第四章

4. (1) 负：$Zn(s) = Zn^{2+}(aq) + 2e^-$

正：$Fe^{2+}(aq) + 2e^- = Fe(s)$

(2) 负：$2I^-(aq) = I_2(s) + 2e^-$

正：$Fe^{3+}(aq) + e^- = Fe^{2+}(aq)$

(3) 负：$Ni(s) = Ni^{2+}(aq) + 2e^-$

正：$Sn^{4+}(aq) + 2e^- = Sn^{2+}(aq)$

(4) 负：$Fe^{2+}(aq) = Fe^{3+}(aq) + e^-$

正：$MnO_4^-(aq) + 8H^+ + 5e^- = Mn^{2+}(aq) + 4H_2O(l)$

5. (1) (-) $Zn | Zn^{2+} || Fe^{2+} | Fe$ (+)

(2) (-) $Pt | I_2 | I^- || Fe^{2+}, Fe^{3+} | Pt$ (+)

(3) (-) $Ni | Ni^{2+} || Sn^{2+}, Sn^{4+} | Pt$ (+)

(4) (-) $Pt | Fe^{2+}, Fe^{3+} || Mn^{2+}, MnO_4^-, H^+ | Pt$ (+)

9. (1) $\varphi^\theta(I_2/I^-) = 0.5355\,V$, $\varphi^\theta(Fe^{3+}/Fe^{2+}) = 0.771\,V$

故 $E = \varphi^\theta(+) - \varphi^\theta(-) = 0.2355\,V$

(2) $\Delta_r G^\theta = -nFE^\theta = -45.44\ kJ/mol$

(3) (-) $Pt | I_2(s), I^-(1mol/L) || Fe^{2+}(1mol/L), Fe^{3+}(1mol/L) | Pt$ (+)

(4) $\varphi(I_2/I^-) = 0.5355\,V + \frac{0.05917}{2} \lg(10^{-2})^2 = 0.6538\,V$

$\varphi(Fe^{3+}/Fe^{2+}) = 0.771\,V + 0.05917 \cdot \lg 10^1 = 0.71183\,V$

$E = \varphi(+) - \varphi(-) = 0.06\,V$

12. (-) $Pt \mid H_2(100kPa) \mid H^+(1mol/L) \parallel H^+(x mol/L) \mid H_2(100kPa) \mid Pt$ (+)

$E = \varphi(+) - \varphi(-) = 0.016V$

解得. $x = 0.19\ mol/L$

17. 因为 $\varphi^\theta(MnO_2/Mn^{2+}) = 1.224V$, $\varphi^\theta(Cl_2/Cl^-) = 1.35827V$

∴反应应该向左进行

但在加热状态下加浓盐酸增加 H^+ 浓度可以使 $\varphi^\theta(MnO_2/Mn^{2+})$ 增大，使 $\varphi^\theta(Cl_2/Cl^-)$ 减小，所以反应可以正向进行.

23. 正: $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$

负: $AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$

∴ $Ag^+(aq) + Br^-(aq) \rightleftharpoons AgBr$, K^θ.

又 $E^\theta = \varphi^\theta(Ag^+/Ag) - \varphi^\theta(AgBr) = 0.726V$

$\lg K^\theta = nE^\theta / 0.0591V = 12.28$

∴ $K_3 = \frac{1}{K^\theta} = 5.13 \times 10^{-13}$