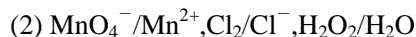
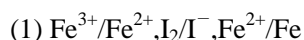


## 习题

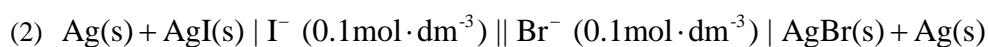
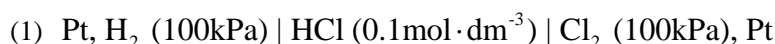
1. 根据表 4-1 中电极的标准电极电势值, 判断下列各组中最强的氧化剂和最强的还原剂分别是哪种物质?



2. 在 298K 时, 已知原电池

$\text{Pt}, \text{O}_2 (100\text{kPa}) | \text{H}^+ (0.10 \text{ mol} \cdot \text{dm}^{-3}) || \text{H}^+ (c) | \text{O}_2 (100\text{kPa}), \text{Pt}$  的电动势为 0.010V。求  $\text{H}^+$  离子的浓度  $c$  为多少?

3. 写出下列电池中各电极上的反应和电池反应, 并计算电极电势



4. 当温度为 298.15K,  $\text{H}_2$  的分压  $p=100 \text{ kPa}$ ,  $\text{H}^+$  离子浓度  $c=0.200 \text{ mol} \cdot \text{dm}^{-3}$  时, 求所组成的氢电极的电极电势。

5. 已知  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e} = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ ,  $E^\circ = +1.232\text{V}$ 。按能斯特方程式计算  $\text{pH}$

$=1$  和  $\text{pH}=5$  时的  $E$  值各为多少? 然后比较溶液酸性对  $\text{Cr}_2\text{O}_7^{2-}$  氧化性强度的影响。

## 部分参考答案

1.

(1)查表得到

$\text{Fe}^{3+} | \text{Fe}^{2+}, \text{I}_2 | \text{I}^-, \text{Fe}^{2+} | \text{Fe}$  的标准电极电势分别为

$$\varphi^\circ (\text{Fe}^{3+} | \text{Fe}^{2+}) = 0.771\text{V}$$

$$\varphi^\circ (\text{I}_2 | \text{I}^-) = 0.5355\text{V}$$

$$\varphi^\circ (\text{Fe}^{2+} | \text{Fe}) = -0.447\text{V}$$

$\text{Fe}^{3+}$  是最强氧化剂,  $\text{Fe}$  是最强还原剂。

(2)查表得到

$\text{MnO}_4^- | \text{Mn}^{2+}, \text{Cl}_2 | \text{Cl}^-, \text{H}_2\text{O}_2 | \text{H}_2\text{O}$  的标准电极电势分别为

$$\varphi^\circ (\text{MnO}_4^- | \text{Mn}^{2+}) = 1.507\text{V}$$

$$\varphi^\circ (\text{Cl}_2 | \text{Cl}^-) = 1.358\text{V}$$

$$\varphi^\circ (\text{H}_2\text{O}_2 | \text{H}_2\text{O}) = 1.776\text{V}$$

$\text{H}_2\text{O}_2$  是最强氧化剂,  $\text{Cl}^-$  是最强还原剂。

2.

阳极反应:  $2\text{H}_2\text{O} - 4\text{e}^- = \text{O}_2 + 4\text{H}^+$

阴极反应:  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$

$$\varphi_{\text{阳}} = \varphi^\circ + \frac{RT}{4F} \ln \left[ \frac{p(\text{O}_2)}{p^\circ} \right] \left[ \frac{c(\text{H}^+)_{\text{阳}}}{c^\circ} \right]^4$$

$$\varphi_{\text{阴}} = \varphi^\circ + \frac{RT}{4F} \ln \left[ \frac{p(\text{O}_2)}{p^\circ} \right] \left[ \frac{c(\text{H}^+)_{\text{阴}}}{c^\circ} \right]^4$$

$$E = \varphi_{\text{阴}} - \varphi_{\text{阳}} = \frac{RT}{4F} \ln \frac{\left[ \frac{c(\text{H}^+)_{\text{阴}}}{c^\circ} \right]^4}{\left[ \frac{c(\text{H}^+)_{\text{阳}}}{c^\circ} \right]^4}$$

$$0.010 = \frac{8.314 \times 298}{4 \times 96500} \ln \left[ \frac{c(\text{H}^+)_{\text{阴}}}{0.10} \right]^4$$

$$c(\text{H}^+)_{\text{阴}} = 0.148 (\text{mol} \cdot \text{dm}^{-3})$$

3.

