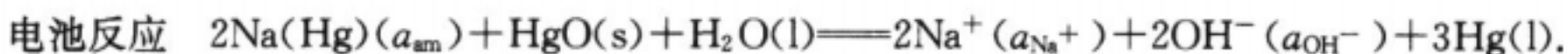
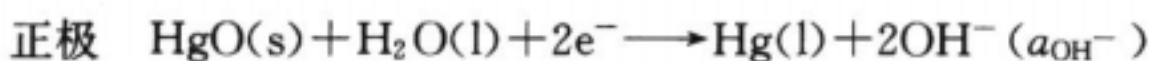
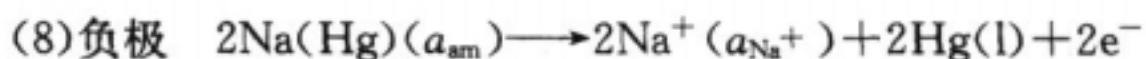
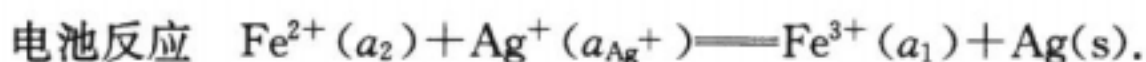
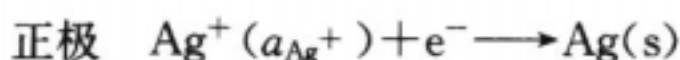
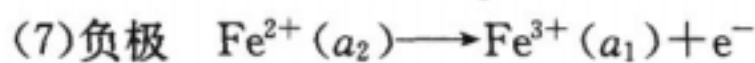
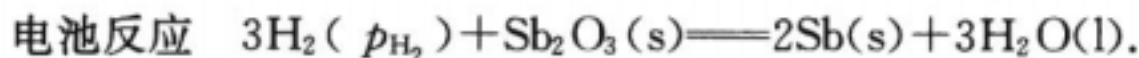
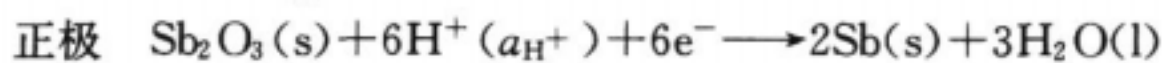
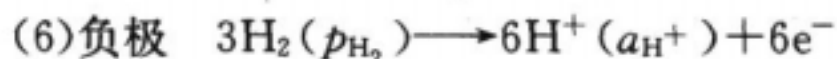
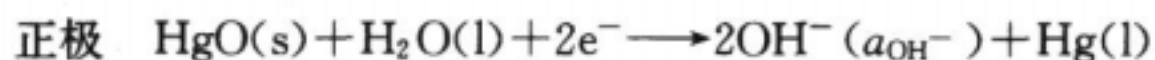
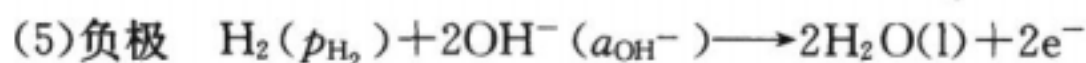
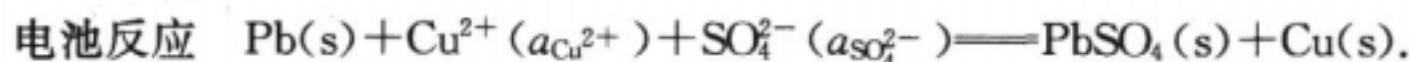
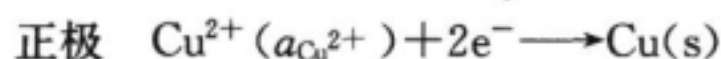
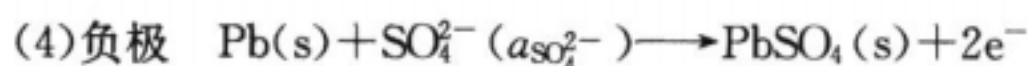
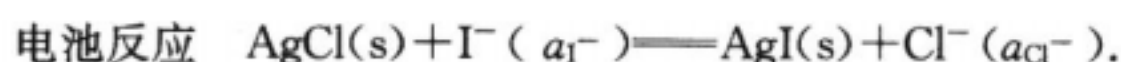
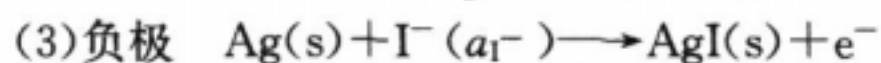
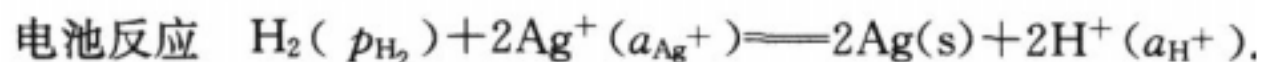
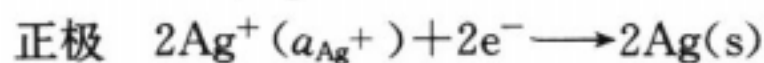
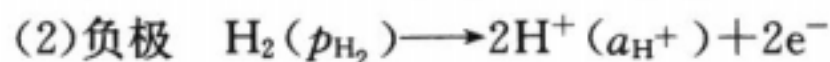
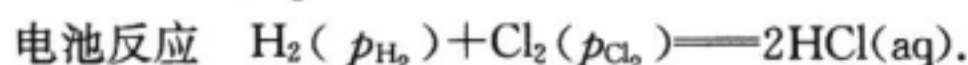
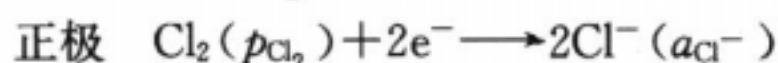
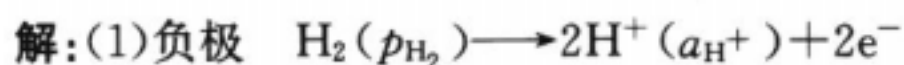
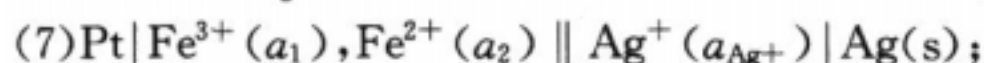
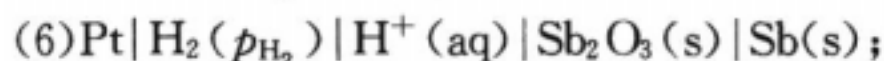
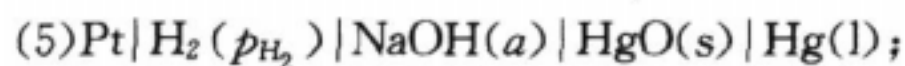
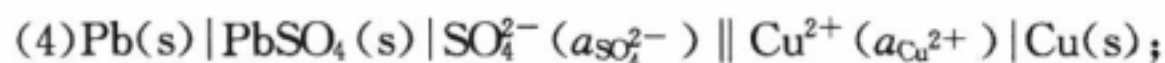
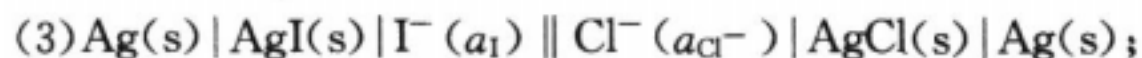
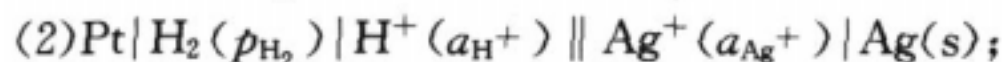
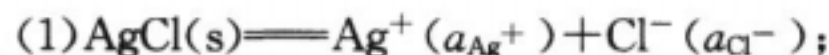


第九章 可逆电池的电动势及其应用

1. 写出下列电池中各电极的反应和电池反应.



2. 试将下述化学反应设计成电池.



- (3) $\text{H}_2(p_{\text{H}_2}) + \text{HgO}(\text{s}) = \text{Hg}(\text{l}) + \text{H}_2\text{O}(\text{l})$;
 (4) $\text{Fe}^{2+}(a_{\text{Fe}^{2+}}) + \text{Ag}^+(a_{\text{Ag}^+}) = \text{Fe}^{3+}(a_{\text{Fe}^{3+}}) + \text{Ag}(\text{s})$;
 (5) $2\text{H}_2(p_{\text{H}_2}) + \text{O}_2(p_{\text{O}_2}) = 2\text{H}_2\text{O}(\text{l})$;
 (6) $\text{Cl}_2(p_{\text{Cl}_2}) + 2\text{I}^-(a_{\text{I}^-}) = \text{I}_2(\text{s}) + 2\text{Cl}^-(a_{\text{Cl}^-})$;
 (7) $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(a_{\text{H}^+}) + \text{OH}^-(a_{\text{OH}^-})$;
 (8) $\text{Mg}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) = \text{Mg}(\text{OH})_2(\text{s})$;
 (9) $\text{Pb}(\text{s}) + \text{HgO}(\text{s}) = \text{Hg}(\text{l}) + \text{PbO}(\text{s})$;
 (10) $\text{Sn}^{2+}(a_{\text{Sn}^{2+}}) + \text{Tl}^{3+}(a_{\text{Tl}^{3+}}) = \text{Sn}^{4+}(a_{\text{Sn}^{4+}}) + \text{Tl}^+(a_{\text{Tl}^+})$.

解:设计电池

- (1) $\text{Ag}(\text{s}) | \text{Ag}^+(a_{\text{Ag}^+}) || \text{Cl}^-(a_{\text{Cl}^-}) | \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$
 (2) $\text{Ag}(\text{s}) | \text{AgI}(\text{s}) | \text{I}^-(a_{\text{I}^-}) || \text{Cl}^-(a_{\text{Cl}^-}) | \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$
 (3) $\text{Pt} | \text{H}_2(p_{\text{H}_2}) | \text{OH}^-(a_{\text{OH}^-}) | \text{HgO}(\text{s}) | \text{Hg}(\text{l})$
 (4) $\text{Pt} | \text{Fe}^{2+}(a_{\text{Fe}^{2+}}), \text{Fe}^{3+}(a_{\text{Fe}^{3+}}) | \text{Ag}^+(a_{\text{Ag}^+}) | \text{Ag}(\text{s})$
 (5) $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+(a_{\text{H}^+}) | \text{O}_2(\text{g}) | \text{Pt}$
 (6) $\text{I}_2(\text{s}) | \text{I}^-(a_{\text{I}^-}) || \text{Cl}^-(a_{\text{Cl}^-}) | \text{Cl}_2(\text{g}) | \text{Pt}$

3. 从饱和 Weston 电池的电动势与温度的关系式, 试求在 298.15 K, 当电池可逆地产生 2 mol 电子的电荷量时, 电池反应的 $\Delta_r G_m$, $\Delta_r H_m$, 和 $\Delta_r S_m$. 已知该关系为

$$E/\text{V} = 1.01845 - 4.05 \times 10^{-5}(T/\text{K} - 293.15) - 9.5 \times 10^{-7}(T/\text{K} - 293.15)^2$$

解: 由 E 的关系式求出 $\left(\frac{\partial E}{\partial T}\right)_p$, 再求出 298.15 K 时 E 的值.

因为: $\Delta_r G_m = -zEF$; $\Delta_r H_m = \Delta_r G_m + T \cdot \Delta_r S_m$.

$$\left(\frac{\partial E}{\partial T}\right)_p = -4.05 \times 10^{-5} - 2 \times 9.5 \times 10^{-7} \times (T - 293.15) \text{V} \cdot \text{K}^{-1}$$

$$\text{当 } T = 298.15 \text{ K 时, } \left(\frac{\partial E}{\partial T}\right)_p = -5.0 \times 10^{-5} \text{V} \cdot \text{K}^{-1}$$

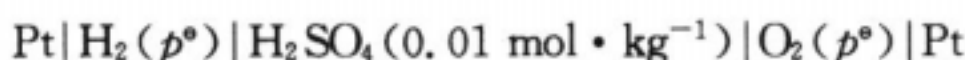
$$E = 1.01815 - 4.05 \times 10^{-5}(298.15 - 293.15) - 9.5 \times 10^{-7}(298.15 - 293.15)^2 = 1.018 \text{ V}$$

$$\Delta_r S_m = zF\left(\frac{\partial E}{\partial T}\right)_p = 2 \times 96500(-5.0 \times 10^{-5}) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -9.65 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m = -zEF = -2 \times 96500 \times 1.018 \text{ J} \cdot \text{mol}^{-1} = -196.5 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta_r H_m &= -zEF + TzF\left(\frac{\partial E}{\partial T}\right)_p = \Delta_r G_m + T \cdot \Delta_r S_m = -196.5 \text{ kJ} \cdot \text{mol}^{-1} \\ &\quad + 298.15 \times (-9.65 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -199.4 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

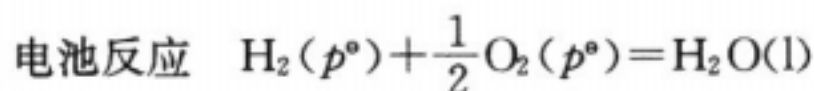
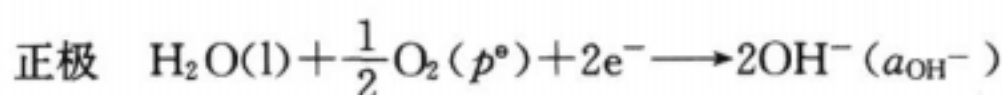
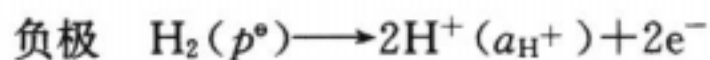
4. 298 K 时, 下述电池的电动势为 1.228 V:



已知 $\text{H}_2\text{O}(\text{l})$ 的标准摩尔生成焓为 $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ} \cdot \text{mol}^{-1}$. 试求:

- (1) 该电池的温度系数;
 (2) 该电池在 273 K 时的电动势. 设反应焓在该温度区间内为常数.

解: (1) 电池反应:



$$\Delta_r G_m = -zFE = -2 \times 96500 \times 1.228 \text{ J} \cdot \text{mol}^{-1} = -237.004 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m = \Delta_r G_m + T \cdot \Delta_r S_m \text{ 其中 } \Delta_r S_m = zF \left(\frac{\partial E}{\partial T} \right)_p$$

$$\Delta_r S_m = \frac{\Delta_r H_m - \Delta_r G_m}{T} = \frac{-286.1 + 237.004}{298 \text{ K}} = -164.75 \text{ J} \cdot \text{mol}^{-1}$$

$$\left(\frac{\partial E}{\partial T} \right)_p = \frac{\Delta_r S_m}{zF} = \frac{-164.75}{2 \times 96500} = -8.54 \times 10^{-4} \text{ V} \cdot \text{K}^{-1}$$

$$(2) \Delta_r H_m = -zFE + zFT \left(\frac{\partial E}{\partial T} \right)_p \quad \Delta_r H_m \text{ 不随温度变化}$$

$$E = \frac{zFT \left(\frac{\partial E}{\partial T} \right)_p - \Delta_r H_m}{zF}$$

$$T = 273 \text{ K 时}, E = 273 \cdot (-8.54 \times 10^{-4}) - \frac{-286.1 \times 10^3}{2 \times 96500} = 1.249 \text{ V.}$$

5. 电池 $\text{Zn(s)} | \text{ZnCl}_2(0.05 \text{ mol} \cdot \text{kg}^{-1}) | \text{AgCl(s)} | \text{Ag(s)}$ 的电动势与温度的关系为

$$E/\text{V} = 1.015 - 4.92 \times 10^{-4} (T/\text{K}) - 298$$

试计算在 298 K 当电池有 2 mol 电子的电荷量输出时, 电池反应的 $\Delta_r G_m$, $\Delta_r H_m$, $\Delta_r S_m$ 和此过程的可逆热效应 Q_R .

