1        $K = K_{\text{KCl}} + K_{\text{H}_2\text{O}} = \dfrac{c\lambda_{\text{KCl}}}{1000} + K_{\text{H}_2\text{O}} = \dfrac{0.001 \times 141.3}{1000} + 1.0 \times 10^{-6} = 142.3 \times 10^{-6} \Omega^{-1} cm^{-1}$

2        $\lambda_i = F\dfrac{V_i}{E}$ $V_i = \dfrac{\lambda_i E}{F}$ $V_{H^+} = 0.0288 cm \cdot s^{-1}$ $V_{K^+} = 0.0050 cm \cdot s^{-1}$ $V_{Cl^-} = 0.0051 cm \cdot s^{-1}$

3        $\lambda_{o,H_2O} = \lambda_{o,KOH} + \lambda_{o,HCl} - \lambda_{o,KCl} = 550.62 \Omega^{-1} cm^2 \cdot eq^{-1}$,

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

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

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

   2          $\lambda_{o,K^+} + \lambda_{o,Cl^-} = 142.82 \Omega^{-1} cm^2 \cdot mol^{-1}$ $\lambda_{o,Na^+} + \lambda_{o,Cl^-} = 126.45 \Omega^{-1} cm^2 \cdot mol^{-1}$

  KCl   NaCl λ_{o,Cl^-}

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

5        $Cu(OH)^2 == Cu^{2+} + 2OH^-$, $c_{Cu^{2+}} = y$ $c_{OH^-} = 2y$ $K_S = 4y^3$

  $u = \Sigma u_i = K_{H_2O} + 10^{-3}[y\lambda_{Cu^{2+}} + 2y\lambda_{OH^-}]$ λ_o λ $y = 1.36 \times 10^{-4} mol/dm^3$

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

6        $AgIO_3 == Ag^+ + IO_3^-$ $c_{Ag^+} = y$ $c_{IO_3^-} = y$ $K_S = y^2$ $K = \Sigma K_i = K_{H_2O} + 10^{-3}$ $y\lambda_{Ag^+} + y\lambda_{IO_3^-}$

            λ_0 $= K_{H_2O} + 10^{-3} y \lambda_{AgIO_3}$

  $y = \dfrac{1.30 \times 10^{-5} - 1.1 \times 10^{-6}}{68.4} \times 10^3 = 1.74 \times 10^{-4} mol/L$; $K_S = y^2 = 3.03 \times 10^{-8} (mol/L)^2$

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

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

8           $IR = iS \cdot \dfrac{l}{KS} = \dfrac{il}{K}$, $K = \dfrac{\lambda c}{1000}$, $IR = \dfrac{il \cdot 1000}{\lambda c} = \dfrac{5 \times 10^{-3} \times 10 \times 10^3}{126 \times 0.5} \approx 0.79V$

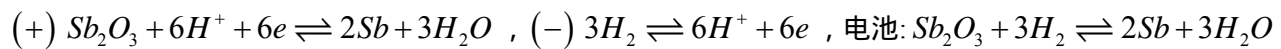9 $\log \gamma_{\pm} = -0.5115 |Z_+||Z_-|\sqrt{I}$ $25\,^{\circ}C$

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

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

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

1

$$(+)\ Sb_2O_3 + 6H^+ + 6e \rightleftharpoons 2Sb + 3H_2O \quad (-)\ 3H_2 \rightleftharpoons 6H^+ + 6e \qquad : Sb_2O_3 + 3H_2 \rightleftharpoons 2Sb + 3H_2O$$

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

$$\varphi_+ = \varphi_{Sb}^0 + \frac{2.3RT}{6F}\log a_{H^+}^6 = \varphi_{Sb}^0 + \frac{2.3RT}{F}\log a_{H^+} \qquad \varphi_- = \frac{2.3RT}{F}\log a_{H^+}$$

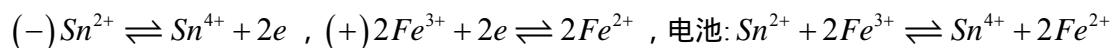$$\therefore E = \varphi_+ - \varphi_- = \varphi_{Sb}^0 = E^0 = 0.0143V$$

2      $(+)\ 4H^+ + O_2 + 4e \rightleftharpoons 2H_2O \quad (-)\ 2H_2 \rightleftharpoons 4H^+ + 4e \qquad : 2H_2 + O_2 \rightleftharpoons 2H_2O$
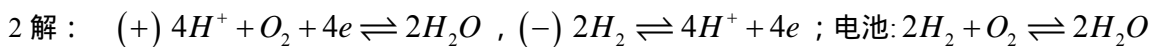
$$E = E^0 + \frac{2.3RT}{4F}\log\frac{P_{H_2} P_{O_2}}{a_{H_2O}^2} = E^0$$

$$\varphi_+^0 = 1.229V \quad \varphi_-^0 = 0.000V \quad \therefore E = \varphi_+^0 - \varphi_-^0 = 1.229V$$

