

## 原电池电动势测定及其应用作业（2）作业点评

1. 已知反应  $\text{Cu}^{2+}(a_1) + \text{Cu}(s) \longrightarrow 2\text{Cu}^+(a_2)$ ，在 298.15K 时，平衡常数为  $1.2 \times 10^{-6}$ ， $\text{Cu}^{2+}$  的

$\Delta_f G_m^\ominus = 64.98 \text{ kJ} \cdot \text{mol}^{-1}$ ，已知  $\text{CuI}$  的活度积为  $1.1 \times 10^{-12}$ ，试求：(1)  $E_{\text{Cu}^+|\text{Cu}}^\ominus$ ；(2)  $E_{\text{I}^-|\text{CuI,Cu}}^\ominus$

解 (1)

$$\Delta_r G_m^\ominus = -RT \ln K^\ominus = \{-8.314 \times 298.15 \times \ln(1.2 \times 10^{-6})\} \text{ kJ} \cdot \text{mol}^{-1} = 33.78 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\ominus = 2\Delta_f G_m^\ominus(\text{Cu}^+) - \Delta_f G_m^\ominus(\text{Cu}^{2+})$$

$$\Delta_f G_m^\ominus(\text{Cu}^+) = [\Delta_r G_m^\ominus + \Delta_f G_m^\ominus(\text{Cu}^{2+})] / 2 = \{(33.78 + 64.98) / 2\} \text{ kJ} \cdot \text{mol}^{-1} = 49.38 \text{ kJ} \cdot \text{mol}^{-1}$$

$$-\Delta_r G_{\text{Cu} \rightarrow \text{Cu}^+}^\ominus = \Delta_r G_{\text{Cu}^+ \rightarrow \text{Cu}}^\ominus = -zFE_{\text{Cu}^+|\text{Cu}}^\ominus$$

$$E_{\text{Cu}^+|\text{Cu}}^\ominus = \frac{\Delta_r G_{\text{Cu} \rightarrow \text{Cu}^+}^\ominus}{F} = \left\{ \frac{49380}{1 \times 96485} \right\} \text{ V} = 0.5118 \text{ V}$$

(2)  $\text{CuI}(s) + e^- \rightarrow \text{Cu}(s) + \text{I}^-(a_{\text{I}^-})$

$$E_{\text{I}^-|\text{CuI,Cu}}^\ominus = E_{\text{Cu}^+|\text{Cu}}^\ominus + \frac{RT}{F} \ln K_{\text{sp}} = \{0.5118 + 0.0592 \lg(1.1 \times 10^{-12})\} \text{ V} = -0.1961 \text{ V}$$

**【点评】** 此题的解题关键是  $\Delta_r G_m^\ominus = -RT \ln K^\ominus = -zFE^\ominus$  以及  $\Delta_r G_m^\ominus = \sum_B \nu_B \Delta_f G_m^\ominus(B)$

2. 电池  $\text{Pt}(s) | \text{H}_2(p^\ominus) | \text{HCl}(m=0.1 \text{ mol} \cdot \text{dm}^{-3}, \gamma_{\pm}=0.7987) | \text{AgCl}(s) | \text{Ag}(s)$  在 298.15K 时的电动势  $E=0.3522 \text{ V}$ ，试计算

(1) 反应  $\text{H}_2(g) + 2\text{AgCl}(s) \longrightarrow \text{Ag}(s) + 2\text{HCl}(0.1 \text{ mol} \cdot \text{dm}^{-3})$  的标准平衡常数；

(2) 金属银在  $1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{HCl}$  溶液中所能产生氢气的平衡压力。已知  $1 \text{ mol} \cdot \text{dm}^{-3}$  的  $\text{HCl}$  的  $\gamma_{\pm}=0.809$ 。

解 (1) 负极  $\text{H}_2(p^\ominus) \longrightarrow 2\text{H}^+(a_{\text{H}^+}) + 2e^-$

正极  $2\text{AgCl}(s) + 2e^- \longrightarrow 2\text{Ag}(s) + 2\text{Cl}^-(a_{\text{Cl}^-})$

电池反应  $\text{H}_2(p^\ominus) + 2\text{AgCl}(s) \longrightarrow \text{Ag}(s) + 2\text{HCl}(a_{\text{HCl}})$

$$\text{因为 } E = E^\ominus - \frac{RT}{2F} \ln \frac{a_{\text{HCl}}^2}{p_{\text{H}_2} / p^\ominus}$$

$$\text{所以 } E^{\ominus} = E^{\ominus} + \frac{RT}{2F} \ln \frac{a_{\text{HCl}}^2}{p_{\text{H}_2} / p^{\ominus}} = \{0.3522 + 2 \times 0.0592 \lg(0.1 \times 0.7987)\} \text{V} = 0.2222 \text{V}$$

$$\text{而 } \ln K^{\ominus} = \frac{zFE^{\ominus}}{RT}$$

$$\text{即 } \lg K^{\ominus} = \frac{zFE^{\ominus}}{2.303RT} = \frac{2 \times 0.2222}{0.0592} = 7.5068$$