解: 298 K 时有 2 mol 电子的电荷量输出

$$E = 1.015 - 4.92 \times 10^{-4} (298 - 298) = 1.015 \text{ V}$$

$$\Delta_r G_m = -zEF = -2 \times 96500 \times 1.015 = -195.9 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m = zF \left(\frac{\partial E}{\partial T} \right)_p = 2 \times 96500 \times (-4.92 \times 10^{-4}) = -95.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta_r H_m = \Delta_r G_m + T \cdot \Delta_r S_m = -195.9 \text{ kJ} \cdot \text{mol}^{-1} + 298 \times (-95.0) \text{ J} \cdot \text{mol}^{-1} = -224.21 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\text{可逆热效应为: } Q_R = T \cdot \Delta_r S_m = 298 \text{ K} \cdot (-95.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = -28.31 \text{ kJ} \cdot \text{mol}^{-1}$$

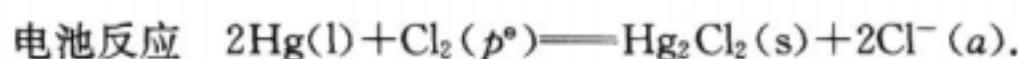
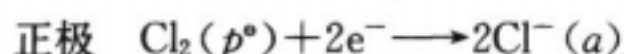
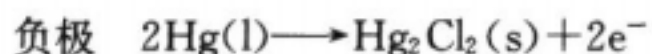
6. 在 298 K 时, 电池 $\text{Hg(l)} | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{HCl(a)} | \text{Cl}_2(p^\circ) | \text{Pt(s)}$ 的电动势为 1.092 V, 温度系数为 $9.427 \times 10^{-4} \text{ V} \cdot \text{K}^{-1}$.

(1) 写出有 2 个电子得失的电极反应和电池的净反应;

(2) 计算与该电池反应相应的 $\Delta_r G_m$, $\Delta_r S_m$, $\Delta_r H_m$ 及可逆热效应 Q_R . 若只有 1 个电子得失, 则这些值又等于多少?

(3) 计算在相同的温度和压力下, 与 2 个电子得失的电池净反应相同的热化学方程式的热效应.

解: (1) 在 298 K 时



$$(2) \Delta_r G_m = -zFE = -2 \times 96500 \times 1.092 = -210.756 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m = zF \left(\frac{\partial E}{\partial T} \right)_p = 2 \times 96500 \times 9.427 \times 10^{-4} = 181.94 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta_r H_m = \Delta_r G_m + T \cdot \Delta_r S_m$$

$$= (-210.756 \times 10^3 + (181.94 \times 298)) = -156.54 \text{ kJ} \cdot \text{mol}^{-1}$$

$$Q_R = T \cdot \Delta_r S_m = 298 \times 181.94 \text{ J} \cdot \text{mol}^{-1} = 54.22 \text{ kJ} \cdot \text{mol}^{-1}$$

若只有一个电子, 则所求的值变为原来的 1/2.

(3) 若在相同温度压力下, 热化学方程式的热效应为

$$Q_p = \Delta_r H_m = -156.54 \text{ kJ} \cdot \text{mol}^{-1}$$

7. 一个可逆电动势为 1.70 V 的原电池, 在恒温槽中恒温至 293 K. 当些电池短路时 (即直接发生化学反应, 不作电功), 相当于有 1000 °C 的电荷量通过. 假定电池中发生的反应与可逆放电时的反应相同, 试求以此电池和恒温槽都看作系统时总的熵变. 如果要分别求算恒温槽和电池的熵变, 还需何种数据?

解: 电池发生的反应与可逆放电时的反应相同.

$$\text{系统的 } \Delta_r G_m = W_{l, \max} = -nEF$$

$$= -(nF)E = -Q \cdot E = +1000 \cdot 1.70 = 1.7 \times 10^3 \text{ J}$$

$$Q_p = \Delta_r H_m$$

$$\Delta S(\text{槽}) = -\frac{Q_p}{T}$$

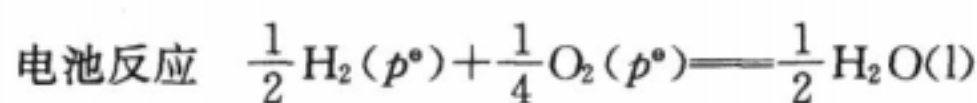
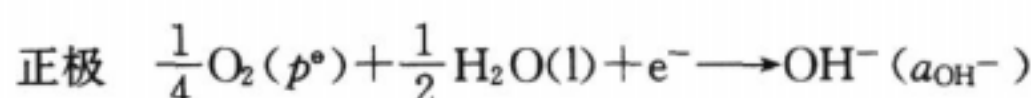
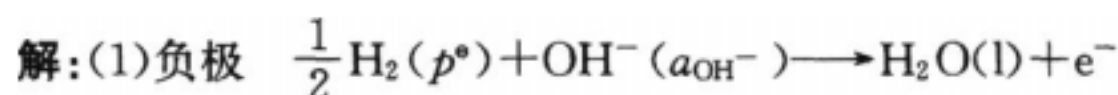
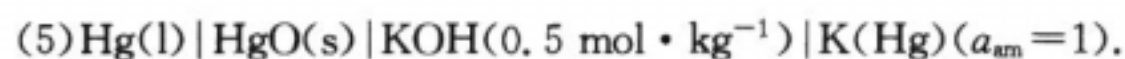
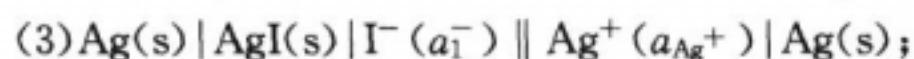
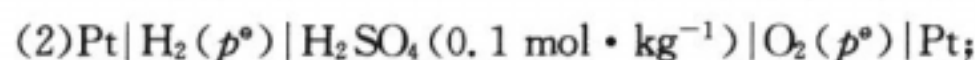
$$\text{体系的 } \Delta_r H = \Delta_r G + T \Delta_r S = 0$$

$$\Delta_r S = \frac{-\Delta_r G}{T} = \frac{W_l}{T} = \frac{1.7 \times 10^3 \text{ J}}{293 \text{ K}} = 5.8 \text{ J} \cdot \text{K}^{-1}$$

若要分别求焓变还需知道电池反应的焓变.

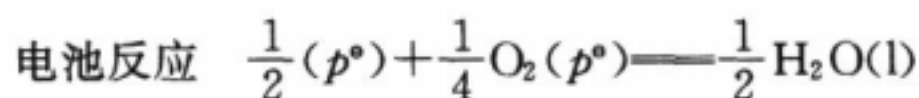
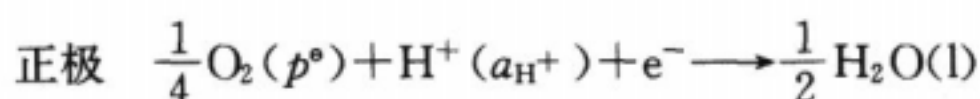
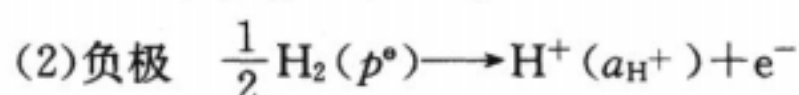
8. 分别写出下列电池的电极反应、电池反应, 列出电动势 E 的计算公式, 并计算电池的标准电动势 E° .

设活度因子均为 1, 气体为理想气体. 所需的标准电极从电极电势表中查阅.

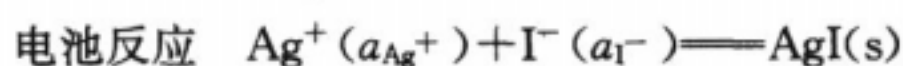
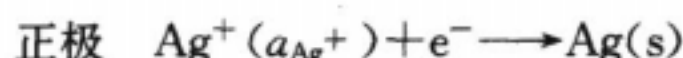
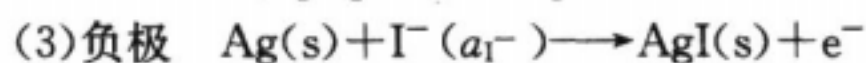


$$\text{电动势 } E = E^\circ - \frac{RT}{F} \ln \left(\frac{a_{\text{H}_2\text{O}}}{a_{\text{H}_2} \cdot a_{\text{O}_2}} \right)^{\frac{1}{2}} = E^\circ$$

$$E^\circ = \varphi_{\text{O}_2 | \text{H}_2\text{O}}^\circ - \varphi_{\text{H}^+ | \text{H}_2}^\circ.$$

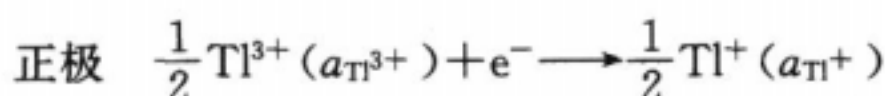
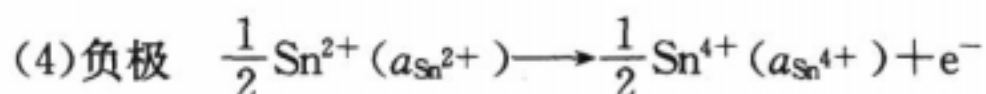


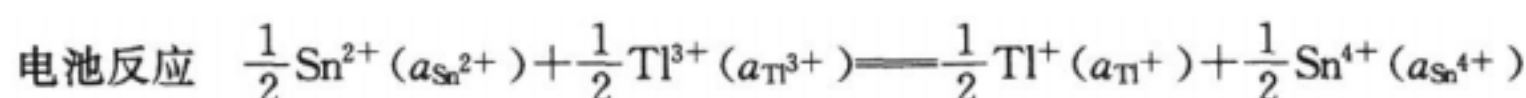
$$E = E^\circ = \varphi_{\text{O}_2 | \text{H}_2\text{O}}^\circ - \varphi_{\text{H}^+ | \text{H}_2}^\circ$$



$$E = E^\circ - \frac{RT}{F} \ln \frac{1}{a_{\text{Ag}^+} a_{\text{I}^-}}$$

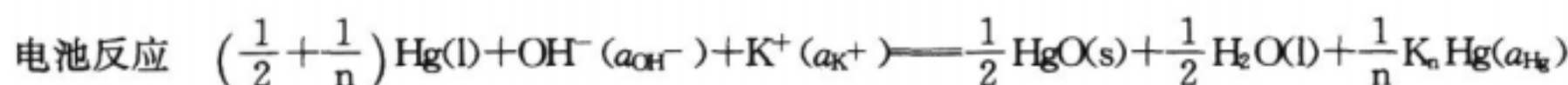
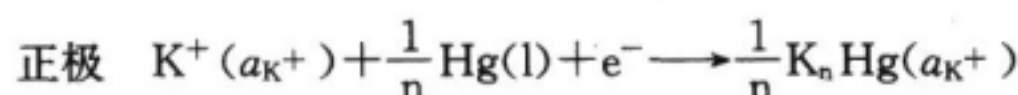
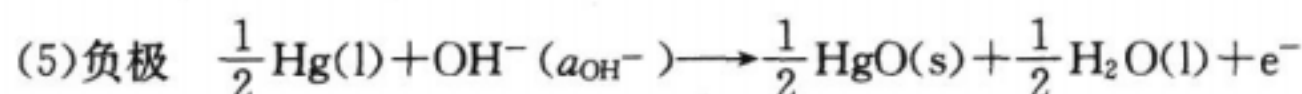
$$E^\circ = \varphi_{\text{Ag}^+ | \text{Ag}}^\circ - \varphi_{\text{AgI} | \text{Ag}}^\circ.$$





$$E = E^{\circ} - \frac{RT}{F} \ln \left(\frac{a_{\text{Sn}^{4+}} \cdot a_{\text{Tl}^{+}}}{a_{\text{Sn}^{2+}} \cdot a_{\text{Tl}^{3+}}} \right)^{\frac{1}{2}}$$

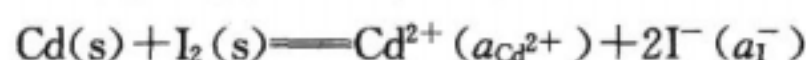
$$E^{\circ} = \varphi_{\text{Tl}^{3+}, \text{Tl}^{+}}^{\circ} + \varphi_{\text{Sn}^{4+}, \text{Sn}^{2+}}^{\circ}$$



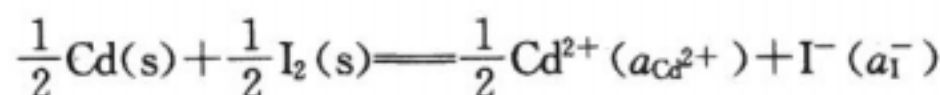
$$E = E^{\circ} - \frac{RT}{F} \ln \frac{1}{a_{\text{K}^{+}} \cdot a_{\text{OH}^{-}}}$$

$$E^{\circ} = \varphi_{\text{K}^{+}, \text{Hg}, \text{K}_n \text{Hg}}^{\circ} - \varphi_{\text{HgO}, \text{Hg}, \text{OH}^{-}}^{\circ}$$

9. 试为下述反应设计一电池

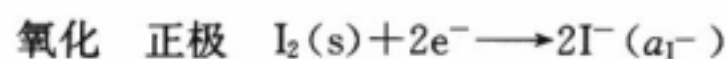
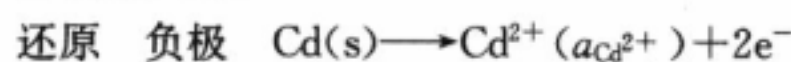


求电池在 298 K 时的标准电动势 E° , 反应的 $\Delta_r G_m^{\circ}$ 和标准平衡常数 K_a° . 如将电池反应写成



再计算 E° , $\Delta_r G_m^{\circ}$ 和 K_a° , 比较两者的结果, 并说明为什么.

解: 设计电池



$$E^{\circ} = \varphi_{\text{I}_2 | \text{I}^{-}}^{\circ} - \varphi_{\text{Cd}^{2+} | \text{Cd}}^{\circ}$$

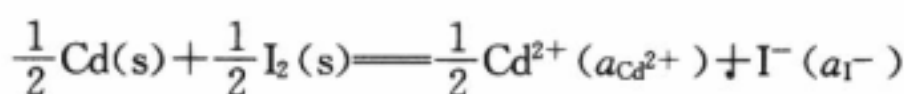
$$= 0.5355 - (-0.4029) = 0.9384 \text{ V}$$

$$\Delta_r G_m^{\circ} = -zE^{\circ}F = -2 \times 96500 \times 0.9384 = -181.11 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln K_a^{\circ} = -\frac{\Delta_r G_m^{\circ}}{RT} = -\frac{-181.11 \times 10^3}{8.314 \times 298} = 73.0958$$

$$K_a^{\circ} = 5.56 \times 10^{31}$$

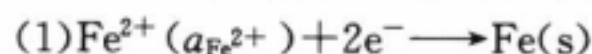
电池反应式写成



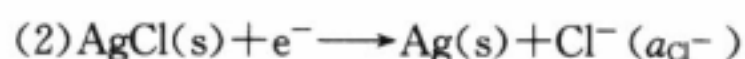
$$E^{\circ} \text{ 不变} \quad \Delta_r G_m^{\circ}(2) = \frac{1}{2} \Delta_r G_m^{\circ}(1) = -90.56 \text{ kJ} \cdot \text{mol}^{-1}$$

$$K_{a(2)}^{\circ} = (K_{a(1)}^{\circ})^{\frac{1}{2}} = 7.46 \times 10^{15}$$

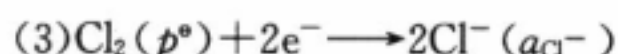
10. 298 K 时, 已知如下三个电极的反应及标准还原电极电势, 如将电极(1)与(3)和(2)与(3)分别组成自发电池(设活度均为 1), 请写出电池的书面表示式; 写出电池反应式并计算电池的标准电动势.



$$\varphi^{\circ}(\text{Fe}^{2+} | \text{Fe}) = -0.440 \text{ V};$$



$$\varphi^{\circ}(\text{Cl}^{-} | \text{AgCl} | \text{Ag}) = 0.2223 \text{ V};$$

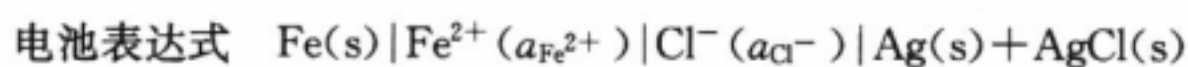
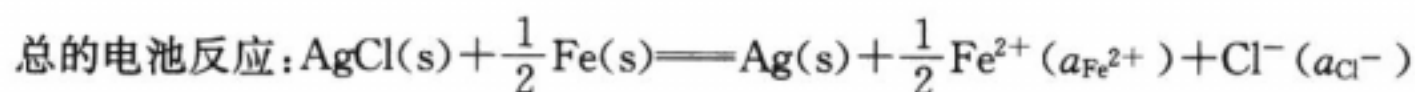
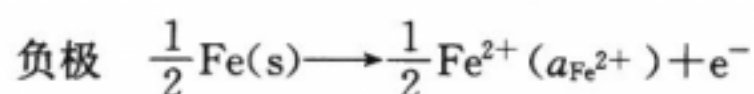


$$\varphi^{\circ}(\text{Cl}_2 | \text{Cl}^{-}) = 1.3583 \text{ V}.$$

解: 自发反应 $E > 0$, 电极电势高的做正极

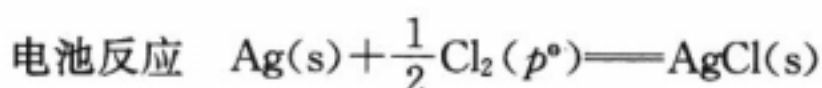
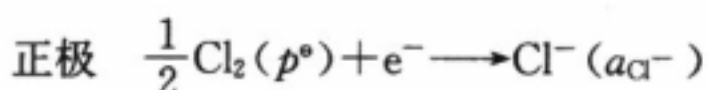
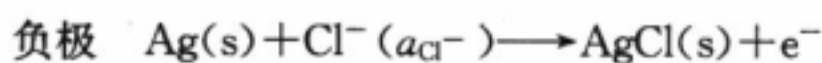
电极(1)的电极电势 < 电极(2)的电极电势.

