



最专业的课后习题答案分享社区

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## 电化学原理第一章习题答案

1、解:  $K_{\text{溶液}} = K_{\text{KCl}} + K_{\text{H}_2\text{O}} = \frac{c\lambda_{\text{KCl}}}{1000} + K_{\text{H}_2\text{O}} = \frac{0.001 \times 141.3}{1000} + 1.0 \times 10^{-6} = 142.3 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$

2、解:  $\lambda_i = F \frac{V_i}{E}$ ,  $V_i = \frac{\lambda_i E}{F}$ ,  $V_{\text{H}^+} = 0.0288 \text{cm} \cdot \text{s}^{-1}$ ,  $V_{\text{K}^+} = 0.0050 \text{cm} \cdot \text{s}^{-1}$ ,  $V_{\text{Cl}^-} = 0.0051 \text{cm} \cdot \text{s}^{-1}$

3、解:  $\lambda_{\text{o}, \text{H}_2\text{O}} = \lambda_{\text{o}, \text{KOH}} + \lambda_{\text{o}, \text{HCl}} - \lambda_{\text{o}, \text{KCl}} = 550.62 \Omega^{-1} \text{cm}^2 \cdot \text{eq}^{-1}$ ,

设  $c^2 = c_{\text{H}^+} c_{\text{OH}^-}$ , 故  $c = \sqrt{K_{\text{w}}} = \sqrt{1.008 \times 10^{-14}} = 1.004$ ,  $\kappa = \frac{\lambda_{\text{o}, \text{H}_2\text{O}} c}{1000} = 5.5 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$

4、(1)  $\because \lambda = \lambda_+ + \lambda_-$ ,  $t_+ + t_- = 1$ ,  $\therefore \lambda_{\text{o}, \text{Cl}^-} = t_{\text{Cl}^-} \lambda_{\text{o}, \text{KCl}} = 76.33 \Omega^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$  (KCl中)

同理:  $\lambda_{\text{o}, \text{K}^+} = 73.49 \Omega^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$ ,  $\lambda_{\text{o}, \text{Na}^+} = 50.14 \Omega^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$ ,  $\lambda_{\text{o}, \text{Cl}^-} = 76.31 \Omega^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$  (NaCl中)

(2) 由上述结果可知:  $\lambda_{\text{o}, \text{K}^+} + \lambda_{\text{o}, \text{Cl}^-} = 142.82 \Omega^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$ ,  $\lambda_{\text{o}, \text{Na}^+} + \lambda_{\text{o}, \text{Cl}^-} = 126.45 \Omega^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$

在 KCl 与 NaCl 溶液中  $\lambda_{\text{o}, \text{Cl}^-}$  相等, 所以证明离子独立移动定律的正确性;

(3)  $u_{\text{o}, i} = \lambda_{\text{o}, \text{Cl}^-} / F$ ,  $u_{\text{o}, \text{Cl}^-} = 7.91 \times 10^{-4} \text{cm}^2 / \text{vs}$ ,  $u_{\text{o}, \text{K}^+} = 7.62 \times 10^{-4} \text{cm}^2 / \text{vs}$ ,  $\lambda_{\text{o}, \text{Na}^+} = 5.20 \times 10^{-4} \text{cm}^2 / \text{vs}$

5、解:  $\text{Cu}(\text{OH})_2 = \text{Cu}^{2+} + 2\text{OH}^-$ , 设  $c_{\text{Cu}^{2+}} = y$ ;  $c_{\text{OH}^-} = 2y$  则  $K_s = 4y^3$

因为  $u = \sum u_i = K \text{H}_2\text{O} + 10^{-3} [y \lambda_{\text{Cu}^{2+}} + 2y \lambda_{\text{OH}^-}]$  以  $\lambda_{\text{o}}$  代替  $\lambda$  (稀溶液) 代入上式, 求得  $y = 1.36 \times 10^{-4} \text{mol/dm}^3$

所以  $K_s = 4y^3 = 1.006 \times 10^{-11} (\text{mol/dm}^3)^3$

6、解:  $\text{AgIO}_3 = \text{Ag}^+ + \text{IO}_3^-$ , 令  $c_{\text{Ag}^+} = y$ ,  $c_{\text{IO}_3^-} = y$ , 则  $K_s = y^2$ ,  $K = \sum K_i = K_{\text{H}_2\text{O}} + 10^{-3} (y \lambda_{\text{Ag}^+} + y \lambda_{\text{IO}_3^-})$

作为无限稀溶液处理, 用  $\lambda_{\text{o}}$  代替,  $= K_{\text{H}_2\text{O}} + 10^{-3} y \lambda_{\text{AgIO}_3}$

则:  $y = \frac{1.30 \times 10^{-5} - 1.1 \times 10^{-6}}{68.4} \times 10^3 = 1.74 \times 10^{-4} \text{mol/L}$ ;  $\therefore K_s = y^2 = 3.03 \times 10^{-8} (\text{mol/L})^2$

7、解:  $\lambda_{\text{o}, \text{HAc}} = \lambda_{\text{o}, \text{HCl}} + \lambda_{\text{o}, \text{NaAc}} - \lambda_{\text{o}, \text{NaCl}} = 390.7 \Omega^{-1} \text{cm}^2 \cdot \text{eq}^{-1}$ ,  $\lambda_{\text{o}, \text{HAc}} = 9.02 \Omega^{-1} \text{cm}^2 \cdot \text{eq}^{-1}$

$\therefore \alpha = \lambda / \lambda_{\text{o}} = 0.023$ ,  $K_a = \alpha^2 / (1 - \alpha) \bar{V} = 1.69 \times 10^{-5}$

8、解: 由欧姆定律  $IR = iS \cdot \frac{l}{KS} = \frac{il}{K}$ ,  $\because K = \frac{\lambda c}{1000}$ ,  $\therefore IR = \frac{il \cdot 1000}{\lambda c} = \frac{5 \times 10^{-3} \times 10 \times 10^3}{126 \times 0.5} \approx 0.79 \text{V}$

9、解: 公式  $\log \gamma_{\pm} = -0.5115 |Z_+||Z_-| \sqrt{I}$  (设  $25^\circ \text{C}$ )

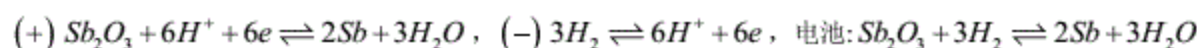
$$(1) \gamma_{\pm}=0.9740, \quad I=\frac{1}{2} \sum m_i z_i^2, I=\frac{1}{2} \sum c_i z_i^2, \quad m_{\pm}=(m_+^{v_+} m_-^{v_-})^{\frac{1}{v}}$$

$$(2) \gamma_{\pm}=0.9101, (3) \gamma_{\pm}=0.6487, (4) \gamma_{\pm}=0.8114$$

$$10、解：a_{H^+}=\gamma_{\pm} m_{H^+}, \quad pH=-\log a_{H^+}=-\log (0.209 \times 0.4)=1.08$$

## 电化学原理第二章习题答案

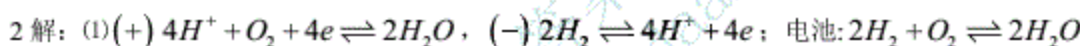
1、解：



$$\text{解法一: } E^0=-\frac{\Delta G^0}{nF}=\frac{8364}{6F} \approx 0.0143V, \quad E=E^0+\frac{2.3RT}{6F} \log \frac{P_{H_2}^3 a_{Sb_2O_3}}{a_{Sb}^2 a_{H_2O}^3}=E^0=0.0143V$$

$$\text{解法二: } \varphi_+^0=\varphi_{Sb}^0+\frac{2.3RT}{6F} \log a_{H^+}^6=\varphi_{Sb}^0+\frac{2.3RT}{F} \log a_{H^+}; \quad \varphi_-^0=\frac{2.3RT}{F} \log a_{H^+}$$

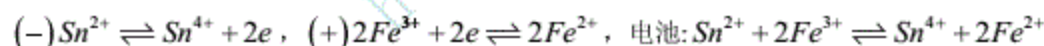
$$\therefore E=\varphi_+-\varphi_-=\varphi_{Sb}^0=E^0=0.0143V$$



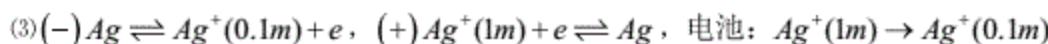
$$E=E^0+\frac{2.3RT}{4F} \log \frac{P_{H_2} P_{O_2}}{a_{H_2O}^2}=E^0$$

$$\text{查表: } \varphi_+^0=1.229V, \quad \varphi_-^0=0.000V, \quad \therefore E=\varphi_+^0-\varphi_-^0=1.229V$$

(2) 视为无限稀释溶液，以浓度代替活度计算

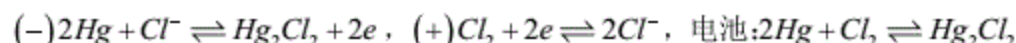
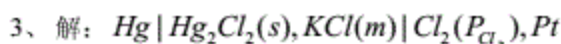


$$E=E^0+\frac{2.3RT}{2F} \log \frac{C_{\text{Sn}^{2+}} C_{\text{Fe}^{3+}}^2}{C_{\text{Sn}^{4+}} C_{\text{Fe}^{2+}}^2}=(0.771-0.15)+\frac{0.0591}{2} \log \frac{0.001 \times (0.01)^2}{0.01 \times (0.001)^2}=0.6505V$$



$$E=E^0+\frac{2.3RT}{F} \log \frac{a_{\text{Ag}^+(1m)}}{a_{\text{Ag}^+(0.1m)}}, \quad (\text{其中}, E^0=0)$$

$$\text{查表: } 1m \text{ AgNO}_3 \text{ 中 } \gamma_{\pm}=0.4V, \quad 0.1m \text{ AgNO}_3 \text{ 中 } \gamma_{\pm}=0.72V, \quad \therefore E=\frac{2.3RT}{F} \log \frac{1 \times 0.4}{0.1 \times 0.72}=0.044V$$



$$\because E = E^0 + \frac{2.3RT}{2F} \log \frac{P_{Cl_2} a_{Hg}^2}{a_{Hg_2Cl_2}} = E^0 = \varphi_+^0 - \varphi_-^0, \therefore E = 1.3595 - 0.2681 = 1.0914V (\text{设 } 25^\circ C)$$

