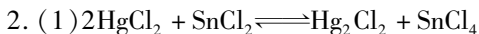
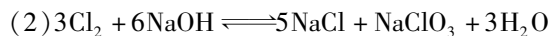


第4章 电化学基础

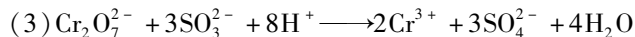
1. 5, -1, 3, 4, 5, 0, 1, -1



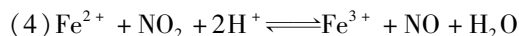
氧化剂: HgCl_2 还原剂: SnCl_2



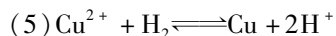
氧化剂: Cl_2 还原剂: Cl_2



氧化剂: $\text{Cr}_2\text{O}_7^{2-}$ 还原剂: SO_3^{2-}



氧化剂: NO_2 还原剂: Fe^{2+}



氧化剂: Cu^{2+} 还原剂: H_2

5. (1) $\varphi = \varphi^\ominus - \frac{RT}{10F} \ln \frac{1}{c_{\text{IO}_3^-}^2 \times c_{\text{H}^+}^{12}}$

(2) $\varphi = \varphi^\ominus - \frac{RT}{2F} \ln \frac{c_{\text{Mn}^{2+}}}{c_{\text{H}^+}^4}$

(3) $E = E^\ominus - \frac{RT}{6F} \ln \frac{c_{\text{Cr}^{3+}}^2 \times c_{\text{SO}_4^{2-}}^3}{c_{\text{Cr}_2\text{O}_7^{2-}} \times c_{\text{SO}_3^{2-}}^3 \times c_{\text{H}^+}^8}$

(4) $E = E^\ominus - \frac{RT}{2F} \ln \frac{c_{\text{Fe}^{3+}}^2 \times c_{\text{Br}^-}^2}{c_{\text{Fe}^{2+}}^3}$

6. H_2O_2 为最强氧化剂, Fe 为最强还原剂;

氧化能力 $\text{H}_2\text{O}_2 > \text{Fe}^{3+} > \text{O}_2 > \text{Fe}^{2+}$; 还原能力 $\text{Fe} > \text{H}_2\text{O}_2 > \text{Fe}^{2+} > \text{H}_2\text{O}$

7. 解: 负极 $\text{H}_2(\text{p}_{\text{H}_2}) \longrightarrow 2\text{H}^+ [c(\text{H}^+)] + 2\text{e}^-$ 正极 $\text{Cu}^{2+}(\text{a}_{\text{Cu}^{2+}}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$

电池反应 $\text{H}_2(\text{p}_{\text{H}_2}) + \text{Cu}^{2+} [c(\text{Cu}^{2+})] \rightleftharpoons \text{Cu}(\text{s}) + 2\text{H}^+ [c(\text{H}^+)]$

8. 解:

$$\text{Fe}^{2+} + \text{Ag}^+ \rightleftharpoons \text{Ag}(\text{s}) + \text{Fe}^{3+}$$

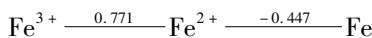
$$E^\ominus = \varphi^\ominus(\text{Ag}^+/\text{Ag}) - \varphi^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+})$$

则

$$\ln K^\ominus = \frac{zE^\ominus F}{RT} \ln K^\ominus = \frac{1 \times (0.7991 - 0.771) \times 96500}{298 \times 8.314} = 1.049$$

$$K^\ominus = 2.988$$

9. 解: 铁的元素电势图为 $\varphi_{\text{A}}^\ominus/\text{V}$



因为 $\varphi_{\text{右}}^\ominus < \varphi_{\text{左}}^\ominus$, 则反应不自发。

10. 解: (1) 已知

$$\varphi_{\text{Fe}^{3+}/\text{Fe}^{2+}} = \varphi_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\ominus + \frac{0.05916}{1} \lg \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 0.771 + 0.05916 \lg \frac{0.5}{0.05} = 0.829 \text{ V}$$

$$\varphi_{\text{MnO}_2/\text{Mn}^{2+}} = \varphi_{\text{MnO}_2/\text{Mn}^{2+}}^\ominus + \frac{0.05916}{2} \lg \frac{[\text{MnO}_2][\text{H}^+]^4}{[\text{Mn}^{2+}]} = 1.208 + \frac{0.05916}{2} \lg \frac{0.1^4}{0.01} = 1.149 \text{ V}$$

$$E = \varphi_+ - \varphi_- = 1.149 - 0.829 = 0.32 \text{ V}$$

(2) 因为 $\varphi(\text{MnO}_2/\text{Mn}^{2+}) > \varphi(\text{Fe}^{3+}/\text{Fe}^{2+})$

故负极反应: $\text{Fe}^{2+} - \text{e} \rightleftharpoons \text{Fe}^{3+}$, 正极反应: $\text{MnO}_2 + 4\text{H}^+ + 2\text{e} \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$

电池反应: $2\text{Fe}^{2+} + \text{MnO}_2 + 4\text{H}^+ \rightleftharpoons 2\text{Fe}^{3+} + \text{Mn}^{2+} + 2\text{H}_2\text{O}$

(3) $\Delta_r G_m = -nFE = -2 \times 9.65 \times 10^4 \times 0.32 = -61760 \text{ J} \cdot \text{mol}^{-1} = -61.76 \text{ kJ} \cdot \text{mol}^{-1}$

$$\lg K^\ominus = \frac{nE^\ominus}{0.05916} = \frac{2(1.208 - 0.770)}{0.05916} = 14.81, K^\ominus = 6.42 \times 10^{14}$$

11. 解: 因纯水的生成反应为 $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$ 则该反应的标准自由能变化值

$\Delta_r G_m^\ominus = -237.191 \text{ kJ} \cdot \text{mol}^{-1}$ 而 $\Delta_r G_m^\ominus = -nFE^\ominus = -1 \times 96485 \times E^\ominus = -237.191 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$

$E^\ominus = 2.458 \text{ V}$ 又因为理论分解电压等于可逆电池电动势, 故电解纯水的理论分解电压为 2.458 V

12. 解: (1) 电极反应 $[\text{Ag}(\text{CN})_2]^- + \text{e}^- \rightleftharpoons \text{Ag} + 2\text{CN}^-$

配位平衡 $\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]^-$

$$[\text{Ag}^+] = \frac{[\text{Ag}(\text{CN})_2^-]}{K_f^\ominus [\text{CN}^-]^2} = \frac{1}{K_f^\ominus \times 1^2} = \frac{1}{K_f^\ominus}$$

$$\varphi^\ominus([\text{Ag}(\text{CN})_2]^-/\text{Ag}) = \varphi(\text{Ag}^+/\text{Ag}) = \varphi^\ominus(\text{Ag}^+/\text{Ag}) + 0.0591 \lg [\text{Ag}^+]$$

$$= 0.7991 + 0.0591 \lg \frac{1}{1.26 \times 10^{21}} = -0.448 \text{ V}$$

$$(2) \varphi([\text{Ag}(\text{CN})_2]^-/\text{Ag}) = \varphi^\ominus([\text{Ag}(\text{CN})_2]^-/\text{Ag}) + 0.0591 \lg \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{CN}^-]^2}$$

$$= -0.448 + 0.0591 \lg \frac{0.20}{(0.50)^2} = -0.454 \text{ V}$$