(2)为正极,电池反应



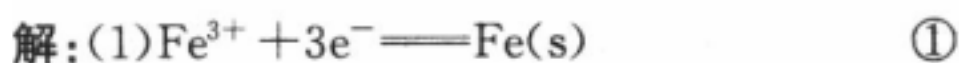
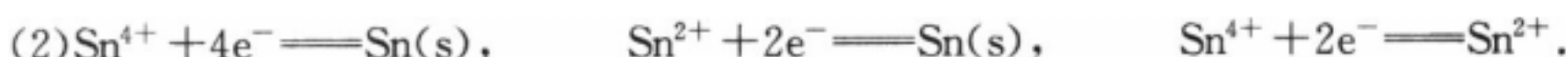
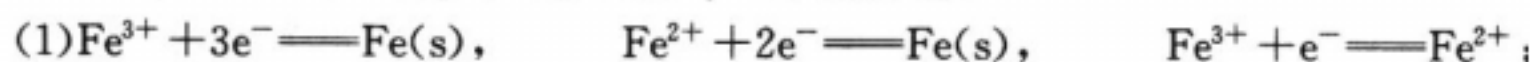
$$E^{\circ} = \varphi_{\text{Cl}^{-} | \text{AgCl} | \text{Ag}}^{\circ} - \varphi_{\text{Fe}^{2+} | \text{Fe}}^{\circ} = 0.2223 - (-0.440) = 0.6623 \text{ V.}$$

同理(2)与(3)组成的自发电池(3)为正极



$$E^{\circ} = \varphi_{\text{Cl}_2 | \text{Cl}^{-}}^{\circ} - \varphi_{\text{Cl}^{-} | \text{AgCl} | \text{Ag}}^{\circ} = (1.3583 - 0.2223) = 1.136 \text{ V.}$$

11. 列式表示下列两组标准电极电势 φ° 之间的关系.



$$\Delta_r G_m^{\circ}(1) - \Delta_r G_m^{\circ}(2) = \Delta_r G_m^{\circ}(3)$$

$$\Delta_r G_m^{\circ}(1) = -3\varphi_{\text{Fe}^{3+} | \text{Fe}}^{\circ} \cdot F$$

$$\because \Delta_r G_m^{\circ} = -zFE^{\circ}$$

E° 为该电极与标准 H_2 电极组成的电池的电动势

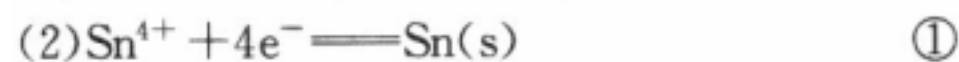
$$E^{\circ} = \varphi^{\circ} - 0$$

$$\therefore \Delta_r G_m^{\circ} = -zF\varphi^{\circ}$$

$$\Delta_r G_m^{\circ}(2) = -2\varphi_{\text{Fe}^{2+} | \text{Fe}}^{\circ} \cdot F$$

$$\begin{aligned} \therefore \Delta_r G_m^{\circ}(3) &= \Delta_r G_m^{\circ}(1) - \Delta_r G_m^{\circ}(2) \\ &= -3\varphi_{\text{Fe}^{3+} | \text{Fe}}^{\circ} \cdot F - (-2\varphi_{\text{Fe}^{2+} | \text{Fe}}^{\circ} \cdot F) \\ &= -1\varphi_{\text{Fe}^{3+} | \text{Fe}^{2+}}^{\circ} \cdot F \end{aligned}$$

$$\therefore \varphi_{\text{Fe}^{3+} | \text{Fe}^{2+}}^{\circ} = 3\varphi_{\text{Fe}^{3+} | \text{Fe}}^{\circ} - 2\varphi_{\text{Fe}^{2+} | \text{Fe}}^{\circ}$$



$$\Delta_r G_m^{\circ}(1) = -4\varphi_{\text{Sn}^{4+} | \text{Sn}}^{\circ} \cdot F$$

$$\Delta_r G_m^{\circ}(2) = -2\varphi_{\text{Sn}^{2+} | \text{Sn}}^{\circ} \cdot F$$

$$\Delta_r G_m^{\circ}(3) = \Delta_r G_m^{\circ}(1) - \Delta_r G_m^{\circ}(2)$$

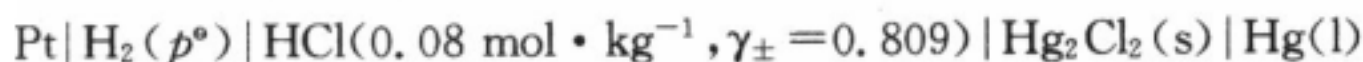
$$\text{同样: } \Delta_r G_m^{\circ} = -zF\varphi^{\circ}$$

$$\Delta_r G_m^{\circ}(3) = -4\varphi_{\text{Sn}^{4+} | \text{Sn}}^{\circ} \cdot F - (-2\varphi_{\text{Sn}^{2+} | \text{Sn}}^{\circ} \cdot F)$$

$$= -2\varphi_{\text{Sn}^{4+}|\text{Sn}^{2+}}^{\ominus} \cdot F$$

$$\therefore \varphi_{\text{Sn}^{4+}|\text{Sn}^{2+}}^{\ominus} = 2\varphi_{\text{Sn}^{4+}|\text{Sn}}^{\ominus} - \varphi_{\text{Sn}^{2+}|\text{Sn}}^{\ominus}$$

12. 298 K 时, 已知如下电池的标准电动势 $E^{\ominus} = 0.2680 \text{ V}$:



(1) 写出电极反应和电池反应.

(2) 计算该电池的电动势.

(3) 计算甘汞电极的标准电极电势.

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

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

总电极反应 $\text{H}_2(p^{\ominus}) + \text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons 2\text{H}^+(a_{\text{H}^+}) + 2\text{Hg}(\text{l}) + 2\text{Cl}^-(a_{\text{Cl}^-})$.

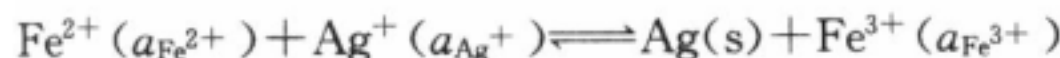
$$(2) E = E^{\ominus} - \frac{RT}{zF} \ln \frac{(a_{\text{H}^+})^2 (a_{\text{Cl}^-})^2}{1}$$

$$= E^{\ominus} - \frac{8.314 \times 298}{2 \times 96500} \ln(0.08 \times 0.809)^4 = 0.409 \text{ V}.$$

$$(3) \varphi_{\text{Hg}_2\text{Cl}_2|\text{Hg}}^{\ominus} - \varphi_{\text{H}^+|\text{H}_2}^{\ominus} = E^{\ominus}$$

$$\varphi_{\text{Hg}_2\text{Cl}_2|\text{Hg}}^{\ominus} = E^{\ominus} = 0.268 \text{ V}.$$

13. 试设计一个电池, 使其中进行下述反应



(1) 写出电池的表示式.

(2) 计算上述电池反应在 298 K、反应进度为 1 mol 时的标准平衡常数 K_a^{\ominus} .

(3) 若将过量磨细的银粉加到浓度为 $0.05 \text{ mol} \cdot \text{kg}^{-1}$ 的 $\text{Fe}(\text{NO}_3)_3$ 溶液中, 求当反应达平衡后, Ag^+ 的浓度为多少? (设活度因子均等于 1.)

解: (1) 电池表示式为 $\text{Pt}|\text{Fe}^{2+}(a_1), \text{Fe}^{3+}(a_2)||\text{Ag}^+(a_3)|\text{Ag}(\text{s})$.

$$(2) \text{平衡常数 } \ln K_a^{\ominus} = \frac{zE^{\ominus}F}{RT}$$

$$E^{\ominus} = \varphi_{\text{Ag}^+|\text{Ag}}^{\ominus} - \varphi_{\text{Fe}^{3+}|\text{Fe}^{2+}}^{\ominus}$$

$$\ln K_a^{\ominus} = \frac{1 \times (0.7991 - 0.771) \cdot 96500}{298 \times 8.314} = 1.094$$

$$K_a^{\ominus} = 2.988.$$

(3) 已知 $\text{Ag}(\text{s}) + \text{Fe}^{3+} \rightleftharpoons \text{Ag}^+ + \text{Fe}^{2+}$

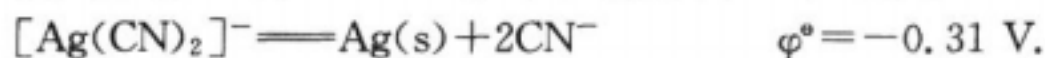
开始 0.05 0 0

平衡 0.05 - a a a

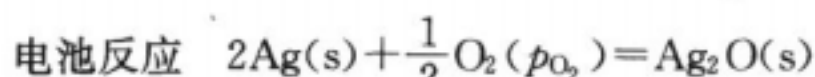
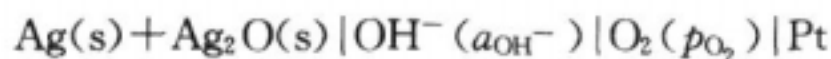
$$K_a^{\ominus} = \frac{a^2}{0.05 - a} = (K_a^{\ominus})^{-1} = (2.988)^{-1}$$

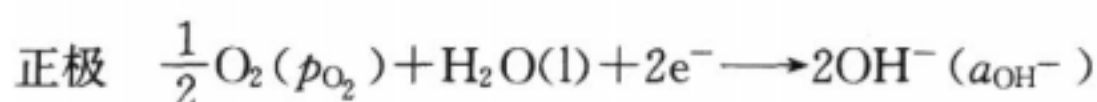
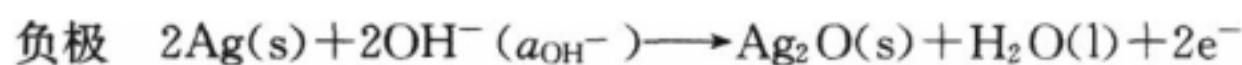
$$a = 4.417 \times 10^{-2} \text{ mol} \cdot \text{kg}^{-1}.$$

14. 试设计合适的电池判断在 298 K 时, 将金属银插在碱溶液中, 在通常的空气中银是否会被氧化? (空气中氧气分压为 21 kPa). 如果在溶液中加入大量的 CN^- , 情况又怎样? 已知:



解: 设计电池



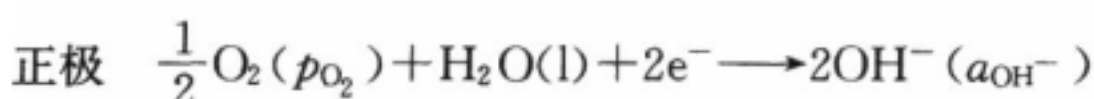
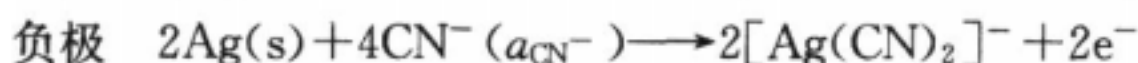
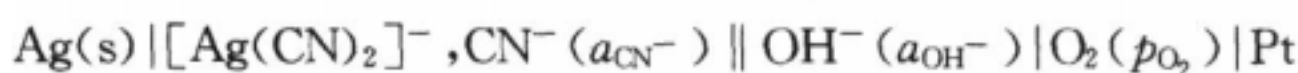


$$E^\ominus = \varphi_{\text{O}_2|\text{OH}^-}^\ominus - \varphi_{\text{Ag}_2\text{O}|\text{Ag}|\text{OH}^-}^\ominus = (0.401 - 0.344) \text{ V} \\ = 0.057 \text{ V}$$

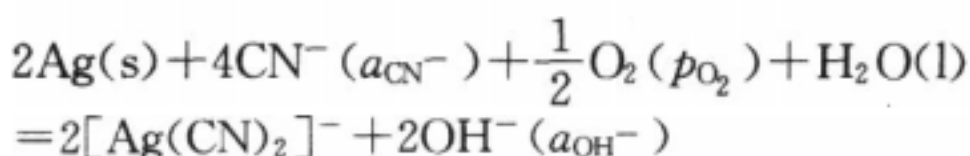
$$E = E^\ominus - \frac{RT}{zF} \ln \frac{1}{a_{\text{O}_2}^{1/2}} = E^\ominus - \frac{RT}{zF} \ln \left(\frac{p_{\text{O}_2}}{p^\ominus} \right)^{-\frac{1}{2}} \text{ V} \\ = 0.057 \text{ V} - \frac{8.314 \times 298}{2 \times 96500} \ln(0.21)^{-\frac{1}{2}} \text{ V} \\ = 0.047 \text{ V} > 0$$

$\Delta_r G_m = -zFE < 0$ 电池是自发的, 在空气中碱性条件下 Ag 能被氧化成氧化银.

加入 CN^- 后, 电池变为



电池反应:



$$\text{电动势 } E = E^\ominus - \frac{RT}{2F} \ln \frac{1}{a_{\text{O}_2}^{1/2}} - \frac{RT}{2F} \ln \frac{(a_{\text{OH}^-})^2 ([\text{Ag}(\text{CN})_2]^-)^2}{(a_{\text{CN}^-})^4}$$

$$E = \varphi_{\text{O}_2|\text{OH}^-}^\ominus - \varphi_{[\text{Ag}(\text{CN})_2]^-|\text{Ag}}^\ominus - \frac{RT}{2F} \ln \frac{1}{a_{\text{O}_2}^{1/2}} - \frac{RT}{2F} \ln \frac{(a_{\text{OH}^-})^2 ([\text{Ag}(\text{CN})_2]^-)^2}{(a_{\text{CN}^-})^4}$$

$$= 0.401 - (-0.31) - 0.01 - \frac{RT}{zF} \ln \frac{(a_{\text{OH}^-})^2 ([\text{Ag}(\text{CN})_2]^-)^2}{(a_{\text{CN}^-})^4}$$

$$= 0.701 - \frac{RT}{zF} \ln \frac{(a_{\text{OH}^-})^2 ([\text{Ag}(\text{CN})_2]^-)^2}{(a_{\text{CN}^-})^4}$$

大量 CN^- 存在, a_{CN^-} 很大, 而 a_{OH^-} 与 $a_{[\text{Ag}(\text{CN})_2]^-}$ 都很小

$$\text{故 } \ln \frac{(a_{\text{OH}^-})^2 ([\text{Ag}(\text{CN})_2]^-)^2}{(a_{\text{CN}^-})^4} < 0$$

$$E > 0.701$$

此时电池电动势大于不加大量 CN^- 离子时的电池电动势.

$$E = \frac{RT \ln K_a^\ominus}{zF} \quad E \text{ 越正 } K_a^\ominus \text{ 越大}$$

反应的趋势越大.

所以, 加入 CN^- 后, Ag 氧化成 $[\text{Ag}(\text{CN})_2]^-$.

15. 在 298 K 时, 分别用金属 Fe 和 Cd 插入下述溶液, 组成电池. 试判断何种金属首先被氧化?

(1) 溶液中含 Fe^{2+} 和 Cd^{2+} 的活度是 0.1.