由于 E 与  $a_{Cr}$  无关, 故两种溶液中的电动势均为上值

其他解法: ①  $E = \varphi_+ - \varphi_-$ , 亦得出  $E = \varphi_+^0 - \varphi_-^0$  ②按  $a_{Cr}$  计算  $\varphi_+$ , 查表得  $\varphi_{甘汞}$ , 则  $E = \varphi_+ - \varphi_{甘汞}$

4、(1)解法一:  $Pt, H_2(1atm) | HCl(a_{H^+} = 1) || AgNO_3(m) | Ag$

$(-) H_2 \rightleftharpoons 2H^+ + 2e, (+) 2Ag^+ + 2e \rightleftharpoons 2Ag$ , 电池:  $H_2 + 2Ag^+ \rightleftharpoons 2H^+ + 2Ag$

有  $E = \varphi_+ - \varphi_- = \varphi_+$ ,  $\therefore \varphi_{Ag/Ag^+}^0 = E - \frac{2.3RT}{F} \log(m_{Ag} \cdot \gamma_{\pm})$ 。

解法二:  $Hg | Hg_2Cl_2(s), KCl(\text{饱和}) || AgNO_3(m) | Ag$ ,  $\varphi_{Ag/Ag^+}^0 = E + \varphi_{甘汞} - \frac{2.3RT}{F} \log(m_{Ag} \cdot \gamma_{\pm})$

(2)同上解法:  $Pt, H_2(1atm) | HCl(a_{H^+} = 1) || PbNO_3(m) | Pb$ , 电池:  $H_2 + Pb^{2+} \rightleftharpoons 2H^+ + Pb$ ,

$\therefore \varphi_{Pb/Pb^{2+}}^0 = E - \frac{2.3RT}{2F} \log(m_{Pb^{2+}} \cdot \gamma_{\pm})$

(3)同上解法:  $Pt, H_2(1atm) | HCl(a_{H^+} = 1) || FeCl_3(m'), FeCl_2(m) | Fe$ , 电池:  $\frac{1}{2} H_2 + Fe^{3+} \rightleftharpoons H^+ + Fe^{2+}$

$\therefore \varphi_{Fe^{2+}/Fe^{3+}}^0 = E - \frac{2.3RT}{F} \log(a_{Fe^{2+}} / a_{Fe^{3+}})$

5、解: (1)  $Zn | ZnSO_4(m), Hg_2SO_4(s) | Hg$ ,  $E = E^0 - \frac{2.3RT}{2F} \log(a_{SO_4^{2-}} a_{Zn^{2+}})$

(2)  $Pb | PbCl_2(s), HCl(m) | H_2(P_{H_2}), Pt$ ;  $E = E^0 + \frac{2.3RT}{2F} \log(a_{H^+}^2 a_{Cl^-}^2 / P_{H_2})$

6、解:  $Pt, H_2(1atm) | HCl(a_{H^+} = 1) || KCl(0.1m'), AgCl(s) | Ag$ ;  $(+) AgCl + e \rightleftharpoons Ag + Cl^-$ ,

$\therefore \varphi_+ = \varphi_+^0 - \frac{2.3RT}{F} \log a_{Cl^-}$ , 查表得:  $\varphi_+^0 = 0.2224V$ ,  $\gamma_{\pm} = 0.79V$ ;

$\therefore E = \varphi_+ = 0.2224 - 0.0591 \log(0.79 \times 0.1) = 0.2876V$ ;

7、解:  $E_a = \frac{2.3RT}{F} \log \frac{1}{a_{Cr}''} - \frac{2.3RT}{F} \log \frac{1}{a_{Cr}'} = \frac{2.3RT}{F} \log \frac{a_{Cr}'}{a_{Cr}''}$  ( $a'' = 0.01m$ ,  $a' = 0.1m$ )

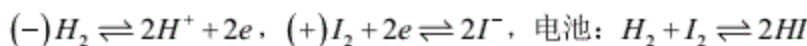
可计算出:  $a_{\pm}' = 0.1 \times 0.78 = 0.078, (a_{\pm}' = a_{Cr}')$ ,  $a_{\pm}'' = 0.01 \times 0.904 = 0.00904, (a_{\pm}'' = a_{Cr}'')$

又  $E_b = 2t_+ \frac{2.3RT}{F} \log(a_{\pm}' / a_{\pm}'')$ ,

$\therefore E_b - E_a = \varphi = (2t_+ - 1) \frac{2.3RT}{F} \log(a_{\pm}' / a_{\pm}'') = (2 \times 0.389 - 1) \times 0.0591 \log \frac{0.078}{0.00904} = -0.0123V$

若用浓度计算, 则  $E_a = 0.0591V, E_b = 0.046V$ ,  $\varphi = E_b - E_a = -0.01V$

8、解: (1)  $Pt, H_2(1atm) | HI(a = 1) | I_2(s), Pt$



$$(2) E = E^0 - \frac{2.3RT}{2F} \log(a_{HI})^2 = E^0, \quad E^0 = 0.5346 - 0.13 \times 10^{-3} \times (35 - 25) = 0.5333V$$

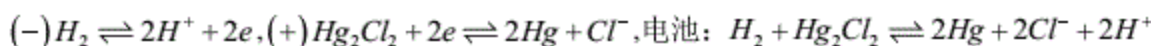
$\therefore E > 0$ ,  $\therefore$  电池表达式中正负极未写错。

$$(3) \Delta G^0 = -nFE^0 = -RT \ln K = -2 \times 96500 \times 0.5333 = -102.9 kJ$$

$$(4) E^0 = \frac{RT}{nF} \ln K, \quad \ln K = \frac{2 \times 96500 \times 0.5333}{8.314 \times 298} = 40.19, \quad K = 2.86 \times 10^{17}$$

$$(5) \text{第(1)(2)问不变 (即 } E \text{ 不变), } \Delta G^{0'} = \frac{1}{2} \Delta G^0 = -51.5 kJ, \quad K' = \sqrt{K} = 5.35 \times 10^8, \text{ 两者均改变。}$$

9、解法一:



$$E = E^0 - \frac{2.3RT}{2F} \log(a_{H^+}^2 a_{Cl^-}^2), \text{查表得 } a_{Cl^-} = 0.79 \times 0.1, \quad -\frac{2.3RT}{F} \log a_{H^+} = E - E^0 + \frac{2.3RT}{F} \log a_{Cl^-}$$

$$\text{得 } -\log a_{H^+} \approx 6.9, \text{ 又 } \log a_{H^+} + \log a_{OH^-} = 14, \text{ 则 } a_{OH^-} = 10^{-7.1} = 7.94 \times 10^{-8}$$

$$\text{解法二: } \varphi_+ = \varphi_+^0 - 0.0591 \log a_{Cl^-}, \quad \varphi_- = 0.0591 \log a_{H^+} = -0.0591 pH, \quad E = \varphi_+ - \varphi_-,$$

$$\therefore pH = \frac{\varphi_+ - E}{0.0591} = 6.9, \quad a_{OH^-} = 10^{-7.1} = 7.94 \times 10^{-8} (\text{mol/dm}^3)$$

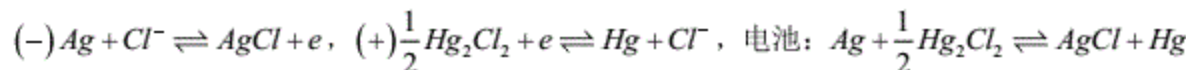


$$\text{按①: } \varphi = \varphi_{Hg/Hg_2^{2+}}^0 + \frac{2.3RT}{2F} \log a_{Hg_2^{2+}} = \varphi_{Hg/Hg_2^{2+}}^0 + \frac{2.3RT}{2F} \log K_s - \frac{2.3RT}{2F} \log a_{SO_4^{2-}}$$

$$\text{按③: } \varphi = \varphi_{Hg/Hg_2SO_4, SO_4^{2-}}^0 - \frac{2.3RT}{2F} \log a_{SO_4^{2-}}$$

$$\therefore \varphi_{Hg/Hg_2SO_4, SO_4^{2-}}^0 = \varphi_{Hg/Hg_2^{2+}}^0 + \frac{2.3RT}{2F} \log K_s = 0.7986 + \frac{0.0591}{2} \log(6.5 \times 10^{-7}) = 0.638V$$