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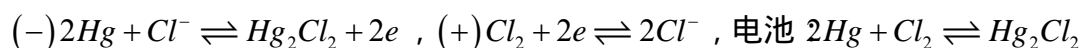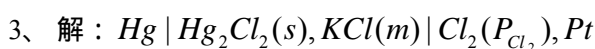
$$E = E^0 + \frac{2.3RT}{2F}\log\frac{C_{Sn^{2+}} C_{Fe^{3+}}^2}{C_{Sn^{4+}} C_{Fe^{2+}}^2} = (0.771-0.15) + \frac{0.0591}{2}\log\frac{0.001\times(0.01)^2}{0.01\times(0.001)^2} = 0.6505V$$

$$(-)Ag \rightleftharpoons Ag^+(0.1m) + e \quad (+)Ag^+(1m) + e \rightleftharpoons Ag \qquad Ag^+(1m) \to Ag^+(0.1m)$$
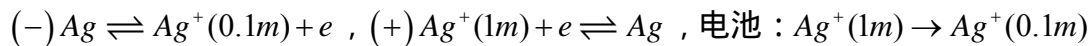
$$E = E^0 + \frac{2.3RT}{F}\log\frac{a_{Ag^+(1m)}}{a_{Ag^+(0.1m)}} \qquad E^0 = 0$$

$$1m\ AgNO_3 \quad \gamma_{\pm} = 0.4V \quad 0.1m\ AgNO_3 \quad \gamma_{\pm} = 0.72V \quad \therefore E = \frac{2.3RT}{F}\log\frac{1\times 0.4}{0.1\times 0.72} = 0.044V$$

3      $Hg \mid Hg_2Cl_2(s), KCl(m) \mid Cl_2(P_{Cl_2}), Pt$

$$(-)2Hg + Cl^- \rightleftharpoons Hg_2Cl_2 + 2e \quad (+)Cl_2 + 2e \rightleftharpoons 2Cl^- \qquad 2Hg + Cl_2 \rightleftharpoons Hg_2Cl_2$$

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

$E \quad a_{Cl^-}$

$$E = \varphi_+ - \varphi_- \qquad E = \varphi_+^0 - \varphi_-^0 \qquad a_{Cl^-} \qquad \varphi_+ \qquad \varphi \qquad E = \varphi_+ - \varphi$$

4 $\qquad Pt, H_2(1atm)\,|\,HCl(a_{H^+}=1)\,\|\,AgNO_3(m)\big|Ag$

$(-)H_2 \rightleftharpoons 2H^+ + 2e \quad (+)2Ag^+ + 2e \rightleftharpoons 2Ag \qquad H_2 + 2Ag^+ \rightleftharpoons 2H^+ + 2Ag$

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

$$Hg\,|\,Hg_2Cl_2(s), KCl(\quad)\,\|\,AgNO_3(m)\big|Ag \quad \varphi_{Ag/Ag^+}^0 = E + \varphi \quad - \frac{2.3RT}{F}\log(m_{Ag^+}\gamma_\pm)$$

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

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

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

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

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

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

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

$$\therefore \varphi_+ = \varphi_+^0 - \frac{2.3RT}{F}\log a_{Cl^-} \qquad \varphi_+^0 = 0.2224V \quad \gamma_\pm = 0.79V$$

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

7 $\qquad E_a = \frac{2.3RT}{F}\log\frac{1}{a_{Cl^-}''} - \frac{2.3RT}{F}\log\frac{1}{a_{Cl^-}'} = \frac{2.3RT}{F}\log\frac{a_{Cl^-}'}{a_{Cl^-}''} \qquad a''=0.01m \quad a'=0.1m$
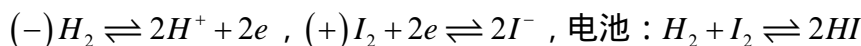
$$a_\pm' = 0.1 \times 0.78 = 0.078, (a_\pm' = a_{Cl^-}') \qquad a_\pm'' = 0.01 \times 0.904 = 0.00904, (a_\pm'' = a_{Cl^-}'')$$

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

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

$$E_a = 0.0591V, E_b = 0.046V \qquad \varphi = E_b - E_a = -0.01V$$

8 $\qquad Pt, H_2(1atm)\,|\,HI(a\ =1)\,|\,I_2(s), Pt$

$$(-)H_2 \rightleftharpoons 2H^+ + 2e \quad (+)I_2 + 2e \rightleftharpoons 2I^- \qquad H_2 + I_2 \rightleftharpoons 2HI$$

$$E = E^0 - \frac{2.3RT}{2F}\log(a_{HI})^2 = E^0 \quad E^0 = 0.5346 - 0.13\times10^{-3}\times(35-25) = 0.5333V$$

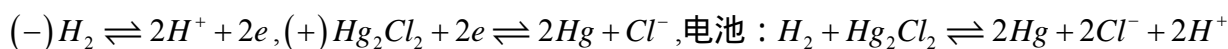$$\because E > 0, \therefore$$

$$\Delta G^0 = -nFE^0 = -RT\ln K = -2\times96500\times0.5333 = -102.9kJ$$

$$E^0 = \frac{RT}{nF}\ln K \quad \ln K = \frac{2\times96500\times0.5333}{8.314\times298} = 40.19 \quad K = 2.86\times10^{17}$$

$$E \qquad \Delta G^{0\prime} = \frac{1}{2}\Delta G^0 = -51.5kJ \quad K' = \sqrt{K} = 5.35\times10^8$$

9   :

$$(-)H_2 \rightleftharpoons 2H^+ + 2e, (+)Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + Cl^-, \qquad H_2 + Hg_2Cl_2 \rightleftharpoons 2Hg + 2Cl^- + 2H^+$$
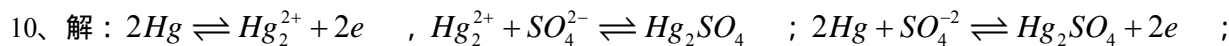
$$E = E^0 - \frac{2.3RT}{2F}\log(a_{H^+}^2 a_{Cl^-}^2), \qquad a_{Cl^-} = 0.79\times0.1 \quad -\frac{2.3RT}{F}\log a_{H^+} = E - E^0 + \frac{2.3RT}{F}\log a_{Cl^-}$$

$$-\log a_{H^+} \approx 6.9 \qquad \log a_{H^+} + \log a_{OH^-} = 14 \qquad a_{OH^-} = 10^{-7.1} = 7.94\times10^{-8}$$

