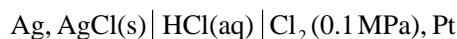


第 17 章 电化学

习题解答

1. 25℃时电池



的电池反应电势为 1.1362 V, 电池反应电势的温度系数为 $-5.95 \times 10^{-4} \text{ V} \cdot \text{K}^{-1}$ 。试计算电池反应



在 25℃时的 $\Delta_r G_m$ 、 $\Delta_r S_m$ 和 $\Delta_r H_m$ 。

解: $\Delta_r G_m = -zFE$

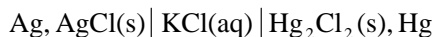
$$= -(1 \times 96485 \times 1.1362) \text{ J} \cdot \text{mol}^{-1} = -109.63 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m = zF \left(\frac{\partial E}{\partial T} \right)_p = [1 \times 96485 \times (-5.95 \times 10^{-4})] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

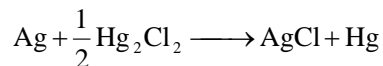
$$= -57.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m = \Delta_r G_m + T \Delta_r S_m = (-109.63 \times 10^3 - 298.15 \times 57.4) \text{ J} \cdot \text{mol}^{-1}$$
$$= -126.74 \text{ kJ} \cdot \text{mol}^{-1}$$

2. 计算电池



在 25℃时的电池反应电势和温度系数。已知 25℃时反应



的 $\Delta_r H_m^\circ = 5.54 \text{ kJ} \cdot \text{mol}^{-1}$, 各物质的标准摩尔熵为: Ag, $42.55 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; AgCl, $96.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; Hg, $76.02 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; Hg_2Cl_2 , $192.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ 。

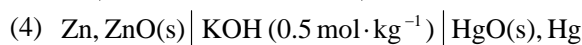
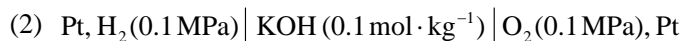
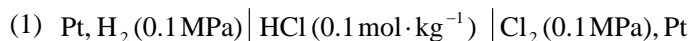
解: $\Delta_r S_m^\circ = \sum \nu_B S_B^\circ$

$$= \left(1 \times 96.2 + 1 \times 76.02 - 1 \times 42.55 - \frac{1}{2} \times 192.5 \right) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$= 33.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\begin{aligned}
 \Delta_r G_m &= \Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T \Delta_r S_m^\ominus \\
 &= (5.54 \times 10^3 - 298.15 \times 33.4) \text{ J} \cdot \text{mol}^{-1} \\
 &= -4.42 \text{ kJ} \cdot \text{mol}^{-1} \\
 E &= -\frac{\Delta_r G_m}{zF} = -\left(\frac{-4.42 \times 10^3}{1 \times 96485}\right) \text{ V} = 0.0458 \text{ V} \\
 \left(\frac{\partial E}{\partial T}\right)_p &= \left(\frac{\partial E^\ominus}{\partial T}\right)_p = \frac{\Delta_r S_m^\ominus}{zF} = \left(\frac{33.4}{1 \times 96485}\right) \text{ V} \cdot \text{K}^{-1} \\
 &= 0.346 \times 10^{-3} \text{ V} \cdot \text{K}^{-1}
 \end{aligned}$$

3. 写出下列电池的电极反应和电池反应:



解: (1) 负极: $\text{H}_2(0.1 \text{ MPa}) \longrightarrow 2\text{H}^+(0.1 \text{ mol} \cdot \text{kg}^{-1}) + 2\text{e}^-$

正极: $\text{Cl}_2(0.1 \text{ MPa}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(0.1 \text{ mol} \cdot \text{kg}^{-1})$

电池: $\text{H}_2(0.1 \text{ MPa}) + \text{Cl}_2(0.1 \text{ MPa}) \longrightarrow$
 $2\text{H}^+(0.1 \text{ mol} \cdot \text{kg}^{-1}) + 2\text{Cl}^-(0.1 \text{ mol} \cdot \text{kg}^{-1})$

(2) 负极: $2\text{H}_2(0.1 \text{ MPa}) + 4\text{OH}^-(0.1 \text{ mol} \cdot \text{kg}^{-1}) \longrightarrow 4\text{H}_2\text{O} + 4\text{e}^-$

正极: $\text{O}_2(0.1 \text{ MPa}) + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-(0.1 \text{ mol} \cdot \text{kg}^{-1})$

电池: $2\text{H}_2(0.1 \text{ MPa}) + \text{O}_2(0.1 \text{ MPa}) \longrightarrow 2\text{H}_2\text{O}$

(3) 负极: $\text{Zn} \longrightarrow \text{Zn}^{2+}(0.1 \text{ mol} \cdot \text{kg}^{-1}) + 2\text{e}^-$

正极: $\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Hg} + 2\text{Cl}^-(0.2 \text{ mol} \cdot \text{kg}^{-1})$

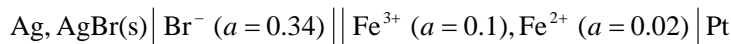
电池: $\text{Zn} + \text{Hg}_2\text{Cl}_2 \longrightarrow$
 $2\text{Hg} + \text{Zn}^{2+}(0.1 \text{ mol} \cdot \text{kg}^{-1}) + 2\text{Cl}^-(0.2 \text{ mol} \cdot \text{kg}^{-1})$

(4) 负极: $\text{Zn} + 2\text{OH}^-(0.5 \text{ mol} \cdot \text{kg}^{-1}) \longrightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-$

正极: $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{Hg} + 2\text{OH}^-(0.5 \text{ mol} \cdot \text{kg}^{-1})$

电池: $\text{Zn} + \text{HgO} \longrightarrow \text{Hg} + \text{ZnO}$

4. 计算电池



在 25℃ 时的电池反应电势。

解：负极： $\text{Ag} + \text{Br}^- (a = 0.34) \longrightarrow \text{AgBr} + \text{e}^-$

正极： $\text{Fe}^{3+} (a = 0.1) + \text{e}^- \longrightarrow \text{Fe}^{2+} (a = 0.02)$