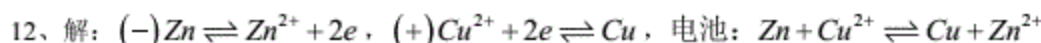
11、解:



$$\Delta G = -nFE = -1 \times 96500 \times 0.0455 = -4.391 kJ/mol$$

$$\Delta H = \Delta G + nFT \left( \frac{\partial E}{\partial T} \right)_p = -4391 + 1 \times 96500 \times 298 \times 0.338 \times 10^{-3} = 5.329 kJ/mol$$

$$\Delta S = nFT \left( \frac{\partial E}{\partial T} \right)_p = 1 \times 96500 \times 298 \times 0.338 \times 10^{-3} = 32.617 J/mol \cdot K$$



$$Q_p = \Delta H = -nFE + nFT \left( \frac{\partial E}{\partial T} \right)_p = -2 \times 96500 \times 1.101 + 2 \times 96500 \times 293 \times \frac{1.103 - 1.101}{298 - 293} = -189.8 \text{ kJ/mol}$$

$$\Delta S = nFT \left( \frac{\partial E}{\partial T} \right)_p = 2 \times 96500 \times \frac{1.103 - 1.101}{298 - 293} = 77.2 \text{ J/mol} \cdot \text{K}$$

$$\because \Delta G = -nFE = -RT \ln K, \quad a_{\text{Zn}^{2+}} = a_{\text{Cu}^{2+}} = 1,$$

$$\therefore E^0 = E, \log K = \frac{nFE^0}{2.3RT} = \frac{2 \times 1.101}{2.3RT \cdot 0.00581} = 37.26, \quad K = 7.95 \times 10^{37}$$

$$13、\text{解法一：} \text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu} + (\varphi_1^0 = 0.337\text{V}) \text{ ①, } \text{Cu}^+ + e \rightleftharpoons \text{Cu} (\varphi_2^0 = 0.520\text{V}) \text{ ②,}$$

$$\text{③} = \text{①} - \text{②}, \therefore \Delta G_3^0 = \Delta G_1^0 - \Delta G_2^0 = -2F\varphi_1^0 + \varphi_2^0 = -2F\varphi_3^0, \therefore \varphi_3^0 = 2\varphi_1^0 - \varphi_2^0 = 0.337 \times 2 - 0.520 = 0.154\text{V};$$

$$\Delta G_3^0 = -F\varphi_3^0 = -0.154 \times 96500 = -14861 \text{ J/mol}, \text{ 所以反应为自发。}$$

$$\text{解法二：由 } \varphi^0 = \frac{RT}{nF} \ln K \text{ 计算由 ③} = \text{①} - \text{②}, \text{ 则 } K_3 = \frac{K_1}{K_2};$$

$$\varphi_3^0 = \frac{RT}{F} \ln K_3 = \frac{RT}{F} (\ln K_1 - \ln K_2) = \frac{RT}{F} \left( \frac{2F}{RT} \varphi_1^0 - \frac{F}{RT} \varphi_2^0 \right) = 2\varphi_1^0 - \varphi_2^0 = 0.154\text{V}$$

$$14、\text{解法一：} (-) 2\text{H}_2 \rightleftharpoons 4\text{H}^+ + 4e, (+) \text{O}_2 + 4\text{H}^+ + 4e \rightleftharpoons 2\text{H}_2\text{O}, \text{ 电池: } 2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}(g)$$

$$\therefore K = \frac{1}{K_p}, \quad ||| \quad E = \frac{RT}{4F} \ln K - \frac{RT}{4F} \ln \frac{p_{\text{H}_2\text{O}}^2}{p_{\text{H}_2}^2 p_{\text{O}_2}}$$

$$\therefore E = \frac{2.3RT}{4F} \log \frac{1}{K_p} - \frac{2.3RT}{4F} \log \frac{p_{\text{H}_2\text{O}}^2}{p_{\text{H}_2}^2 p_{\text{O}_2}} = \frac{-0.0591}{4} \log(9.7 \times 10^{-81}) - \frac{-0.0591}{4} \log \frac{(24/760)^2}{1^2 \times 1} = 1.226\text{V}$$

$$\text{解法二：} \varphi_{\text{H}_2} = \frac{2.3RT}{2F} \log a_{\text{H}^+} = \frac{0.0591}{2} \log(0.02 \times 0.544) = -0.06\text{V},$$

$$\varphi_{\text{O}_2} = \varphi_{\text{O}_2}^0 + \frac{2.3RT}{2F} (\log a_{\text{H}^+}^2 - \log p_{\text{H}_2\text{O}}) = 1.229 + \frac{0.0591}{2} [\log(0.02 \times 0.544)^2 - \log(24/760)] = 1.16\text{V}$$

$$\therefore E = \varphi_{\text{O}_2} - \varphi_{\text{H}_2} = 1.16 - (-0.06) = 1.22\text{V}$$

$$15、\text{解：(1)有 } \text{Zn}^{2+} \text{ Cu}^{2+} \text{ H}^+ \text{ 三种离子可在阴极还原，}$$

$$\varphi_{\text{Zn}^{2+}} = \varphi_{\text{Zn}^{2+}}^0 + \frac{2.3RT}{2F} \log a_{\text{Zn}^{2+}} = -0.763 + \frac{0.0591}{2} \log(0.01 \times 0.39) = -0.83\text{V}$$

$$\varphi_{\text{Cu}^{2+}} = \varphi_{\text{Cu}^{2+}}^0 + \frac{2.3RT}{2F} \log a_{\text{Cu}^{2+}} = 0.337 + \frac{0.0591}{2} \log(0.01 \times 0.41) = 0.27\text{V}$$

$$\varphi_{\text{H}^+} = \frac{2.3RT}{F} \log a_{\text{H}^+} = 0.0591 \times (-5) = -0.30\text{V}$$

所以，阴极析出的顺序为：Cu、H<sub>2</sub>、Zn

(2) 当  $Zn$  析出时电位为  $-0.83V$ , (由  $i \rightarrow 0$ , 故可用平衡电位替代析出电位, 即可忽略电极的极化)

$$\therefore -0.83 = \varphi_{Cu^{2+}} + \frac{0.0591}{2} \log a_{Cu^{2+}}, \quad \log a_{Cu^{2+}} = \frac{2}{0.0591} (-0.83 - 0.337) = -39.49, \quad a_{Cu^{2+}} = 3.24 \times 10^{-40}$$

$$C = \frac{a_{Cu^{2+}}}{\gamma_{\pm}} = \frac{3.24 \times 10^{-40}}{0.41} = 7.9 \times 10^{-40} \text{ mol/L}, \text{ 说明铜离子几乎完全极化了}$$

16、解:  $\because Pb \rightleftharpoons Pb^{2+} + 2e^-$  ①,  $Pb^{2+} + 2F^- \rightleftharpoons PbF_2$ ;  $Pb + 2F^- \rightleftharpoons PbF_2 + 2e^-$  ②;

$$\therefore \varphi_2^0 = \varphi_1^0 + \frac{2.3RT}{2F} \log K_s,$$

$$\log K_s = \frac{2F}{2.3RT} (\varphi_2^0 - \varphi_1^0) = \frac{2}{0.0591} (-0.3502 + 0.1263) = -7.58, \quad \text{得, } K_s = 2.63 \times 10^{-8}$$

17、 $(-)\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2e^-$ ,  $(+)\text{Hg}_2\text{Cl}_2 + 2e^- \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$  电池:  $\text{Hg}_2\text{Cl}_2 + \text{Zn} \rightleftharpoons 2\text{Hg} + 2\text{Cl}^- + \text{Zn}^{2+}$

$$E_a = E^0 + \frac{2.3RT}{2F} \log \frac{1}{a_{Zn^{2+}} a_{Cl^-}^2} = E^0 - \frac{2.3RT}{2F} \log [(m_a \gamma_{\pm,a}) (2m_a \gamma_{\pm,a})^2] = E^0 - \frac{0.0591}{2} \log 4 (m_a \gamma_{\pm,a})^3$$

$$E_b = E^0 - \frac{0.0591}{2} \log 4 (m_b \gamma_{\pm,b})^3, \quad E_b - E_a = \frac{0.0591}{2} \log \frac{4 (m_a \gamma_{\pm,a})^3}{4 (m_b \gamma_{\pm,b})^3} = \frac{3 \times 0.0591}{2} \left[ \log \frac{m_a}{m_b} + \log \frac{\gamma_{\pm,a}}{\gamma_{\pm,b}} \right],$$

$$\log \frac{\gamma_{\pm,a}}{\gamma_{\pm,b}} = \frac{2 \times (E_b - E_a)}{3 \times 0.0591} - \log \frac{m_a}{m_b} = \frac{2 \times (1.0044 - 1.10085)}{3 \times 0.0591} - \log \frac{0.25148}{0.00500} = -0.31, \quad \frac{\gamma_{\pm,a}}{\gamma_{\pm,b}} = 0.49$$

18、解: 电池  $a$  为无迁移浓差电池, 电极对负离子 ( $Cl^-$ ) 可逆。

电池  $b$  为有迁移浓差电池, 电极对负离子 ( $Cl^-$ ) 可逆。

$$(1) E_a = -\frac{2.3RT}{F} \log \frac{a_{\pm,2}}{a_{\pm,1}} = -\frac{2.3RT}{F} \log \frac{m_2 \gamma_{\pm,2}}{m_1 \gamma_{\pm,1}},$$

$$\log \frac{\gamma_{\pm,2}}{\gamma_{\pm,1}} = -\frac{FE_a}{2.3RT} - \log \frac{m_2}{m_1} = -\frac{0.0822}{2 \times 0.0591} - \log \frac{0.0082}{0.082} = 1.695, \quad \frac{\gamma_{\pm,2}}{\gamma_{\pm,1}} = 2.02。$$

$$(2) E_b = -2t_+ \frac{RT}{F} \ln \frac{a_{\pm,2}}{a_{\pm,1}},$$

$$t_+ = -\frac{E_b}{2 \frac{RT}{F} \ln \frac{m_2 \gamma_{\pm,2}}{m_1 \gamma_{\pm,1}}} = -\frac{E_b}{E_a} = \frac{57.9 \times 10^{-3}}{82.8 \times 10^{-3}} = 0.7044$$

$$(3) t_+ = \frac{\lambda_{0,H^+}}{\lambda_{0,H^+} + \lambda_{0,Cl^-}} = \frac{\lambda_{0,H^+}}{\lambda_{0,HCl}}$$

$$\lambda_{0,H^+} = t_+ \lambda_{0,HCl} = 0.7044 \times 83.8 = 59.03 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}, \quad \lambda_{0,Cl^-} = (1 - t_+) \lambda_{0,HCl} = 24.77 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$$