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

$$\therefore pH = \frac{\varphi_+ - E}{0.0591} = 6.9 \quad a_{OH^-} = 10^{-7.1} = 7.94\times10^{-8}(mol/dm^3)$$

10      $2Hg \rightleftharpoons Hg_2^{2+} + 2e \qquad Hg_2^{2+} + SO_4^{2-} \rightleftharpoons Hg_2SO_4 \qquad 2Hg + SO_4^{-2} \rightleftharpoons Hg_2SO_4 + 2e$
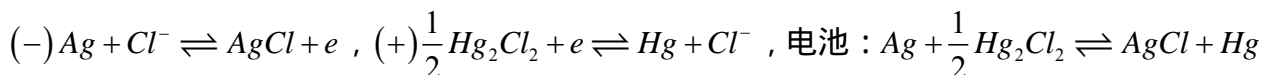
$$\varphi = \varphi_{Hg/Hg_2^{2+}}^0 + \frac{2.3RT}{2F}\log a_{Hg_2^{2+}} = \varphi_{Hg/Hg_2^{2+}}^0 + \frac{2.3RT}{2F}\log Ks - \frac{2.3RT}{2F}\log a_{SO_4^{2-}}$$

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

$$\therefore \varphi_{Hg/Hg_2SO_4,SO_4^{2-}}^0 = \varphi_{Hg/Hg_2^{2+}}^0 + \frac{2.3RT}{2F}\log Ks = 0.7986 + \frac{0.0591}{2}\log(6.5\times10^{-7}) = 0.638V$$

11

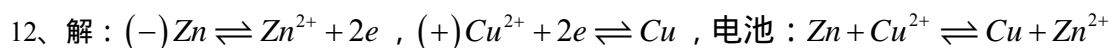$$(-)Ag + Cl^- \rightleftharpoons AgCl + e \quad (+)\frac{1}{2}Hg_2Cl_2 + e \rightleftharpoons Hg + Cl^- \qquad Ag + \frac{1}{2}Hg_2Cl_2 \rightleftharpoons AgCl + Hg$$

$$\Delta G = -nFE = -1\times96500\times0.0455 = -4.391kJ/mol$$

$$\Delta H = \Delta G + nFT\left(\frac{\partial E}{\partial T}\right)_P = -4391 + 1\times96500\times298\times0.338\times10^{-3} = 5.329\,kJ/mol$$

$$\Delta S = nFT\left(\frac{\partial E}{\partial T}\right)_P = 1\times96500\times298\times0.338\times10^{-3} = 32.617\,J/mol\cdot K$$

12       $(-)Zn \rightleftharpoons Zn^{2+} + 2e \quad (+)Cu^{2+} + 2e \rightleftharpoons Cu \qquad Zn + Cu^{2+} \rightleftharpoons Cu + Zn^{2+}$

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

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

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

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

13          $Cu^{2+} + 2e \rightleftharpoons Cu+ \quad \varphi_1^0 = 0.337V \qquad Cu^+ + e \rightleftharpoons Cu \quad \varphi_2^0 = 0.520V$

    =   - $\because \Delta G_3^0 = \Delta G_1^0 - \Delta G_2^0 = -2F\varphi_1^0 + \varphi_2^0 = -2F\varphi_3^0 \quad \therefore \varphi_3^0 = 2\varphi_1^0 - \varphi_2^0 = 0.337 \times 2 - 0.520 = 0.154V$

$$\Delta G_3^0 = -F\varphi_3^0 = -0.154 \times 96500 = -14861\,J/mol$$

$$\varphi^0 = \frac{RT}{nF}\ln K \qquad = \quad - \qquad K_3 = \frac{K_1}{K_2}$$

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

14          $(-)2H_2 \rightleftharpoons 4H^+ + 4e \quad (+)O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O \qquad 2H_2 + O_2 \rightleftharpoons 2H_2O(g)$

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

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

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

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

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

15          $Zn^{2+} \; Cu^{2+} \; H^+$

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

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

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

                 $Cu \quad H_2 \quad Zn$

Zn $-0.83V$ $i \to 0$

$$\therefore -0.83 = \varphi_{Cu^{2+}} + \frac{0.0591}{2}\log a_{Cu^{2+}} \quad \log a_{Cu^{2+}} = \frac{2}{0.0591}(-0.83-0.337) = -39.49 \quad a_{Cu^{2+}} = 3.24\times10^{-40}$$

$$C = \frac{a_{Cu^{2+}}}{\gamma_\pm} = \frac{3.24\times10^{-40}}{0.41} = 7.9\times10^{-40} \; mol/L$$

16       $\because Pb \rightleftharpoons Pb^{2+} + 2e \quad Pb^{2+} + 2F^- \rightleftharpoons PbF_2 \quad Pb + 2F^- \rightleftharpoons PbF_2 + 2e$

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

$$\log Ks = \frac{2F}{2.3RT}(\varphi_2^0 - \varphi_1^0) = \frac{2}{0.0591}(-0.3502+0.1263) = -7.58 \qquad\qquad Ks = 2.63\times10^{-8}$$

17   $(-)Zn \rightleftharpoons Zn^{2+} + 2e \quad (+)Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^- \qquad\qquad Hg_2Cl_2 + Zn \rightleftharpoons 2Hg + 2Cl^- + Zn^{2+}$