电池： $\text{Ag} + \text{Br}^- (a = 0.34) + \text{Fe}^{3+} (a = 0.1) \longrightarrow$

$\text{AgBr} + \text{Fe}^{2+} (a = 0.02)$

$$E^\circ = E^\circ \{ \text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt} \} - E^\circ \{ \text{Br}^- | \text{AgBr(s)}, \text{Ag} \}$$

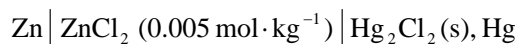
$$= (0.771 - 0.07116) \text{ V} = 0.700 \text{ V}$$

$$E = E^\circ - \frac{RT}{zF} \ln \frac{a_{\text{Fe}^{2+}}}{a_{\text{Br}^-} a_{\text{Fe}^{3+}}}$$

$$= \left(0.700 - 0.05916 \times \lg \frac{0.02}{0.34 \times 0.1} \right) \text{ V}$$

$$= 0.714 \text{ V}$$

5. 25℃ 时电池



的电池反应电势为 1.227 V, $0.005 \text{ mol} \cdot \text{kg}^{-1}$ ZnCl_2 溶液的离子平均活度因子 $\gamma_{\pm} = 0.789$ 。计算该电池在 25℃ 时电池反应的标准电势。

解：负极： $\text{Zn} \longrightarrow \text{Zn}^{2+} (0.005 \text{ mol} \cdot \text{kg}^{-1}) + 2\text{e}^-$

正极： $\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Hg} + 2\text{Cl}^- (0.010 \text{ mol} \cdot \text{kg}^{-1})$

电池： $\text{Zn} + \text{Hg}_2\text{Cl}_2 \longrightarrow$

$2\text{Hg} + \text{Zn}^{2+} (0.005 \text{ mol} \cdot \text{kg}^{-1}) + 2\text{Cl}^- (0.010 \text{ mol} \cdot \text{kg}^{-1})$

$$E^\circ = E + \frac{RT}{zF} \ln a_{\text{Zn}^{2+}} a_{\text{Cl}^-}^2 = E + \frac{RT}{zF} \ln \left[4 \left(\frac{b}{b^\circ} \right)^3 \gamma_{\pm}^3 \right]$$

$$= \left[1.227 + \frac{0.05916}{2} \lg (4 \times 0.005^3 \times 0.789^3) \right] \text{ V}$$

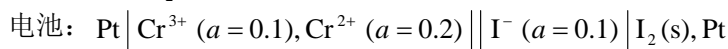
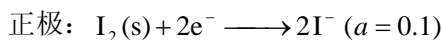
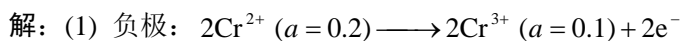
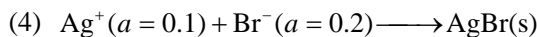
$$= 1.031 \text{ V}$$

6. 将下列反应设计成电池，并计算 25℃ 时电池反应的电势。已知 $E^\circ \{ \text{Cr}^{3+}, \text{Cr}^{2+} | \text{Pt} \} = -0.407 \text{ V}$ ，其他数据可查表 17-3。

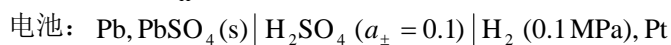
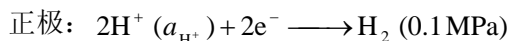
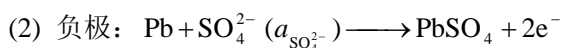
(1) $2\text{Cr}^{2+} (a = 0.2) + \text{I}_2(\text{s}) \longrightarrow 2\text{Cr}^{3+} (a = 0.1) + 2\text{I}^- (a = 0.1)$

(2) $\text{Pb}(\text{s}) + \text{H}_2\text{SO}_4 (a_{\pm} = 0.1) \longrightarrow \text{PbSO}_4(\text{s}) + \text{H}_2 (0.1 \text{ MPa})$

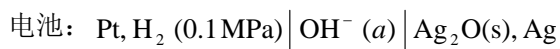
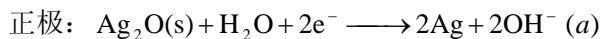
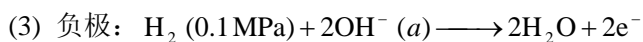
(3) $\text{H}_2 (0.1 \text{ MPa}) + \text{Ag}_2\text{O}(\text{s}) \longrightarrow 2\text{Ag}(\text{s}) + \text{H}_2\text{O}(\text{l})$



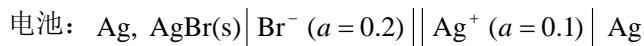
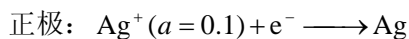
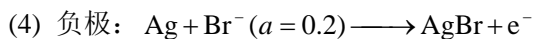
$$\begin{aligned} E &= E^\ominus - \frac{RT}{zF} \ln \frac{a_{\text{Cr}^{3+}}^2 a_{\text{I}^-}^2}{a_{\text{Cr}^{2+}}^2} \\ &= \left[(0.5353 + 0.407) - 0.05916 \lg \left(\frac{0.1 \times 0.1}{0.2} \right) \right] \text{V} \\ &= 1.019 \text{ V} \end{aligned}$$



$$\begin{aligned} E &= E^\ominus - \frac{RT}{zF} \ln \frac{p_{\text{H}_2} / p^\ominus}{a_{\text{H}^+}^2 \cdot a_{\text{SO}_4^{2-}}} = E^\ominus - \frac{RT}{zF} \ln \frac{p_{\text{H}_2} / p^\ominus}{a_{\pm}^3} \\ &= \left[(0 + 0.3590) - \frac{0.05916}{2} \lg \frac{1}{0.1^3} \right] \text{V} \\ &= 0.2703 \text{ V} \end{aligned}$$

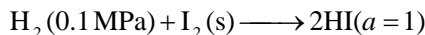


$$\begin{aligned} E &= E^\ominus - \frac{RT}{zF} \ln \frac{1}{p_{\text{H}_2} / p^\ominus} = (0.342 + 0.8277) \text{ V} \\ &= 1.170 \text{ V} \end{aligned}$$