(2) 溶液中含 Fe^{2+} 的活度是 0.1, 而含 Cd^{2+} 的活度是 0.0036.

$$\text{解: (1) } \varphi_1^\ominus = \varphi_{\text{Cd}^{2+}|\text{Cd}}^\ominus = -0.4029 \text{ V}$$

$$\varphi_2^\ominus = \varphi_{\text{Fe}^{2+}|\text{Fe}}^\ominus = -0.4402 \text{ V}$$

$\varphi_1^\ominus > \varphi_2^\ominus$, 以 φ_1^\ominus 为正极

设计电池 $\text{Fe(s)} | \text{Fe}^{2+}(a_{\text{Fe}^{2+}}), \text{Cd}^{2+}(a_{\text{Cd}^{2+}}) | \text{Cd(s)}$

负极 $\text{Fe(s)} \longrightarrow \text{Fe}^{2+}(a_{\text{Fe}^{2+}}) + 2\text{e}^-$

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

电池反应 $\text{Fe(s)} + \text{Cd}^{2+}(a_{\text{Cd}^{2+}}) \rightleftharpoons \text{Cd(s)} + \text{Fe}^{2+}(a_{\text{Fe}^{2+}})$

$$\text{电池电动势: } E = E^\ominus - \frac{RT}{zF} \ln \frac{a_{\text{Fe}^{2+}}}{a_{\text{Cd}^{2+}}}$$

$$= \varphi_{\text{Cd}^{2+}|\text{Cd}}^\ominus - \varphi_{\text{Fe}^{2+}|\text{Fe}}^\ominus - \frac{RT}{zF} \ln \frac{a_{\text{Fe}^{2+}}}{a_{\text{Cd}^{2+}}}$$

$$= -0.4029 + 0.4402 - \frac{8.314 \times 298}{2 \times 96500} \ln 1$$

$$= 0.0383 \text{ V} > 0, \Delta_r G_m = -zEF < 0$$

电池反应能发生首先 Fe(s) 被氧化成 Fe^{2+} .

$$(2) E = E^\ominus - \frac{RT}{2F} \ln \frac{a_{\text{Fe}^{2+}}}{a_{\text{Cd}^{2+}}}$$

$$= 0.0383 \text{ V} - \frac{8.314 \times 298}{96500 \times 2} \ln \frac{0.1}{0.0036}$$

$$= -0.0044 \text{ V} < 0$$

$$\Delta_r G_m > 0$$

反应不能发生, 而其逆反应可以发生.

Cd 首先被氧化成 Cd^{2+} .

16. 在 298 K 时, 有电池: $\text{Ag(s)} | \text{AgCl(s)} | \text{NaCl(aq)} | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg(l)}$, 已知化合物的标准生成 Gibbs 自由能分别为: $\Delta_f G_m^\ominus(\text{AgCl, s}) = -109.79 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f G_m^\ominus(\text{Hg}_2\text{Cl}_2, \text{s}) = -210.75 \text{ kJ} \cdot \text{mol}^{-1}$. 试写出该电池的电极和电池反应, 并计算电池的电动势.

解: 负极 $\text{Ag(s)} + \text{Cl}^-(a_{\text{Cl}^-}) \longrightarrow \text{AgCl(s)} + \text{e}^-$

正极 $\frac{1}{2} \text{Hg}_2\text{Cl}_2(\text{s}) + \text{e}^- \longrightarrow \text{Hg(l)} + \text{Cl}^-(a_{\text{Cl}^-})$

电池反应 $\text{Ag(s)} + \frac{1}{2} \text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{AgCl(s)} + \text{Hg(l)}$

$$\Delta_r G_m^\ominus = \Delta_f G_m^\ominus(\text{AgCl, s}) - \frac{1}{2} \Delta_f G_m^\ominus(\text{Hg}_2\text{Cl}_2, \text{s})$$

$$= -109.79 - \frac{1}{2} \times (-210.75)$$

$$= -4.415 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\text{标准态下 } E = E^\ominus = -\frac{\Delta_r G_m^\ominus}{zF} = \frac{4.415 \times 10^3}{1 \times 96500} = 0.04575 \text{ V}$$

17. 根据下列在 298 K 和标准压力下的热力学数据, 计算 HgO(s) 在该温度时的解离压. 已知:

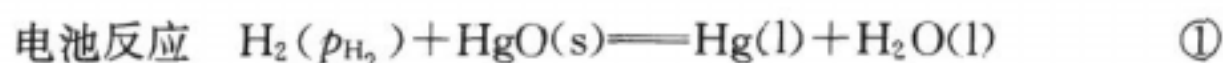
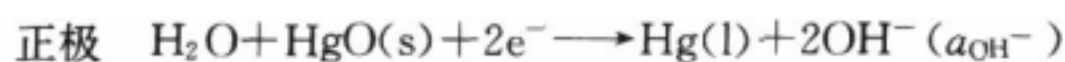
(1) 电池 $\text{Pt} | \text{H}_2(p_{\text{H}_2}) | \text{NaOH(a)} | \text{Hg(l)}$ 的标准电动势 $E^\ominus = 0.9265 \text{ V}$;

(2) 反应 $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{l}) \rightleftharpoons \text{H}_2\text{O(l)}$ 的 $\Delta_r H_m^\ominus = -285.83 \text{ kJ} \cdot \text{mol}^{-1}$;

(3) 298 K 时, 下表为各物质的标准摩尔熵值

化合物	HgO(s)	$\text{O}_2(\text{g})$	$\text{H}_2\text{O(l)}$	Hg(l)	$\text{H}_2(\text{g})$
$S_m^\ominus / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	70.29	205.1	69.91	77.4	130.7

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



$$\Delta_r G_m^\circ = -zE^\circ F = (-2 \times 96500 \times 0.9265) = -178.84 \text{ kJ} \cdot \text{mol}^{-1}$$

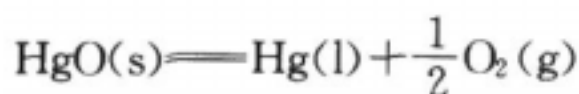


$$\Delta_r G_m^\circ = \Delta_r H_m^\circ - T \cdot \Delta_r S_m^\circ$$

$$\Delta_r S_m^\circ = 69.91 - 130.7 - \frac{1}{2}(205.1) = -163.34 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\circ = (-285.83 \times 10^3 - 298.(-163.34)) = -237.15 \text{ kJ} \cdot \text{mol}^{-1}$$

①-②式得



$$\Delta_r G_m^\circ = \Delta_r G_m^\circ(1) - \Delta_r G_m^\circ(2)$$

$$= -178.81 + 237.15 = 58.34 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln K^\circ = \frac{\Delta_r G_m^\circ}{RT} = \frac{58.34 \times 10^3}{8.314 \times 298} = -23.547$$

$$K^\circ = 5.94 \times 10^{-11}$$

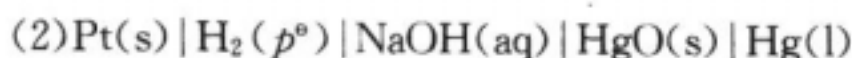
$$K^\circ = \left(\frac{p_{\text{O}_2}}{p^\circ} \right)^{\frac{1}{2}} = 5.94 \times 10^{-11}$$

$$p_{\text{O}_2} = 3.575 \times 10^{-16} \text{ Pa.}$$

18. 在 273~318 K 的温度范围内, 下述电池的电动势与温度的关系可由所列公式表示:

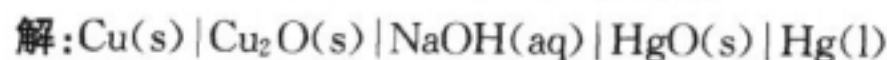


$$E/\text{mV} = 461.7 - 0.144(T/\text{K} - 298) + 1.4 \times 10^{-4}(T/\text{K} - 298)^2$$

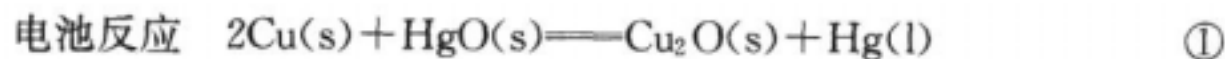
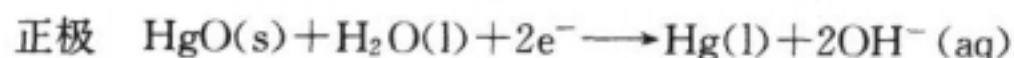
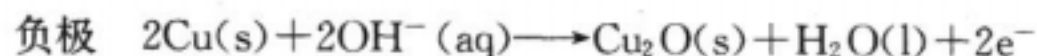


$$E/\text{mV} = 925.65 - 0.2948(T/\text{K} - 298) + 4.9 \times 10^{-4}(T/\text{K} - 298)^2$$

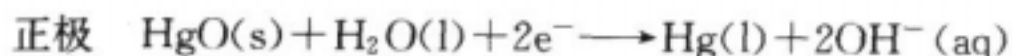
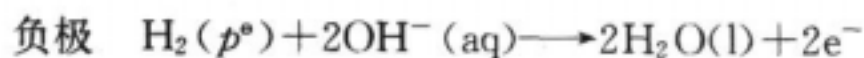
已知 $\Delta_r H_m^\circ(\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_r G_m^\circ(\text{H}_2\text{O}, \text{l}) = -237.13 \text{ kJ} \cdot \text{mol}^{-1}$, 试分别计算 $\text{HgO}(\text{s})$ 和 $\text{Cu}_2\text{O}(\text{s})$ 在 298 K 时的 $\Delta_r G_m^\circ$ 和 $\Delta_r H_m^\circ$ 的值.



(1) 的电池反应为



(2) 的电池反应为:



在 298 K 时①、②的电池电动势分别为

$$E_1 = 461.7 - 0.114(T - 298) + 1.4 \times 10^{-4}(T - 298)^2 \text{ mV}$$

$$= 461.7 \text{ mV}$$

$$E_2 = 925.65 \text{ mV}$$

$$\Delta_r G_m^\circ(1) = -zE_1 F = 0.4617 \times 96500 \times 2 = -89.11 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\circ(2) = -zE_2 F = 0.92565 \times 96500 \times 2 = -178.65 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\text{在 } 298 \text{ K 时 } \Delta_r S_m^\circ(1) = zF \left(\frac{\partial E_1}{\partial T} \right)_p = 2 \times 96500 \times (-0.144) \times 10^{-3} = -27.792 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m^\circ(1) = zF \left(\frac{\partial E_1}{\partial T} \right)_p = 2 \times 96500 \times (-0.2948) \times 10^{-3} = -56.896 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta_r H_m(1) &= \Delta_r G_m(1) + T \cdot \Delta_r S_m(1) \\ &= -89.11 \times 10^3 \text{ J} \cdot \text{mol}^{-1} + 298 \times (-27.792 \text{ J} \cdot \text{K} \cdot \text{mol}^{-1}) \\ &= -97.39 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r H_m(2) &= \Delta_r G_m(2) + T \cdot \Delta_r S_m(2) \\ &= -178.65 \times 10^3 + (-56.896) \times 298 \\ &= -195.61 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\text{已知 } \text{H}_2(p^\circ) + \frac{1}{2} \text{O}_2(p^\circ) = \text{H}_2\text{O(l)} \quad (3)$$

$$\Delta_r G_m^\circ(3) = -237.13 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m^\circ(3) = -285.85 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\text{②} - \text{③} \text{ 得 } \text{HgO(s)} = \text{Hg(l)} + \frac{1}{2} \text{O}_2(p^\circ) \quad (4)$$

$$\Delta_r G_m^\circ(4) = -\Delta_f G_m^\circ(\text{HgO, s}) = \Delta_r G_m^\circ(2) - \Delta_r G_m^\circ(3)$$

$$\begin{aligned} \text{故 } \Delta_f G_m^\circ(\text{HgO, s}) &= \Delta_r G_m^\circ(3) - \Delta_r G_m^\circ(2) \\ &= -237.13 + 178.65 = -58.48 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_f H_m^\circ(\text{HgO, s}) &= \Delta_r H_m^\circ(3) - \Delta_r H_m^\circ(2) \\ &= -285.83 + 195.61 = -90.22 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\text{同样 } \text{①} + \text{③} - \text{②} \text{ 得 } 2\text{Cu(s)} + \frac{1}{2} \text{O}_2(p^\circ) = \text{Cu}_2\text{O(s)} \quad (5)$$

$$\begin{aligned} \Delta_f G_m^\circ(\text{Cu}_2\text{O, s}) &= \Delta_r G_m^\circ(1) - \Delta_r G_m^\circ(2) + \Delta_r G_m^\circ(3) \\ &= -89.11 - (-178.65) + (-237.13) = -147.59 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_f H_m^\circ(\text{Cu}_2\text{O, s}) &= \Delta_r H_m^\circ(1) - \Delta_r H_m^\circ(2) + \Delta_r H_m^\circ(3) \\ &= -97.39 - (-195.61) + (-285.83) \\ &= -187.61 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

19. 有电池 $\text{Pt} | \text{H}_2(p^\circ) | \text{H}^+(a_{\text{H}^+}) || \text{OH}^-(a_{\text{OH}^-}) | \text{O}_2(p^\circ) | \text{Pt}$, 在 298 K 时, 已知该电池的标准电动势 $E^\circ = 0.40 \text{ V}$, $\Delta_f G_m^\circ(\text{H}_2\text{O, l}) = -237.13 \text{ kJ} \cdot \text{mol}^{-1}$. 试计算这时 $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+(a_{\text{H}^+}) + \text{OH}^-(a_{\text{OH}^-})$ 的离子积常数 K_w° 的值.

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

正极 $\text{H}_2\text{O(l)} + \frac{1}{2} \text{O}_2(p^\circ) + 2\text{e}^- \longrightarrow 2\text{OH}^-(a_{\text{OH}^-})$

$$\text{电池反应 } \text{H}_2(p^\circ) + \text{H}_2\text{O(l)} + \frac{1}{2} \text{O}_2(p^\circ) = 2\text{H}^+(a_{\text{H}^+}) + 2\text{OH}^-(a_{\text{OH}^-}) \quad (1)$$

$$\text{而 } \text{H}_2(p^\circ) + \frac{1}{2} \text{O}_2(p^\circ) = \text{H}_2\text{O(l)} \quad (2)$$

$$\Delta_r G_m^\circ(1) = -zEF = -2 \times 96500 \times 0.4 = -77.2 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\circ(2) = \Delta_f G_m^\circ(\text{H}_2\text{O, l}) = -237.13 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\text{①} - \text{②} \text{ 得 } \text{H}_2\text{O(l)} = \text{H}^+(a_1) + \text{OH}^-(a_2) \quad (3)$$

$$\begin{aligned} \Delta_r G_m^\circ(3) &= \frac{\Delta_r G_m^\circ(1) - \Delta_r G_m^\circ(2)}{2} = \frac{237.13 - 77.2}{2} \\ &= 80.0 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\ln K^\circ = -\frac{\Delta_r G_m^\circ(3)}{RT} = -\frac{80 \times 10^3}{8.314 \times 298} = -32.2897$$

$$K_w^\circ = K^\circ = 9.5 \times 10^{-15}.$$

20. 有电池 $\text{Zn(s)} | \text{ZnCl}_2 (m = 0.005 \text{ mol} \cdot \text{kg}^{-1}) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg(l)}$, 已知在 298 K 时的电动势 $E = 1.227 \text{ V}$, Debye-Hückel 极限公式中的常数 $A = 0.509 (\text{mol} \cdot \text{kg}^{-1})^{-\frac{1}{2}}$, 试求:

(1) 电极反应和电池的净反应;

(2) 电池的标准电动势 E° (要考虑 γ_\pm 的影响);

(3) 按电池反应有 2 个电子得失, 当反应进度为 1 mol 时的 $\Delta_r G_m^\circ$.

解: 负极 $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(a_{\text{Zn}^{2+}}) + 2\text{e}^-$

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

电池净反应 $\text{Zn(s)} + \text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{Zn}^{2+}(a_{\text{Zn}^{2+}}) + 2\text{Cl}^-(a_{\text{Cl}^-}) + 2\text{Hg(l)}$

在 $m = 0.005 \text{ mol} \cdot \text{kg}^{-1}$ 的 ZnCl_2 溶液中

$$I = \frac{1}{2} \sum_B m_B z_B^2 = \frac{1}{2} (2^2 + 1^2) \times 0.005 = 0.0125 \text{ mol} \cdot \text{kg}^{-1}$$

$$\lg \gamma_\pm = -A |z_+ \cdot z_-| \sqrt{I} = -0.509 \times |2| \sqrt{0.0125} = -0.1138$$

$$\gamma_\pm = 0.7695$$

$$E = E^\circ + \frac{RT}{zF} \ln a_{\text{Zn}^{2+}} \cdot a_{\text{Cl}^-}^2 \quad \text{其中 } a_{\text{Zn}^{2+}} = m_{\text{ZnCl}_2} \cdot \gamma_\pm = E^\circ + \frac{RT}{zF} \ln 4 \cdot m_{\text{ZnCl}_2}^3 \cdot \gamma_\pm^3 = 1.227 \text{ V}$$

$$E^\circ = 1.227 \text{ V} - \frac{8.314 \times 298}{2 \times 96500} \ln 4 \cdot (0.005)^3 (0.7695)^3$$

$$= 1.227 + 0.196 = 1.423 \text{ V}$$

当有 2 mol 电子得失, 如上的电池反应进度为 1 mol 时

$$\Delta_r G_m^\circ = -zFE^\circ = -2 \times 96500 \times 1.423 = -274.64 \text{ kJ} \cdot \text{mol}^{-1}.$$

21. 写出下列浓差电池的电池反应, 并计算在 298 K 时的电动势.