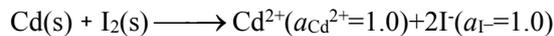
$$\text{所以 } K^{\ominus} = 3.21 \times 10^7$$

$$(2) \quad K^{\ominus} = \frac{a_{\text{HCl}}^2}{p_{\text{H}_2} / p^{\ominus}}$$

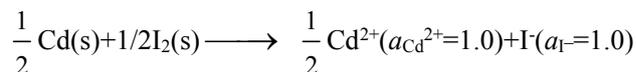
$$p_{\text{H}_2} = \frac{a_{\text{HCl}}^2 \cdot p^{\ominus}}{K^{\ominus}} = \frac{a_{\pm}^4 \cdot p^{\ominus}}{K^{\ominus}} = \left\{ \frac{(0.809 \times 1)^4 \times 100}{3.212 \times 10^7} \right\} \text{kPa} = 1.33 \times 10^{-3} \text{Pa}$$

**【点评】** 此题的解题关键是利用电池反应的能斯特方程求算  $E^{\ominus}$ ，然后从  $\Delta_r G_m^{\ominus} = -RT \ln K^{\ominus} = -zFE^{\ominus}$  以及  $K^{\ominus}$  的表达式进行计算。

3. 试为下述反应设计一电池

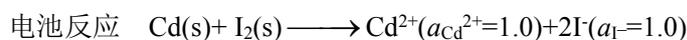
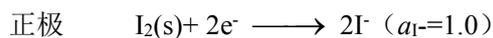
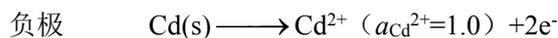
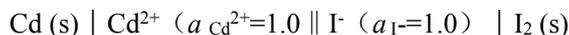


求电池在298.15K时的  $E^{\ominus}$ 、反应的  $\Delta_r G_m^{\ominus}$  和平衡常数  $K^{\ominus}$ 。如将反应写成



再计算  $E^{\ominus}$ 、 $\Delta_r G_m^{\ominus}$  和  $K^{\ominus}$ ，以此了解反应方程式的写法对这些物理量的影响。

**解** 设计电池如下



电池反应与所给的化学反应方程式一致，说明所设计的电池是正确的。

$$E^{\ominus} = E_{\text{I}_2|\text{I}^{-}}^{\ominus} - E_{\text{Cd}^{2+}|\text{Cd}}^{\ominus} = \{0.5355 - (-0.4029)\} \text{V} = 0.9384 \text{V}$$

$$\Delta_r G_m^\ominus = -zFE^\ominus = \{-2 \times 96485 \times (0.9384)\} \text{J} \cdot \text{mol}^{-1} = -181.1 \text{kJ} \cdot \text{mol}^{-1}$$

$$\ln K^\ominus = \frac{-\Delta_r G_m^\ominus}{RT} = \frac{181100}{8.314} = 73.10$$

$$K^\ominus = 5.58 \times 10^{31}$$

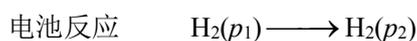
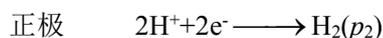
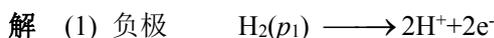
如果反应式的各项系数均缩小至原来的一半， $E^\ominus$  的值保持不变，而

$$\Delta_r G_m^\ominus(2) = \frac{1}{2} \Delta_r G_m^\ominus(1) = -90.55 \text{kJ} \cdot \text{mol}^{-1}$$

$$K^\ominus(2) = \sqrt{K^\ominus(1)} = 7.47 \times 10^{15}$$

**【点评】** 对同一反应系统，当反应方程式间存在倍数关系时， $\Delta_r G_m^\ominus$  与  $K^\ominus$  值发生变化，但  $E^\ominus$  与  $E^\ominus$  值不变。

4. 下列电池  $\text{Pt(s)} \mid \text{H}_2(p_1) \mid \text{H}_2\text{SO}_4(m) \mid \text{H}_2(p_2) \mid \text{Pt(s)}$ ，假定  $\text{H}_2$  遵从的状态方程为  $pV_m = RT + ap$ ，其中  $a = 0.0148 \text{dm}^3 \cdot \text{mol}^{-1}$ ，且与温度、压力无关，当  $\text{H}_2$  的压力  $p_1 = 2026.5 \text{kPa}$ ， $p_2 = 101.325 \text{kPa}$  时：  
(1) 计算以上电池在  $298.15 \text{K}$  时的电动势；(2) 当电池可逆放电时，是吸热还是放热？为什么？



因 
$$-2FE = \Delta_r G_m = \int_{p_1}^{p_2} V_m dp,$$

而 
$$V_m = \frac{RT}{p} + a$$

所以 
$$-2FE = \int_{p_1}^{p_2} \left( \frac{RT}{p} + a \right) dp$$

即 
$$E = \frac{RT}{2F} \ln \frac{p_1}{p_2} + \frac{a}{2F} (p_1 - p_2)$$

代入数据可求得  $E = 0.0386 \text{V}$

(2) 由 
$$-\Delta_r S_m = \left( \frac{\partial \Delta_r G_m}{\partial T} \right)_p = -zF \left( \frac{\partial E}{\partial T} \right)_p$$