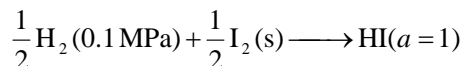


$$\begin{aligned}
 E &= E^\ominus - \frac{RT}{zF} \ln \frac{1}{a_{\text{Ag}^+} \cdot a_{\text{Br}^-}} \\
 &= \left[(0.7994 - 0.07116) - 0.05916 \lg \left(\frac{1}{0.1 \times 0.2} \right) \right] \text{V} \\
 &= 0.6277 \text{ V}
 \end{aligned}$$

7. 试为反应



设计电池, 并计算 25℃时 (1) 电池反应的标准电势 E^\ominus ; (2) 标准摩尔反应吉布斯函数 $\Delta_r G_m^\ominus$; (3) 标准平衡常数 K^\ominus ; (4) 若将上述反应写成



所得结果有何变化?

解: 负极: $\text{H}_2(0.1 \text{ MPa}) \longrightarrow 2\text{H}^+(a) + 2\text{e}^-$

正极: $\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(a)$

电池: $\text{Pt}, \text{H}_2(0.1 \text{ MPa}) | \text{HI}(a=1) | \text{I}_2(\text{s}), \text{Pt}$

$$(1) E^\ominus = E^\ominus \{ \text{I}^- | \text{I}_2(\text{s}), \text{Pt} \} - E^\ominus \{ \text{H}^+ | \text{H}_2, \text{Pt} \} = 0.5353 \text{ V}$$

$$\begin{aligned}
 (2) \Delta_r G_m^\ominus &= -zFE^\ominus = -(2 \times 96485 \times 0.5353) \text{ J} \cdot \text{mol}^{-1} \\
 &= -103.3 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

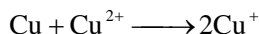
$$\begin{aligned}
 (3) K^\ominus &= \exp \left(-\frac{\Delta_r G_m^\ominus}{RT} \right) = \exp \left(-\frac{-103.3 \times 10^3}{8.3145 \times 298.15} \right) \\
 &= 1.25 \times 10^{18}
 \end{aligned}$$

$$(4) E^\ominus = 0.5353 \text{ V}$$

$$\Delta_r G_m^\ominus = -51.65 \text{ kJ} \cdot \text{mol}^{-1}$$

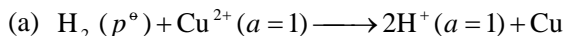
$$K^\ominus = 1.12 \times 10^9$$

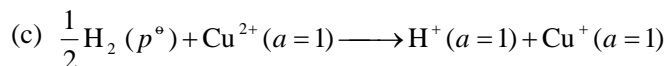
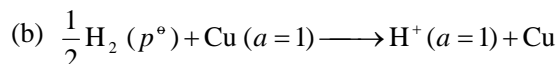
8. 试利用表 17-3 中的 $E^\ominus \{ \text{Cu}^{2+} | \text{Cu} \}$ 和 $E^\ominus \{ \text{Cu}^+ | \text{Cu} \}$ 数据, 求 25℃时的 $E^\ominus \{ \text{Cu}^{2+}, \text{Cu}^+ | \text{Pt} \}$, 并计算反应



在 25℃时的标准平衡常数。

解: 三个电极对应的电池反应为:





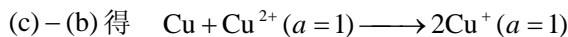
$$\Delta_r G_m^\ominus (c) = \Delta_r G_m^\ominus (a) - \Delta_r G_m^\ominus (b)$$

$$\text{即} \quad -FE^\ominus \{ \text{Cu}^{2+}, \text{Cu}^+ | \text{Pt} \} = -2FE^\ominus \{ \text{Cu}^{2+} | \text{Cu} \} - (-FE^\ominus \{ \text{Cu}^+ | \text{Cu} \})$$

$$\therefore E^\ominus \{ \text{Cu}^{2+}, \text{Cu}^+ | \text{Pt} \} = 2E^\ominus \{ \text{Cu}^{2+} | \text{Cu} \} - E^\ominus \{ \text{Cu}^+ | \text{Cu} \}$$

$$= (2 \times 0.3417 - 0.521) \text{V}$$

$$= 0.162 \text{V}$$



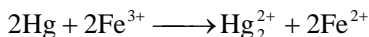
$$E^\ominus = E^\ominus \{ \text{Cu}^{2+}, \text{Cu}^+ | \text{Pt} \} - E^\ominus \{ \text{Cu}^+ | \text{Cu} \}$$

$$= (0.162 - 0.521) \text{V}$$

$$= -0.359 \text{V}$$

$$K^\ominus = \exp\left(\frac{zFE^\ominus}{RT}\right) = \exp\left[\frac{1 \times 96485 \times (-0.359)}{8.3145 \times 298.15}\right] = 8.5 \times 10^{-7}$$

9. 试由表 17-3 的数据计算反应



在 25℃ 时的标准平衡常数。若所有物质均处于标准状态，指出反应进行的方向。

$$\text{解: } K^\ominus = \exp\left(\frac{zFE^\ominus}{RT}\right) = \exp\left(\frac{2 \times 96485 \times (0.771 - 0.7971)}{8.3145 \times 298.15}\right)$$