(1) $\text{Pt} | \text{H}_2(\text{g}, 200 \text{ kPa}) | \text{H}^+(a_{\text{H}^+}) | \text{H}_2(\text{g}, 100 \text{ kPa}) | \text{Pt}$;

(2) $\text{Pt} | \text{H}_2(p^\circ) | \text{H}^+(a_{\text{H}^+, 1} = 0.01) \parallel \text{H}^+(a_{\text{H}^+, 2} = 0.1) | \text{H}_2(p^\circ) | \text{Pt}$;

(3) $\text{Pt} | \text{Cl}_2(\text{g}, 100 \text{ kPa}) | \text{Cl}^-(a_{\text{Cl}^-}) | \text{Cl}_2(\text{g}, 200 \text{ kPa}) | \text{Pt}$;

(4) $\text{Pt} | \text{Cl}_2(p^\circ) | \text{Cl}^-(a_{\text{Cl}^-, 1} = 0.1) \parallel \text{Cl}^-(a_{\text{Cl}^-, 2} = 0.01) | \text{Cl}_2(p^\circ) | \text{Pt}$;

(5) $\text{Zn(s)} | \text{Zn}^{2+}(a_{\text{Zn}^{2+}, 1} = 0.004) \parallel \text{Zn}^{2+}(a_{\text{Zn}^{2+}, 2} = 0.02) | \text{Zn(s)}$;

(6) $\text{Pb(s)} | \text{PbSO}_4(\text{s}) | \text{SO}_4^{2-}(a_1 = 0.01) \parallel \text{SO}_4^{2-}(a_2 = 0.001) | \text{PbSO}_4(\text{s}) | \text{Pb(s)}$.

解: 浓差电池由浓度之间的差异造成的电池电动势

两电极标准电势相等

$$E^\circ = 0$$

(1) 负极 $\text{H}_2(200 \text{ kPa}) \longrightarrow 2\text{H}^+(a_{\text{H}^+}) + 2\text{e}^-$

正极 $2\text{H}^+(a_{\text{H}^+}) + 2\text{e}^- \longrightarrow \text{H}_2(100 \text{ kPa})$

电池反应 $\text{H}_2(200 \text{ kPa}) \rightleftharpoons \text{H}_2(100 \text{ kPa})$

$$E = -\frac{RT}{zF} \ln \frac{p_{\text{H}_2}(1)}{p_{\text{H}_2}(2)} = -\frac{8.314 \times 298}{2 \times 96500} \ln \frac{1}{2} = 0.0089 \text{ V}.$$

(2) 负极 $\text{H}_2(p^\circ) \longrightarrow 2\text{H}^+(a_1) + 2\text{e}^-$

正极 $2\text{H}^+(a_2) + 2\text{e}^- \longrightarrow \text{H}_2(p^\circ)$

电池反应 $2\text{H}^+(a_2) \rightleftharpoons 2\text{H}^+(a_1)$

$$E = -\frac{RT}{zF} \ln \left(\frac{a_1}{a_2} \right)^2 = -\frac{8.314 \times 298}{96500 \times 2} \ln \left(\frac{0.01}{0.1} \right)^2 = 0.0591 \text{ V}.$$

(3) 负极 $2\text{Cl}^-(a_1) \longrightarrow \text{Cl}_2(100 \text{ kPa}) + 2\text{e}^-$

正极 $\text{Cl}_2(200 \text{ kPa}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(a_1)$

电池反应 $\text{Cl}_2(200 \text{ kPa}) \rightleftharpoons \text{Cl}_2(100 \text{ kPa})$

$$E = -\frac{RT}{zF} \ln \frac{p_{\text{Cl}_2}(1)}{p_{\text{Cl}_2}(2)} = -\frac{8.314}{2 \times 96500} \ln \frac{1}{2} = 0.0089 \text{ V.}$$

(4) 负极 $2\text{Cl}^-(a_1) \longrightarrow \text{Cl}_2(p^\circ) + 2e^-$

正极 $\text{Cl}_2(p^\circ) + 2e^- \longrightarrow 2\text{Cl}^-(a_2)$

电池反应 $2\text{Cl}^-(a_1) \rightleftharpoons 2\text{Cl}^-(a_2)$

$$E = -\frac{RT}{zF} \ln \left(\frac{a_2}{a_1} \right)^2 = -\frac{8.314}{96500} \times 298 \ln \frac{0.01}{0.1} = 0.0591.$$

(5) 负极 $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(a_1) + 2e^-$

正极 $\text{Zn}^{2+}(a_2) + 2e^- \longrightarrow \text{Zn(s)}$

电池反应 $\text{Zn}^{2+}(a_2) \rightleftharpoons \text{Zn}^{2+}(a_1)$

$$E = -\frac{RT}{zF} \ln \frac{a_1}{a_2} = -\frac{8.314 \times 298}{2 \times 96500} \ln \frac{0.004}{0.02} = 0.0207 \text{ V.}$$

(6) 负极 $\text{Pb(s)} + \text{SO}_4^{2-}(a_1) \longrightarrow \text{PbSO}_4(\text{s}) + 2e^-$

正极 $\text{PbSO}_4(\text{s}) + 2e^- \longrightarrow \text{Pb(s)} + \text{SO}_4^{2-}(a_2)$

电池反应 $\text{SO}_4^{2-}(a_1) \rightleftharpoons \text{SO}_4^{2-}(a_2)$

$$E = -\frac{RT}{zF} \ln(a_2/a_1) = -\frac{-298 \times 8.314}{2 \times 96500} \ln \frac{0.001}{0.01} = 0.0296 \text{ V.}$$

22. 298 K 时, 有下述电池:

$\text{Ag(s)} | \text{AgCl(s)} | \text{KCl}(0.5 \text{ mol} \cdot \text{kg}^{-1}) || \text{KCl}(0.05 \text{ mol} \cdot \text{kg}^{-1}) | \text{AgCl(s)} | \text{Ag(s)}$

已知该电池的实测电动势为 0.0536 V, 在 $0.5 \text{ mol} \cdot \text{kg}^{-1}$ 的 KCl 溶液中, γ_{\pm} 值分别为 0.649 和 0.812, 计算 Cl^- 的迁移数.

解: 电池 负极 $\text{Ag(s)} + \text{Cl}^-(m_1) \longrightarrow \text{AgCl(s)} + e^-$

正极 $\text{AgCl(s)} + e^- \longrightarrow \text{Ag(s)} + \text{Cl}^-(m_2)$

电池反应 $\text{Cl}^-(m_1) \longrightarrow \text{Cl}^-(m_2)$

离子由高浓度向低浓度迁移

电动势为浓差电势 E_c 与液接电势之和

$$E_c = -\frac{RT}{zF} \ln \frac{a_2}{a_1} = -\frac{8.314 \times 298}{96500} \ln \frac{0.05 \times 0.812}{0.5 \times 0.649} = 0.05336 \text{ V}$$

$$E_j = E - E_c = (0.0536 - 0.05336) = 0.00024 \text{ V}$$

由液接电势的计算公式

$$E_j = (t_+ - t_-) \frac{RT}{zF} \ln(a_1/a_2) = (1 - 2t_-) \frac{RT}{zF} \ln(a_1/a_2) = 0.00024 \text{ V}$$

解得 $t_- = 0.4998$.

注: 迁移过程的自由变化 ΔG_j 为

$$t_+ RT \ln a_{\text{K}^+}/a'_{\text{K}^+} + t_- RT \ln a_{\text{Cl}^-}/a'_{\text{Cl}^-} = -zE_j F$$

K^+ 活度由 $a_{\text{K}^+} \longrightarrow a'_{\text{K}^+}$, t_+ 个离子由不同浓度变化引起自由能的变化

$$a'_{\text{K}^+} = a'_{\text{Cl}^-} = m' \gamma_{\pm}$$

$$a_{\text{K}^+} = a_{\text{Cl}^-} = m \cdot \gamma_{\pm}$$

而 $t_+ + t_- = 1$ 得出

$$E_j = (t_+ + t_-) \frac{RT}{zF} \ln(a_1/a_2).$$

23. 常用的铅蓄电池可表示为

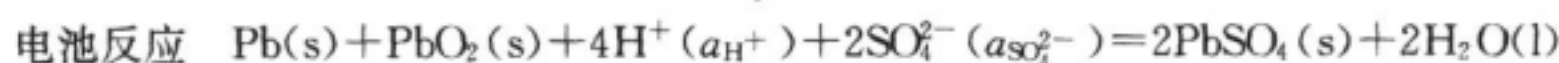
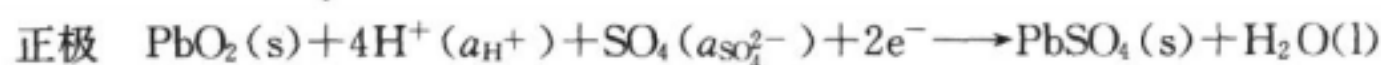
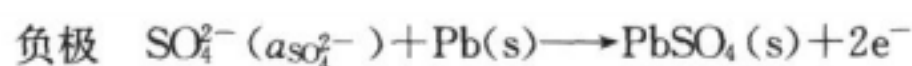
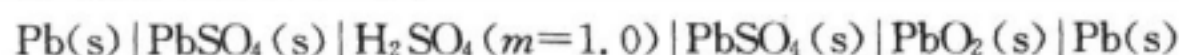
$\text{Pb(s)} | \text{PbSO}_4(\text{s}) | \text{H}_2\text{SO}_4(m=1.0 \text{ mol} \cdot \text{kg}^{-1}) | \text{PbSO}_4(\text{s}) | \text{PbSO}_4 | \text{Pb(s)}$

已知在 $0\sim 60^{\circ}\text{C}$ 的温度区内,电动势 E 与温度的关系式为

$$E/\text{V}=1.917\ 37+56.1\times 10^{-6}(t/^{\circ}\text{C})+1.08\times 10^{-8}(t/^{\circ}\text{C})^2$$

在 25°C 时,电池的 $E^{\ominus}=2.041\ \text{V}$,试计算这时电解质溶液 $\text{H}_2\text{SO}_4(m=1.0\ \text{mol}\cdot\text{kg}^{-1})$ 的平均活度因子 γ_{\pm} .

解:铅蓄电池表示式为:



$$E=E^{\ominus}-\frac{RT}{zF}\ln\frac{1}{(a_{\text{H}^{+}})^4(a_{\text{SO}_4^{2-}})^2}$$

$$\text{酸性溶液}\quad a_{\text{H}^{+}}=\gamma_{+}\cdot m_{\text{H}^{+}}=\gamma_{+}\cdot 2m$$

$$a_{\text{SO}_4^{2-}}=\gamma_{-}\cdot m_{\text{SO}_4^{2-}}=\gamma_{-}\cdot m$$

$$\gamma_{\pm}=(\gamma_{\text{H}^{+}}^2\cdot\gamma_{\text{SO}_4^{2-}})^{\frac{1}{3}}$$

$$E=E^{\ominus}-\frac{RT}{zF}\ln\frac{1}{(\gamma_{+}\cdot 2m)^4(\gamma_{-}\cdot m)^2}(\gamma_{+})^2(\gamma_{-})=\gamma_{\pm}^3$$

$$E=E^{\ominus}-\frac{RT}{zF}\ln(\gamma_{\pm}^3\cdot 4m^2\cdot m)^2$$

$$\text{在 } 298\ \text{K 时}, E=1.9188\ \text{V}$$

$$E=E^{\ominus}+\frac{8.314\times 298}{96500}\ln\gamma_{\pm}^3\cdot 4m^2\cdot m=1.9188\ \text{V}$$

$$1.9188-2.041=\frac{8.314\times 298}{96500}\ln 4\gamma_{\pm}^3$$

$$\ln 4\gamma_{\pm}^3=-4.760$$

$$\gamma_{\pm}=0.129.$$

* 24. 在 $298\ \text{K}$ 和 $100\ \text{kPa}$ 时,试求电极 $\text{Pt}|\text{S}_2\text{O}_3^{2-},\text{S}_4\text{O}_6^{2-}$ 的标准电极电势.已知

(1) $1\ \text{mol}\ \text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}(\text{s})$ 溶于大量水中, $\Delta_r H_{\text{m},1}^{\ominus}=46.735\ \text{kJ}\cdot\text{mol}^{-1}$;

(2) $1\ \text{mol}\ \text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}(\text{s})$ 溶于过量的 I_3^{-} 离子溶液中, $\Delta_r H_{\text{m},2}^{\ominus}=28.786\ \text{kJ}\cdot\text{mol}^{-1}$;

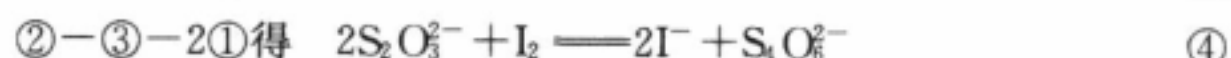
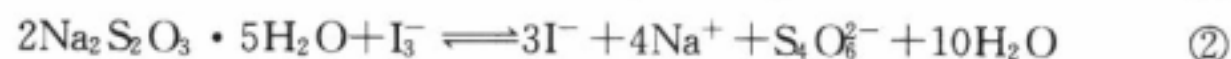
(3) $1\ \text{mol}\ \text{I}_2(\text{s})$ 溶于过量的 I^{-} 离子溶液中, $\Delta_r H_{\text{m},3}^{\ominus}=3.431\ \text{kJ}\cdot\text{mol}^{-1}$;

(4) $\text{Pt}|\text{I}_2(\text{s})|\text{I}^{-},\varphi_{\text{I}}^{\ominus}=0.535\ \text{V}$;

(5) 各物质在 $298\ \text{K}$ 时的标准摩尔熵为

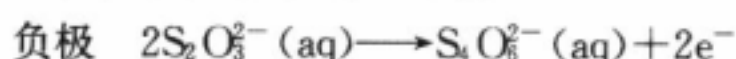
化合物	$\text{S}_2\text{O}_3^{2-}$	$\text{S}_4\text{O}_6^{2-}$	I^{-}	$\text{I}_2(\text{s})$
$S_{\text{m}}^{\ominus}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	33.47	146.0	105.9	116.7

解:(1)的化学反应式为



④的转移电子数为 2

把两电极组成电池



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

电池反应 $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{s}) \rightleftharpoons 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$

④的 $\Delta_r H_m^\circ(4) = \Delta_r H_m^\circ(2) - \Delta_r H_m^\circ(3) - 2\Delta_r H_m^\circ(1)$

$$= (28.786 - 3.431 - 2 \times 46.735) = -68.115 \text{ kJ} \cdot \text{mol}^{-1}$$

熵变为 $\Delta_r S_m^\circ(4) = \sum_B S_m^\circ = 105.9 \times 2 + 146 - 33.47 \times 2 - 116.7 = 174.16 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

$\Delta_r G_m^\circ(4) = \Delta_r H_m^\circ(4) - T\Delta_r S_m^\circ(4)$

$$= -68.115 \times 10^3 - 298 \times 174.16 = -120.01 \text{ kJ} \cdot \text{mol}^{-1}$$

电池电动势为 $E^\circ = -\frac{\Delta_r G_m^\circ(4)}{zF} = \frac{120.01 \times 10^3}{96500 \times 2} = 0.6218 \text{ V}$

$$E^\circ = \varphi^\circ - \varphi_{\text{S}_2\text{O}_3^{2-}, \text{S}_4\text{O}_6^{2-}}^\circ$$

$$\therefore \varphi_{\text{S}_2\text{O}_3^{2-}, \text{S}_4\text{O}_6^{2-}}^\circ = \varphi^\circ - E^\circ = 0.535 - 0.6218 = -0.0868 \text{ V}$$

25. 已知 298 K 时, 反应 $2\text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$ 的平衡常数为 9.7×10^{-81} , 这时 $\text{H}_2\text{O}(\text{l})$ 的饱和蒸气为 3200 Pa, 试求 298 K 时下述电池的电动势 E .

$\text{Pt} | \text{H}_2(p^\circ) | \text{H}_2\text{SO}_4(0.01 \text{ mol} \cdot \text{kg}^{-1}) | \text{O}_2(p^\circ) | \text{Pt}$

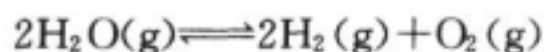
(298 K 时的平衡常数是根据高温下的数据间接求出的. 由于氧电极上的电极反应不易达到平衡, 不能测出电动势 E 的精确值, 所以可通过上法来计算 E 值.)