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

$$E_b = E^0 - \frac{0.0591}{2}\log 4(m_b\gamma_{\pm,b})^3, E_b - E_a = \frac{0.0591}{2}\log\frac{4(m_a\gamma_{\pm,a})^3}{4(m_b\gamma_{\pm,b})^3} = \frac{3\times0.0591}{2}\left[\log\frac{m_a}{m_b}+\log\frac{\gamma_{\pm,a}}{\gamma_{\pm,b}}\right],$$

$$\log\frac{\gamma_{\pm,a}}{\gamma_{\pm,b}} = \frac{2\times(E_b-E_a)}{3\times0.0591} - \log\frac{m_a}{m_b} = \frac{2\times(1.0044-1.10085)}{3\times0.0591} - \log\frac{0.25148}{0.00500} = -0.31, \qquad \frac{\gamma_{\pm,a}}{\gamma_{\pm,b}} = 0.49$$

18   a Cl^-

        b Cl^-

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

$$\log\frac{\gamma_{\pm,2}}{\gamma_{\pm,1}} = -\frac{FE_a}{2.3RT} - \log\frac{m_2}{m_1} = -\frac{0.0822}{2\times0.0591} - \log\frac{0.0082}{0.082} = 1.695 \quad \frac{\gamma_{\pm,2}}{\gamma_{\pm,1}} = 2.02$$

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

$$t_+ = -\frac{E_b}{2\frac{RT}{F}\ln\frac{m_2\gamma_{\pm,2}}{m_2\gamma_{\pm,1}}} = -\frac{E_b}{E_a} = \frac{57.9\times10^{-3}}{82.8\times10^{-3}} = 0.7044$$

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

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

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

$$= 1.33 - \frac{0.0591 \times 14}{6}pH + \frac{0.0591}{6}\log\frac{a_{Cr_2O_3^{2-}}}{a_{Cr^{3+}}^2} = 1.33 - 0.138pH - 0.00985\log\frac{a_{Cr_2O_3^{2-}}}{a_{Cr^{3+}}^2}$$
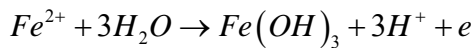
$$\varphi = \varphi^0 + \frac{2.3RT}{nF}\log\frac{a_A^a}{b_B^b} = 0.2681 - \frac{0.0591}{2}\log a_{Cl^-}^2 = 0.2681 - 0.0591\log a_{Cl^-}$$

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

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

20   : $pH = 7.68$

$8.7 < pH < 14.5 \qquad -0.85 < \varphi < -0.25 \qquad\qquad Fe(OH)_2$

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

21                      $a_i = 10^{-6}$

$Zn^{2+} + 2e \rightleftharpoons Zn$	$\varphi = -0.94V \qquad 2pH = -0.763 + 0.0295\log a_{Zn^{2+}}$
$Zn(OH)_2 + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O$	$pH = 8.48 \qquad 2pH = 10.96 - \log a_{Zn^{2+}}$
$ZnO_2^{2-} + 2H^+ \rightleftharpoons Zn(OH)_2$	$pH = 11.89 \qquad 2pH = 29.78 + \log a_{Zn^{2+}}$
$Zn(OH)_2 + 2H^+ + 2e \rightleftharpoons Zn + 2H_2O$	$\varphi = -0.437 - 0.0591pH$
$ZnO_2^{2-} + 4H^+ + 2e \rightleftharpoons Zn + 2H_2O$	$\varphi = 0.44 - 0.118pH + 0.0296\log a_{ZnO_2^{2-}} = 0.263 - 0.118pH$
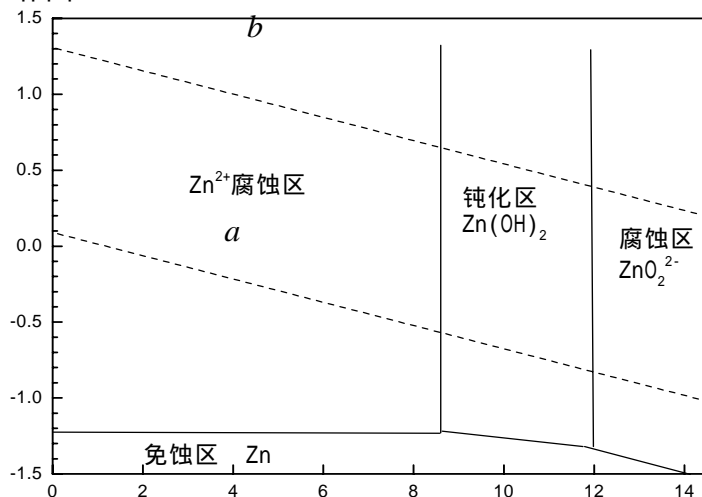
$\varphi = -0.82V \qquad\qquad 8.48 < pH < 11.89$

Zn

$\varphi = -1.0V \qquad\qquad pH < 11.89$

1          $E = \dfrac{q}{\varepsilon_0 \varepsilon_r}$ $:\varepsilon_0 = 8.85 \times 10^{-12}$, $E = \dfrac{2 \times 10^{-5} \times 10^{-4}}{8.85 \times 10^{-12} \times 40} = 5.6 \times 10^8 \, V/m$

2       $\varphi = -0.35V$ $\dfrac{d\sigma}{d\varphi} = \dfrac{\sigma_{(-0.2V)} - \sigma_{(-0.4V)}}{-0.2 - (-0.4)}$ -0.2~-0.4