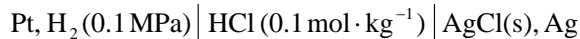
$$= 0.13$$

若所有物质均处于标准状态，则

$$E = E^\ominus = (0.771 - 0.7971) \text{V} = -0.026 \text{V} < 0$$

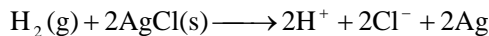
\therefore 反应由右向左进行。

10. 25℃ 时，电池



的电池反应电势为 0.3522 V。

(1) 求反应



在 25℃ 时的标准平衡常数。已知 0.1 mol · kg⁻¹ HCl 溶液的 $\gamma_{\pm} = 0.798$ 。

(2) 求金属银在 $1 \text{ mol} \cdot \text{kg}^{-1} \text{HCl}$ 溶液中产生 H_2 的平衡压力。已知 25°C 时 $1 \text{ mol} \cdot \text{kg}^{-1} \text{HCl}$ 溶液的 $\gamma_{\pm} = 0.809$ 。

$$\begin{aligned} \text{解: (1)} \quad E^\circ &= E + \frac{RT}{zF} \ln \frac{a_{\text{H}^+}^2 \cdot a_{\text{Cl}^-}^2}{p_{\text{H}_2} / p^\circ} \\ &= [0.3522 + 0.05916 \lg(0.1 \times 0.798)^2] \text{V} \\ &= 0.2223 \text{V} \end{aligned}$$

$$\begin{aligned} K^\circ &= \exp\left(\frac{zFE^\circ}{RT}\right) = \exp\left(\frac{2 \times 96485 \times 0.2223}{8.3145 \times 298.15}\right) \\ &= 3.28 \times 10^7 \end{aligned}$$

$$\begin{aligned} \text{(2)} \quad K^\circ &= \frac{a_{\text{H}^+}^2 \cdot a_{\text{Cl}^-}^2}{p_{\text{H}_2} / p^\circ} = \frac{a_{\pm}^4}{p_{\text{H}_2} / p^\circ} = \frac{[(b_{\pm} / b^\circ) \gamma_{\pm}]^4}{p_{\text{H}_2} / p^\circ} \\ p_{\text{H}_2} &= \left[\frac{(1 \times 0.809)^4}{3.28 \times 10^7} \times 100 \right] \text{kPa} = 1.31 \times 10^{-6} \text{kPa} \end{aligned}$$

11. 已知电池

$\text{Pt}, \text{H}_2(0.1 \text{ MPa}) \mid \text{NaOH}(0.01 \text{ mol} \cdot \text{kg}^{-1}) \parallel \text{HCl}(0.01 \text{ mol} \cdot \text{kg}^{-1}) \mid \text{H}_2(0.1 \text{ MPa}), \text{Pt}$

在 25°C 时的电池反应电势为 0.587 V ，同温度下 $0.01 \text{ mol} \cdot \text{kg}^{-1} \text{NaOH}$ 和 $0.01 \text{ mol} \cdot \text{kg}^{-1} \text{HCl}$ 溶液的 γ_{\pm} 都等于 0.904 ，求水的离子积 K_w° 。

解：负极： $\text{H}_2(0.1 \text{ MPa}) + 2\text{OH}^-(a_{\text{OH}^-}) \longrightarrow 2\text{H}_2\text{O} + 2\text{e}^-$

正极： $2\text{H}^+(a_{\text{H}^+}) + 2\text{e}^- \longrightarrow \text{H}_2(0.1 \text{ MPa})$

电池： $2\text{H}^+(a_{\text{H}^+}) + 2\text{OH}^-(a_{\text{OH}^-}) \longrightarrow 2\text{H}_2\text{O}$

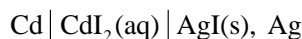
$$\begin{aligned} E^\circ &= E + \frac{RT}{F} \ln \frac{1}{a_{\text{H}^+} \cdot a_{\text{OH}^-}} \\ &= \left[0.587 + 0.05916 \lg \frac{1}{(0.01 \times 0.904)^2} \right] \text{V} = 0.829 \text{V} \end{aligned}$$

$$E^\circ = \frac{RT}{F} \ln \frac{1}{K_w^\circ}$$

$$\lg K_w^\circ = \frac{0.829}{0.05916} = -14.01$$

$$K_w^\circ = 0.98 \times 10^{-14}$$

12. 已知电池



在 25°C 时的电池反应电势为 0.2860 V, 求 CdI_2 溶液的离子平均活度 a_{\pm} 及电解质作为整体的活度 a_B 。

解: 电池反应: $\text{Cd}(\text{s}) + 2\text{AgI}(\text{s}) \longrightarrow 2\text{Ag}(\text{s}) + \text{CdI}_2(\text{aq})$

$$E = E^\circ - \frac{RT}{zF} \ln(a_{\text{Cd}^{2+}} \cdot a_{\text{I}^-}^2) = E^\circ - \frac{RT}{zF} \ln a_{\pm}^3$$

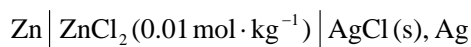
$$\lg a_{\pm} = \frac{2(E^\circ - E)/V}{3 \times 0.05916} = \frac{2 \times (-0.15241 + 0.4032 - 0.2860)}{3 \times 0.05916}$$

$$= -0.3968$$

$$a_{\pm} = 0.401$$

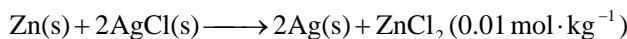
$$a_B = a_{\pm}^3 = 0.0645$$

13. 已知电池



在 25°C 时的电池反应电势为 1.1566 V, 其他数据可查表 17-3, 求 $0.01 \text{ mol} \cdot \text{kg}^{-1} \text{ ZnCl}_2$ 溶液的离子平均活度、离子平均活度因子及 ZnCl_2 的活度。

解: 电池反应:



$$E = E^\circ - \frac{RT}{zF} \ln(a_{\text{Zn}^{2+}} \cdot a_{\text{Cl}^-}^2) = E^\circ - \frac{RT}{zF} \ln a_{\pm}^3$$

$$\lg a_{\pm} = \frac{2(E^\circ - E)/V}{3 \times 0.05916}$$

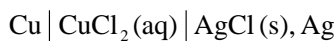
$$= \frac{2 \times (0.22216 + 0.7620 - 1.1566)}{3 \times 0.05916} = -1.9432$$

$$a_{\pm} = 0.0114$$

$$a_B = a_{\pm}^3 = 1.48 \times 10^{-6}$$

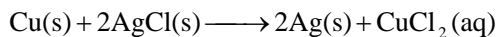
$$\gamma_{\pm} = \frac{a_{\pm}}{(b_{\pm}/b^\circ)} = \frac{0.0114}{\sqrt[3]{4} \times 0.01} = 0.718$$