19、解：(1)  $\varphi = \varphi^0 - \frac{2.3RT}{nF} \text{mpH} + \frac{2.3RT}{nF} \log \frac{a_A}{b_B^b}$

$$= 1.33 - \frac{0.0591 \times 14}{6} \text{pH} + \frac{0.0591}{6} \log \frac{a_{\text{Cr}_2\text{O}_7^{2-}}}{a_{\text{Cr}^{3+}}^2} = 1.33 - 0.138 \text{pH} - 0.00985 \log \frac{a_{\text{Cr}_2\text{O}_7^{2-}}}{a_{\text{Cr}^{3+}}^2}$$

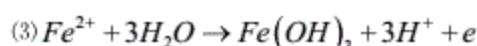
(2)  $\varphi = \varphi^0 + \frac{2.3RT}{nF} \log \frac{a_A}{b_B^b} = 0.2681 - \frac{0.0591}{2} \log a_{\text{Cr}^{3+}}^2 = 0.2681 - 0.0591 \log a_{\text{Cr}^{3+}}$

(3)  $\log a_{\text{Cd}(\text{OH})_2} - \log a_{\text{OH}^-} + \log a_{\text{H}_2\text{O}} + \log a_{\text{H}_2\text{O}} = \log K$ ，即  $\log a_{\text{H}_2\text{O}} - \log a_{\text{OH}^-} = \log K$

由  $\text{pH} = 14 + \log a_{\text{OH}^-}$ ， $\text{pH} = 14 + \log a_{\text{H}_2\text{O}} - \log K$

20、解：(1) 线①与线②大约在  $\text{pH} = 7.68$  时相交

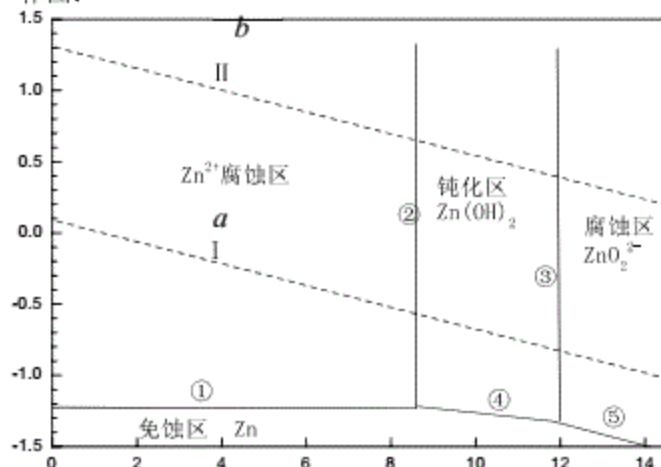
(2) 在  $8.7 < \text{pH} < 14.5$ ， $-0.85 < \varphi < -0.25$  时可能生成  $\text{Fe}(\text{OH})_2$  沉淀



21、解：因作腐蚀图，故取  $a_i = 10^{-6}$

$\text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn}$	$\varphi = -0.94\text{V}$ ， $2\text{pH} = -0.763 + 0.0295 \log a_{\text{Zn}^{2+}}$
$\text{Zn}(\text{OH})_2 + 2\text{H}^+ \rightleftharpoons \text{Zn}^{2+} + 2\text{H}_2\text{O}$	$\text{pH} = 8.48$ ， $2\text{pH} = 10.96 - \log a_{\text{Zn}^{2+}}$
$\text{ZnO}_2^{2-} + 2\text{H}^+ \rightleftharpoons \text{Zn}(\text{OH})_2$	$\text{pH} = 11.89$ ， $2\text{pH} = 29.78 + \log a_{\text{Zn}^{2+}}$
$\text{Zn}(\text{OH})_2 + 2\text{H}^+ + 2e \rightleftharpoons \text{Zn} + 2\text{H}_2\text{O}$	$\varphi = -0.437 - 0.0591 \text{pH}$
$\text{ZnO}_2^{2-} + 4\text{H}^+ + 2e \rightleftharpoons \text{Zn} + 2\text{H}_2\text{O}$	$\varphi = 0.44 - 0.118 \text{pH} + 0.0296 \log a_{\text{ZnO}_2^{2-}} = 0.263 - 0.118 \text{pH}$
反应	平衡条件

作图：



当  $\varphi = -0.82\text{V}$  时，在  $8.48 < \text{pH} < 11.89$  时

$\text{Zn}$  可能因钝化而免于腐蚀。

当  $\varphi = -1.0\text{V}$  时，在  $\text{pH} < 11.89$  时

可因处于热力学稳定区或钝化区而免于腐蚀。



# 电化学原理第三章习题答案

## 原创力文档

1、解：由高斯定律： $E = \frac{q}{\epsilon_0 \epsilon_r}$ ，查表： $\epsilon_0 = 8.85 \times 10^{-12}$ ，则  $E = \frac{2 \times 10^{-5} \times 10^{-4}}{8.85 \times 10^{-12} \times 40} = 5.6 \times 10^8 \text{ V/m}$

预览与源文档一致, 下载高清无水印

2、解： $\varphi = -0.35 \text{ V}$  处， $\frac{d\sigma}{d\varphi} = \frac{\sigma_{(-0.2 \text{ V})} - \sigma_{(-0.4 \text{ V})}}{-0.2 - (-0.4)}$ （-0.2~-0.4 之间近似为直线），则

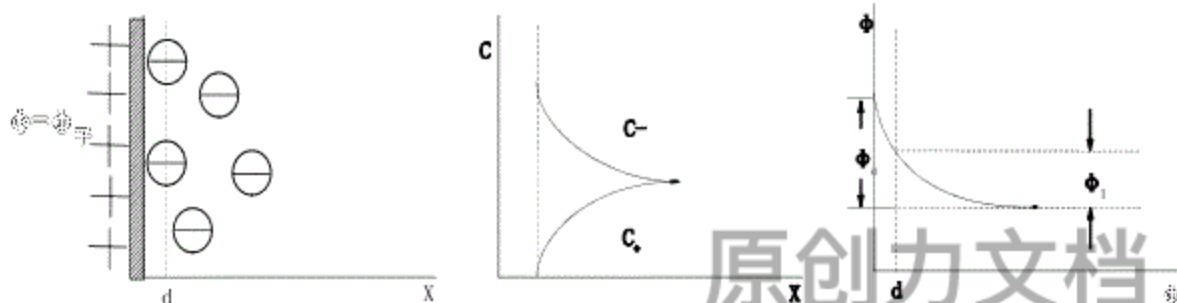
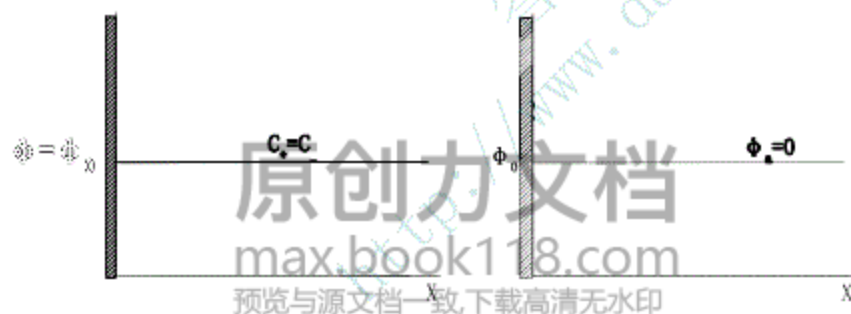
$$\frac{d\sigma}{d\varphi} = \frac{0.413 - 0.392}{-0.2 + 0.4} = 0.13 \text{ J/mV} \quad , \quad q = -\frac{d\sigma}{d\varphi} = -0.13 \text{ C/m}^2$$

3、解：(1)  $q = C\varphi = C(\varphi_{\text{平}} - \varphi_0) = 36 \times (-0.763 + 0.63) = -4.79 \mu\text{C/cm}^2$

(2)  $q$  不变， $Cd$  增大，因此有  $\text{Cl}^-$  吸附，是紧密层厚度减小，故  $C = \frac{\epsilon_0 \epsilon_r}{d}$  将增大到，它可认为  $\varphi_{\text{平}} < \varphi_0$ ， $q > 0$  时  $\text{Cl}^-$  吸附很少， $Cd$  变化不大，但  $q$  与此无关

(3)  $q = C(\varphi - \varphi_0) = 36 \times (0.32 + 0.64) = 34.2 \mu\text{C/cm}^2$

4、解： $\text{Ag}^+ + e \rightleftharpoons \text{Ag}$ ， $\varphi_{\text{平}} = \varphi_0 + 0.591 \log(0.002) = 0.64 \text{ V} > \varphi_0$ ，所以金属表面带正电荷。