$\dfrac{d\sigma}{d\varphi} = \dfrac{0.413 - 0.392}{-0.2 + 0.4} = 0.13 \, J/mV$ $q = -\dfrac{d\sigma}{d\varphi} = -0.13 \, C/m^2$
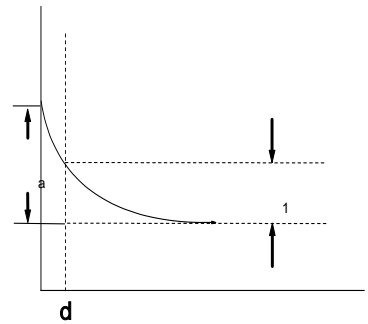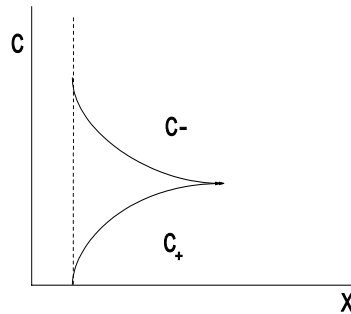
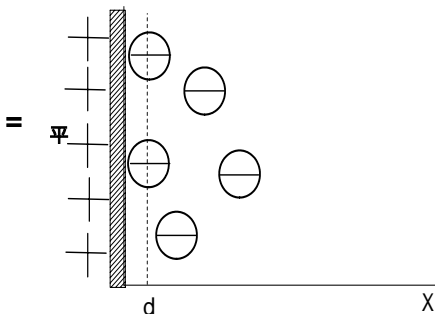3 $q = C\varphi = C(\varphi - \varphi_0) = 36 \times (-0.763 + 0.63) = -4.79 \, \mu C/cm^2$

  q Cd Cl^- $C = \dfrac{\varepsilon_0 \varepsilon_r}{d}$ $\varphi < \varphi_0$ $q > 0$

  Cl^- Cd q

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

4       $Ag^+ + e \rightleftharpoons Ag$ $\varphi = \varphi_0 + 0.591 \log(0.002) = 0.64V > \varphi_0$

5

$$\varphi_0 = 0 \qquad\qquad \varphi_1 = - \quad + \frac{2RT}{F}\ln\varphi_a - \frac{RT}{F}\ln C \qquad\qquad \varphi_1 = 0$$

6 $\qquad \varphi \geq \varphi_0 \qquad\qquad \sigma\downarrow Cd\uparrow \qquad\qquad q>0 \qquad q=0$

7 $\qquad\qquad Cd = \dfrac{dq}{d\varphi}$

$\varphi_a \qquad q_1 = -\dfrac{\partial\sigma}{\partial\varphi} \approx \dfrac{-\sigma_2+\sigma_3}{\varphi_a-(\varphi_a+b)} = \dfrac{\sigma_2-\sigma_3}{b}$

$(\varphi_a-b) \qquad q_2 = \dfrac{\sigma_1-\sigma_2}{\varphi_a-(\varphi_a-b)} = \dfrac{\sigma_1-\sigma_2}{b}$

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

$$q_1 \qquad\qquad \varphi_1 = \frac{(\varphi_a - b) + \varphi_a}{2} = \varphi_a - \frac{1}{2}b$$

$$q_2 \qquad\qquad \varphi_2 = \frac{(\varphi_a + b) + \varphi_a}{2} = \varphi_a + \frac{1}{2}b$$

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

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

8 $\qquad\qquad \varphi_a = \varphi - \varphi_0 = 0.11 - (-0.119) = 0.30V \quad \therefore \varphi_1 > 0 \qquad\qquad q \quad c$

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

$$\varphi_1 = -\frac{2RT}{F}\ln\frac{\varphi_a}{q}\sqrt{2\varepsilon_0\varepsilon_r RT} + \frac{2RT}{F}\ln\varphi_a - \frac{RT}{F}\ln c$$

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

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

$$c = 0.001\,mol/L \qquad \varphi_1 = 0.222V \quad \varphi_1 : \varphi_a = 0.222 : 0.3 > \frac{2}{3}$$

$$c = 0.1\,mol/L \qquad \varphi_1 = 0.1038V \quad \varphi_1 : \varphi_a = \frac{1}{3}$$

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

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

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

$$c = 0.1\,mol/L \qquad \varphi_1 \approx 0.1038V$$

9 $\qquad Cd \sim \varphi \qquad\qquad \varphi_0 = -0.37V \qquad\quad NaCl \qquad \varphi = -0.25 \sim -0.27V > \varphi_0$

$$NaCl \qquad Cl^- \qquad\qquad\qquad Cl^-$$

1        $Cu^{2+} + 2e \rightleftharpoons Cu$ $T = 25^{o}C$ $\varphi = \varphi^{0} + \dfrac{2.3RT}{2F}\log a_{Cu^{2+}} = 0.337 + \dfrac{2.3RT}{2F}10^{-7} \approx 0.13V$

$H^{+} + e \rightarrow \dfrac{1}{2}H_{2}$ $T = 25^{o}C$ $\gamma_{\pm} = 0.130$ $\eta_{a} = \varphi - \varphi$ $\eta_{c} = \varphi - \varphi$

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

$-0.28V$

2        $2H^{+} + 2e \rightarrow H_{2}$ $-\log a_{H^{+}} = 6.5$ $\therefore \eta_{c} = \varphi_{H^{+},} - \varphi = 0.0591\log a_{H^{+}} - (-1.23) \approx 0.846V$