14. 25°C 时电池



当 CuCl_2 溶液的浓度 $b = 0.0001 \text{ mol} \cdot \text{kg}^{-1}$ 时, 电池反应电势 $E = 0.191 \text{ V}$; $b = 0.2 \text{ mol} \cdot \text{kg}^{-1}$ 时, $E = -0.074 \text{ V}$ 。设 $0.0001 \text{ mol} \cdot \text{kg}^{-1}$ CuCl_2 溶液的离子平均活度因子 $\gamma_{\pm} = 0.960$, 试求 $0.2 \text{ mol} \cdot \text{kg}^{-1}$ CuCl_2 溶液的 γ_{\pm} 。

解: 电池反应



$$E_1 = E^\ominus - \frac{RT}{zF} \ln \left(\frac{4b_1^3 \gamma_{\pm,1}^3}{b^{\ominus 3}} \right)$$

$$E_2 = E^\ominus - \frac{RT}{zF} \ln \left(\frac{4b_2^3 \gamma_{\pm,2}^3}{b^{\ominus 3}} \right)$$

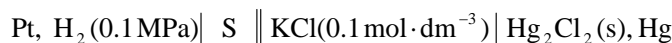
$$E_1 - E_2 = \frac{3RT}{zF} \ln \left(\frac{b_2 \gamma_{\pm,2}}{b_1 \gamma_{\pm,1}} \right)$$

$$\lg \left(\frac{b_2 \gamma_{\pm,2}}{b_1 \gamma_{\pm,1}} \right) = \frac{2 \times (0.191 + 0.074)}{3 \times 0.05916} = 2.986$$

$$\frac{b_2 \gamma_{\pm,2}}{b_1 \gamma_{\pm,1}} = 968$$

$$\therefore \gamma_{\pm,2} = 968 \times \frac{0.0001}{0.2} \times 0.960 = 0.465$$

15. 在电池



中, 当 S 是 pH 为 6.86 的缓冲溶液时, 测得 25°C 时电池反应的电势为 0.7409 V ; 现将 S 换以一 pH 未知的溶液, 同温度下测得电池反应的电势为 0.6097 V , 求该溶液的 pH。

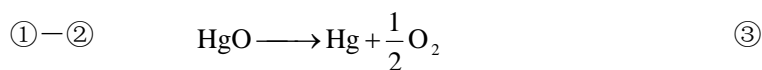
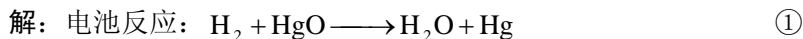
$$\begin{aligned} \text{解: } (\text{pH})_x &= (\text{pH})_s + \frac{(E_x - E_s)F}{RT \ln 10} = 6.86 + \frac{0.6097 - 0.7409}{0.05916} \\ &= 4.64 \end{aligned}$$

16. 已知 25°C 时电池



的电池反应电势为 0.9265 V , $\text{H}_2\text{O(l)}$ 的标准摩尔生成焓为 $-285.830 \text{ kJ} \cdot \text{mol}^{-1}$ 。各物质的标准摩尔熵为: HgO , $70.29 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; Hg(l) , $76.02 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $\text{O}_2(\text{g})$, $205.138 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $\text{H}_2(\text{g})$, $130.684 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $\text{H}_2\text{O(l)}$, $69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ 。求 25°C 时 HgO 的分

解压。



$$\begin{aligned} \Delta_r G_m^\ominus(1) &= \Delta_r G_m^\ominus(1) = -zFE \\ &= (-2 \times 96485 \times 0.9265) \text{ J} \cdot \text{mol}^{-1} \\ &= -178.79 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r G_m^\ominus(2) &= \Delta_r H_m^\ominus(2) - T\Delta_r S_m^\ominus(2) \\ &= \left[-285.830 \times 10^3 - 298.15 \times \left(69.91 - 130.684 \right. \right. \\ &\quad \left. \left. - \frac{1}{2} \times 205.138 \right) \right] \text{ J} \cdot \text{mol}^{-1} \\ &= -237.13 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r G_m^\ominus(3) &= \Delta_r G_m^\ominus(1) - \Delta_r G_m^\ominus(2) \\ &= (-178.79 + 237.13) \text{ kJ} \cdot \text{mol}^{-1} \\ &= 58.34 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

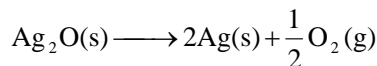
$$\ln K^\ominus = -\frac{\Delta_r G_m^\ominus(3)}{RT} = -\frac{58.34 \times 10^3}{8.3145 \times 298.15} = -23.53$$

$$K^\ominus = 6.0 \times 10^{-11}$$

$$\therefore K^\ominus = \left(\frac{p_{\text{O}_2}}{p^\ominus} \right)^{1/2}$$

$$\therefore p_{\text{O}_2} = K^{\ominus 2} p^\ominus = \left[(6.0 \times 10^{-11})^2 \times 100 \right] \text{ kPa} = 3.6 \times 10^{-19} \text{ kPa}$$

17. 试计算 $\text{Ag}_2\text{O}(\text{s})$ 在空气中开始分解的温度。反应式为



设空气的压力为 101.3 kPa，空气中 O_2 的摩尔分数为 0.21， $\text{Ag}_2\text{O}(\text{s})$ 的标准摩尔生成焓为 $-31.05 \text{ kJ} \cdot \text{mol}^{-1}$ ，分解反应的标准摩尔反应焓不随温度变化。

解：设计电池 $\text{Pt}, \text{O}_2(\text{g}) \mid \text{OH}^-(\text{aq}) \mid \text{Ag}_2\text{O}(\text{s}), \text{Ag}$

$$\ln K^\circ(298.15 \text{ K}) = \frac{zFE^\circ}{RT} = \frac{2 \times 96485 \times (0.342 - 0.401)}{8.3145 \times 298.15} = -4.59$$

