电化学原理第一章习题答案

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

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

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

设
$$c^2 = c_{H^+} c_{OH^-}$$
,故 $c = \sqrt{K_W} = \sqrt{1.008 \times 10^{-14}} = 1.004$, $\kappa = \frac{\lambda_{o,H_2O} c}{1000} = 5.5 \times 10^{-8} \Omega^{-1} cm^{-1}$

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

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

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

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

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

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

因为u=Σu_i=KH₂O+10⁻³[yλCu²⁺+2yλOH⁻]以 λ_o 代替 λ (稀溶液)代入上式,求得y=1.36 × 10⁻⁴mol/dm³ 所以Ks=4y³=1.006 × 10⁻¹¹ (mol/dm³)³

6、解:
$$AgIO_3 == Ag^+ + IO_3^-$$
,令 $c_{Ag^+} = y$, $c_{IO_3^-} = y$,则 $K_S = y^2$, $K = \sum K_i = K_{H_2O} + 10^{-3}$ ($y \lambda_{Ag^+} + y \lambda_{IO_3^-}$)

作为无限稀溶液处理,用 λ_0 代替,

$$= K_{H_2O} + 10^{-3} \,\mathrm{y} \,\lambda_{AgIO_3}$$

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

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

$$\alpha = \lambda/\lambda_0 = 0.023$$
 , $K_\alpha = \alpha^2/(1-\alpha)\bar{V} = 1.69 \times 10^{-5}$

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

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

(1)
$$\gamma_{\pm} = 0.9740$$
, $I = \frac{1}{2} \sum m_i z_i^2$, $I = \frac{1}{2} \sum c_i z_i^2$, $m_{\pm} = (m_{\pm}^{\nu_{\pm}} m_{-}^{\nu_{\pm}})^{\frac{1}{\nu}}$

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

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

电化学原理第二章习题答案

1、解:

$$\left(+\right)Sb_2O_3+6H^++6e \rightleftharpoons 2Sb+3H_2O \text{ , } \left(-\right)3H_2 \rightleftharpoons 6H^++6e \text{ , 电池: } Sb_2O_3+3H_2 \rightleftharpoons 2Sb+3H_2O$$

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

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

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

2解:
$$(+)4H^+ + O_2 + 4e \rightleftharpoons 2H_2O$$
, $(-)2H_2 \rightleftharpoons 4H^+ + 4e$; 电池: $2H_2 + O_2 \rightleftharpoons 2H_2O$

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

查表:
$$\varphi_+^0$$
 =1.229 V , φ_-^0 =0.000 V , $\therefore E = \varphi_+^0 - \varphi_-^0 = 1.229V$

视为无限稀释溶液,以浓度代替活度计算

$$(-)Sn^{2+} \Longrightarrow Sn^{4+} + 2e$$
 , $(+)2Fe^{3+} + 2e \Longrightarrow 2Fe^{2+}$, 电池: $Sn^{2+} + 2Fe^{3+} \Longrightarrow Sn^{4+} + 2Fe^{2+}$

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

$$(-) Ag \rightleftharpoons Ag^+(0.1m) + e \text{ , } (+) Ag^+(1m) + e \rightleftharpoons Ag \text{ , 电池} : Ag^+(1m) \rightarrow Ag^+(0.1m)$$

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

查表:
$$1 \text{m} \, AgNO_3 \, \oplus \, \gamma_\pm = 0.4V$$
 , $0.1 \text{m} \, AgNO_3 \, \oplus \, \gamma_\pm = 0.72V$, $\therefore E = \frac{2.3RT}{F} \log \frac{1 \times 0.4}{0.1 \times 0.72} = 0.044V$

3、
$$\mathbf{H}$$
: $Hg | Hg_2Cl_2(s), KCl(m) | Cl_2(P_{Cl_2}), Pt$

$$(-)2Hg+Cl^- \Longrightarrow Hg_2Cl_2+2e$$
 , $(+)Cl_2+2e \Longrightarrow 2Cl^-$, 电池 $2Hg+Cl_2 \Longrightarrow Hg_2Cl_2$

$$:: E = E^{0} + \frac{2.3RT}{2F} \log \frac{P_{Cl_{2}} a_{Hg}^{2}}{a_{Hg,Cl_{2}}} = E^{0} = \varphi_{+}^{0} - \varphi_{-}^{0} , :: E = 1.3595 - 0.2681 = 1.0914V (12.25^{\circ}C)$$