解: 负极 $2\text{H}_2(p^\circ) \longrightarrow 4\text{H}^+(a_{\text{H}^+}) + 4\text{e}^-$

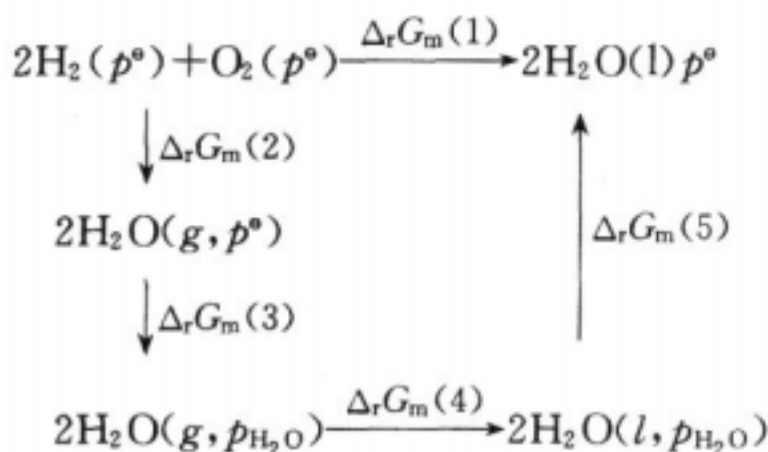
正极 $\text{O}_2(p^\circ) + 4\text{H}^+(a_{\text{H}^+}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}(\text{l})$

电池反应 $2\text{H}_2(p^\circ) + \text{O}_2(p^\circ) \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$

高温水分解的方程式为



此计算需设计过程如下:



$$\Delta_r G_m(1) = \Delta_r G_m(2) + \Delta_r G_m(3) + \Delta_r G_m(4) + \Delta_r G_m(5)$$

$$= \Delta_r G_m(2) + \Delta_r G_m(3) + 0 + 0$$

$$\Delta_r G_m(2) = RT \ln K_w$$

$$\Delta_r G_m(3) = nRT \ln \frac{p_{\text{H}_2\text{O}}}{p^\circ}$$

$$\therefore \Delta_r G_m(1) = RT \ln K_w + nRT \ln \frac{p_{\text{H}_2\text{O}}}{p^\circ}$$

$$\begin{aligned} &= 8.314 \times 298 \ln 9.7 \times 10^{-81} + 2 \times 8.314 \times 298 \ln \frac{3200}{101325} \\ &= -473.58 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$E = -\frac{\Delta_r G_m(1)}{zF} = -\frac{-473.58}{4 \times 96500} = 1.227 \text{ V}$$

26. 计算 298 K 时下述电池的电动势 E :

$\text{Pb}(\text{s}) | \text{PbCl}_2(\text{s}) | \text{HCl}(0.01 \text{ mol} \cdot \text{kg}^{-1}) || \text{H}_2(10 \text{ kPa}) | \text{Pt}(\text{s})$

已知 $\varphi^\circ(\text{Pb}^{2+} | \text{Pb}) = -0.126 \text{ V}$, 该温度下 $\text{PbCl}_2(\text{s})$ 在水中饱和溶液的浓度为 $0.039 \text{ mol} \cdot \text{kg}^{-1}$ (用 Debye

—Hückel 极限公式求活度因子后再计算电动势)。

解: 负极 $\text{Pb(s)} + 2\text{Cl}^-(a_{\text{Cl}^-}) \longrightarrow \text{PbCl}_2(\text{s}) + 2\text{e}^-$

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

电池反应 $\text{Pb(s)} + 2\text{H}^+(a_{\text{H}^+}) + 2\text{Cl}^-(a_{\text{Cl}^-}) \rightleftharpoons \text{H}_2(p_{\text{H}_2}) + \text{PbCl}_2(\text{s}) \quad (1)$

电池的一极为氢电极, 需求出 $\varphi_{\text{PbCl}_2|\text{Pb}|\text{Cl}^-}$ 的电极电势, 与 $\varphi_{\text{Pb}^{2+}|\text{Pb}}$ 组成电池。

设计电池 $\text{Pb(s)}|\text{Pb}^{2+}(a_{\text{Pb}^{2+}})||\text{Cl}^-(a_{\text{Cl}^-})|\text{PbCl}_2(\text{s})+\text{Pb(s)}$

负极 $\text{Pb(s)} \longrightarrow \text{Pb}^{2+}(a_{\text{Pb}^{2+}}) + 2\text{e}^-$

正极 $\text{PbCl}_2(\text{s}) + 2\text{e}^- \longrightarrow \text{Pb(s)} + 2\text{Cl}^-(a_{\text{Cl}^-})$

电池反应 $\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(a_{\text{Pb}^{2+}}) + \text{Cl}^-(a_{\text{Cl}^-})$

$$E = \varphi_{\text{PbCl}_2|\text{Pb}|\text{Cl}^-} - \varphi_{\text{Pb}^{2+}|\text{Pb}} = \frac{RT}{zF} \ln a_{\text{Pb}^{2+}} \cdot a_{\text{Cl}^-}^2$$

PbCl_2 溶液的浓度为 $0.039 \text{ mol} \cdot \text{kg}^{-1}$

$$\text{离子强度为 } I = \frac{1}{2} \sum_B m_B z_B^2 = \frac{1}{2} m(2^2 + 1^2) = 2.5 m = 0.0975 \text{ mol} \cdot \text{kg}^{-1}$$

$$\lg \gamma_{\pm} = -0.509 \times |z^+ \cdot z^-| \sqrt{I} = -0.509 \times 2 \sqrt{0.0975} = -0.3179$$

$$\gamma_{\pm} = 0.481$$

$$a_{\text{Pb}^{2+}} = m_{\text{Pb}^{2+}} \cdot \gamma_+, a_{\text{Cl}^-} = \gamma_- \cdot m_{\text{Cl}^-}$$

$$\therefore E = \varphi_{\text{PbCl}_2|\text{Pb}|\text{Cl}^-} - \varphi_{\text{Pb}^{2+}|\text{Pb}} = \frac{RT}{zF} \ln \gamma_+ \cdot m_{\text{Pb}^{2+}} \cdot (\gamma_-)^2 \cdot m_{\text{Cl}^-}^2$$

$$\gamma_+ \cdot \gamma_-^2 = \gamma_{\pm}^3$$

$$\therefore E = \frac{RT}{zF} \ln \gamma_{\pm}^3 m \cdot 4m^2 = \frac{RT}{zF} \ln (0.481)^3 \cdot 0.039^3 \cdot 4 = -0.1353 \text{ V}$$

$$\varphi_{\text{PbCl}_2|\text{Pb}|\text{Cl}^-} = E + \varphi_{\text{Pb}^{2+}|\text{Pb}} = -0.1353 + (-0.126) = -0.2613 \text{ V}$$

电池反应(1)的电池电动势为

$$E = \varphi_{\text{H}^+|\text{H}_2} - \varphi_{\text{PbCl}_2|\text{Pb}|\text{Cl}^-} - \frac{RT}{zF} \ln \frac{a_{\text{H}_2}}{a_{\text{H}^+}^2 \cdot a_{\text{Cl}^-}^2}$$

同样计算出 $0.01 \text{ mol} \cdot \text{kg}^{-1}$ 的 HCl 的离子强度为 γ_{\pm}

$$I = \frac{1}{2} \sum_B m_B z_B^2 = m = 0.01 \text{ mol} \cdot \text{kg}^{-1}$$

$$\lg \gamma_{\pm} = -0.509 |z^+ \cdot z^-| \sqrt{I} = -0.509 \times \sqrt{0.01} = -0.0509$$

$$\gamma_{\pm} \approx 1$$

$$\begin{aligned} E &= \varphi_{\text{H}^+|\text{H}_2} - \varphi_{\text{PbCl}_2|\text{Pb}|\text{Cl}^-} - \frac{8.314 \times 298}{2 \times 96500} \ln \frac{10 \text{ kPa}}{101.325 \text{ kPa} \cdot (0.01)^2 (0.01)^2} \\ &= 0 - (-0.2613) - 0.2067 = 0.0546 \text{ V} \end{aligned}$$

27. 有如下电池



已知 298 K 时该电池的电动势 $E(298 \text{ K}) = 0.372 \text{ V}$, 温度为 308 K 时, $E(308 \text{ K}) = 0.374 \text{ V}$,

设电动势 E 随温度的变化是均匀的。又知 298 K 时, $\varphi^\circ(\text{Ag}^+|\text{Ag}) = 0.799 \text{ V}$, $\varphi^\circ(\text{Cu}^{2+}|\text{Cu}) = 0.337 \text{ V}$ 。

(1) 写出电极反应和电池反应;

(2) 当电池可逆地输出 2 mol 电子的电荷量时, 求电池反应的 $\Delta_r G_m$, $\Delta_r H_m$ 和 $\Delta_r S_m$;

(3) 求醋酸根 AgAc(s) 的溶度积 K_{sp}° (设活度因子均为 1)。

解: (1) 电池 负极 $\text{Cu(s)} \longrightarrow \text{Cu}^{2+}(a_{\text{Cu}^{2+}}) + 2\text{e}^-$

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

电池反应 $\text{Cu(s)} + 2\text{AgAc(s)} \rightleftharpoons \text{Cu}^{2+}(a_{\text{Cu}^{2+}}) + 2\text{Ag(s)} + 2\text{Ac}^-(a_{\text{Ac}^-})$ 。

(2) 电动势随温度均匀变化

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{E(308) - E(298)}{308 - 298} = 0.002 \text{ V} \cdot \text{K}^{-1}$$

$$\text{在 } 298 \text{ K 时 } \Delta_r G_m = -zFE = -2 \times 96500 \times (0.372) = -71.796 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m = zF \left(\frac{\partial E}{\partial T}\right)_p = 2 \times 96500 \times 0.0002 = 38.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m = \Delta_r G_m + T \cdot \Delta_r S_m = -60.29 \text{ kJ} \cdot \text{mol}^{-1}$$

$$E^\circ = \varphi_{\text{AgAc(s)}|\text{Ag}}^\circ - \varphi_{\text{Cu}^{2+}|\text{Cu}}^\circ$$

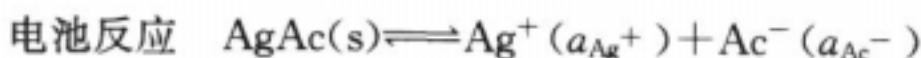
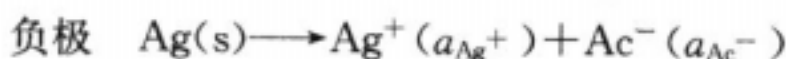
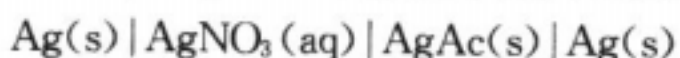
$$\varphi_{\text{AgAc(s)}|\text{Ag}}^\circ = E^\circ + \varphi_{\text{Cu}^{2+}|\text{Cu}}^\circ \quad (1)$$

$$E = E^\circ - \frac{RT}{zF} \ln(a_{\text{Cu}^{2+}} \cdot a_{\text{Ac}^-}^2)$$

$$E^\circ = E + \frac{RT}{zF} \ln a_{\text{Cu}^{2+}} \quad (2)$$

$$\begin{aligned} \text{②代入①得 } \varphi_{\text{AgAc}|\text{Ag}}^\circ &= E + \frac{RT}{zF} \ln(a_{\text{Cu}^{2+}} \cdot a_{\text{Ac}^-}^2) + \varphi_{\text{Cu}^{2+}|\text{Cu}}^\circ \\ &= 0.372 + \frac{8.314 \times 298}{2 \times 96500} \ln 0.1 \cdot (0.2)^2 + 0.337 = 0.638 \text{ V} \end{aligned}$$

(3) 要求 AgAc(s) 的溶度积设计电池如下:



$$E^\circ = \varphi_{\text{AgAc}|\text{Ag}}^\circ - \varphi_{\text{Ag}^+|\text{Ag}}^\circ$$

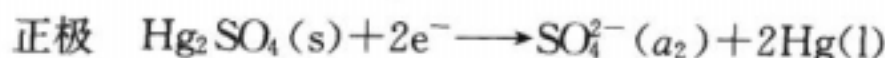
$$= 0.638 - 0.799 = 0.161 \text{ V}$$

$$\ln K_{\text{sp}} = \frac{zFE^\circ}{RT} = \frac{-0.161 \times 96500}{8.314 \times 298} = -6.271$$

$$K_{\text{sp}} = 1.89 \times 10^{-3}$$

28. 已知 298 K 时, 电极 $\text{Hg}_2^{2+}(a_{\text{Hg}_2^{2+}}) | \text{Hg(l)}$ 的标准还原电极电势为 0.789 V, $\text{Hg}_2\text{SO}_4(\text{s})$ 的活度积 $K_{\text{sp}}^\circ = 8.2 \times 10^{-7}$, 试求电极 $\text{SO}_4^{2-} | \text{Hg}_2\text{SO}_4(\text{s}) | \text{Hg(l)}$ 的标准电势 φ° .

解: 设计电池 $\text{Hg(l)} | \text{Hg}_2^{2+}(a_1) || \text{SO}_4^{2-}(a_2) | \text{Hg}_2\text{SO}_4(\text{s}) | \text{Hg(l)}$



$$E^\circ = \frac{RT \ln K_{\text{sp}}^\circ}{zF} = \frac{8.314 \times 298 \ln 8.2 \times 10^{-7}}{96500 \times 2} = -0.180 \text{ V}$$

$$E^\circ = \varphi_{\text{Hg}_2\text{SO}_4|\text{Hg}|\text{SO}_4^{2-}}^\circ - \varphi_{\text{Hg}_2^{2+}|\text{Hg}}^\circ = -0.180 \text{ V}$$

$$\varphi_{\text{Hg}_2\text{SO}_4|\text{Hg}|\text{SO}_4^{2-}}^\circ = -0.180 + 0.789 = 0.609 \text{ V}$$

29. 298 K 时, 试设计合适的电池, 用电动势测定下列各热力学函数值. 要求写出电池的表示和列出所求函数的计算式.

(1) $\text{Ag(s)} + \text{Fe}^{3+}(a_{\text{Fe}^{3+}}) \rightleftharpoons \text{Ag}^+(a_{\text{Ag}^+}) + \text{Fe}^{2+}(a_{\text{Fe}^{2+}})$ 的平衡常数;

(2) $\text{Hg}_2\text{Cl}_2(\text{s})$ 的标准活度积常数 K_{sp}° ;

(3) $\text{HBr}(0.01 \text{ mol} \cdot \text{kg}^{-1})$ 溶液的离子平均活度系数 γ_{\pm} ;

(4) $\text{Ag}_2\text{O(s)}$ 的分解温度;

(5) $\text{H}_2\text{O}(\text{l})$ 的标准摩尔生成 Gibbs 自由能;

(6) 弱酸 HA 的解离常数.

解: (1) 设计电池 $\text{Ag}(\text{s}) | \text{Ag}^+(\text{a}_1) || \text{Fe}^{3+}(\text{a}_2), \text{Fe}^{2+}(\text{a}_3) | \text{Pt}$

$$E^\circ = \varphi_{\text{Fe}^{3+} | \text{Fe}^{2+}}^\circ - \varphi_{\text{Ag}^+ | \text{Ag}}^\circ = \frac{RT}{zF} \ln K^\circ.$$

(2) 设计电池为 $\text{Hg}(\text{l}) | \text{Hg}_2^{2+}(\text{a}_1) || \text{Cl}^-(\text{a}_2) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}(\text{l})$

$$E^\circ = \varphi_{\text{Hg}_2\text{Cl}_2 | \text{Hg} | \text{Cl}^-}^\circ - \varphi_{\text{Hg}_2^{2+} | \text{Hg}}^\circ = \frac{RT}{zF} \ln K_{\text{sp}}.$$

(3) 设计电池为 $\text{Pt} | \text{H}_2(p^\circ) | \text{HBr}(m) | \text{AgBr}(\text{s}) | \text{Ag}(\text{s})$

电池反应为 $\frac{1}{2} \text{H}_2(p^\circ) + \text{AgBr}(\text{s}) \rightleftharpoons \text{H}^+(\text{a}_1) + \text{Br}^-(\text{a}_2) + \text{Ag}(\text{s})$

$$E = E^\circ - \frac{RT}{F} \ln \frac{a_1 a_2}{(p_{\text{H}_2}/p^\circ)^{\frac{1}{2}}} = E^\circ - \frac{RT}{F} \ln \gamma_{\pm}^2 m^2.$$

(4) 设计电池为 $\text{Pt} | \text{O}_2(p_{\text{O}_2}) | \text{OH}^-(\text{a}_1) | \text{Ag}_2\text{O}(\text{s}) | \text{Ag}(\text{s})$

电池反应 $\text{Ag}_2\text{O}(\text{s}) \rightleftharpoons 2\text{Ag}(\text{s}) + \frac{1}{2} \text{O}_2(p_{\text{O}_2})$

$$E^\circ = \varphi_{\text{Ag}_2\text{O} | \text{Ag} | \text{OH}^-}^\circ - \varphi_{\text{O}_2 | \text{OH}^-}^\circ$$

还应测出 $(\partial E / \partial T)_p$ 根据

$$\Delta_r S_m^\circ = \frac{zF}{RT} (\partial E / \partial T)_p$$

$$\Delta_r H_m^\circ(298 \text{ K}) = \Delta_r G_m^\circ(298 \text{ K}) + T \Delta_r S_m^\circ(298 \text{ K})$$

设 $\Delta_r H_m^\circ$ 与 $\Delta_r S_m^\circ$ 不随温度变化而变化

$$\text{由 } \Delta_r G_m^\circ(T) = \Delta_r H_m^\circ(298 \text{ K}) - T \cdot \Delta_r S_m^\circ(298 \text{ K}) = 0$$

求出 T 值.