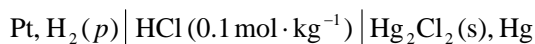
$$K^\circ(298.15 \text{ K}) = 0.0102$$

$$K^\circ(T) = \left(\frac{p_{\text{O}_2}}{p^\circ} \right)^{1/2} = \sqrt{\frac{101.3 \times 0.21}{100}} = 0.46$$

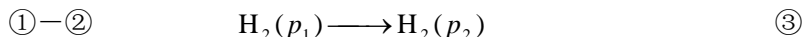
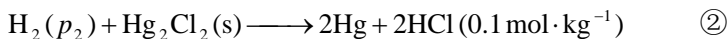
$$\begin{aligned} \ln \frac{K^\circ(T)}{K^\circ(298.15 \text{ K})} &= \frac{\Delta_r H_m^\circ}{R} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T} \right) \\ &= \frac{31.05 \times 10^3}{8.3145} \left(\frac{1}{298.15} - \frac{1}{T/\text{K}} \right) \end{aligned}$$

$$T = 428 \text{ K}$$

18. 电池



在 25°C 测得 $p = 0.1013 \text{ MPa}$ 时, $E = 0.3990 \text{ V}$; $p = 11.16 \text{ MPa}$ 时, $E = 0.4596 \text{ V}$ 。试求 H_2 在 25°C 、 11.16 MPa 时的逸度因子。设 0.1013 MPa 时 H_2 可当作理想气体。



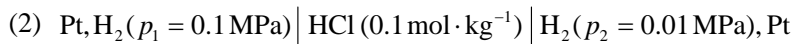
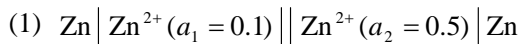
$$\Delta_r G_m^\circ(3) = \Delta_r G_m(1) - \Delta_r G_m(2) = -zF(E_1 - E_2)$$

$$\text{又} \quad \Delta_r G_m(3) = RT \ln \frac{f_2^*}{f_1^*} = RT \ln \frac{p_2 \phi_2}{p_1 \phi_1}$$

$$\therefore \lg \frac{p_2 \phi_2}{p_1 \phi_1} = -\frac{2 \times (0.3990 - 0.4596)}{0.05916} = 2.049$$

$$\frac{p_2}{p_1} \cdot \frac{\phi_2}{\phi_1} = 112$$

$$\phi_2 = 112 \times \frac{0.1013}{11.16} \times 1 = 1.02$$

19. 计算下列浓差电池在 18°C 时的电池反应电势:

解: (1) 电池反应: $\text{Zn}^{2+}(a=0.5) \longrightarrow \text{Zn}^{2+}(a=0.1)$

$$E = -\frac{RT}{zF} \ln \frac{a_1}{a_2} = \left[-\frac{8.3145 \times 291.15}{2 \times 96485} \ln \frac{0.1}{0.5} \right] \text{V}$$

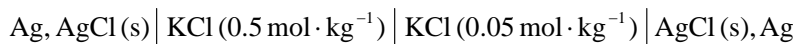
$$= 0.0202 \text{ V}$$

(2) 电池反应: $\text{H}_2(p_1 = 0.1 \text{ MPa}) \longrightarrow \text{H}_2(p_2 = 0.01 \text{ MPa})$

$$E = -\frac{RT}{zF} \ln \frac{p_2}{p_1} = \left[-\frac{8.3145 \times 291.15}{2 \times 96485} \ln \frac{0.01}{0.1} \right] \text{V}$$

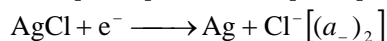
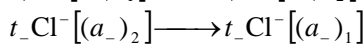
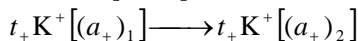
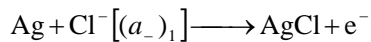
$$= 0.0289 \text{ V}$$

20. 已知 25°C 时电池



的电池反应电势为 0.0536 V, $0.5 \text{ mol} \cdot \text{kg}^{-1}$ 和 $0.05 \text{ mol} \cdot \text{kg}^{-1}$ KCl 溶液的离子平均活度因子分别为 0.649 和 0.812。试计算 K^+ 的迁移数及该电池的液接电势。

解: 当电池中有 96485 C 电量通过时, 发生的变化为:



总变化为: $t_+ \text{K}^+[(a_+)_1] + t_- \text{Cl}^-[(a_-)_1] \longrightarrow t_+ \text{K}^+[(a_+)_2] + t_- \text{Cl}^-[(a_-)_2]$

$$\Delta_r G_m = t_+ RT \ln \frac{(a_+)_2 (a_-)_2}{(a_+)_1 (a_-)_1} = 2t_+ RT \ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

$$E = -\frac{\Delta_r G_m}{zF} = -2t_+ \frac{RT}{F} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1} = 2t_+ \frac{RT}{F} \ln \frac{b_1 \gamma_{\pm,1}}{b_2 \gamma_{\pm,2}}$$

即
$$0.0536 \text{ V} = \left[2t_+ \times 0.05916 \lg \frac{0.5 \times 0.649}{0.05 \times 0.812} \right] \text{V}$$

解得 $t_+ = 0.502$

$$E_{\text{液接}} = E - \frac{RT}{F} \ln \frac{(a_{\pm})_1}{(a_{\pm})_2} = (2t_+ - 1) \frac{RT}{F} \ln \frac{b_1 \gamma_{\pm,1}}{b_2 \gamma_{\pm,2}}$$

$$= \left[(2 \times 0.502 - 1) \times 0.05916 \lg \frac{0.5 \times 0.649}{0.05 \times 0.812} \right] \text{V}$$

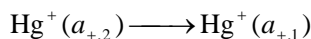
$$= 0.2 \text{ mV}$$

21. 电池



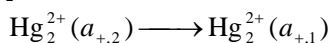
在 18℃ 时的电池反应电势为 0.029 V, 1 dm³ S₁ 溶液中含有 6.30 g 硝酸和 0.263 g 硝酸亚汞, 1 dm³ S₂ 溶液中含有 6.30 g 硝酸和 2.63 g 硝酸亚汞。试确定在溶液中的亚汞离子是 Hg⁺ 还是 Hg₂²⁺。