3        $(-)Zn^{2+} + 2e \rightarrow Zn$ $(+)Zn \rightarrow Zn^{2+} + 2e$

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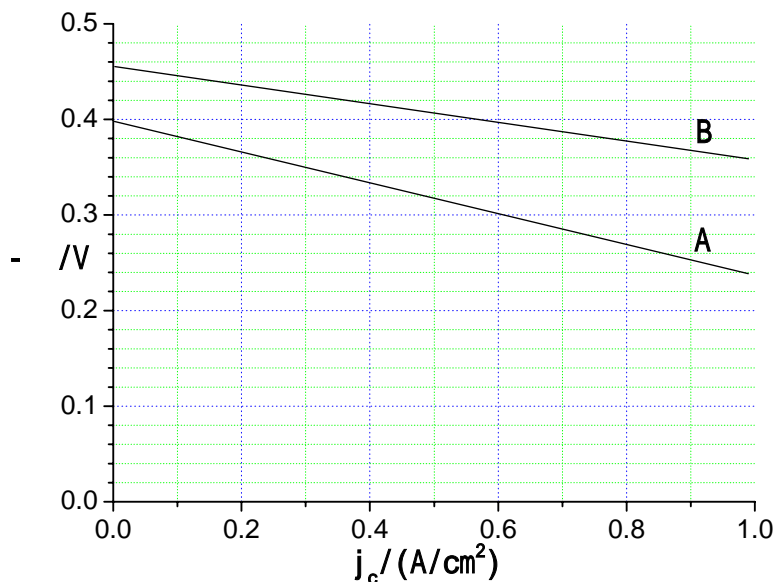
$2H^{+} + 2e \rightarrow H_{2}$

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

$\varphi_{c} > \varphi_{c}{}'$ $\varphi_{c} = -1.135V$ $\eta_{Zn} = \varphi_{Zn,} - \varphi_{c} = -0.817 - (-1.135) = 0.318V$

$V = \varphi_{a} - \varphi_{c} + IR = -0.817 - (-1.135) + 0.5 = 0.818V$

4   B   A   B

5   j_{1} j_{2} $j_{1} = nFv_{1} = nfKc\exp\left(-\dfrac{w_{1}}{RT}\right)$ $j_{2} = nFv_{2} = nFKc\exp\left(-\dfrac{w_{2}}{RT}\right)$

$\dfrac{j_{2}}{j_{1}} = \exp\left(\dfrac{w_{1} - w_{2}}{RT}\right) = \exp\left(-\dfrac{w_{1}}{RT}\right) = \exp\left(-\dfrac{4 \times 10^{3}}{8.31 \times 293}\right) \approx 0.193$ $j_{2} = 0.193 j_{1} = 18.6\, mA/cm^{2}$ 81%

6      $j \quad = nFv \quad = 2\times 96500\times 1\times 10^{-3} = 193\,A/m^2 \quad j \quad = nFv \quad = 2\times 96500\times 0.25 = 48250\,A/m^2$

$j = 193\,A/m^2$

$\because j = j \quad = 193\,A/m^2 \quad j \quad - j = 48250 - 193 = 48057\,A/m^2$

$\therefore j \quad \approx j \quad - j$

7   v_1 W_1 v_2 W_2

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

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

$17106\,J/mol$

8         $\varphi_c = \varphi_{Zn}^0 + \dfrac{2.3RT}{2F}\log\left(\gamma_\pm m_{Zn^{2+}}\right) = -0.763 + \dfrac{0.0591}{2}\log(0.33\times 1) = -0.77V \quad \varphi_a = \varphi_H^0 = 0$

$\because E = \varphi_a - \varphi_c = 0.777V \qquad V=1.24V \quad \therefore V > E$

Zn

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

1

            Cu

2               $j_{d1} \qquad j_{d2} \qquad j_{d3} \quad \because j_d = nFD\dfrac{c^0}{\delta} \quad \therefore j_{d3} \approx 2j_{d2}$

        $j_{d1} < j_{d3}$ $j_{d1} \neq j_{d2}$

3       $j_d = nFD\dfrac{c^0}{\delta} = \dfrac{4\times 96500\times 6\times 10^{-5}\times 0.1\times 10^{-3}}{5\times 10^{-2}} = 0.046\,A/cm^2$

4           $\left(Cd^{2+}\right)$ $t_{Cd^{2+}}$ j_c

         $j_c \propto \omega^{0.5}$

5
$$\begin{cases} j = j_d\left(\dfrac{c^0 - c^s}{c^0}\right)\cdots\cdots \\ j_d = nFDc^0/\delta \cdots\cdots\cdots \\ \delta = \dfrac{c^0 - c^s}{(dc/dx)_{x=0}}\cdots\cdots \end{cases}$$

$$j = nFD(dc/dx)_{x=0} = 2 \times 96500 \times 0.5 \times 10^{-5} \times 8 \times 10^{-2} = 0.077\,A/cm^2$$

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

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

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

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

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

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

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

8 $$t = \frac{n^2F^2\pi D\left(c^0\right)^2}{4v^2j^2} \quad \frac{4^2 \times 96500^2 \times 3.14 \times 1.2 \times 10^{-5} \times \left(0.1 \times 10^{-3}\right)^2}{4 \times 1 \times \left(0.5\right)^2} = 5.6 \times 10^{-2}s$$

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

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

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

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

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

13

10

$$\begin{cases} j = j_d\left(\dfrac{c^0 - c^s}{c^0}\right)\cdots\cdots \\ j_d = nFDc^0\big/\delta \quad\cdots\cdots\cdots \\ \delta = \dfrac{c^0 - c^s}{(dc/dx)_{x=0}}\cdots\cdots \end{cases}$$

