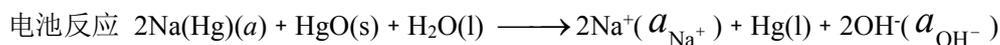
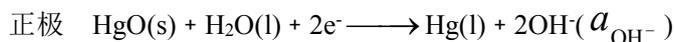
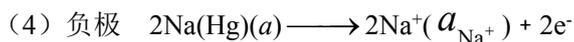
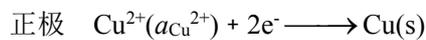
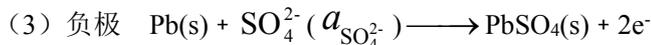
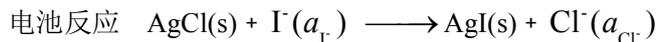
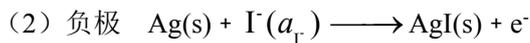
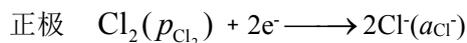
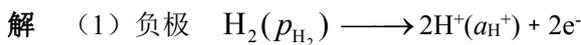
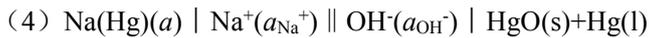
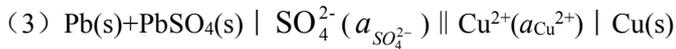
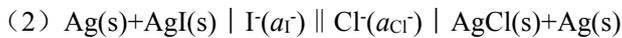


## 可逆电池电动势及其应用-作业(1) 作业点评

1. 写出下列电池中各电极上的反应和电池反应



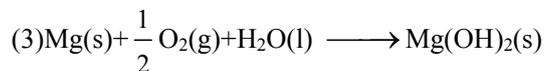
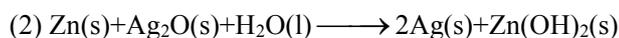
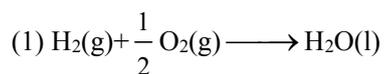
**【点评】**在电池表达式中规定最左边写负极，最右边写正极，因此若未作说明，我们通常默认电池按此规定表达。在写电极反应和电池反应时应遵循如下要求：

(1) 左侧的负极发生氧化反应，右侧的正极发生还原反应。两电极反应都必须满足质量守恒和电荷守恒，同时两电极反应中的得失电子数应相等。

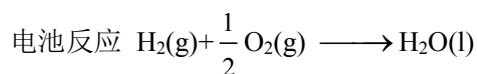
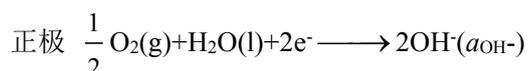
(2) 各参加反应的物种状态必须标出，气体还应标出压力，液体或固体还应标出浓度或活度。

(3) 在单液电池或有盐桥存在的电池中正极反应和负极反应相加的结果即为总电池反应。

2. 将下列化学反应设计成电池，并求出298.15K时电池的标准电动势

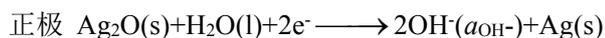
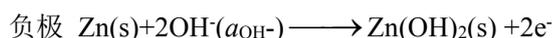


解 (1) (Pt)H<sub>2</sub>(g) | OH<sup>-</sup>(a<sub>OH<sup>-</sup>) | O<sub>2</sub>(g)(Pt)</sub>



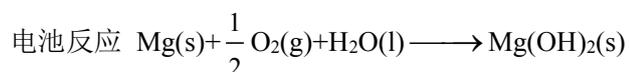
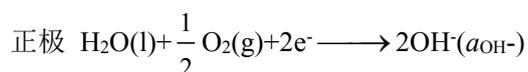
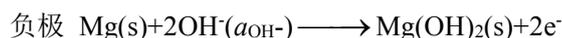
$$E^\ominus = E_+^\ominus - E_-^\ominus = \{0.401 - (-0.828)\} \text{V} = 1.229 \text{V}$$

(2) Zn(s) | Zn(OH)<sub>2</sub>(s) | OH<sup>-</sup>(a<sub>OH<sup>-</sup>) | Ag<sub>2</sub>O(s), Ag(s)</sub>



$$E^\ominus = E_+^\ominus - E_-^\ominus = \{0.344 - (-1.245)\} \text{V} = 1.589 \text{V}$$

(3) Mg(s) | Mg(OH)<sub>2</sub>(s) | OH<sup>-</sup>(a<sub>OH<sup>-</sup>) | O<sub>2</sub>(g)(Pt)</sub>