解: 设亚汞离子为 Hg⁺, 则电池反应为:



$$\begin{aligned} E &= -\frac{RT}{F} \ln \frac{a_{+,1}}{a_{+,2}} \approx -\frac{RT}{F} \ln \frac{b_{+,1}}{b_{+,2}} \\ &= \left(\frac{8.3145 \times 291.15}{96485} \times \ln \frac{2.63}{0.263} \right) \text{V} \\ &= 0.0578 \text{V} \end{aligned}$$

设亚汞离子为 Hg₂²⁺, 则电池反应为:



$$E = -\frac{RT}{2F} \ln \frac{a_{+,1}}{a_{+,2}} \approx -\frac{RT}{2F} \ln \frac{b_{+,1}}{b_{+,2}} = 0.0289 \text{V}$$

因后一假设求得的反应电势与实验值相符, 故亚汞离子应为 Hg₂²⁺。

22. 25℃ 时用铅作电极电解 pH = 4.76 的硫酸溶液。当阴极电流密度为 1 A·cm⁻² 时, 测得铅阴极的电极电势为 -1.8416 V, 阴极电流密度为 0.01 A·cm⁻² 时, 铅阴极的电极电势为 -1.6216 V。求当阴极电流密度为 0.1 A·cm⁻² 时, 氢在铅阴极上的超电势。

解: 阴极反应: $\text{H}^+(\text{pH} = 4.76) + \text{e}^- \longrightarrow \frac{1}{2} \text{H}_2(p^\circ)$

$$\begin{aligned} E_c(0) &= E^\circ - \frac{RT}{F} \ln \frac{1}{a_{\text{H}^+}} = \left(0 - 0.05916 \lg \frac{1}{a_{\text{H}^+}} \right) \text{V} \\ &= (-0.05916 \cdot \text{pH}) \text{V} = -(0.05916 \times 4.76) \text{V} \\ &= -0.282 \text{V} \end{aligned}$$

$$\eta_c = E_c(j) - E_c(0)$$

$$j = 1 \text{ A} \cdot \text{cm}^{-2}, \quad \eta_c = (-1.8416 + 0.282) \text{V} = -1.560 \text{V}$$

$$j = 0.01 \text{ A} \cdot \text{cm}^{-2}, \quad \eta_c = (-1.6216 + 0.282) \text{V} = -1.340 \text{V}$$

代入塔菲尔公式 $|\eta| = a + b \ln\{j\}$

$$\begin{aligned} 1.560 \text{ V} &= a + b \ln(1 \times 10^3) \\ 1.340 \text{ V} &= a + b \ln(0.01 \times 10^3) \end{aligned}$$

解得 $a = 1.230 \text{ V}$

$$b = 0.0478 \text{ V}$$

$$j = 0.1 \text{ A} \cdot \text{cm}^2, \quad |\eta_c| = [1.230 + 0.0478 \times \ln(0.1 \times 10^3)] \text{ V} = 1.450 \text{ V}$$

$$\therefore \eta_c = -1.450 \text{ V}$$

23. 25°C 时, 以汞为阴极电解含有浓度为 $0.01 \text{ mol} \cdot \text{dm}^{-3}$ 的 NaCl 溶液, 阴极反应 $\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$ 受传质控制, 极限电流密度为 $25.0 \text{ mA} \cdot \text{cm}^{-2}$, 求阴极上 Na^+ 的传质系数以及扩散层厚度。已知溶液中 Na^+ 的扩散系数 $D = 1.33 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ 。

$$\begin{aligned} \text{解: } k_d &= \frac{j_l}{|z| F C_{\text{B}\infty}} \\ &= \frac{25.0 \times 10^{-3} \times 10^4 \text{ A} \cdot \text{m}^{-2}}{1 \times 96485 \text{ C} \cdot \text{mol}^{-1} \times 0.01 \times 10^3 \text{ mol} \cdot \text{m}^{-3}} = 2.59 \times 10^{-4} \text{ m} \cdot \text{s}^{-1} \\ \delta &= \frac{D}{k_d} = \left(\frac{1.33 \times 10^{-5} \times 10^{-4}}{2.59 \times 10^{-4}} \right) \text{ m} = 5.14 \times 10^{-6} \text{ m} \end{aligned}$$

24. 25°C 时以铂电极电解含有 $\text{NiCl}_2 (0.01 \text{ mol} \cdot \text{kg}^{-1})$ 和 $\text{CuCl}_2 (0.02 \text{ mol} \cdot \text{kg}^{-1})$ 的水溶液。若电解过程中不断搅拌溶液, 金属在铂电极上的超电势可忽略不计, 并设活度可用浓度代替, 问: (1) 阴极上何种金属先析出? (2) 第二种金属析出时, 第一种金属在溶液中的浓度是多少? 所需的标准电极反应电势可查表 17-3。

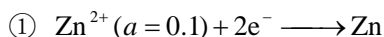
$$\begin{aligned} \text{解: (1) } E\{\text{Ni}^{2+}|\text{Ni}\} &= E^\circ\{\text{Ni}^{2+}|\text{Ni}\} - \frac{RT}{zF} \ln \frac{1}{a_{\text{Ni}^{2+}}} \\ &= \left(-0.257 + \frac{0.05916}{2} \lg 0.01 \right) \text{ V} \\ &= -0.316 \text{ V} \\ E\{\text{Cu}^{2+}|\text{Cu}\} &= E^\circ\{\text{Cu}^{2+}|\text{Cu}\} - \frac{RT}{zF} \ln \frac{1}{a_{\text{Cu}^{2+}}} \\ &= \left(0.3417 + \frac{0.05916}{2} \lg 0.02 \right) \text{ V} \\ &= 0.291 \text{ V} \end{aligned}$$