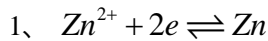$$j = FD\left(\frac{dc}{dx}\right)_{x=0} = 96500 \times 6 \times 10^{-5} \times 7 \times 10^{-2} = 0.405\,A\big/cm^2$$

$$\delta = \frac{c^0 - c^s}{(dc/dx)_{x=0}} = \frac{(1-0.1)\times 10^{-3}}{7 \times 10^{-2}} = 1.29 \times 10^{-2}\,cm$$
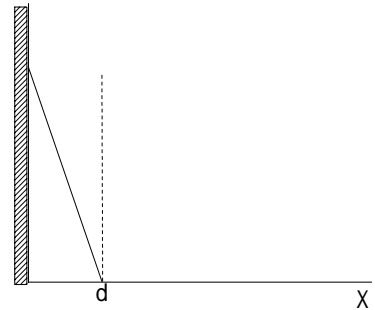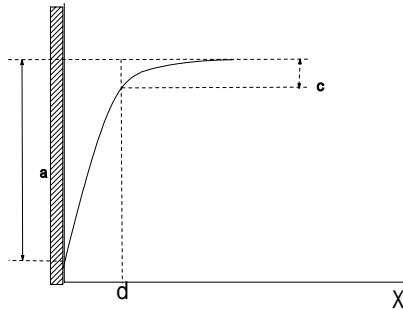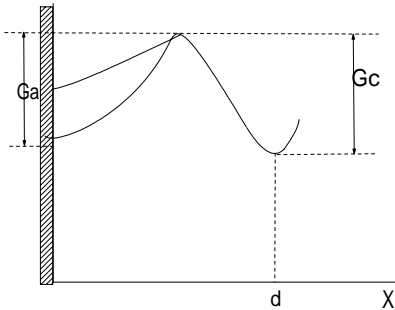
$$\eta = \varphi - \varphi = \frac{2.3RT}{F}\log\left(1 - \frac{j}{j_d}\right) \quad \log\left(1 - \frac{j}{j_d}\right) = \frac{\eta\,F}{2.3RT} = \frac{-0.059}{0.0591} = -1$$

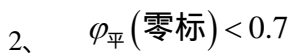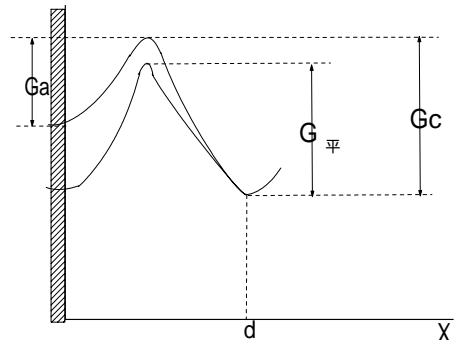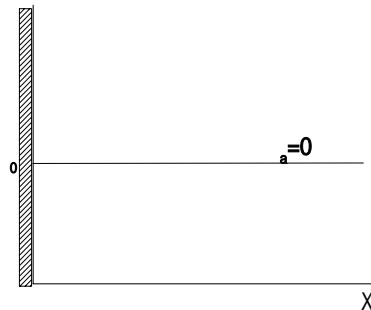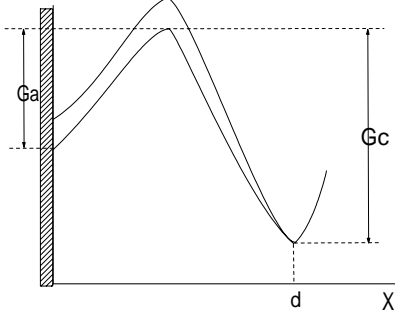$$c^s = c^0\left(1 - \frac{j}{j_d}\right) = 1 \times 10^1 = 0.1\,mol\big/L$$

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

$\Delta\varphi > 0$

$\varphi = \varphi_0$

2    $\varphi\ (\quad) < 0.7$

14

$$j_a = \overrightarrow{j} - \overleftarrow{j} = j^0 \left[\exp\left(\frac{\overrightarrow{\alpha} F \eta_a}{RT} \right) - \exp\left(-\frac{\overleftarrow{\alpha} F \eta_a}{RT} \right) \right] \qquad\qquad j_a = j^0 \left[\exp\left(\frac{\beta 2 F \eta_a}{RT} \right) - \exp\left(-\frac{\alpha 2 F \eta_a}{RT} \right) \right]$$

3      $NaCN$ $Zn(CN)_4^{2-}$

   j_1 (W)

4    $Ni^{2+} + 2e \rightarrow Ni$ Tafel $j_c >> j^0$

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

5                     $Zn \rightarrow Zn^{2+} + 2e$

$$\because \eta_a = 0.05V \qquad\qquad \overrightarrow{\alpha} = \frac{n}{\nu} - \overleftarrow{\alpha} = 1.1$$

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

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

             TAFEL $\left(\because j_a : j^0 \approx 50:1 \right)$

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

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

$$a_{Cu^{2+}} = 0.116 \, mol/L \qquad\qquad \varphi^0 = 0.3448V \qquad a_{Cu^{2+}} = 0.06 \, mol/L$$

$$\eta_c = \varphi - \varphi = -\frac{2.3RT}{\overrightarrow{\alpha} F} \log j^0 + \frac{2.3RT}{\overrightarrow{\alpha} F} \log j_c$$

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

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

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

15

j_c φ j j_d $j_d{}'$

8                        $j_c \gg j^0$ TAFEL η_c

$$\eta_c = \frac{2.3RT}{\overrightarrow{\alpha}F}\log\frac{j}{j^0} = 0.0591\left[\log 1 - \log\left(1\times10^{-9}\right)\right] = 0.532V \quad E = V_{j=0} = 0.832V$$