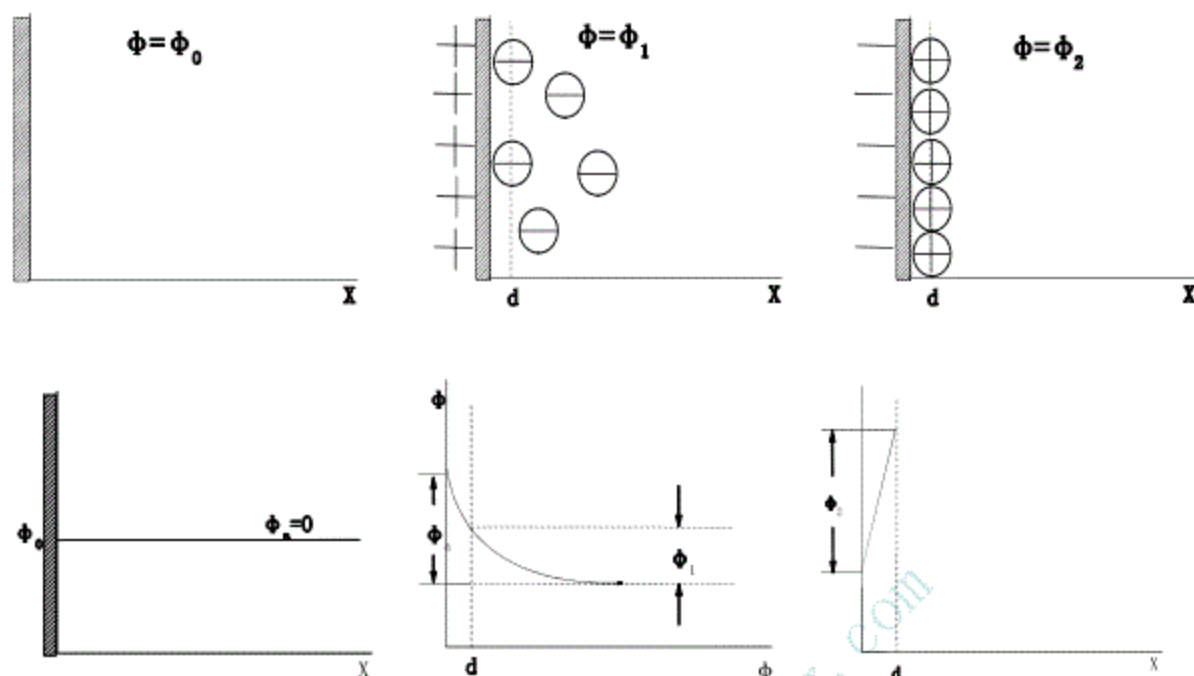


## 原创力文档

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5、解：

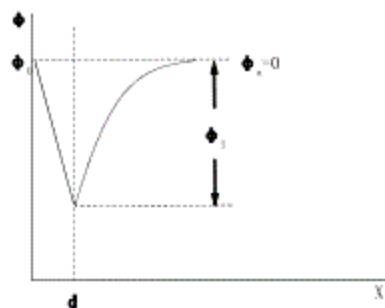
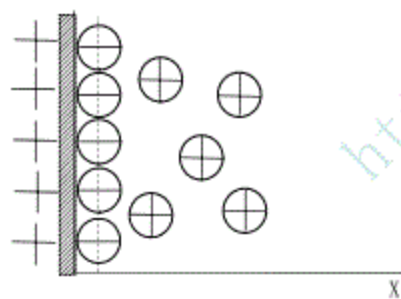


$$\phi_0 = 0$$

$$\phi_1 = -\text{常数} + \frac{2RT}{F} \ln \phi_s - \frac{RT}{F} \ln C$$

$$\phi_2 = 0$$

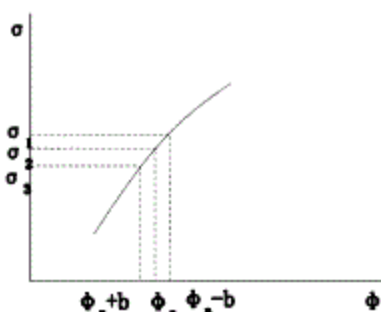
6、解：在  $\phi \geq \phi_0$  的范围内  $\sigma \downarrow$   $Cd \uparrow$ ，表明在  $q > 0$  和接近  $q = 0$  的电极表面有阴离子吸附，故为加入了表面活性阴离子（无机离子）



7、解法一：根据  $Cd = \frac{dq}{d\phi}$ ，如图所示，

$$\text{在 } \phi_a \text{ 点: } q_1 = -\frac{\partial \sigma}{\partial \phi} \approx \frac{-\sigma_2 + \sigma_3}{\phi_a - (\phi_a + b)} = \frac{\sigma_2 - \sigma_3}{b};$$

$$\text{在 } (\phi_a - b) \text{ 点: } q_2 = \frac{\sigma_1 - \sigma_2}{\phi_a - (\phi_a - b)} = \frac{\sigma_1 - \sigma_2}{b};$$



$$\Delta q = q_1 - q_2 = \frac{2\sigma_2 - \sigma_1 - \sigma_3}{b}; \because \Delta \varphi = \varphi_a - (\varphi_a - b) = b, \therefore C = \frac{\Delta q}{\Delta \varphi} = \frac{2\sigma_2 - \sigma_1 - \sigma_3}{b^2}.$$

解法二：取  $q_1$  的平均电位  $\varphi_1 = \frac{(\varphi_a - b) + \varphi_a}{2} = \varphi_a - \frac{1}{2}b$  处的表面电荷密度：

取  $q_2$  的平均电位  $\varphi_2 = \frac{(\varphi_a + b) + \varphi_a}{2} = \varphi_a + \frac{1}{2}b$  处的表面电荷密度：

$$\text{则 } q_1 = -\left(\frac{\partial \sigma}{\partial \varphi_a}\right)_1 \approx -\frac{\sigma_1 - \sigma_2}{b}, \quad q_2 = -\left(\frac{\partial \sigma}{\partial \varphi_a}\right)_2 \approx -\frac{\sigma_2 - \sigma_3}{b}.$$

$$\text{则有, } C = -\left(\frac{\partial^2 \sigma}{\partial \varphi^2}\right) = -\frac{\Delta q}{\Delta \varphi} = -\frac{q_1 - q_2}{\varphi_a - b/2 - \varphi_a - b/2} = \frac{q_1 - q_2}{b} = -\frac{\sigma_1 + \sigma_3 - 2\sigma_2}{b^2}.$$

8、解法一：  $\varphi_a = \varphi - \varphi_0 = 0.11 - (-0.119) = 0.30V$ ,  $\therefore \varphi_1 > 0$ , 且由题给数据知  $q$ ,  $c$  较大。

$$\varphi_1 = -\frac{2RT}{F} \ln \frac{1}{C_{1y}} \sqrt{2\varepsilon_0 \varepsilon_r RT} + \frac{2RT}{F} \ln \varphi_a - \frac{RT}{F} \ln c, \quad C_{1y} = \frac{q}{\varphi_a - \varphi_1} \approx \frac{q}{\varphi_a};$$

$$\begin{aligned} \varphi_1 &= -\frac{2RT}{F} \ln \frac{\varphi_a}{q} \sqrt{2\varepsilon_0 \varepsilon_r RT} + \frac{2RT}{F} \ln \varphi_a - \frac{RT}{F} \ln c \\ &= 0.0591 \left[ -2 \log \frac{0.3 \times \sqrt{2 \times 8.85 \times 10^{-12} \times 40 \times 298 \times 8.31}}{0.1} + 2 \log 0.3 - \log(c \times 10^3) \right] \\ &= 0.222 - 0.0591 \log(c \times 10^3) \end{aligned}$$

当  $c = 0.001 \text{ mol/L}$  时,  $\varphi_1 = 0.222V$ ,  $\varphi_1 : \varphi_a = 0.222 : 0.3 > \frac{2}{3}$ , 双层结构较分散;

当  $c = 0.1 \text{ mol/L}$  时,  $\varphi_1 = 0.1038V$ ,  $\varphi_1 : \varphi_a = \frac{1}{3}$ , 分散层较小。

解法二：  $q = \sqrt{8\varepsilon_0 \varepsilon_r c RT} Sh \left( \frac{\varphi_1 F}{2RT} \right)$ , 令  $\frac{\varphi_1 F}{2RT} = Z$ , 则  $q = 2.648 \times 10^{-3} \sqrt{c} ShZ$ ;

$$\text{当 } c = 0.001 \text{ mol/L 时, } ShZ = \frac{q}{2.648 \times 10^{-3} \times 1} \approx 37.764,$$

$$Z = Sh^{-1}(37.764) = \ln(37.764 + \sqrt{37.764^2 + 1}) \approx 2.3 \log 75.5 \approx 4.325, \quad \varphi_1 = \frac{Z \times 2RT}{F} \approx 0.222V$$

同理可求  $c = 0.1 \text{ mol/L}$  时,  $\varphi_1 \approx 0.1038V$ 。

9、解：从  $Cd \sim \varphi$  曲线可知  $\varphi_0 = -0.37V$ ；未加  $NaCl$  时,  $\varphi_{\text{测}} = -0.25 \sim -0.27V > \varphi_0$ , 电极（钢）表面带正电荷，缓蚀剂为阳离子型，难吸附，不起缓蚀作用；加  $NaCl$  以后,  $Cl^-$  吸附，缓蚀剂离子在  $Cl^-$  层吸附，故有缓蚀作用。

## 电化学原理第四章习题答案

1、解：①  $\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$ ，设  $T = 25^\circ\text{C}$ ， $\varphi = \varphi^0 + \frac{2.3RT}{2F} \log a_{\text{Cu}^{2+}} = 0.337 + \frac{2.3RT}{2F} 10^{-7} \approx 0.13\text{V}$

②  $\text{H}^+ + e \rightarrow \frac{1}{2}\text{H}_2$ ，设  $T = 25^\circ\text{C}$ ，查表  $\gamma_{\pm} = 0.130$ ， $\eta_a = \varphi - \varphi_{\text{H}^+}$ ， $\eta_c = \varphi_{\text{H}^+} - \varphi$  则：

$$\varphi = \frac{2.3RT}{F} \log a_{\text{H}^+} - \eta_c = 0.0591 \log (2 \times 0.130) - 0.23 \approx -0.28\text{V}$$

为使氢气不析出，阴极电位不可负于  $-0.28\text{V}$ 。

2、解： $2\text{H}^+ + 2e \rightarrow \text{H}_2$ ，已知  $-\log a_{\text{H}^+} = 6.5$ ， $\therefore \eta_c = \varphi_{\text{H}^+} - \varphi = 0.0591 \log a_{\text{H}^+} - (-1.23) \approx 0.846\text{V}$