由于 $E 与 a_{CL}$ 无关,故两种溶液中的电动势均为上值

其他解法: $E=\varphi_+-\varphi_-$,亦得出 $E=\varphi_+^0-\varphi_-^0$ 按 a_{Cl^-} 计算 φ_+ ,查表得 $\varphi_{
m fl}$,则 $E=\varphi_+-\varphi_{
m fl}$

4、 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
$$E = \varphi_+ - \varphi_- = \varphi_+$$
 , $\therefore \varphi_{Ag/Ag^+}^0 = E - \frac{2.3RT}{F} \log(m_{Ag^+} \gamma_\pm)$ 。

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

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

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

同上解法: Pt, $H_2(1atm) \mid HCl(a_{H^+} = 1) \parallel \text{FeCl}_3(m')$, $\text{FeCl}_2(m) \mid \text{Fe}$, 电池 $\frac{1}{2}H_2 + \text{Fe}^{3+} \rightleftharpoons H^+ + \text{Fe}^{2+}$

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

5. **AR**:
$$Zn|ZnSO_4(m), Hg_2SO_4(s)|Hg$$
, $E = E^0 - \frac{2.3RT}{2F}\log(a_{SO_4^{2-}}a_{Zn^{2+}})$
 $Pb|PbCl_2(s), HCl(m)|H_2(P_{H_2}), Pt$; $E = E^0 + \frac{2.3RT}{2F}\log(a_{H^+}^2a_{CL}^2/P_{H_2})$

$$6, \ \ \textbf{$M:$ Pt}, \\ H_{2}(1atm) \ | \ HCl(a_{_{H^{^{+}}}}=1) \ \big\| \ KCl(0.1m^{'}), \\ AgCl(s) \ \big| \ Ag\ \ ;\ \big(+\big) \ AgCl + e \Longrightarrow Ag + Cl^{^{-}} \ \ ,$$

$$\therefore \varphi_+ = \varphi_+^0 - \frac{2.3RT}{F} \log a_{Cl^-}$$
,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.
$$\mathbf{M}: E_a = \frac{2.3RT}{F} \log \frac{1}{a_{Cl^-}} - \frac{2.3RT}{F} \log \frac{1}{a_{Cl^-}} = \frac{2.3RT}{F} \log \frac{a_{Cl^-}}{a_{Cl^-}}$$
 ($a'' = 0.01$ m , $a' = 0.1$ m)

可计算出:
$$a_{\pm}^{'}=0.1\times0.78=0.078, (a_{\pm}^{'}=a_{Cl^{-}}^{'})$$
 , $a_{\pm}^{''}=0.01\times0.904=0.00904, (a_{\pm}^{''}=a_{Cl^{-}}^{''})$

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

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

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

8, **$$\mathbf{m}$$**: $Pt, H_2(1atm) | HI(a = 1) | I_2(s), Pt$

$$(-)H_2 \Longrightarrow 2H^+ + 2e$$
 , $(+)I_2 + 2e \Longrightarrow 2I^-$, 电池: $H_2 + I_2 \Longrightarrow 2HI$
$$E = E^0 - \frac{2.3RT}{2E} \log(a_{HI})^2 = E^0 \text{ , } E^0 = 0.5346 - 0.13 \times 10^{-3} \times (35 - 25) = 0.5333V$$

:: E > 0, ∴ 电池表达式中正负极未写错。

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

$$E^0 = \frac{RT}{nF} \ln K$$
, $\ln K = \frac{2 \times 96500 \times 0.5333}{8314 \times 298} = 40.19$, $K = 2.86 \times 10^{17}$

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

9、解法一:

$$(-)H_2 \rightleftharpoons 2H^+ + 2e$$
, $(+)Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + Cl^-$,电池: $H_2 + Hg_2Cl_2 \rightleftharpoons 2Hg + 2Cl^- + 2H^+$

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

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

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

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

10、
$$\mathbf{H}: 2Hg \rightleftharpoons Hg_2^{2+} + 2e$$
 , $Hg_2^{2+} + SO_4^{2-} \rightleftharpoons Hg_2SO_4$; $2Hg + SO_4^{-2} \rightleftharpoons Hg_2SO_4 + 2e$;