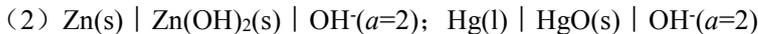
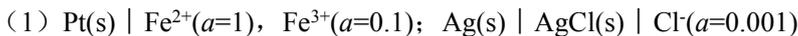


$$E^\ominus = E_+^\ominus - E_-^\ominus = \{0.401 - (-2.690)\} \text{V} = 3.091 \text{V}$$

**【点评】**将指定的过程(包括化学反应)设计成原电池是基本的要求，其关键是要设法从中分解出发生氧化作用的部分和发生还原作用的部分，连接两部分的电解液为相同电解液时优先考虑(此即单液电池)，若无法避免两部分使用不同电解液时，中间必须使用盐桥将其连接起来。电池表达式中规定最左边写负极，最右边写正极。

3. 根据标准电极电势及能斯特方程，计算298.15K时下列电极的电极电势，以及将第(1)组内

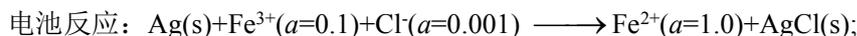
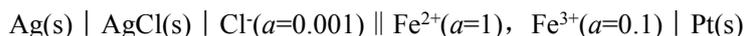
和第(2)内电极各自组成的电池的电动势，并写出电池反应。



解 (1)  $E_{\text{Fe}^{3+}|\text{Fe}^{2+}} = E_{\text{Fe}^{3+}|\text{Fe}^{2+}}^{\ominus} - \frac{RT}{F} \ln \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} = \{0.771 - 0.0592 \lg \frac{1.0}{0.1}\} \text{V} = 0.712 \text{V}$

$$E_{\text{AgCl,Ag}|\text{Cl}^-} = E_{\text{AgCl,Ag}|\text{Cl}^-}^{\ominus} - \frac{RT}{F} \ln a_{\text{Cl}^-} = \{0.222 - 0.0592 \lg 0.001\} \text{V} = 0.400 \text{V}$$

组成的电池为



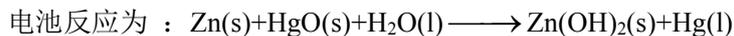
$$E = E_+ - E_- = \{0.712 - 0.400\} \text{V} = 0.312 \text{V}$$

(2)

$$E_{\text{Zn,Zn(OH)}_2|\text{OH}^-} = E_{\text{Zn,Zn(OH)}_2|\text{OH}^-}^{\ominus} - \frac{RT}{2F} \ln a_{\text{OH}^-}^2 = \{-1.245 - 0.0592 \lg 2\} \text{V} = -1.263 \text{V};$$

$$E_{\text{Hg,HgO}|\text{OH}^-} = E_{\text{Hg,HgO}|\text{OH}^-}^{\ominus} - \frac{RT}{2F} \ln a_{\text{OH}^-}^2 = \{0.0984 - 0.0592 \lg 2\} \text{V} = 0.0806 \text{V}$$

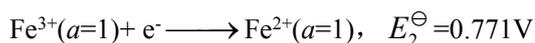
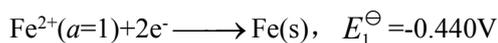
组成的电池为



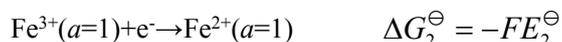
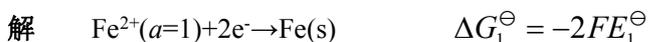
$$E = E_+ - E_- = \{0.0806 - (-1.263)\} \text{V} = 1.343 \text{V}$$

**【点评】**由不同的电极组成电池时，电池的电动势必须为正值；若连接正负极的电解液不同时，中间必须使用盐桥将其连接起来。

4. 试根据下列电极反应的  $E^{\ominus}$  (电极) 值



计算电极反应  $\text{Fe}^{3+}(a=1) + 3\text{e}^- \longrightarrow \text{Fe(s)}$  的  $E_3^{\ominus}$  值。



$$(1)+(2)\text{得: } \text{Fe}^{3+}(a=1)+3\text{e}^{-}\rightarrow\text{Fe}(\text{s}) \quad \Delta G_3^{\ominus} = -3FE_3^{\ominus}$$

$$\Delta G_3^{\ominus} = \Delta G_1^{\ominus} + \Delta G_2^{\ominus}$$

$$-3FE_3^{\ominus} = -2FE_1^{\ominus} - FE_2^{\ominus}$$

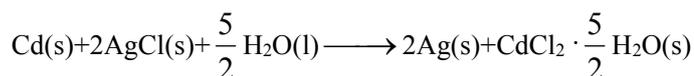
$$E_3^{\ominus} = \frac{2E_1^{\ominus} + E_2^{\ominus}}{3} = \left\{ \frac{-2 \times 0.440 + 0.771}{3} \right\} \text{V} = -0.036 \text{V}$$