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

η_a $$j^0 = \frac{RTj_a}{nF\eta_a} = \frac{8.31\times298\times1}{2\times96500\times0.001} = 12.83\,A\big/cm^2$$

j^0 j^0 j^0
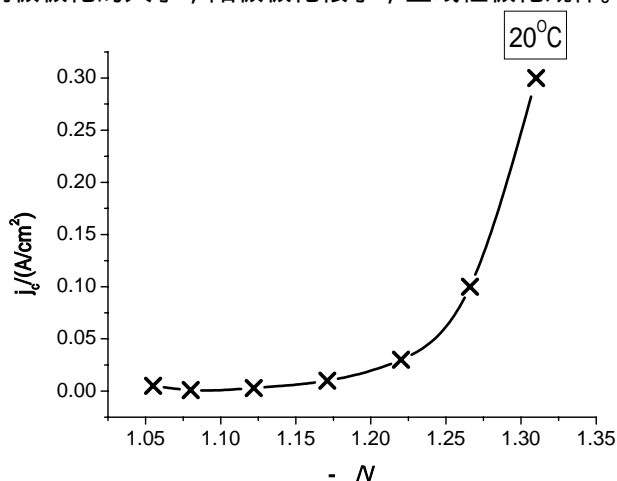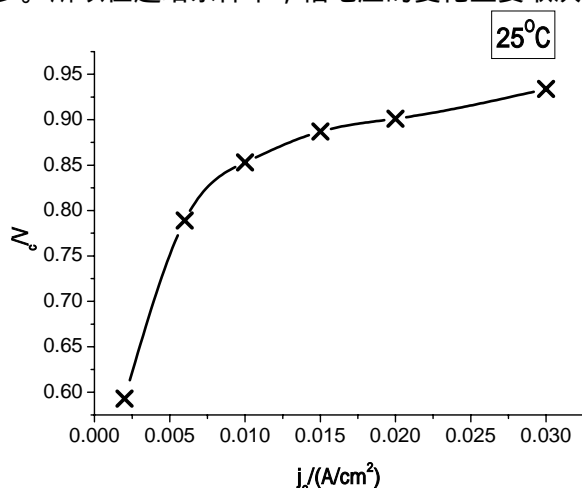
9                        $2H_2O + O_2 + 4e \rightarrow 4OH^-$

$\log j = 0$ $\eta_c = 0.36V$ $\therefore a = 0.36V$ TAFEL $tg\alpha$

$$\therefore b = tg\alpha = \frac{\Delta\varphi}{\Delta\log j} = 0.093 \quad \log j^0 = -\frac{a}{b} = -\frac{0.36}{0.093} = -3.87 \quad \therefore j^0 = 1.35\times10^{-4}\,A\big/cm^2$$

10                        $\log j = 0$ $\eta_c = 1.185V$ $\therefore a = 1.185V$ TAFEL $tg\alpha$

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

$$\log j^0 = -\frac{a}{b} = -\frac{1.185}{0.289} = -4.10 \quad \therefore j^0 = 7.94\times10^{-5}\,A\big/cm^2$$

1    $\eta_H = \varphi - \varphi = \frac{2.3RT}{F}\log a_{H^+} - \varphi = 0.0581\log\left(0.5\times2\times0.154\right) - \left(-0.479\right) = 0.432V \quad \left(\gamma_\pm = 0.154\right)$

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

2    $\because \eta_H = \qquad -\frac{1-\alpha}{\alpha}\varphi_1 + \frac{RT}{\alpha F}\ln j$

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

$pH = 5 \qquad\qquad \eta_H \qquad pH = 3 \qquad 0.128V \qquad\qquad pH$

$$\frac{1-\alpha}{\alpha}\varphi_1 = \qquad + \frac{1-\alpha}{\alpha}\frac{RT}{F}\ln c \qquad\qquad pH = 3 \qquad\qquad\qquad pH = 5$$

3    $H^+ + e \to \frac{1}{2}H_2 \qquad\qquad 25^{O}C$

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

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

4   OH (A) (B)

$(B) \qquad\qquad\qquad (A) \qquad\qquad\qquad (A) \qquad \varphi = \varphi^0 + \frac{RT}{F}\ln\frac{a_{OH}^0 a_{H^+}^0}{a_{H_2O}^0} \quad \varphi = \varphi^0 + \frac{RT}{F}\ln\frac{a_{OH}^s a_{H^+}^s}{a_{H_2O}^s}$

$$a_{H_2O}^0 \approx a_{H_2O}^s \quad a_{H^+}^s \approx a_{H^+}^0 \left(\because pH \qquad\right)$$

$$\therefore \varphi - \varphi = \Delta\varphi = \frac{RT}{F}\ln\frac{a_{OH}^s}{a_{OH}^0} \qquad\qquad c_{OH}^s = c_{OH}^0 \exp\left(\frac{F\Delta\varphi}{RT}\right)$$

$(B) \qquad\qquad \overleftarrow{j_B} = FKc_{OH}^s \exp\left(\frac{\beta F\Delta\varphi}{RT}\right) = FKc_{OH}^0 \exp\left(\frac{F\Delta\varphi}{RT}\right) \bullet \exp\left(\frac{\beta F\Delta\varphi}{RT}\right)$

$$\beta = 0.5 \quad \overleftarrow{j_B} = FKc_{OH}^0 \exp\left(\frac{3}{2}\frac{F\Delta\varphi}{RT}\right)$$

$$\Delta\varphi = \qquad + \frac{2RT}{3F}\ln\overleftarrow{j_B} \qquad j = \overleftarrow{j_B}$$

$$\therefore \Delta\varphi = \qquad + \frac{2RT}{3F}\ln j = \qquad + \frac{4.6RT}{3F}\log j \qquad b = \frac{4.6RT}{3F}$$

5         $25^{O}C$ TAFEL $b \approx 0.118V$

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

$$\varphi = \varphi - \eta_c = \frac{2.3RT}{F}\log a_{H^+} - \left(a + b\log j\right) = 0.375V$$