接 :
$$\varphi = \varphi_{Hg/Hg_2^{2+}}^0 + \frac{2.3RT}{2F} \log a_{Hg_2^{2+}}^2 = \varphi_{Hg/Hg_2^{2+}}^0 + \frac{2.3RT}{2F} \log Ks - \frac{2.3RT}{2F} \log a_{SO_4^{2-}}^2$$

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

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

11、解

$$(-) Ag + Cl^- \Longrightarrow AgCl + e \text{ , } (+) \frac{1}{2} Hg_2Cl_2 + e \Longrightarrow Hg + Cl^- \text{ , } 电池: Ag + \frac{1}{2} Hg_2Cl_2 \Longrightarrow AgCl + Hg$$

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

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

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

12、解:
$$(-)Zn \rightleftharpoons Zn^{2+} + 2e$$
 , $(+)Cu^{2+} + 2e \rightleftharpoons Cu$, 电池: $Zn + Cu^{2+} \rightleftharpoons Cu + Zn^{2+}$

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

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

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

$$\therefore E^0 = E, \log K = \frac{nFE^0}{2.3RT} = \frac{2 \times 1.101}{2.3RT0.00581} = 37.26 , K = 7.95 \times 10^{37}$$

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

$$= - , :: \Delta G_3^0 = \Delta G_1^0 - \Delta G_2^0 = -2F\varphi_1^0 + \varphi_2^0 = -2F\varphi_3^0 , :: \varphi_3^0 = 2\varphi_1^0 - \varphi_2^0 = 0.337 \times 2 - 0.520 = 0.154V ;$$

$$\Delta G_{\rm 3}^{\rm 0} = -F \varphi_{\rm 3}^{\rm 0} = -0.154 \times 96500 = -14861 J/mol$$
 ,所以反应为自发。

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

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

14、解法
$$-: (-)2H_2 \Longrightarrow 4H^+ + 4e$$
 , $(+)O_2 + 4H^+ + 4e \Longrightarrow 2H_2O$, 电池 $2H_2 + O_2 \Longrightarrow 2H_2O(g)$

$$\therefore K = \frac{1}{Kp} , \qquad \qquad ||| \qquad E = \frac{RT}{4F} \ln K - \frac{RT}{4F} \ln \frac{p_{H_2O}^2}{p_{H_2}^2 p_{O_2}}$$

$$\therefore E = \frac{2.3RT}{4F} \log \frac{1}{Kp} - \frac{2.3RT}{4F} \log \frac{p_{H_2O}^2}{p_{H_2}^2 p_{O_2}} = \frac{-0.0591}{4} \log(9.7 \times 10^{-81}) - \frac{-0.0591}{4} \log \frac{\left(24/760\right)^2}{1^2 \times 1} = 1.226V$$

解法二:
$$\varphi_{H_2} = \frac{2.3RT}{2F} \log a_{H^+} = \frac{0.0591}{2} \log(0.02 \times 0.544) = -0.06V$$
 ,

$$\varphi_{O_2} = \varphi_{O_2}^0 + \frac{2.3RT}{2F} (\log a_{H^+}^2 - \log p_{H_2O}) = 1.229 + \frac{0.0591}{2} \left[\log(0.02 \times 0.544)^2 - \log(24/760) \right] = 1.16V$$

$$\therefore E = \varphi_{O_2} - \varphi_{H_2} = 1.16 - (-0.06) = 1.22V$$

15、 \mathbf{m} : 有 $\mathbf{Z}n^{2+}$ $\mathbf{C}u^{2+}$ \mathbf{H}^{+} 三种离子可在阴极还原,

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

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

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

所以,阴极析出的顺序为: $Cu \, \subset \, H_2 \subset Zn$

当 Zn 析出时电位为-0.83 V, (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)

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

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

16、
$$\mathbf{m}: : Pb \rightleftharpoons Pb^{2+} + 2e$$
 , $Pb^{2+} + 2F^- \rightleftharpoons PbF_2$; $Pb + 2F^- \rightleftharpoons PbF_2 + 2e$;

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

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

17、
$$(-)Zn \rightleftharpoons Zn^{2+} + 2e$$
 , $(+)Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$ 电池 : $Hg_2Cl_2 + Zn \rightleftharpoons 2Hg + 2Cl^- + Zn^{2+}$