**【点评】**此题为通过热力学与电化学的原理、方法及公式的综合应用解决问题的典型例题，其中隐含了盖斯定律的应用、吉布斯自由能变与电动势的关系的使用，数据的查阅与应用。

此解题过程是解决此类问题的典型思路，读者充分理解后可以触类旁通。

5.298.15K时，电池 $\text{Cd}(\text{s}) \mid \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}(\text{饱和溶液}) \mid \text{AgCl}(\text{s}) \mid \text{Ag}(\text{s})$ 的电动势为0.6753V，温度系数为 $-6.5 \times 10^{-4} \text{V} \cdot \text{K}^{-1}$ ，试计算此温度时电池反应的 $\Delta_r G_m$ 、 $\Delta_r H_m$ 、 $\Delta_r S_m$ 、 $Q_R$ 值。

**解** 电池反应为



$$\Delta_r G_m = -zFE = \{-2 \times 96485 \times 0.6753\} \text{J} \cdot \text{mol}^{-1} = -130.3 \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m = zF \left( \frac{\partial E}{\partial T} \right)_p = \{2 \times 96485 \times (-6.5 \times 10^{-4})\} \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -0.125 \text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m = -zFE + zFT \left( \frac{\partial E}{\partial T} \right)_p = \{-130.3 - 0.125 \times 298.15\} \text{kJ} \cdot \text{mol}^{-1} = -167.7 \text{kJ} \cdot \text{mol}^{-1}$$

$$Q_R = T\Delta_r S_m = \{298.15 \times (-0.125)\} \text{kJ} \cdot \text{mol}^{-1} = -37.27 \text{kJ} \cdot \text{mol}^{-1}$$

**【点评】**此题集中体现了原电池热力学所能解决的问题，其关键在于写出给定电池的电池反应，有确定的 $z$ 值后代入相关公式后即可求得结果。

6. 电池 $\text{Pt}(\text{s}) \mid \text{H}_2(p^{\ominus}) \mid \text{NaOH}(\text{稀}) \mid \text{Bi}_2\text{O}_3(\text{s}) \mid \text{Bi}(\text{s})$ 在291.15K时的电动势 $E=384.6\text{mV}$ ，在283.15K ~ 308.15K， $dE/dT=-0.39\text{mV} \cdot \text{K}^{-1}$ ，若291.15K时液态水的摩尔生成焓 $\Delta_f H_m = -285.84 \text{kJ} \cdot \text{mol}^{-1}$ ，试求 $\text{Bi}_2\text{O}_3(\text{s})$ 在相同温度时的 $\Delta_f H_m$ 值。

**解** 电池反应为  $3\text{H}_2(p^{\ominus}) + \text{Bi}_2\text{O}_3(\text{s}) \longrightarrow 2\text{Bi}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$

$$\begin{aligned} \Delta_r H_m &= 3\Delta_f H_m(\text{H}_2\text{O}) - \Delta_f H_m(\text{Bi}_2\text{O}_3) \\ \Delta_f H_m(\text{Bi}_2\text{O}_3) &= 3\Delta_f H_m(\text{H}_2\text{O}) - \Delta_r H_m \\ \text{而 } \Delta_r H_m &= -zEF + zFT\left(\frac{\partial E}{\partial T}\right)_p = zF\left[T\left(\frac{\partial E}{\partial T}\right)_p - E\right] \\ &= \{6 \times 96485 \times [291.15 \times (-0.00039) - 0.3846]\} \text{J} \cdot \text{mol}^{-1} \\ &= -288.3 \text{kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\text{所以 } \Delta_f H_m(\text{Bi}_2\text{O}_3) = \{3 \times (-285.84) - (-288.3)\} \text{kJ} \cdot \text{mol}^{-1} = -569.2 \text{kJ} \cdot \text{mol}^{-1}$$

**【点评】** 此题为通过电化学的方法就算热力学数据。此题的解题关键是

$$\Delta_r H_m = -zEF + zFT\left(\frac{\partial E}{\partial T}\right)_p \text{ 以及 } \Delta_r H_m = \sum_{\text{B}} \nu_{\text{B}} \Delta_f H_m(\text{B})。$$