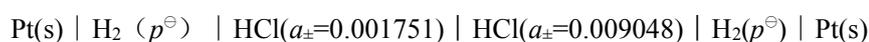
可得  $\Delta_r S_m = zF \left( \frac{\partial E}{\partial T} \right)_p = R \ln \frac{p_1}{p_2} > 0$ ,  $Q_R = T \Delta_r S_m > 0$

所以, 该电池可逆放电时吸热。

**【点评】**此题的电池反应为  $H_2$  的扩散过程, 即  $H_2(p_1) \longrightarrow H_2(p_2)$ , 该过程的  $\Delta_r G_m = \int_{p_1}^{p_2} V_m dp$  是

解题的关键, 即当作  $H_2$  的等温变压过程来计算。

### 5. 有迁移的浓差电池



测得 298.15K 时电动势为 0.01428V, 计算液接电势和  $H^+$  的迁移数。

**解**  $E_1 = E_{\text{有液接}} - E_{\text{无液接}} = \{0.01428 + 0.0592 \lg(0.00175/0.009048)\} \text{V} = -0.02795 \text{V}$

$$\text{又 } E_1 = (2t_+ - 1) \frac{RT}{F} \ln \frac{(a_{\pm})_1}{(a_{\pm})_2} \quad (a_2 > a_1 \text{ 时})$$

$$\text{所以 } 2t_+ + 1 = \frac{-0.02795}{0.0592 \lg \frac{0.001751}{0.009048}} = 0.6619$$

$$\text{即 } 2t_+ = 1.6619$$

$$\text{因此 } t_+ = 0.8310$$

**【点评】**有液体接界电势存在的电池的电动势必须考虑液体接界电势的贡献。

### 6. 电池 $\text{Pt(s)} \mid \text{H}_2(\text{g}) \mid \text{HCl}(\text{aq}) \mid \text{Hg}_2\text{Cl}_2(\text{s}) \mid \text{Hg}(\text{l})$

(1) 写出电池反应;

(2) 已知 298.15K 时  $E^\ominus = 0.2688 \text{V}$ ,  $\Delta_f G_m^\ominus [\text{Cl}^-(\text{aq})] = -131.26 \text{kJ} \cdot \text{mol}^{-1}$ , 计算  $\text{Hg}_2\text{Cl}_2(\text{s})$  的

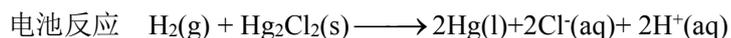
$$\Delta_f G_m^\ominus;$$

(3) 计算 298.15K 时反应  $\text{Hg}_2\text{Cl}_2(\text{s}) \longrightarrow \text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$  的平衡常数  $K^\ominus$ 。

已知 298.15K 时  $\Delta_f G_m^\ominus [\text{Hg}_2^{2+}(\text{aq})] = 152.0 \text{kJ} \cdot \text{mol}^{-1}$ 。

**解** (1) 负极  $\text{H}_2(\text{g}) \longrightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$

正极  $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^-(\text{aq})$



$$(2) \Delta_r G_m^\ominus = -zFE^\ominus = \{-2 \times 96485 \times 0.2680\} \text{J} \cdot \text{mol}^{-1} = -5.17 \times 10^4 \text{J} \cdot \text{mol}^{-1}$$

又  $\Delta_r G_m^\ominus = 2\Delta_f G_m^\ominus[\text{Cl}^-(\text{aq})] - \Delta_f G_m^\ominus[\text{Hg}_2\text{Cl}_2(\text{s})]$

即  $-5.17 \times 10^4 = 2 \times (-131.26 \times 10^3) - \Delta_f G_m^\ominus[\text{Hg}_2\text{Cl}_2(\text{s})] / \text{kJ} \cdot \text{mol}^{-1}$

解得  $\Delta_f G_m^\ominus[\text{Hg}_2\text{Cl}_2(\text{s})] = -210.8 \text{kJ} \cdot \text{mol}^{-1}$

$$(3) \Delta_r G_m^\ominus = \Delta_f G_m^\ominus[\text{Hg}_2^{2+}(\text{aq})] + 2\Delta_f G_m^\ominus[\text{Cl}^-(\text{aq})] - \Delta_f G_m^\ominus[\text{Hg}_2\text{Cl}_2(\text{s})]$$

$$= \{152.0 + 2 \times (-131.26) - (-210.8)\} \text{kJ} \cdot \text{mol}^{-1} = 100.3 \text{kJ} \cdot \text{mol}^{-1}$$

$$\ln K^\ominus = \frac{-\Delta_r G_m^\ominus}{RT} = \frac{-100300}{8.314 \times 298.15} = -40.48$$

$$K^\ominus = 2.63 \times 10^{-18}$$

**【点评】** 本题涉及电池反应中各物质的不同状态 (g、l、s、aq)，计算时应注意。另外，稀溶液中  $\text{H}^+$  的标准生成吉布斯自由能  $\Delta_f G_m^\ominus[\text{H}^+(\text{aq})] = 0$