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

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

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

18、解:电池 a 为无迁移浓差电池,电极对负离子($c\bar{c}$)可逆。 电池 b 为有迁移浓差电池,电极对负离子($c\bar{c}$)可逆。

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

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

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

$$t_{+} = -\frac{E_{b}}{2\frac{RT}{F} \ln \frac{m_{2}\gamma_{\pm,2}}{m_{2}\gamma_{\pm,1}}} = -\frac{E_{b}}{E_{a}} = \frac{57.9 \times 10^{-3}}{82.8 \times 10^{-3}} = 0.7044$$

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

$$\lambda_{_{0,H^{+}}}=t_{_{+}}\lambda_{_{0,HCl}}=0.7044\times83.8=59.03\Omega^{^{-1}}cm^{2}eq^{^{-1}}\ \ ,\ \ \lambda_{_{0,Cl^{-}}}=(1-t_{_{+}})\lambda_{_{0,HCl}}=24.77\Omega^{^{-1}}cm^{2}eq^{^{-1}}$$

19,
$$\varphi = \varphi^0 - \frac{2.3RT}{nF} mpH + \frac{2.3RT}{nF} \log \frac{a_A^a}{b_B^b}$$

$$=1.33-\frac{0.0591\times14}{6}pH+\frac{0.0591}{6}\log\frac{a_{Cr_2O_3^{2-}}}{a_{Cr^{3+}}^2}=1.33-0.138pH-0.00985\log\frac{a_{Cr_2O_3^{2-}}}{a_{Cr^{3+}}^2}$$

$$\varphi = \varphi^0 + \frac{2.3RT}{nF} \log \frac{a_A^a}{b_B^b} = 0.2681 - \frac{0.0591}{2} \log a_{Cl^-}^2 = 0.2681 - 0.0591 \log a_{Cl^-}$$

$$\log a_{Cd(OH)_2} - \log a_{OH^-} + \log a_{HCdO_2^-} + \log a_{H_2O} = \log K \ \ \text{, } \\ \log \log a_{HCdO_2^-} - \log a_{OH^-} = \log K$$

由
$$pH = 14 + \log a_{OH^-}$$
 , $pH = 14 + \log a_{HCdO_2^-} - \log K$

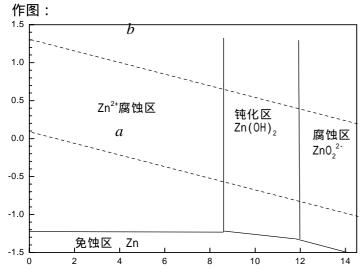
20、解: 线 与线 大约在 pH = 7.68 时相交

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

$$Fe^{2+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + e^{-2H}$$

21、解:因作腐蚀图,故取 $a_i = 10^{-6}$

$Zn^{2+} + 2e \rightleftharpoons Zn$	$\varphi = -0.94V$, $2pH = -0.763 + 0.0295 \log a_{Zn^{2+}}$
$Zn(OH)_2 + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O$	$pH = 8.48$, $2pH = 10.96 - \log a_{Zn^{2+}}$
$ZnO_2^{2-} + 2H^+ \rightleftharpoons Zn(OH)_2$	$pH = 11.89$, $2pH = 29.78 + \log a_{Zn^{2+}}$
$Zn(OH)_2 + 2H^+ + 2e \rightleftharpoons Zn + 2H_2O$	$\varphi = -0.437 - 0.0591 pH$
$ZnO_2^{2-} + 4H^+ + 2e \rightleftharpoons Zn + 2H_2O$	$\varphi = 0.44 - 0.118 pH + 0.0296 \log a_{ZnO_2^{2-}} = 0.263 - 0.118 pH$
反应	平衡条件



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

电化学原理第三章习题答案

1、 解:由高斯定律:
$$E=\frac{q}{\varepsilon_0\varepsilon_r}$$
 , 查表: $\varepsilon_0=8.85\times 10^{-12}$,则 $E=\frac{2\times 10^{-5}\times 10^{-4}}{8.85\times 10^{-12}\times 40}=5.6\times 10^8 \, V/m$

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

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

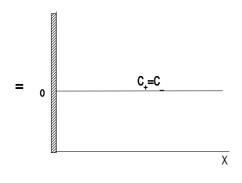
3、 解:
$$q = C\varphi = C(\varphi_{\text{TF}} - \varphi_0) = 36 \times (-0.763 + 0.63) = -4.79 \,\mu\text{C/cm}^2$$