(1) 两电极反应和标准电极电势分别为

阳极反应  $\text{H}_2 - 2\text{e}^- = 2\text{H}^+ \quad \varphi^\circ (\text{H}^+/\text{H}_2) = 0\text{V}$

阴极反应  $\text{Cl}_2 + 2\text{e}^- = 2\text{Cl}^- \quad \varphi^\circ (\text{Cl}_2/\text{Cl}^-) = 1.35827\text{V}$

该原电池反应为



$$\begin{aligned} \varphi(\text{H}^+/\text{H}_2) &= \varphi^\circ(\text{H}^+/\text{H}_2) + \frac{RT}{2F} \ln \frac{\left[ \frac{c(\text{H}^+)}{c^\circ} \right]^2}{\left[ \frac{p(\text{H}_2)}{p^\circ} \right]} & \varphi(\text{Cl}_2/\text{Cl}^-) &= \varphi^\circ(\text{Cl}_2/\text{Cl}^-) - \frac{RT}{2F} \ln \frac{\left[ \frac{c(\text{Cl}^-)}{c^\circ} \right]^2}{\left[ \frac{p(\text{Cl}_2)}{p^\circ} \right]} \\ &= \frac{8.314 \times 298.15}{2 \times 96485} \ln 0.01 & &= 1.35827 - \frac{8.314 \times 298.15}{2 \times 96485} \ln 0.01 \\ &= -0.0592 & &= 1.4174 \end{aligned}$$

(2) 两电极反应和标准电极电势分别为

阳极反应  $\text{Ag} + \text{I}^- - \text{e}^- = \text{AgI} \quad \varphi^\circ (\text{AgI}/\text{Ag}) = -0.15224\text{V}$

阴极反应  $\text{AgBr} + \text{e}^- = \text{Ag} + \text{Br}^- \quad \varphi^\circ (\text{AgBr}/\text{Ag}) = 0.07133\text{V}$

该原电池反应为



$$\begin{aligned} \varphi(\text{AgI}/\text{Ag}) &= \varphi^\circ(\text{AgI}/\text{Ag}) - \frac{RT}{F} \ln \left[ \frac{c(\text{I}^-)}{c^\circ} \right] & \varphi(\text{AgBr}/\text{Ag}) &= \varphi^\circ(\text{AgBr}/\text{Ag}) - \frac{RT}{F} \ln \left[ \frac{c(\text{Br}^-)}{c^\circ} \right] \\ &= -0.15224 - \frac{8.314 \times 298.15}{96485} \ln 0.1 & &= 0.071 - \frac{8.314 \times 298.15}{96485} \ln 0.1 \\ &= -0.15224 + 0.0592 & &= 0.071 - 0.0592 \\ &= -0.093(\text{V}) & &= 0.1302(\text{V}) \end{aligned}$$

4.

$$\begin{aligned}\varphi(\text{H}^+/\text{H}_2) &= \varphi^\theta(\text{H}^+/\text{H}_2) + \frac{RT}{2F} \ln \frac{[\frac{c(\text{H}^+)}{c^\theta}]^2}{[\frac{P(\text{H}_2)}{P^\theta}]} \\ &= \frac{8.314 \times 298.15}{2 \times 96485} \ln 0.2^2 \\ &= -0.041\end{aligned}$$

5.

$$\text{pH}=1, [\text{H}^+]=0.1 \text{ mol} \cdot \text{dm}^{-3}$$

$$\begin{aligned}E &= E^\theta - \frac{8.314 \times 298.15}{6 \times 96485} \ln \frac{[\frac{c(\text{Cr}^{3+})}{c^\theta}]^2}{[\frac{c(\text{Cr}_2\text{O}_7^{2-})}{c^\theta}][\frac{c(\text{H}^+)}{c^\theta}]^{14}} \\ &= 1.232 - 0.138 \\ &= 1.094\end{aligned}$$

$$\text{pH}=5, [\text{H}^+]=10^{-5} \text{ mol} \cdot \text{dm}^{-3}$$

$$\begin{aligned}E &= E^\theta - \frac{8.314 \times 298.15}{6 \times 96485} \ln \frac{[\frac{c(\text{Cr}^{3+})}{c^\theta}]^2}{[\frac{c(\text{Cr}_2\text{O}_7^{2-})}{c^\theta}][\frac{c(\text{H}^+)}{c^\theta}]^{14}} \\ &= 1.232 - 0.690 \\ &= 0.542\end{aligned}$$