3、解： $(-)\text{Zn}^{2+} + 2e \rightarrow \text{Zn}$ ， $(+)\text{Zn} \rightarrow \text{Zn}^{2+} + 2e$

$$\varphi_{a,\text{Zn}} = \varphi_{\text{Zn}}^0 + \frac{2.3RT}{2F} \log a_{\text{Zn}^{2+}} = -0.763 + \frac{0.0591}{2} \log (0.1 \times 0.15) = -0.817\text{V}$$

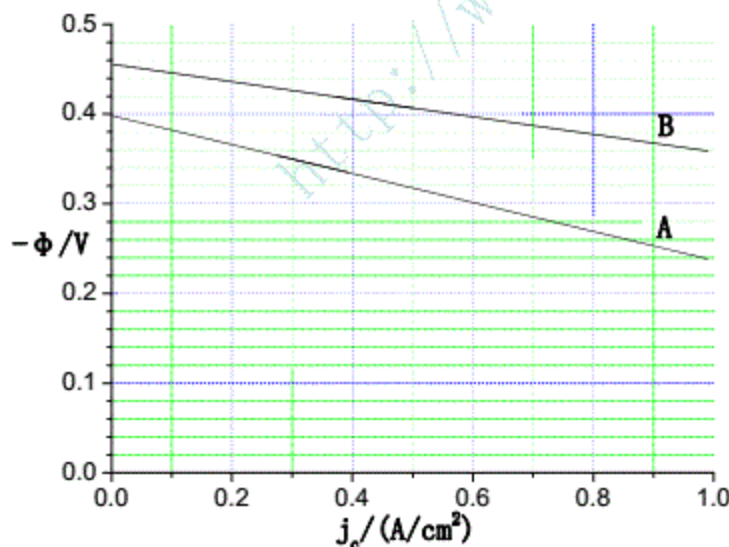
若阴极上析氢： $2\text{H}^+ + 2e \rightarrow \text{H}_2$ ，

$$\varphi_c' = \varphi_{\text{H}^+} - \eta_{\text{H}} = 0.0591 \log a_{\text{H}^+} - \eta = 0.0591 \log (0.2 \times 0.265) - 1.06 = -1.1354\text{V}$$

不使氢析出，则需  $\varphi_c > \varphi_c'$ ，设  $\varphi_c = -1.135\text{V}$ ，则： $\eta_{\text{Zn}} = \varphi_{\text{Zn}} - \varphi_c = -0.817 - (-1.135) = 0.318\text{V}$

最高槽压： $V = \varphi_a - \varphi_c + IR = -0.817 - (-1.135) + 0.5 = 0.818\text{V}$

4、解：因为在 B 液中极化度小于 A 液，所以铁在 B 溶液中易于腐蚀溶解



5、解：设初始速度为  $j_1$ ，改编后速度为  $j_2$ ： $j_1 = nFv_1 = nFKc \exp\left(-\frac{w_1}{RT}\right)$ ， $j_2 = nFv_2 = nFKc \exp\left(-\frac{w_2}{RT}\right)$

$$\frac{j_2}{j_1} = \exp\left(\frac{w_1 - w_2}{RT}\right) = \exp\left(-\frac{w_1}{RT}\right) = \exp\left(-\frac{4 \times 10^3}{8.31 \times 293}\right) \approx 0.193, j_2 = 0.193 j_1 = 18.6 \text{ mA/cm}^2, \text{比原来低 } 81\%$$

6、解：(1)  $j_{\text{扩散}} = nFv_{\text{扩散}} = 2 \times 96500 \times 1 \times 10^{-3} = 193 \text{ A/m}^2$ ,  $j_{\text{电子}} = nFv_{\text{电子}} = 2 \times 96500 \times 0.25 = 48250 \text{ A/m}^2$

与  $j = 193 \text{ A/m}^2$  比较：该电极过程的控制步骤是扩散步骤。

(2)  $\because j = j_{\text{扩散}} = 193 \text{ A/m}^2$ ,  $j_{\text{电子}} - j = 48250 - 193 = 48057 \text{ A/m}^2$

$\therefore j_{\text{电子}} \approx j_{\text{电子}} - j$ , 电子转移步骤为非控制步骤, 处于准平衡态。

7、解：设原扩散速度为  $v_1$ , 活化能为  $W_1$ ; 搅拌后速度为  $v_2$ , 活化能为  $W_2$ 。

$$v_1 = Kc \exp\left(-\frac{W_1}{RT}\right), v_2 = Kc \exp\left(-\frac{W_2}{RT}\right), v_2/v_1 = \exp\left(\frac{W_1 - W_2}{RT}\right) = 1000,$$

$$\therefore \Delta W = W_1 - W_2 = RT \ln(v_2/v_1) = \ln 10^3 \times 8.31 \times 298 = 17106 \text{ J/mol}$$

扩散活化能应降低  $17106 \text{ J/mol}$ 。

8、解：(1)  $\varphi_c = \varphi_{\text{Zn}}^0 + \frac{2.3RT}{2F} \log(\gamma_{\pm} m_{\text{Zn}^{2+}}) = -0.763 + \frac{0.0591}{2} \log(0.33 \times 1) = -0.777 \text{ V}$ ,  $\varphi_a = \varphi_H^0 = 0$ 。

$\because E = \varphi_a - \varphi_c = 0.777 \text{ V}$ , 而  $V = 1.24 \text{ V}$ ,  $\therefore V > E$ , 是电解池。

(2) 作为电解池, 负极为阴极, 故  $\text{Zn}$  电极发生阴极极化

$$(3) V = E + (\eta_a + \eta_c) + IR, \eta_c = V - (E + \eta_a + IR) = 1.24 - (0.777 + 0.164 + 0.1) = 0.199 \text{ V}$$

## 电化学原理第五章习题答案

1、解：出现铜红色, 表明锡离子扩散速度较小, 在凹处离子浓度降低较多, 采用间隙电流有助于消除凹处锡离子浓度与体浓度之差, 而避免镀层中  $\text{Cu}$  含量过高。

2、解：设(1)的极限扩散电流为  $j_{d1}$  (2)为  $j_{d2}$  (3)为  $j_{d3}$ ;  $\because j_d = nFD \frac{c^0}{\delta}$ ,  $\therefore j_{d3} \approx 2j_{d2}$

又由于正离子在阴极还原时, 反应粒子的电迁移将使稳态电流密度增大, 所以(1)中有大量高外电解质, 可忽略电迁移影响,  $j_{d1} < j_{d3}$ , 其反应不同于(2)故  $j_{d1} \neq j_{d2}$ 。所以三者的值是不等的

$$3、解：j_d = nFD \frac{c^0}{\delta} = \frac{4 \times 96500 \times 6 \times 10^{-5} \times 0.1 \times 10^{-3}}{5 \times 10^{-2}} = 0.046 \text{ A/cm}^2$$

4、解：因是正离子 ( $\text{Cd}^{2+}$ ) 在阴极还原, 故加入大量局外电解质时, 将使  $t_{\text{Cd}^{2+}}$  减小, 使  $j_c$  减小, 表现了电迁移对扩散速度影响的规律; 又因  $j_c \propto \omega^{0.5}$ 。所以, 判断是扩散步骤控制, 当很大时, 速度控制步骤将转变为混合控制 (扩散控制与电化学步骤控制), 直至成为电化学步骤控制。

$$5、解：(1)列方程组 \begin{cases} j = j_d \left( \frac{c^0 - c^s}{c^0} \right) \dots\dots ① \\ j_d = nFDc^0/\delta \dots\dots ② \\ \delta = \frac{c^0 - c^s}{(dc/dx)_{x=0}} \dots\dots ③ \end{cases}$$

将②③代入①解得：  $j = nFD(dc/dx)_{x=0} = 2 \times 96500 \times 0.5 \times 10^{-5} \times 8 \times 10^{-2} = 0.077 A/cm^2$

$$(2) -\eta_{浓差} = \varphi - \varphi_{平} = \frac{2.3RT}{2F} \log \left( 1 - \frac{j}{j_d} \right), \quad \log \left( 1 - \frac{j}{j_d} \right) = -\frac{2F\eta_{浓差}}{2.3RT} = -\frac{2 \times 0.056}{0.0577} = -1.94, \quad 1 - \frac{j}{j_d} = 0.0115$$

$$c^s = c^0 \left( 1 - \frac{j}{j_d} \right) = 2 \times 0.0115 = 0.023 mol/L$$

$$6、解： j_d = nFD \frac{c^0}{\delta} = \frac{2 \times 96500 \times 1 \times 10^{-2} \times 0.5 \times 10^{-3}}{1.1 \times 10^{-2}} = 0.088 A/cm^2,$$

$$\Delta\varphi = -\eta_c = \frac{2.3RT}{nF} \log \left( 1 - \frac{j}{j_d} \right) = \frac{0.0591}{2} \log \left( 1 - \frac{0.044}{0.088} \right) = -0.009V = -9mV$$

$$7、解：(1) j_d = 0.62nFD^{2/3}v^{-1/6}\omega^{1/2}c^0, \quad \omega = 2\pi n = 62.8^\circ/s;$$

$$\therefore j_d = 0.62 \times 2 \times 96500 \times (1 \times 10^{-5})^{2/3} (1.09 \times 10^{-2})^{-1/6} (62.8)^{1/2} \times 0.1 \times 10^{-3} = 0.0935 A/cm^2$$

$$(2) 静止时： j_d' = nFD \frac{c^0}{\delta} = \frac{2 \times 96500 \times 1 \times 10^{-5} \times 0.1 \times 10^{-3}}{5 \times 10^{-3}} = 0.0386 A/cm^2, \quad \therefore \frac{j_d}{j_d'} = \frac{0.0935}{0.0386} = 2.42$$