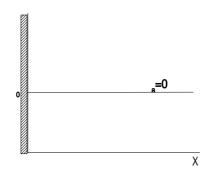
q不变,Cd 增大,因此有 Cl^- 吸附,是紧密层厚度减小,故 $C=rac{\mathcal{E}_0\mathcal{E}_r}{d}$ 将增大到,它可认为 $\varphi_{\Psi}<\varphi_0$,q>0

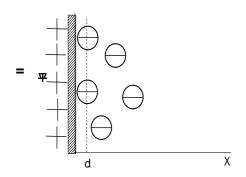
时 Cl^- 吸附很少,Cd 变化不大,但q与此无关

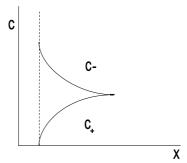
$$q = C(\varphi - \varphi_0) = 36 \times (0.32 + 0.64) = 34.2 \,\mu\text{C/cm}^2$$

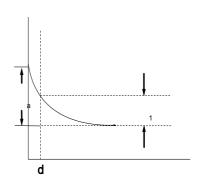
4、 解: $Ag^+ + e \Longrightarrow Ag$, $\varphi_{\mp} = \varphi_0 + 0.591\log(0.002) = 0.64V > \varphi_0$,所以金属表面带正电荷。



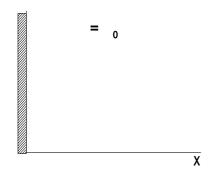


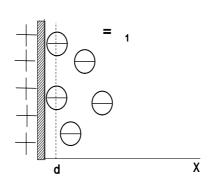


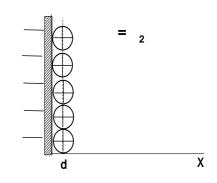


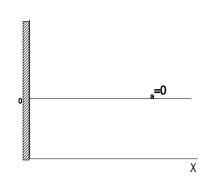


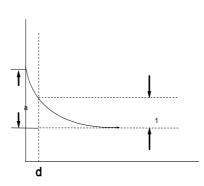
5、解:

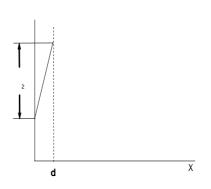










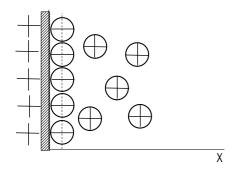


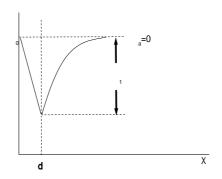
$$\varphi_0 = 0$$

$$\varphi_1 = -$$
常数 + $\frac{2RT}{F}$ ln $\varphi_a - \frac{RT}{F}$ ln C

$$\varphi_1 = 0$$

6、解:在 $\varphi\geq\varphi_0$ 的范围内 $\sigma\downarrow Cd$ 个,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)

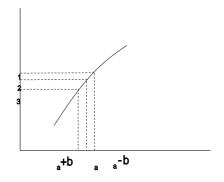




7、 解法一:根据 $Cd = \frac{dq}{d\varphi}$,如图所示,

在
$$\varphi_{\rm a}$$
点: $q_{\rm l} = -rac{\partial\sigma}{\partial\varphi} pprox rac{-\sigma_{\rm 2} + \sigma_{\rm 3}}{\varphi_{\rm a} - \left(\varphi_{\rm a} + b
ight)} = rac{\sigma_{\rm 2} - \sigma_{\rm 3}}{b}$;

在
$$\left(\varphi_{\mathsf{a}}-b\right)$$
点: $q_2=rac{\sigma_1-\sigma_2}{\varphi_{\mathsf{a}}-\left(\varphi_{\mathsf{a}}-b\right)}=rac{\sigma_1-\sigma_2}{b}$;



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

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;