(5) 设计电池 $\text{Pt} | \text{H}_2(p^\circ) | \text{H}^+(\text{a}_1) | \text{O}_2(p^\circ) | \text{Pt}$

电池反应 $\text{H}_2(p^\circ) + \frac{1}{2} \text{O}_2(p^\circ) = \text{H}_2\text{O}(\text{l})$

$$\Delta_r G_m^\circ(\text{H}_2\text{O}, \text{l}) = \Delta_r G_m^\circ = -zFE^\circ.$$

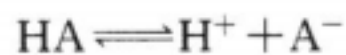
(6) 设计电池为 $\text{Pt} | \text{H}_2(p^\circ) | \text{HA}(m), \text{A}^-(m_{\text{A}^-}), \text{Cl}^-(\text{a}_1) | \text{AgCl}(\text{s}) + \text{Ag}(\text{s})$

电池反应 $\text{AgCl}(\text{s}) + \frac{1}{2} \text{H}_2(p^\circ) \rightleftharpoons \text{Ag}(\text{s}) + \text{H}^+(\text{a}_{\text{H}^+}) + \text{Cl}^-(\text{a}_1)$

$$E = E^\circ - \frac{RT}{zF} \ln \frac{a_{\text{H}^+} \cdot a_1}{(p_{\text{H}_2}/p^\circ)^{\frac{1}{2}}} \text{ 测出 } E \text{ 值即得 } a_{\text{H}^+} \text{ 的值.}$$

$$a_{\text{H}^+} = m_{\text{H}^+}$$

根据 HA 的电离平衡



$$t=0 \quad m_{\text{HA}} \quad 0 \quad m_{\text{A}^-}$$

平衡 $m_{\text{HA}} - m_{\text{H}^+} \quad m_{\text{H}^+} \quad m_{\text{A}^-} + m_{\text{H}^+}$ 设活度系数均为 1

$$K_{\text{a}} = \frac{a_{\text{H}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}} = \frac{m_{\text{H}^+} \times (m_{\text{A}^-} + m_{\text{H}^+})}{m_{\text{HA}} - m_{\text{H}^+}}.$$

* 30. 298 K 时, 测得如下电池的电动势 E 与 HBr 浓度的关系如表所示:

$\text{Pt} | \text{H}_2(p^\circ) | \text{HBr}(m) | \text{AgBr}(\text{s}) | \text{Ag}(\text{s})$

$m/(\text{mol} \cdot \text{kg}^{-1})$	0.01	0.02	0.05	0.10
E/V	0.3127	0.2786	0.2340	0.2005

试计算:

(1) 电极 $\text{Br}^-(a_{\text{Br}^-}) | \text{AgBr}(\text{s}) | \text{Ag}(\text{s})$ 的标准电极电势 φ° ;

(2) $0.1 \text{ mol} \cdot \text{kg}^{-1}$ 的 HBr 溶液的离子平均活度系数 γ_{\pm} .

解: (1) 负极 $\frac{1}{2} \text{H}_2(p^\circ) \longrightarrow \text{H}^+(a_1) + \text{e}^-$

正极 $\text{AgBr}(\text{s}) + \text{e}^- \longrightarrow \text{Ag}(\text{s}) + \text{Br}^-(a_2)$

电池反应 $\frac{1}{2} \text{H}_2(p^\circ) + \text{AgBr}(\text{s}) \rightleftharpoons \text{Ag}(\text{s}) + \text{H}^+(a_1) + \text{Br}^-(a_2)$

$$E = \varphi_{\text{AgBr}|\text{Ag}|\text{Br}^-}^\circ - \varphi_{\text{H}^+|\text{H}_2} - \frac{RT}{F} \ln(a_1 \cdot a_2)$$

$$= \varphi_{\text{AgBr}|\text{Ag}|\text{Br}^-}^\circ - \frac{RT}{F} \ln \gamma_{\pm}^2 m^2$$

$$\lg \gamma_{\pm} = -A |z^+ \cdot z^-| \sqrt{I}; I = \frac{1}{2} \sum_B m_B z_B^2 = m$$

$$\lg \gamma_{\pm} = -A \sqrt{m}$$

$$\therefore E = \varphi_{\text{AgBr}|\text{Ag}|\text{Br}^-}^\circ - \frac{2RT}{F} (\ln \gamma_{\pm} + \ln m)$$

以 $E + \frac{2RT}{F} \ln 10^{-A\sqrt{m}}$ 对 $\ln m$ 作图。(图略)

截距即为 $\varphi_{\text{AgBr}|\text{Ag}|\text{Br}^-}^\circ$ 的值, 约为 0.0728 V .

(2) 把任意一组数据代入上式解得 $\lg \gamma_{\pm} = -0.0795$, 即 $\gamma_{\pm} = 0.833$.

* 31. 电池 $\text{Pt} | \text{H}_2(p_1) | \text{HCl}(m) | \text{H}_2(p_2) | \text{Pt}$ 中, 设氢气遵从的状态方程为 $pV_m = RT + \alpha p$, 式中 $\alpha = 1.48 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$, 且与温度、压力无关. 当氢气的压力 $p_1 = 2000 \text{ kPa}$, $p_2 = 100 \text{ kPa}$ 时,

(1) 写出电极反应和电池反应;

(2) 计算电池在 298 K 时的电动势;

(3) 当电池放电时, 是吸热还是放热? 为什么?

解: (1) 负极 $\text{H}_2(p_1) \longrightarrow 2\text{H}^+(a_1) + 2\text{e}^-$

正极 $2\text{H}^+(a_1) + 2\text{e}^- \longrightarrow \text{H}_2(p_2)$.

电池反应 $\text{H}_2(p_1) \rightleftharpoons \text{H}_2(p_2)$.

$$(2) E = -\frac{\Delta_r G_m}{zF}$$

$$\begin{aligned} \text{非理气 } \Delta_r G_m &= \int_{p_1}^{p_2} V dp = \int_{p_1}^{p_2} \left(\frac{RT}{p} + \alpha \right) dp \\ &= RT \ln(p_2/p_1) + \alpha(p_2 - p_1) \\ &= 8.314 \times 298 \ln \frac{2000}{100} + 1.48 \times 10^{-5} (2000 - 100) \text{ kPa} \\ &= 7422.14 + 0.02812 = 7422.17 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

$$E = -\frac{\Delta_r G_m}{zF} = -\frac{7422.17}{2 \times 96500} = -0.0385 \text{ V}.$$

$$(3) \Delta_r S_m = zF(\partial E / \partial T)_p$$

$$E = -\frac{\Delta_r G_m}{zF} = -\frac{RT \ln(p_2/p_1) + a(p_2 - p_1)}{zF}$$

$$(\partial E / \partial T)_p = -\frac{R}{zF} \ln(p_2/p_1)$$

$$\Delta_r S_m = zF(\partial E / \partial T)_p = -R \ln(p_2/p_1) = 24.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$Q_R = T \cdot \Delta_r S_m = 298 \times 24.91$$

$$= 7422.14 \text{ J} \cdot \text{mol}^{-1} > 0$$

即电池可逆放电时吸热。

32. 在 298 K 时, 有电池 $\text{Pt(s)} | \text{H}_2(p^\circ) | \text{HI}(m) | \text{AuI(s)} | \text{Au(s)}$, 已知当 HI 浓度 $m = 1.0 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ 时, $E = 0.97 \text{ V}$; 当 $m = 3.0 \text{ mol} \cdot \text{kg}^{-1}$ 时, $E = 0.41 \text{ V}$; 电极 $\text{Au}^+ | \text{Au(s)}$ 的标准电极电势为 $\varphi^\circ(\text{Au}^+ | \text{Au}) = 1.68 \text{ V}$. 试求:

(1) HI 溶液浓度为 $3.0 \text{ mol} \cdot \text{kg}^{-1}$ 时的平均离子活度因子 γ_{\pm} ;

(2) AuI(s) 的活度积常数 K_{sp}° .

解: (1) 负极 $\frac{1}{2} \text{H}_2(p^\circ) \longrightarrow \text{H}^+(a_1) + \text{e}^-$

正极 $\text{AuI(s)} + \text{e}^- \longrightarrow \text{Au(s)} + \text{I}^-(a_2)$

电池反应 $\frac{1}{2} \text{H}_2(p^\circ) + \text{AuI(s)} \rightleftharpoons \text{Au(s)} + \text{H}^+(a_1) + \text{I}^-(a_2)$

当 $m = 1.0 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ 时, 一价稀溶液

$$\lg \gamma_{\pm} = -0.509 |z^+ \cdot z^-| \sqrt{I} = -0.509 \sqrt{1 \times 10^{-4}} = -0.00509$$

$$\gamma_{\pm} = 0.988 \approx 1. (m \longrightarrow 0, I \longrightarrow 0, \lg \gamma_{\pm} \longrightarrow 0, \gamma_{\pm} \longrightarrow 1)$$

而若要准确求出 $m = 3.0 \text{ mol} \cdot \text{kg}^{-1}$ 时的 γ_{\pm} 则应用

$$E = E^\circ - \frac{RT}{zF} \ln(a_1 \cdot a_2)$$

$$= E^\circ - \frac{RT}{zF} \ln(\gamma_{\pm} \cdot m)^2$$

当 $m = 1.0 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ 时,

$$E^\circ = E_1 - \frac{RT}{zF} \ln(1 \times 10^{-4})^2 = 0.97 - \frac{2 \times 8.314 \times 298}{96500} \ln 1 \times 10^{-4} = 0.497 \text{ V}$$

$m = 3.0 \text{ mol} \cdot \text{kg}^{-1}$ 时

$$E_2 = E^\circ - \frac{RT}{zF} \ln(\gamma_{\pm} \cdot m)^2$$

$$0.41 \text{ V} = 0.497 \text{ V} - \frac{2 \times 8.314 \times 298}{96500} \ln(3.0 \cdot \gamma_{\pm})$$

$$-0.087 = -\frac{2 \times 8.314 \times 298}{96500} \ln(\gamma_{\pm} \cdot 3)$$

$$\gamma_{\pm} = 1.814.$$

(2) 计算 AuI 的活度积设计电池如下

$\text{Au(s)} | \text{Au}^+(a_1) | \text{I}^-(a_2) | \text{AuI(s)} | \text{Au(s)}$

负极 $\text{Au(s)} \longrightarrow \text{Au}^+(a_1) + \text{e}^-$

正极 $\text{AuI(s)} + \text{e}^- \rightleftharpoons \text{Au(s)} + \text{I}^-(a_2)$

电池反应 $\text{AuI(s)} \longrightarrow \text{Au}^+(a_1) + \text{I}^-(a_2)$

$$E^\circ = \varphi_{\text{AuI}|\text{Au}}^\circ - \varphi_{\text{Au}^+|\text{Au}}^\circ$$

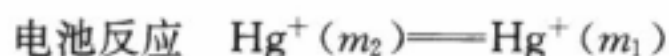
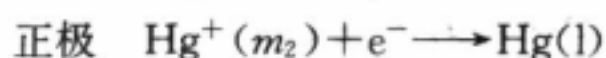
$$=0.497-1.68=-1.183 \text{ V}$$

$$\ln K_{\text{ap}}^{\circ} = \frac{zEF}{RT} = \frac{-1.183 \times 96500}{8.314 \times 298} = -46.077$$

$$K_{\text{ap}}^{\circ} = 9.749 \times 10^{-21}.$$

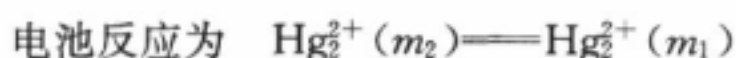
33. 有电池 $\text{Hg(l)} | \text{硝酸亚汞}(m_1), \text{HNO}_3(m) \parallel \text{硝酸亚汞}(m_2), \text{HNO}_3(m) | \text{Hg(l)}$, 电池中 HNO_3 的浓度均为 $m=0.1 \text{ mol} \cdot \text{kg}^{-1}$. 在 291 K 时, 维持 $m_2/m_1=10$ 的情况下, Ogg(奥格)对该电池进行了一系列测定, 求得电动势的平均值为 0.029 V. 试根据这些数据确定亚汞离子在溶液中是以 Hg_2^{2+} 还是 Hg^+ 形式存在.

解: 设亚汞仅以 Hg^+ 形式存在, 则电池反应应为



$$E_0 = -\frac{RT}{zF} \ln \frac{a_1}{a_2} \approx \frac{RT}{F} \ln \frac{m_2}{m_1} = 0.0578 \text{ V}$$

若以 Hg_2^{2+} 形式存在



$$E_1 = -\frac{RT}{2F} \ln \frac{a_1}{a_2} \approx \frac{RT}{2F} \ln \frac{m_2}{m_1} = \frac{1}{2} E_0 = 0.0289 \text{ V}$$

可见亚汞以 Hg_2^{2+} 的形式存在.

34. 298 K 时测定下述电池的电动势:

玻璃电极 | pH 缓冲溶液 | 饱和甘汞电极

当所用缓冲溶液的 $\text{pH}=4.00$ 时, 测得电池的电动势为 0.1120 V. 若换用另一缓冲溶液重测电动势, 得 $E=0.3865 \text{ V}$. 试求该缓冲溶液的 pH . 当电池换用 $\text{pH}=2.50$ 的缓冲溶液时, 计算电池的电动势 E .

解: $\varphi_{\text{玻}} = \varphi_{\text{玻}}^{\circ} - 0.05915 \times \text{pH}$

$$E_1 = \varphi_{\text{甘汞}} - \varphi_{\text{玻},1}$$

$$E_2 = \varphi_{\text{甘汞}} - \varphi_{\text{玻},2}$$

$$E_2 - E_1 = 0.05915(\text{pH}_2 - \text{pH}_1)$$

$$\text{pH}_2 = \frac{0.3865 - 0.112}{0.05915} + 4.0 = 8.64$$

$\text{pH}=2.5$ 时

$$E = E_1 + 0.05915 \times (2.5 - 4.0)$$

$$= 0.112 + 0.05915 \times (2.5 - 4.0)$$

$$= 0.0233 \text{ V}.$$

35. 用电动势测定丁酸解离常数. 在 298 K 时安排成如下电池:

$\text{Pt} | \text{H}_2(p^{\circ}) | \text{HA}(m_1), \text{NaA}(m_2), \text{NaCl}(m_3) | \text{AgCl(s)} | \text{Ag(s)}$

其中 HA 代表丁酸, NaA 为丁酸钠. 实验数据如下:

$m_1/(\text{mol} \cdot \text{kg}^{-1})$	$m_2/(\text{mol} \cdot \text{kg}^{-1})$	$m_3/(\text{mol} \cdot \text{kg}^{-1})$	E/V
0.007 17	0.006 87	0.007 06	0.633 87
0.012 73	0.012 20	0.012 54	0.619 22
0.015 15	0.014 53	0.014 93	0.615 01

试求反应 $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ 的平衡常数 K_a° . 设活度因子均为 1.

