$= 0.9456\text{V}$$

改变量 **0.414V**



结论

$$E = E^{\ominus} + \frac{0.0592\text{V}}{z} \lg \frac{c^{\text{a}}(\text{氧化态})}{c^{\text{b}}(\text{还原态})}$$

◆ 离子浓度对电极电势的影响

一般不大

◆ 若 H^+ 或 OH^- 也参与了电极反应，则溶液的
酸度往往对电极电势的影响

较大