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

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: $\varphi_{\rm a}=\varphi_{\rm 0}=0.11-(-0.119)=0.30V$, \therefore $\varphi_{\rm 1}>0$,且由题给数据知 q , c 较大。

$$\varphi_{1} = -\frac{2RT}{F} \ln \frac{1}{C_{1y}} \sqrt{2\varepsilon_{0}\varepsilon_{r}RT} + \frac{2RT}{F} \ln \varphi_{a} - \frac{RT}{F} \ln c , \qquad C_{1y} = \frac{q}{\varphi_{a} - \varphi_{1}} \approx \frac{q}{\varphi_{a}} ;$$

$$\varphi_{1} = -\frac{2RT}{F} \ln \frac{\varphi_{a}}{q} \sqrt{2\varepsilon_{0}\varepsilon_{r}RT} + \frac{2RT}{F} \ln \varphi_{a} - \frac{RT}{F} \ln c$$

$$= 0.0591 \left[-2\log \frac{0.3 \times \sqrt{2 \times 8.85 \times 10^{-12} \times 40 \times 298 \times 8.31}}{0.1} + 2\log 0.3 - \log(c \times 10^{3}) \right]$$

 $= 0.222 - 0.0591\log(c \times 10^3)$

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

当 c=0.1mol/L 时, $\varphi_{\rm l}=0.1038V$, $\varphi_{\rm l}:\varphi_{\rm a}=\frac{1}{3}$,分散层较小。

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

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

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

同理可求 c=0.1 mol/L 时 , $\varphi_{\rm l} \approx 0.1038 V$ 。

9、解:从 $Cd\sim \varphi$ 曲线可知 $\varphi_0=-0.37V$;未加 NaCl 时 , $\varphi_{\rm th}=-0.25\sim -0.27V>\varphi_0$,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:
$$Cu^{2+} + 2e \rightleftharpoons Cu$$
 ,设 $T = 25\,^{\circ}C$, $\varphi = \varphi^{0} + \frac{2.3RT}{2F}\log a_{cu^{2+}} = 0.337 + \frac{2.3RT}{2F}10^{-7} \approx 0.13V$
$$H^{+} + e \to \frac{1}{2}H_{2} \text{ ,设} T = 25\,^{\circ}C \text{ ,查表} \gamma_{\pm} = 0.130 \text{ ,} \eta_{a} = \varphi - \varphi_{\Psi} \text{ ,} \eta_{c} = \varphi_{\Psi} - \varphi \text{ 回}:$$

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

为使氢气不析出,阴极电位不可负于-0.28V。

2、 解:
$$2H^+ + 2e \rightarrow H_2$$
 ,已知 $-\log a_{H^+} = 6.5$, $\therefore \eta_c = \varphi_{H^+,\Psi} - \varphi = 0.0591 \log a_{H^+} - \left(-1.23\right) \approx 0.846 V$

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

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

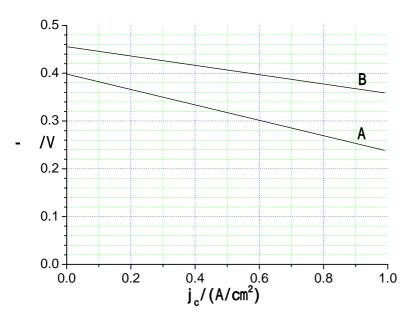
若阴极上析氢: $2H^+ + 2e \rightarrow H_2$,

$$\varphi_c^{\;\prime} = \varphi_{H, \Psi} - \eta_H = 0.0591 \log a_{H^+} - \eta = 0.0591 \log \left(0.2 \times 0.265\right) - 1.06 = -1.1354 V$$

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

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

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 ; $j_1=nFv_1=nfKc\exp\left(-\frac{w_1}{RT}\right)$, $j_2=nFv_2=nFKc\exp\left(-\frac{w_2}{RT}\right)$

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

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

与 $j = 193 A/m^2$ 比较:该电极过程的控制步骤是扩散步骤。

$$: j = j_{\text{H}} = 193 \, \text{A/m}^2$$
 , $j_{\text{ph}} = -j = 48250 - 193 = 48057 \, \text{A/m}^2$

 $\therefore j_{\text{pr}} \approx j_{\text{pr}} - j$,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 。

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

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

扩散活化能应降低17106 J/mol。

8. **\textbf{K}**:
$$\varphi_c = \varphi_{Zn}^0 + \frac{2.3RT}{2F} \log \left(\gamma_{\pm} m_{Zn^{2+}} \right) = -0.763 + \frac{0.0591}{2} \log \left(0.33 \times 1 \right) = -0.77V$$
, $\varphi_a = \varphi_H^0 = 0$.