酸性越大，则氧化性越强

8.

$$\begin{aligned}\text{阳极反应 } \text{Ag} - \text{e}^- &= \text{Ag}^+ & \varphi^\theta(\text{Ag}^+/\text{Ag}) &= 0.7996 \text{ V} \\ \text{阴极反应 } \text{Fe}^{3+} + \text{e}^- &= \text{Fe}^{2+} & \varphi^\theta(\text{Fe}^{3+}/\text{Fe}^{2+}) &= 0.771 \text{ V} \\ \text{该原电池的标准电动势 } E^\theta &= \varphi^\theta(\text{Fe}^{3+}/\text{Fe}^{2+}) - \varphi^\theta(\text{Ag}^+/\text{Ag}) \\ &= 0.771 \text{ V} - 0.7996 \text{ V} = -0.0286 \text{ V}\end{aligned}$$

$$\begin{aligned}\ln K^\theta &= ZE^\theta F/RT = -0.0286 \times 96485 \times 1/8.314 \times 298.15 \\ &= -1.13\end{aligned}$$

$$K^\theta = 0.328$$

9.

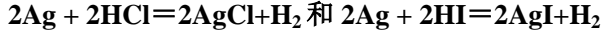
$$\begin{aligned}\text{阳极反应 } 2\text{Cl}^- - 2\text{e}^- &= \text{Cl}_2 & \varphi^\theta(\text{Cl}_2/\text{Cl}^-) &= 1.36 \text{ V} \\ \text{阴极反应 } \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- &= \text{Mn}^{2+} + 2\text{H}_2\text{O} & \varphi^\theta(\text{MnO}_2/\text{Mn}^{2+}) &= 1.23 \text{ V} \\ \text{该原电池的标准电动势 } E^\theta &= \varphi^\theta(\text{MnO}_2/\text{Mn}^{2+}) - \varphi^\theta(\text{Cl}_2/\text{Cl}^-)\end{aligned}$$

$$= 1.23\text{V} - 1.36\text{V} = -0.13 < 0$$

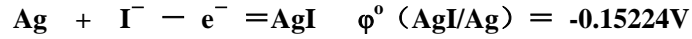
标准条件下不能自发进行

10.

置换反应为



则阳极反应分别为:  $\text{Ag} + \text{Cl}^- - \text{e}^- = \text{AgCl} \quad \varphi^\circ (\text{AgCl}/\text{Ag}) = 0.22233\text{V}$



阴极反应  $2\text{H}^+ + 2\text{e}^- = \text{H}_2 \quad \varphi^\circ (\text{H}^+/\text{H}_2) = 0\text{V}$

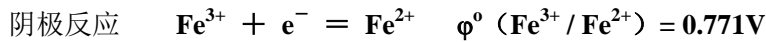
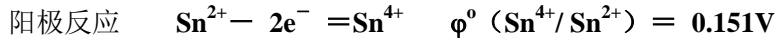
$$E_1 = \varphi^\circ (\text{H}^+/\text{H}_2) - \varphi^\circ (\text{AgCl}/\text{Ag}) = -0.22233\text{V} < 0$$

$$E_2 = \varphi^\circ (\text{H}^+/\text{H}_2) - \varphi^\circ (\text{AgI}/\text{Ag}) = 0.15224\text{V} > 0$$

所以银难以置换  $\text{HCl}$  中的  $\text{H}$  而很容易置换  $\text{HI}$  中的  $\text{H}$ 。

11.

电池反应可以表示为



$$E^\circ = \varphi^\circ (\text{Fe}^{3+}/\text{Fe}^{2+}) - \varphi^\circ (\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.771 - 0.151 = 0.620\text{V}$$

$$\Delta G = -nE^\circ F = -0.620 \times 96485 \times 2 = -1.196 \times 10^5 \text{ (J/mol)}$$