

第 17 章 电化学

基本概念

1. 电势较高的电极为正极，电势较低的电极为负极；正离子趋向或负离子离开的电极为阴极，负离子趋向或正离子离开的电极为阳极；错；对。

2. 电流为零（达到平衡）时原电池的电池电势称为电动势；只决定于参与反应的各物质的化学势的电池电势；在两种含有不同溶质或溶质相同而浓度不同的溶液界面上存在的电势差；避免使用有液接界面的原电池或使用盐桥。

$$3. \mu_i + z_i F \phi; -SdT + Vdp + \sum_{\alpha=1}^{\pi} \sum_{i=1}^K \tilde{\mu}_i^{(\alpha)} dn_i^{(\alpha)} + \sigma dA_s; \sum_{\alpha=1}^{\pi} \sum_B \nu_B \tilde{\mu}_B^{(\alpha)} = W'_R。$$

$$4. -zFE; zF\left(\frac{\partial E}{\partial T}\right)_p; -zF\left[E - T\left(\frac{\partial E}{\partial T}\right)_p\right]; \text{错。}$$

$$5. E = E^\circ - \frac{RT}{zF} \sum_B \nu_B \ln a_B; \text{参加反应的所有物质均处于标准状态的电池反应电势}; E^\circ = \frac{RT}{zF} \ln K^\circ。$$

6.

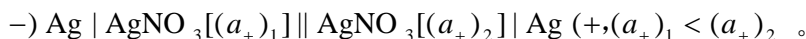
电极	电极反应	$E^\circ/V(25^\circ\text{C})$
(1) $\text{H}^+ \text{H}_2 \text{Pt}$	$\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2$	0
(2) $\text{OH}^- \text{H}_2 \text{Pt}$	$\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^-$	-0.8277
(3) $\text{H}^+ \text{O}_2 \text{Pt}$	$4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.229
(4) $\text{OH}^- \text{O}_2 \text{Pt}$	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.401
(5) $\text{Ag}^+ \text{Ag}$	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.7994
(6) $\text{Cl}^- \text{AgCl(s)} \text{Ag}$	$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	0.22216

(1) 与 (2)，(3) 与 (4) 构成的电池反应均为水的解离反应，(5) 与 (6) 构成的电池反应为微溶盐的溶解；水的 K_w° 与 AgCl 的 K_{sp}° 。

$$7. \frac{RT}{2F} \ln K_{sp}^\circ = -0.2326 \text{ V}。$$

8. (4)

9. 浓差电池的反应是物理变化，化学电池的反应是化学变化。



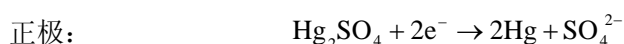
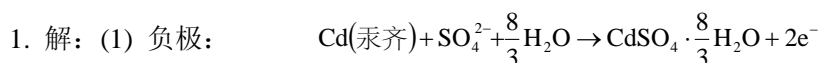
10. 实际电极电势与电极反应电势有显著差别的现象；传质超电势，活化超电势。

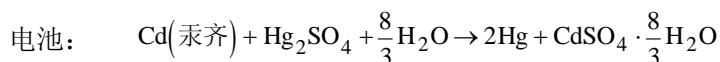
11. 实际的电极电势与平衡的电极反应电势之差 $\eta = E(j) - E(0)$ ； $|\eta| = a + b \ln \{j\}$ ；

$$E_a(0) + \eta_a - E_c(0) - \eta_c + IR; E_c(0) + \eta_c - E_a(0) - \eta_a - IR。$$

12. (3)

计算题





(2) $E/\text{V} = 1.018646 - 4.06 \times 10^{-5}(t/^\circ\text{C} - 20)$

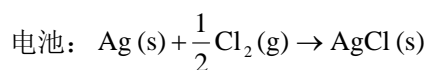
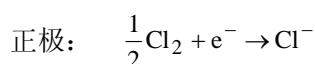
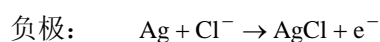
(3) $\Delta_r G_m = -zFE = -2 \times 96485 \times 1.018646 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} = -196.568 \text{ kJ} \cdot \text{mol}^{-1}$

$$\Delta_r S_m = zF \left(\frac{\partial E}{\partial T} \right)_p = 2 \times 96485 \times (-4.06 \times 10^{-5}) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -7.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m = [-196.568 + 293.15 \times (-7.83) \times 10^{-3}] \text{ kJ} \cdot \text{mol}^{-1} = -198.863 \text{ kJ} \cdot \text{mol}^{-1}$$

(4) $Q_R = T\Delta_r S_m = 293.15 \times (-7.83) \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} = -2.295 \text{ kJ} \cdot \text{mol}^{-1}$

2. 解: 一) $\text{Ag} | \text{AgCl} | \text{Cl}^- | \text{Cl}_2 | \text{Pt}$ (+)



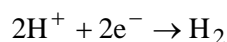
$$E^\ominus = 1.3579 - 0.2222 = 1.1357 \text{ V},$$

$$\Delta_r G_m^\ominus = \Delta_r G_m^\ominus = -zFE^\ominus = -1 \times 96485 \times 1.1357 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} = -109.58 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\lg K^\ominus = \frac{1.1357}{0.05916} = 19.197, \quad K^\ominus = 1.57 \times 10^{19},$$

$$K^\ominus = \frac{1}{\left(\frac{p_{\text{Cl}_2}}{p^\ominus} \right)^{1/2}}, \quad \frac{p_{\text{Cl}_2}}{p^\ominus} = \frac{1}{(K^\ominus)^2} = 4.06 \times 10^{-39}, \quad \therefore p_{\text{Cl}_2} = 4.06 \times 10^{-37} \text{ kPa}.$$

3. 解: (1) 阴极反应: $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$



$$E\{\text{Zn}^{2+} | \text{Zn}\} = \left[-0.762 - \frac{0.05916}{2} \lg \frac{1}{0.1} \right] \text{ V} = -0.792 \text{ V}$$

$$E\{\text{H}^+ | \text{H}_2\} = [0 + 0.05916 \lg(10^{-7}) + (-0.726)] \text{ V} = -1.140 \text{ V}, \quad \text{故先析出 Zn}.$$

(2) $E\{\text{Br}^- | \text{Br}_2\} = [1.065 - 0.05916 \lg(0.1 \times 0.01)] \text{ V} = 1.242 \text{ V}$

(3) $E\{\text{OH}^- | \text{O}_2\} = [0.401 - 0.05916 \lg(10^{-7}) + 0.480] \text{ V} = 1.295 \text{ V}$

$$1.295 = 1.065 - 0.05916 \lg x, \quad x = 1.29 \times 10^{-4},$$

即此时溶液中溴离子浓度为 $1.29 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ 。