$$8、解：(1) 非稳态恒流极化下： t = \frac{n^2 F^2 \pi D (c^0)^2}{4v^2 j^2} = \frac{4^2 \times 96500^2 \times 3.14 \times 1.2 \times 10^{-5} \times (0.1 \times 10^{-3})^2}{4 \times 1 \times (0.5)^2} = 5.6 \times 10^{-2} s$$

$$(2) c_O^s = c_O^0 \left[ 1 - \left( \frac{t}{\tau} \right)^{1/2} \right] = 0.1 \times 10^{-3} \left[ 1 - \left( \frac{1 \times 10^{-3}}{5.6 \times 10^{-2}} \right)^{1/2} \right] = 8.66 \times 10^{-2} mol/L$$

$$\text{或 } c_O^s = c_O^0 - \frac{2j}{nF} \sqrt{\frac{t}{\pi D}} = 8.67 \times 10^{-2} mol/L$$

$$9、解：(1) j_d = nFD \frac{c^0}{\delta} = \frac{2 \times 96500 \times 1.5 \times 10^{-4} \times 0.1 \times 10^{-3}}{0.01} = 0.2895 A/cm^2, \quad \varphi = \varphi_{1/2} + \frac{RT}{nF} \ln \left( \frac{j_d - j}{j} \right),$$

$$\therefore \varphi_{1/2} = \varphi - \frac{2.3RT}{2F} \log \left( \frac{j_d - j}{j} \right) = -0.12 - \frac{0.0591}{2} \log \left( \frac{0.2895 - 0.08}{0.08} \right) = -0.132V$$

$$(2) j = 0.2 A/cm^2 \text{ 时, } \varphi = \varphi_{1/2} + \frac{2.3RT}{2F} \log \left( \frac{j_d - j}{j} \right) = -0.132 + \frac{0.0591}{2} \log \left( \frac{0.2895 - 0.2}{0.2} \right) = -0.142V$$

10、解：设方程组

$$\begin{cases} j = j_d \left( \frac{c^0 - c^s}{c^0} \right) \dots\dots ① \\ j_d = nFDc^0 / \delta_{\text{有效}} \dots\dots ② \\ \delta_{\text{有效}} = \frac{c^0 - c^s}{(dc/dx)_{x=0}} \dots\dots ③ \end{cases}$$

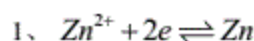
(1)将②③代入①得：  $j = FD \left( \frac{dc}{dx} \right)_{x=0} = 96500 \times 6 \times 10^{-5} \times 7 \times 10^{-2} = 0.405 \text{ A/cm}^2$

(2)  $\delta_{\text{有效}} = \frac{c^0 - c^s}{(dc/dx)_{x=0}} = \frac{(1-0.1) \times 10^{-3}}{7 \times 10^{-2}} = 1.29 \times 10^{-2} \text{ cm}$

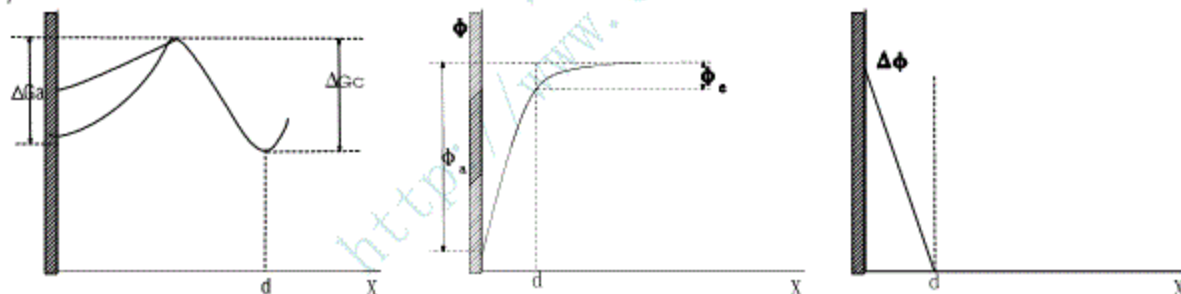
(3)  $\eta_{\text{浓}} = \varphi - \varphi_{\text{平}} = \frac{2.3RT}{F} \log \left( 1 - \frac{j}{j_d} \right)$ ,  $\log \left( 1 - \frac{j}{j_d} \right) = \frac{\eta_{\text{浓}} F}{2.3RT} = \frac{-0.059}{0.0591} = -1$ ,

$c^s = c^0 \left( 1 - \frac{j}{j_d} \right) = 1 \times 10^{-1} = 0.1 \text{ mol/L}$

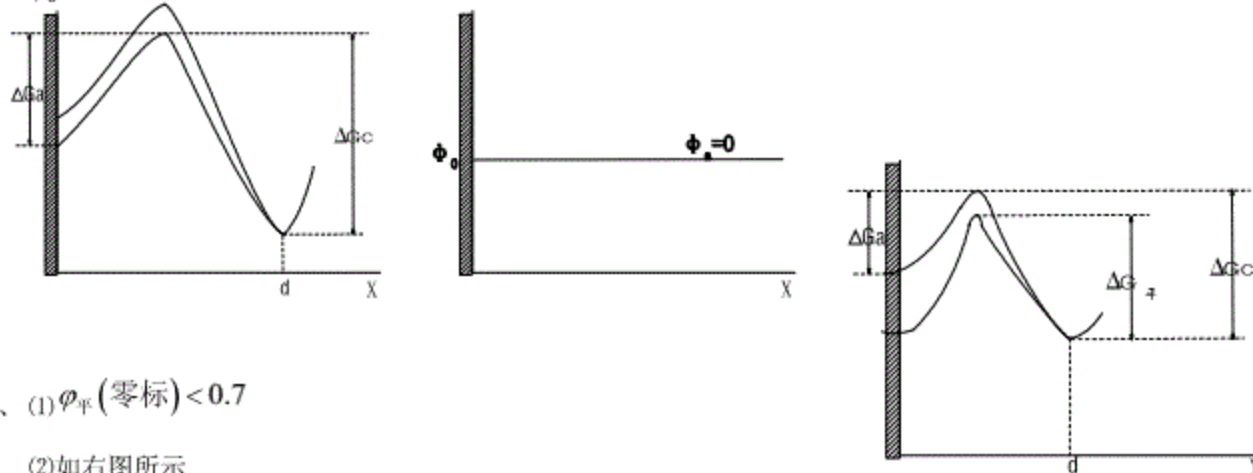
## 电化学原理第六章习题答案



$\Delta\varphi > 0$  :



$\varphi = \varphi_0$  :



2、(1)  $\varphi_{\text{平}}(\text{零标}) < 0.7$

(2) 如右图所示



(3)阳极极化

$$j_a = \bar{j} - \bar{j} = j^0 \left[ \exp\left(\frac{\bar{\alpha}F\eta_a}{RT}\right) - \exp\left(-\frac{\bar{\alpha}F\eta_a}{RT}\right) \right], \text{ 也可写成 } j_a = j^0 \left[ \exp\left(\frac{\beta 2F\eta_a}{RT}\right) - \exp\left(-\frac{\alpha 2F\eta_a}{RT}\right) \right]$$

3、加入  $\text{NaCN}$ ：将因吸附而影响电子转移步骤活化能；生成部分  $\text{Zn}(\text{CN})_4^{2-}$  络离子，影响还原过程机理（增加强制转化步骤），所以阴极过程电化学反应速度减小，阴极极化曲线会改变。

在  $j_1$  处，由上所述，控制步骤有可能从混合步骤转化为电子转移步骤。（当  $W_{\text{电}}$  增加较多时）

4、 $\text{Ni}^{2+} + 2e \rightarrow \text{Ni}$ ，在较高电流密度下，可用 Tafel 关系计算（即  $j_c \gg j^0$ ）：

$$\eta_c = -\frac{2.3RT}{\alpha F} \log j^0 + \frac{2.3RT}{\alpha F} \log j = -\frac{0.0581}{1} \log(2 \times 10^{-9}) + \frac{0.0581}{1} \log 0.04 = 0.424V$$

5、牺牲阳极反应： $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e$

$\because \eta_a = 0.05V$ ，估计在弱极化区，且  $\bar{\alpha} = \frac{n}{v} - \alpha = 1.1$ ，

$$\therefore j_a = j^0 \left[ \exp\left(\frac{0.9 \times 96500 \times 0.05}{8.31 \times 298}\right) - \exp\left(-\frac{1.1 \times 96500 \times 0.05}{8.31 \times 298}\right) \right] = 1.13 \times 10^{-4} A/cm^2,$$

$$R_p = \frac{\Delta \phi}{\Delta j} = \frac{0.05}{1.13 \times 10^{-4}} = 442.5 \Omega/cm^2$$

（本题可用 TAFEL 公式近似计算（ $\because j_a : j^0 \approx 50:1$ ），不可以用线性极化公式计算。）

6、 $\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$

$$(1) \varphi_{\text{平}} = \varphi^0 + \frac{2F}{2.3RT} \log a_{\text{Cu}^{2+}}, \log a_{\text{Cu}^{2+}} = \frac{2F}{2.3RT} (\varphi_{\text{平}} - \varphi^0) = \frac{2 \times (0.31 - 0.337)}{0.0577} = -0.94,$$