故阴极先析出 Cu 。

$$\begin{aligned}
 (2) \quad & 0.3417 + \frac{0.05916}{2} \lg a_{\text{Cu}^{2+}} = -0.316 \\
 & a_{\text{Cu}^{2+}} = 5.8 \times 10^{-23} \\
 & b_{\text{Cu}^{2+}} = \left(\frac{a_{\text{Cu}^{2+}}}{\gamma_{\pm}} \right) \cdot b^{\ominus} = a_{\text{Cu}^{2+}} \cdot b^{\ominus} = 5.8 \times 10^{-23} \text{ mol} \cdot \text{kg}^{-1}
 \end{aligned}$$

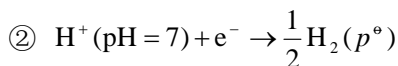
25. 25℃时用铜片作阴极, 石墨作阳极, 电解浓度为 $0.1 \text{ mol} \cdot \text{kg}^{-1}$ 的 ZnCl_2 溶液, 若电流密度为 $10 \text{ mA} \cdot \text{cm}^{-2}$, 问在阴极上首先析出什么物质? 在阳极上又析出什么物质? 已知此电流密度下 H_2 在铜电极上的超电势为 -0.584 V , O_2 在石墨电极上的超电势为 0.896 V , 并假定 Cl_2 在石墨电极上的超电势可略而不计, 活度可用浓度代替。

解: 可能的阴极反应:



$$\begin{aligned}
 E(0) &= E^{\ominus} - \frac{RT}{zF} \ln \frac{1}{a_{\text{Zn}^{2+}}} = \left(-0.7620 - \frac{0.05916}{2} \lg \frac{1}{0.1} \right) \text{V} \\
 &= -0.792 \text{ V}
 \end{aligned}$$

$$E(j) = E(0) = -0.792 \text{ V}$$

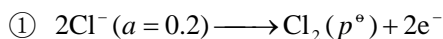


$$\begin{aligned}
 E(0) &= E^{\ominus} - \frac{RT}{F} \ln \frac{1}{a_{\text{H}^{+}}} \\
 &= -(0.05916 \times 7) \text{ V} = -0.414 \text{ V}
 \end{aligned}$$

$$\begin{aligned}
 E(j) &= E(0) + \eta_c \\
 &= (-0.414 - 0.584) \text{ V} = -0.998 \text{ V}
 \end{aligned}$$

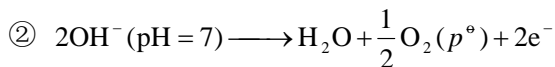
∴ Zn 先析出。

可能的阳极反应:



$$\begin{aligned}
 E(0) &= E^{\ominus} - \frac{RT}{F} \ln a_{\text{Cl}^{-}} = (1.35793 - 0.05916 \times \lg 0.2) \text{ V} \\
 &= 1.399 \text{ V}
 \end{aligned}$$

$$E(j) = E(0) = 1.399 \text{ V}$$



$$E(0) = E^\circ - \frac{RT}{zF} \ln a_{\text{OH}^-}^2 = [0.401 - 0.05916 \times (-7)] \text{V}$$

$$= 0.815 \text{V}$$

$$E(j) = E(0) + \eta_a = (0.815 + 0.896) \text{V} = 1.711 \text{V}$$

∴ Cl_2 先析出。

26. 25°C 时用铂片为电极电解 $0.5 \text{ mol} \cdot \text{kg}^{-1}$ 的 CuSO_4 溶液 (其中含 H_2SO_4 为 $0.01 \text{ kg} \cdot \text{mol}^{-1}$)。若氢在铜上的超电势为 -0.23 V , 活度可用浓度代替, 问在阴极上析出 H_2 时, 残留在溶液中的 Cu^{2+} 浓度是多少? (注意由于阳极反应产生 O_2 , 溶液中 H^+ 浓度在 Cu 析出的过程中是不断增大的)。

解: 阴极: $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$

阳极: $\text{H}_2\text{O} \longrightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^-$

电池反应: $\text{Cu}^{2+} + \text{H}_2\text{O} \longrightarrow \text{Cu} + 2\text{H}^+ + \frac{1}{2}\text{O}_2$

设阴极上析出氢气时, Cu^{2+} 的浓度为 $x \text{ mol} \cdot \text{kg}^{-1}$, 则 H^+ 的浓度应为

$$[0.02 + (0.5 - x) \times 2] \text{ mol} \cdot \text{kg}^{-1} = (1.02 - 2x) \text{ mol} \cdot \text{kg}^{-1}$$

此时, 电极 $\text{Cu}^{2+} (x \text{ mol} \cdot \text{kg}^{-1}) | \text{Cu}$ 的电极电势为

$$\begin{aligned} E(j)_1 &= E(0) = E^\circ \left\{ \text{Cu}^{2+} | \text{Cu} \right\} - \frac{RT}{2F} \ln \frac{1}{a_{\text{Cu}^{2+}}} \\ &= \left(0.337 - \frac{0.05916}{2} \lg \frac{1}{x} \right) \text{V} \end{aligned}$$

电极 $\text{H}^+ [(1.02 - 2x) \text{ mol} \cdot \text{kg}^{-1}] | \text{H}_2 (p^\circ), \text{Pt}$ 的电极电势为

$$\begin{aligned} E(j)_2 &= E(0) + \eta_c = E^\circ \left\{ \text{H}^+ | \text{H}_2, \text{Pt} \right\} - \frac{RT}{zF} \ln \frac{1}{a_{\text{H}^+}^2} + \eta_c \\ &= \left[0 - \frac{0.05916}{2} \lg \frac{1}{(1.02 - 2x)^2} - 0.23 \right] \text{V} \end{aligned}$$

$E(j)_1 = E(j)_2$, 即

$$0.337 - \frac{0.05916}{2} \lg \frac{1}{x} = -\frac{0.05916}{2} \lg \frac{1}{(1.02 - 2x)^2} - 0.23$$

$$\frac{(1.02 - 2x)^2}{x} = 1.5 \times 10^{19}$$

这说明 x 是一个极小的数，与 1.02 相比， $2x$ 可以略去。

$$\therefore x = 7 \times 10^{-20}$$

即残留在溶液中的 Cu^{2+} 浓度为 $7 \times 10^{-20} \text{ mol} \cdot \text{kg}^{-1}$ 。