 $:: E = \varphi_a - \varphi_c = 0.777V$, 而 V=1.24V , :: V > E , 是电解池。

作为电解池,负极为阴极,故Zn 电极发生阴极极化

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

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 Cu 含量过高。

2、解:设 的极限扩散电流为
$$j_{d1}$$
 为 j_{d2} 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 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 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 $\left(Cd^{2+}\right)$ 在阴极还原,故加入大量局外电解质时,将使 $t_{cd^{2+}}$ 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。

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

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

$$-\eta_{\not\!\!\!\!/\!\!\!/\!\!\!/} = \varphi - \varphi_{\not\!\!\!/\!\!\!/} = \frac{2.3RT}{2F} \log \left(1 - \frac{j}{j_d}\right) \; , \; \log \left(1 - \frac{j}{j_d}\right) = -\frac{2F\eta_{\not\!\!\!/\!\!\!/\!\!\!/\!\!\!/}}{2.3RT} = -\frac{2\times0.056}{0.0577} = -1.94 \;\; , \; 1 - \frac{j}{j_d} = 0.0115$$

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

$$6, \quad \text{fif} \ : \ j_d = nFD \frac{c^0}{\mathcal{S}} = \frac{2 \times 96500 \times 1 \times 10^{-2} \times 0.5 \times 10^{-3}}{1.1 \times 10^{-2}} = 0.088 \, A/cm^2 \quad ,$$

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

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

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

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

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

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

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

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

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

$$j = 0.2 \, A/cm^2 \, \mathrm{Fl} \quad , \\ \varphi = \varphi_{\mathrm{I/2}} + \frac{2.3 RT}{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) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.2895 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591}{2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591 - 0.2}{0.2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591 - 0.2}{0.2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591 - 0.2}{0.2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591 - 0.2}{0.2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591 - 0.2}{0.2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591 - 0.2}{0.2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591 - 0.2}{0.2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591 - 0.2}{0.2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.142 V + \frac{0.0591 - 0.2}{0.2} \log \left(\frac{0.0591 - 0.2}{0.2} \right) = -0.014 V + \frac{0.059$$

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

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

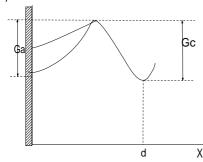
$$\eta_{ix} = \varphi - \varphi_{ix} = \frac{2.3RT}{F} \log \left(1 - \frac{j}{j_d} \right), \log \left(1 - \frac{j}{j_d} \right) = \frac{\eta_{ix}F}{2.3RT} = \frac{-0.059}{0.0591} = -1,$$

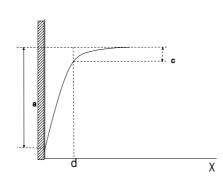
$$c^{s} = c^{0} \left(1 - \frac{j}{j_{d}} \right) = 1 \times 10^{1} = 0.1 \, mol/L$$

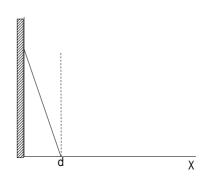
电化学原理第六章习题答案

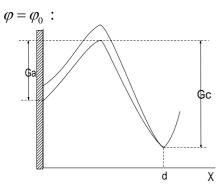
$$1, \quad Zn^{2+} + 2e \rightleftharpoons Zn$$

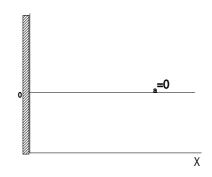
 $\Delta \varphi > 0$:

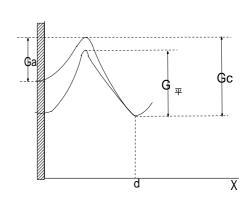












 $_{2}$ 、 φ_{Ψ} (零标)<0.7

如右图所示

阳极极化

$$j_a = \overline{j} - \overline{j} = j^0 \Bigg[\exp \Bigg(rac{\overline{lpha} F \eta_a}{RT} \Bigg) - \exp \Bigg(- rac{\overline{lpha} F \eta_a}{RT} \Bigg) \Bigg]$$
,也可写成 $j_a = j^0 \Bigg[\exp \Bigg(rac{eta 2 F \eta_a}{RT} \Bigg) - \exp \Bigg(- rac{lpha 2 F \eta_a}{RT} \Bigg) \Bigg]$

3、 加入 NaCN : 将因吸附而影响电子转移步骤活化能; 生成部分 $Zn(CN)_4^{2-}$ 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 $W_{\rm B}$ 增加较多时)