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

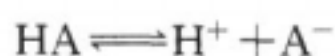
正极 $\text{AgCl(s)} + \text{e}^- \longrightarrow \text{Ag(s)} + \text{Cl}^-(a_{\text{Cl}^-})$

电池反应 $\text{AgCl(s)} + \frac{1}{2} \text{H}_2(p^\circ) \rightleftharpoons \text{Ag(s)} + \text{H}^+(a_{\text{H}^+}) + \text{Cl}^-(a_{\text{Cl}^-})$

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

$$\begin{aligned} \ln a_{\text{H}^+} &= \frac{zF(E^\circ - E)}{RT} - \ln a_{\text{Cl}^-} \\ &= \frac{96500 \times (0.2224 - 0.6339)}{8.314 \times 298} - \ln 0.0076 \end{aligned}$$

$$a_{\text{H}^+} = 1.553 \times 10^{-5}$$



开始 $m_1 \quad 0 \quad m_2$

平衡 $m_1 - m_{\text{H}^+} \quad m_{\text{H}^+} \quad m_2 + m_{\text{H}^+}$

$$K_a = \frac{a_{\text{H}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}} \quad \text{浓度均很稀, 活度系数近似为 1.}$$

$$\begin{aligned} K_a &= \frac{1.553 \times 10^{-5} \times (0.00687 + 1.553 \times 10^{-5})}{0.00717 - 1.553 \times 10^{-5}} \\ &= 1.472 \times 10^{-5} \end{aligned}$$

对其余数据作同样的计算, 取平均值为 $\overline{K_a} = 1.48 \times 10^{-5}$.

36. 298 K 时, 下述电池的实验数据如表所示:

$\text{Pt} | \text{H}_2(p^\circ) | \text{Ba(OH)}_2(0.00500 \text{ mol} \cdot \text{kg}^{-1}), \text{BaCl}_2(m) | \text{AgCl(s)} | \text{Ag(s)}$

$m/(\text{mol} \cdot \text{kg}^{-1})$	0.005 00	0.011 66	0.018 33	0.028 33
E/V	1.049 83	1.027 83	1.015 97	1.004 44

试求 298 K 时水的离子积常数 K_w° . 设活度因子均为 1.

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

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

电池反应 $\frac{1}{2} \text{H}_2(p^\circ) + \text{AgCl(s)} \rightleftharpoons \text{Ag(s)} + \text{H}^+(a_{\text{H}^+}) + \text{Cl}^-(a_{\text{Cl}^-})$

$$E = E^\circ - \frac{RT}{zF} \ln(a_{\text{H}^+} \cdot a_{\text{Cl}^-}), \text{ 其中 } a_{\text{H}^+} \cdot a_{\text{OH}^-} = K_w$$

$$\therefore E = E^\circ - \frac{RT}{F} \ln \frac{K_w \cdot a_{\text{Cl}^-}}{a_{\text{OH}^-}}$$

$$\text{解出 } K_w(1) = 1.0 \times 10^{-14}$$

同理理解出其余 K_w 值, 取平均值为 $\overline{K_w} = 1.03 \times 10^{-14}$.

37. 在 298 K 时, 有下列两个电池:

(1) $\text{Ag(s)} | \text{AgCl(s)} | \text{HCl 乙醇溶液}(m_1) | \text{H}_2(p^\circ) \text{Pt} | \text{H}_2(p^\circ) | \text{HCl 乙醇溶液}(m_2) | \text{AgCl(s)} | \text{Ag(s)}$

(2) $\text{Ag(s)} | \text{AgCl(s)} | \text{HCl 乙醇溶液}(m_1) | \text{HCl 乙醇溶液}(m_2) | \text{AgCl(s)} | \text{Ag(s)}$

已知 HCl 乙醇溶液的浓度分别为: $m_1 = 8.238 \times 10^{-2} \text{ mol} \cdot \text{kg}^{-1}$, $m_2 = 8.224 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$, 两电池

电动势分别为 $E_1=0.082\text{ V}$, $E_2=0.0577\text{ V}$.

试求:

(1)在两种 HCl 的乙醇溶液中离子平均活度因子的比值 $\gamma_{\pm,1}/\gamma_{\pm,2}$;

(2) H^+ 在 HCl 乙醇溶液中的迁移数 t_{H^+} ;

(3) H^+ 和 Cl^- 的无限稀释离子摩尔电导率 $\Lambda_m^\infty(\text{H}^+)$ 和 $\Lambda_m^\infty(\text{Cl}^-)$ 的值. 已知 $\Lambda_m^\infty(\text{HCl})=8.38\times 10^{-3}\text{ S}\cdot\text{m}^2\cdot\text{mol}^{-1}$.

解:(1)电池为串联电池

反应式为 $\text{H}^+(a_1)+\text{Cl}^-(a_2)\longrightarrow\text{H}^+(a_1')+\text{Cl}^-(a_2')$

$$E=-\frac{RT}{zF}\ln\frac{a_1'\cdot a_2'}{a_1\cdot a_2}$$

$$a_1\cdot a_2=(\gamma_{\pm}m)^2$$

$$\therefore E=-\frac{RT}{zF}\ln\left(\frac{\gamma_{\pm}'m'}{\gamma_{\pm}m}\right)=0.0822\text{ V}$$

$$\text{即 } \ln\left(\frac{\gamma_{\pm}'}{\gamma_{\pm}}\times\frac{8.224\times 10^{-3}}{8.238\times 10^{-2}}\right)^2=-\frac{0.0822\times 96500}{8.314\times 298}$$

$$\gamma_{\pm}'/\gamma_{\pm}=2.021.$$

(2)电池(2)负极 $\text{Ag}(\text{s})+\text{Cl}^-(m_1)\longrightarrow\text{AgCl}(\text{s})+\text{e}^-$

正极 $\text{AgCl}(\text{s})+\text{e}^-\longrightarrow\text{Ag}(\text{s})+\text{Cl}^-(m_2)$

电池反应 $\text{Cl}^-(m_1)\rightleftharpoons\text{Cl}^-(m_2)$

$$\text{实测电动势 } E_{\text{实}}=E_c+E_j=-2t+\frac{RT}{F}\ln\left(\frac{\gamma_{\pm}m_2}{\gamma_{\pm}m_1}\right)$$

$$=5.77\times 10^{-2}\text{ V}-2t+\frac{8.314\times 298}{96500}\ln(2.02\times\frac{8.224\times 10^{-3}}{8.238\times 10^{-2}})$$

$$=5.77\times 10^{-2}\text{ V}$$

$$t_+=0.702.$$

(3) $t_+\Lambda_m^\infty(\text{HCl})=\lambda_m^\infty(\text{H}^+)$

$$\lambda_m^\infty(\text{H}^+)=0.702\times 8.38\times 10^{-3}=5.882\times 10^{-3}\text{ S}\cdot\text{m}^2\cdot\text{mol}^{-1}$$

$t_-\Lambda_m^\infty(\text{HCl})=\lambda_m^\infty(\text{Cl}^-)$ 其中 $t_-=1-t_+$

$$\lambda_m^\infty(\text{Cl}^-)=(1-0.702)\times 8.38\times 10^{-3}\text{ S}\cdot\text{m}^2\cdot\text{mol}^{-1}=2.497\times 10^{-3}\text{ S}\cdot\text{m}^2\cdot\text{mol}^{-1}.$$

38. 已知 298 K 时 100 kPa 时, C(石墨)的标准摩尔燃烧焓为 $\Delta_c H_m^\circ=-393.5\text{ kJ}\cdot\text{mol}^{-1}$. 如将 C(石墨)的燃烧反应安排成燃料电池

C(石墨, s) | 熔融氧化物 | $\text{O}_2(\text{g})$ | M(s)

则能量的利用率将大大提高, 也防止了热电厂用煤直接发电所造成的能源浪费和环境污染. 试根据一些热力学数据计算该燃料电池的电动势. 已知这些物质的标准摩尔熵为:

物质	C(石墨, s)	$\text{CO}_2(\text{g})$	$\text{O}_2(\text{g})$
$S_m^\circ/(\text{J}\cdot\text{K}^{-1}\text{mol}^{-1})$	5.74	213.74	205.14

解: 电池负极 $\text{C}(\text{s})+2\text{O}^{2-}\longrightarrow\text{CO}_2(p_{\text{CO}_2})+4\text{e}^-$

正极 $\text{O}_2(p_{\text{O}_2})+4\text{e}^-\longrightarrow2\text{O}^{2-}$

总的电池反应 $\text{C}(\text{s})+\text{O}_2(p_{\text{O}_2})\rightleftharpoons\text{CO}_2(p_{\text{CO}_2})$

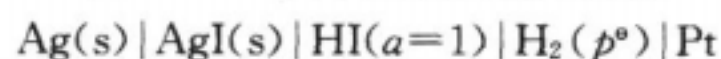
$$\Delta_r H_m^\circ = \Delta_c H_m^\circ = -393.15 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta_r S_m^\circ &= S_m^\circ(\text{CO}_2) - S_m^\circ(\text{C(石墨)}) - S_m^\circ(\text{O}_2, g) \\ &= 213.74 - 5.74 - 205.14 = 2.86 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

$$\text{在 } 298 \text{ K 时, } \Delta_r G_m^\circ = \Delta_r H_m^\circ - T \cdot \Delta_r S_m^\circ = (-393.5 \times 10^3 - 298 \times 2.86) \text{ J} \cdot \text{mol}^{-1} = -394.35 \text{ kJ} \cdot \text{mol}^{-1}$$

$$E^\circ = -\frac{\Delta_r G_m^\circ}{zF} = \frac{394.35 \times 10^3}{96500 \times 4} = 1.022 \text{ V.}$$

39. 在 298 K 时, 下述电池的电动势 $E=0.1519 \text{ V}$,



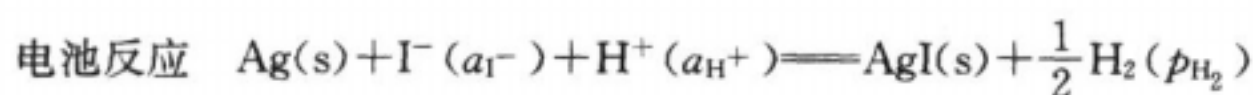
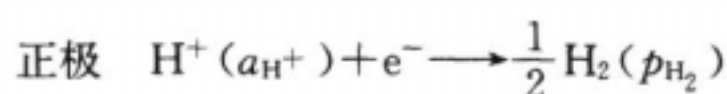
并已知下列物质的标准摩尔生成焓:

物质	AgI(s)	Ag ⁺	I ⁻
$\Delta_f H_m^\circ (\text{kJ} \cdot \text{mol}^{-1})$	-61.84	105.58	-55.94

试求:

(1) 当电池可逆输出 1 mol 电子的电荷量时, 试计算 Q, W_e (膨胀功), W_i (电功) 和电池反应的 $\Delta_r U_m, \Delta_r H_m, \Delta_r S_m, \Delta_r A_m$, 和 $\Delta_r G_m$ 的值各为多少?

(2) 如果让电池短路, 不作电功, 则在发生同样的反应时上述各函数的变量又为多少?



$$\text{可逆输出 1 mol 电子 } \Delta_r H_m^\circ = \Delta_r G_m^\circ + \Delta_r S_m^\circ \cdot T$$

$$\begin{aligned} \Delta_r H_m^\circ &= \Delta_r H_m^\circ(\text{AgI(s)}) - \Delta_f H_m^\circ(\text{Ag}) - \Delta_f H_m^\circ(\text{I}^-) - \Delta_f H_m^\circ(\text{H}^+) \\ &= -61.84 + 55.94 = -5.9 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\Delta_r G_m^\circ = -zFE^\circ = -zFE = -96500 \times (0.1519) = -14.66 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m^\circ = \frac{\Delta_r H_m^\circ - \Delta_r G_m^\circ}{T} = 29.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta_r U_m^\circ = \Delta_r H_m^\circ - \sum \nu RT = -5.9 - \frac{1}{2} \times 8.314 \times 298 \times 10^{-3} = -7.14 \text{ kJ} \cdot \text{mol}^{-1}$$

$$W_i = zEF = 96500 \times 0.1519 = 14.66 \text{ kJ} \cdot \text{mol}^{-1}$$

$$W_e = p \cdot \Delta V = \sum \nu RT = 1.24 \text{ kJ} \cdot \text{mol}^{-1}$$

$$Q_R = T \cdot \Delta_r S_m^\circ = 298 \times 29.4 = 8.76 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r A_m^\circ = -W_{\text{max}} = W_e + W_i = 14.66 + 1.24 = -15.9 \text{ kJ} \cdot \text{mol}^{-1}.$$

(2) 电池短路, 发生同样反应, 体系状态与可逆输出时相同.

故状态函数 $\Delta_r H_m^\circ, \Delta_r G_m^\circ, \Delta_r S_m^\circ, \Delta_r U_m^\circ, \Delta_r A_m^\circ$ 均不变

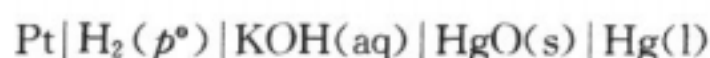
膨胀功 W_e 也不变, 但 $W_i = 0$ (不做电功)

$$Q_p = \Delta_r H_m^\circ = -5.9 \text{ kJ} \cdot \text{mol}^{-1}.$$

40. 已知水的离子积常数 K_w° 在 293 K 和 303 K 时分别为: $K_w^\circ(293 \text{ K}) = 0.67 \times 10^{-14}$, $K_w^\circ(303 \text{ K}) = 1.45 \times 10^{-14}$. 试求:

(1) 在 298 K 和标准压力时, 中和反应 $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O(l)}$ 的 $\Delta_r H_m^\circ$ 和 $\Delta_r S_m^\circ$ 的值 (设 $\Delta_r H_m^\circ$ 与温度的关系可以忽略).

(2) 298 K 时, OH^- 的标准摩尔生成 Gibbs 自由能 $\Delta_f G_m^\ominus$ 的值. 已知下述电池的标准的电动势 $E^\ominus = 0.927$ V;



并已知反应 $\text{Hg(l)} + \frac{1}{2} \text{O}_2(\text{g}, p^\ominus) = \text{HgO(s)}$ 的 $\Delta_r G_m^\ominus(298 \text{ K}) = -58.5 \text{ kJ} \cdot \text{mol}^{-1}$.

解: (1) $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_w = a_{\text{H}^+} \cdot a_{\text{OH}^-}$$

$$\ln \frac{K_w(T_2)}{K_w(T_1)} = \frac{\Delta_r H_m^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{1.45 \times 10^{-14}}{0.67 \times 10^{-14}} = \frac{\Delta_r H_m^\ominus}{8.314} \left(\frac{1}{293 \text{ K}} - \frac{1}{303 \text{ K}} \right)$$

$$\Delta_r H_m^\ominus = 56.99 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\ominus(293 \text{ K}) = -RT_1 \ln \frac{1}{K_w(T_1)}$$

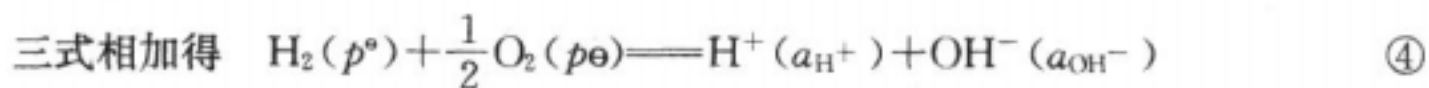
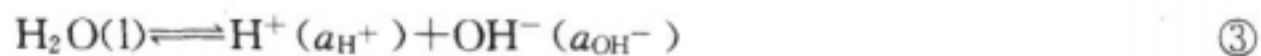
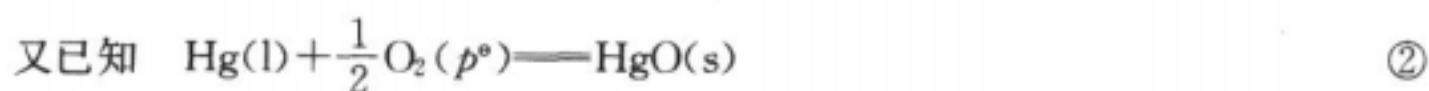
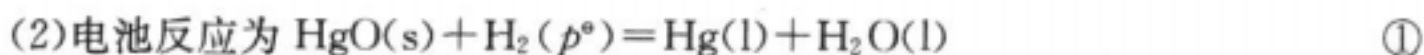
$$= 79.62 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\ominus(303 \text{ K}) = -80.27 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\ominus(298 \text{ K}) = \frac{1}{2} [\Delta_r G_m^\ominus(303 \text{ K}) + \Delta_r G_m^\ominus(293 \text{ K})]$$

$$= -79.95 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m^\ominus = \frac{\Delta_r H_m^\ominus - \Delta_r G_m^\ominus}{T} = 77.06 \text{ kJ} \cdot \text{mol}^{-1}.$$



$$\Delta_r G_m^\ominus(4) = \Delta_f G_m^\ominus(\text{OH}^-) = \Delta_r G_m^\ominus(1) + \Delta_r G_m^\ominus(2) + \Delta_r G_m^\ominus(3)$$

$$= -2 \times 0.927 \times 96500 - 58.5 \times 10^3 - 79.95 \times 10^3$$

$$= -317.36 \text{ kJ} \cdot \text{mol}^{-1}.$$