$a_{\text{Cu}^{2+}} = 0.116 \text{ mol/L}$ ，（若查得  $\varphi^0 = 0.3448V$ ，则  $a_{\text{Cu}^{2+}} = 0.06 \text{ mol/L}$ ）

$$(2) \eta_c = \varphi_{\text{平}} - \varphi = -\frac{2.3RT}{\alpha F} \log j^0 + \frac{2.3RT}{\alpha F} \log j_c,$$

$$\log j_c = \frac{\bar{\alpha}F}{2.3RT} (\varphi_{\text{平}} - \varphi) + \log j^0 = \frac{1 \times (0.31 + 0.23)}{0.0577} + \log(1.3 \times 10^{-9}) = 0.473, j_c = 2.97 A/cm^2$$

$$7、(1) \eta_c = \frac{2.3RT}{\alpha F} \log \frac{j}{j^0}, \bar{\alpha} = \frac{2.3RT}{\eta_c F} \log \frac{j}{j^0} = \frac{0.0581 \times (\log 1 - \log 10^{-9})}{0.556} = 0.94$$

$$(2) \log j'_c = \frac{\bar{\alpha}F}{2.3RT} \eta'_c + \log j^0 = \frac{0.94 \times 2 \times 0.556}{0.0581} + \log 10^{-9} = 8.99, j'_c = 9.8 \times 10^8 A/cm^2$$

比原来速度 ( $j_c$ ) 增加了近九个数量级, 可见  $\phi$  对  $j$  影响之大, 但实际中将受  $j_d$  所限, 不会达到  $j_d'$  值

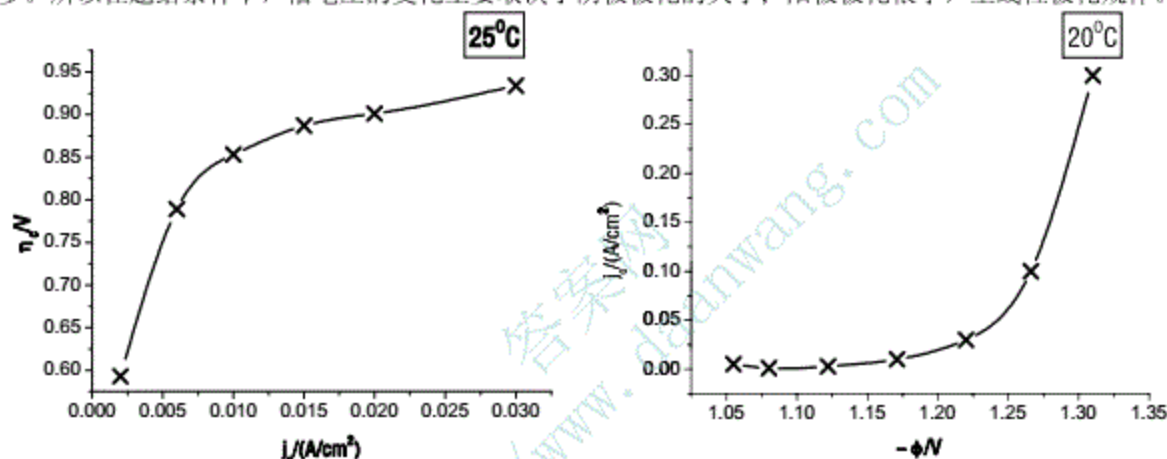
8、(1) 由于对阴极反应:  $j_c \gg j^0$ , 故可用 TAFEL 关系计算  $\eta_c$ :

$$\eta_c = \frac{2.3RT}{\alpha F} \log \frac{j}{j^0} = 0.0591 [\log 1 - \log (1 \times 10^{-9})] = 0.532V, \quad E = V_{j=0} = 0.832V,$$

$$\therefore \eta_a = V - (E + \eta_c - IR) = 1.765 - (0.832 + 0.532 + 0.4) = 0.001V$$

$$(2) \text{ 由于 } \eta_a \text{ 很小, 故应按线性极化或弱极化区进行计算 } j^0 = \frac{RTj_a}{nF\eta_a} = \frac{8.31 \times 298 \times 1}{2 \times 96500 \times 0.001} = 12.83 A/cm^2$$

(3) 上述计算结果表明: 阳极反应过程的可逆性很好 ( $j^0$  很大); 且阳极过程之  $j^0$  比阴极反应过程的  $j^0$  大得多。所以在题给条件下, 槽电压的变化主要取决于阴极极化的大小; 阳极极化很小, 呈线性极化规律。



9、电极反应:  $2H_2O + O_2 + 4e \rightarrow 4OH^-$

用作图法求解:  $\log j = 0$  时  $\eta_c = 0.36V$ ,  $\therefore a = 0.36V$ 。设 TAFEL 区斜率为  $tg\alpha$ ,

$$\therefore b = tg\alpha = \frac{\Delta\phi}{\Delta\log j} = 0.093, \quad \log j^0 = -\frac{a}{b} = -\frac{0.36}{0.093} = -3.87, \quad \therefore j^0 = 1.35 \times 10^{-4} A/cm^2$$

10、由作图法求解:  $\log j = 0$  时  $\eta_c = 1.185V$ ,  $\therefore a = 1.185V$ 。设 TAFEL 区斜率为  $tg\alpha$ ,

$$\therefore b = tg\alpha = \frac{\Delta\phi}{\Delta\log j} = 0.289, \quad \alpha = \frac{2.3RT}{bF} = \frac{0.0591}{0.289} \approx 0.20$$

$$\log j^0 = -\frac{a}{b} = -\frac{1.185}{0.289} = -4.10, \quad \therefore j^0 = 7.94 \times 10^{-5} A/cm^2$$

## 电化学原理第七章习题答案

$$1、\eta_H = \phi_{\text{平}} - \phi = \frac{2.3RT}{F} \log a_{H^+} - \phi = 0.0581 \log (0.5 \times 2 \times 0.154) - (-0.479) = 0.432V, \quad (\gamma_{\pm} = 0.154)$$

$$\log j = \frac{\eta_H - a}{b} = \frac{0.432 - 0.63}{0.11} = -1.8,$$

$$j = 0.016 \text{ A/cm}^2$$

$$2、\because \eta_H = \text{常数} - \frac{1-\alpha}{\alpha} \phi_1 + \frac{RT}{\alpha F} \ln j,$$

$$\therefore \eta_H' - \eta_H = -\frac{1-\alpha}{\alpha} \frac{RT}{F} (\ln c_{H^+}' - \ln c_{H^+}) = -\frac{(1-0.48) \times 0.0591}{0.48} (-5+3) = 0.128V$$

在  $pH = 5$  的溶液中的  $\eta_H$  值比  $pH = 3$  时高  $0.128V$ ，当保持  $pH$  不变时，可通过增加溶液总浓度（加入中性盐）

使  $\frac{1-\alpha}{\alpha} \phi_1 = \text{常数} + \frac{1-\alpha}{\alpha} \frac{RT}{F} \ln c_{\Sigma}$  增大而使  $pH = 3$  溶液中的析氢过电位增加至与  $pH = 5$  时一样。

$$3、H^+ + e \rightarrow \frac{1}{2} H_2, \text{ 设温度为 } 25^\circ C$$

$$\text{当 } j_1 = 5 \times 10^{-3} \text{ A/cm}^2 \text{ 时, } \eta_1 = \frac{2.3RT}{\alpha F} \log \frac{j}{j^0} = \frac{0.0591}{0.5} [\log(5 \times 10^{-3}) - \log(1 \times 10^{-4})] = 0.201V$$

$$\text{当 } j_2 = 3.2 \times 10^{-2} \text{ A/cm}^2 \text{ 时, } \eta_2 = 0.296V$$

4、检测出少量  $OH^-$ ，说明步骤(A)比(B)快

$$\text{假设(B)为控制步骤, 则(A)为准平衡态, 故对反应(A)有: } \phi_{\pi} = \phi^0 + \frac{RT}{F} \ln \frac{a_{OH}^0 a_{H^+}^0}{a_{H_2O}^0}, \phi = \phi^0 + \frac{RT}{F} \ln \frac{a_{OH}^s a_{H^+}^s}{a_{H_2O}^s}$$

$$\text{设 } a_{H_2O}^0 \approx a_{H_2O}^s, a_{H^+}^s \approx a_{H^+}^0 (\because pH \text{ 未变}),$$

$$\therefore \phi - \phi_{\pi} = \Delta\phi = \frac{RT}{F} \ln \frac{a_{OH}^s}{a_{OH}^0} \text{ 用浓度代替活度: } c_{OH}^s = c_{OH}^0 \exp\left(\frac{F\Delta\phi}{RT}\right)$$

$$\text{对(B)步骤有: } \bar{j}_B = FKc_{OH}^s \exp\left(\frac{\beta F\Delta\phi}{RT}\right) = FKc_{OH}^0 \exp\left(\frac{F\Delta\phi}{RT}\right) \cdot \exp\left(\frac{\beta F\Delta\phi}{RT}\right)$$

$$\text{设 } \beta = 0.5, \bar{j}_B = FKc_{OH}^0 \exp\left(\frac{3}{2} \frac{F\Delta\phi}{RT}\right);$$

$$\text{取对数: } \Delta\phi = \text{常数} + \frac{2RT}{3F} \ln \bar{j}_B, \text{ 由于 } j_{\Sigma} = \bar{j}_B,$$

$$\therefore \Delta\phi = \text{常数} + \frac{2RT}{3F} \ln j_{\Sigma} = \text{常数} + \frac{4.6RT}{3F} \log j_{\Sigma}, \text{ 即 } b = \frac{4.6RT}{3F}, \text{ 与实验值吻合。}$$

5、由于  $25^\circ C$  时迟缓放电理论之 TAFEL 斜率  $b \approx 0.118V$ ，则该过程机理为记录迟缓放电机理。

$$\log j^0 = -\frac{a}{b} = -\frac{0.7}{0.128} = -5.47, \quad j^0 = 3.39 \times 10^{-6} \text{ A/cm}^2,$$

$$\phi = \phi_{\pi} - \eta_c = \frac{2.3RT}{F} \log a_{H^+} - (a + b \log j) = 0.375V$$