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

$$\eta_c = -\frac{2.3RT}{\vec{\alpha}F}\log j^0 + \frac{2.3RT}{\vec{\alpha}F}\log j = -\frac{0.0581}{1}\log(2\times10^{-9}) + \frac{0.0581}{1}\log0.04 = 0.424V$$

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

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

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

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

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

6, $Cu^{2+} + 2e \rightleftharpoons Cu$

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

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

$$\eta_c = \varphi_{\mp} - \varphi = -\frac{2.3RT}{\vec{\alpha}F} \log j^0 + \frac{2.3RT}{\vec{\alpha}F} \log j_c ,$$

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

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

$$\log j_c' = \frac{\vec{\alpha}F}{2.3RT} \eta_c' + \log j^0 = \frac{0.94 \times 2 \times 0.556}{0.0581} + \log 10^{-9} = 8.99 , j_c' = 9.8 \times 10^8 A/cm^2$$

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

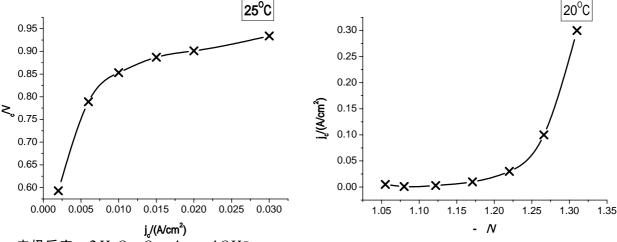
8、 由于对阴极反应: $j_c >> j^0$, 故可用 TAFEL 关系计算 η_c :

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

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

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

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: $2H_2O + O_2 + 4e \rightarrow 4OH^{-1}$

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

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

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 $tg\alpha$,

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

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

电化学原理第七章习题答案

1.
$$\eta_H = \varphi_{\mp} - \varphi = \frac{2.3RT}{F} \log a_{H^+} - \varphi = 0.0581 \log (0.5 \times 2 \times 0.154) - (-0.479) = 0.432V$$
, $(\gamma_{\pm} = 0.154)$

$$\log j = \frac{\eta_H - a}{b} = \frac{0.432 - 0.63}{0.11} = -1.8 , \qquad j = 0.016 \, A/cm^2$$

2、
$$: \eta_H =$$
常数 $-\frac{1-\alpha}{\alpha} \varphi_1 + \frac{RT}{\alpha F} \ln j$,

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

在 pH=5 的溶液中的 η_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
$$\frac{1-\alpha}{\alpha}\varphi_1$$
 = 常数 + $\frac{1-\alpha}{\alpha}\frac{RT}{F}\ln c_{\dot{\mathbb{S}}}$ 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、
$$H^+ + e \rightarrow \frac{1}{2}H_2$$
,设温度为 $25^{\circ}C$

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

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

4、 检测出少量 OH , 说明步骤 (A) 比 (B) 快

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

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

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

对
$$(B)$$
步骤有: $\overleftarrow{j_B} = FKc_{OH}^s \exp\left(\frac{\beta F\Delta \varphi}{RT}\right) = FKc_{OH}^0 \exp\left(\frac{F\Delta \varphi}{RT}\right) \cdot \exp\left(\frac{\beta F\Delta \varphi}{RT}\right)$

ਪੋਲ੍ਹ
$$\beta = 0.5$$
 , $\dot{j}_B = FKc_{OH}^0 \exp\left(\frac{3}{2}\frac{F\Delta\varphi}{RT}\right)$;

取对数:
$$\Delta \varphi =$$
常数 $+ \frac{2RT}{3E} \ln \frac{\dot{j}_B}{\dot{j}_B}$, 由于 $j_{\stackrel{.}{\bowtie}} = \frac{\dot{j}_B}{\dot{j}_B}$,

$$\therefore \Delta \varphi = 常数 + \frac{2RT}{3F} \ln j_{\stackrel{\circ}{\bowtie}} = 常数 + \frac{4.6RT}{3F} \log j_{\stackrel{\circ}{\bowtie}} , \quad Db = \frac{4.6RT}{3F} , \quad 5$$
 与实验值吻合。

5、 由于 $25^{o}C$ 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。

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

$$\varphi = \varphi_{\Psi} - \eta_{c} = \frac{2.3RT}{F} \log a_{H^{+}} - (a + b \log j) = 0.375V$$