1. 计算氢标准电极的标准电极 $2H^+ + 2e^- = H_2$ $\varphi^\ominus = 0V$

$$\varphi(H^+/H_2) = \varphi^\ominus - \frac{RT}{nF}\ln\frac{P_{H_2}/P^\ominus}{(c_{H^+}/c^\ominus)^2}$$

$$= 0 - \frac{8.314 \times 293.15}{2 \times 96485}\ln\frac{100000/101325}{(0.2)^2} = -0.041\text{ V}$$

2. 电对络合 $Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$ $\varphi^\ominus = 1.232V$

$$\varphi = \varphi^\ominus - \frac{RT}{6F}\ln\frac{(C_{Cr^{3+}}/c^\ominus)^2}{(\frac{C_{Cr_2O_7^{2-}}}{c^\ominus})(\frac{C_{H^+}}{c^\ominus})^{14}}$$

$C_{Cr^{3+}} = C_{Cr_2O_7^{2-}} = 1 mol/L$

pH=1 $C_{H^+} = 0.1 mol/L$ $\varphi = 1.232 + \frac{14 \times 8.314 \times 293}{6 \times 96485}\ln 0.1 = 1.094\text{ V}$

pH=5 $C_{H^+} = 10^{-5} mol/L$ $\varphi = 1.232 + \frac{14 \times 8.314 \times 293}{6 \times 96485}\ln 10^{-5} = 0.547\text{ V}$

因此，溶液酸性电减，即pH改变，$Cr_2O_7^{2-}$ 的氧化性增强。

3. 电对络合 $O_3 + 4H^+ + 4e^- = 2H_2O$ $\varphi^\ominus(O_3/H_2O) = 1.229V$ 其中 $P_{O_3} = P^\ominus$

$$\varphi = \varphi^\ominus - \frac{RT}{4F}\ln\frac{1}{(\frac{P_{O_3}}{P^\ominus})(\frac{C_{H^+}}{c^\ominus})^4}$$

$$\varphi = \varphi^\ominus + \frac{RT}{F}\ln C_{H^+}$$

pH=1 $\varphi = \varphi^\ominus + \frac{RT}{F}\ln 10^{-1}$

pH=3 $\varphi' = \varphi^\ominus + \frac{RT}{F}\ln 10^{-3}$

$$\varphi - \varphi' = \frac{RT}{F}(\ln 10^{-1} - \frac{RT}{F}\ln 10^{-3})$$

$$= \frac{RT}{F}\ln\frac{10^{-1}}{10^{-3}}$$

$$= \frac{8.314 \times 293}{96485}\ln 100 = 0.118V$$

即pH升高3个单位，氧化电位增了3×0.118V.

4.(1) 原电池 $Pt|H_2(100kPa)|HCl(0.1 mol\cdot L^{-1})||Cl_2(100kPa)|Pt$

电极反应
阳极 $H_2 - 2e^- = 2H^+$ $\varphi^\ominus = 0V$
阴极 $Cl_2 + 2e^- = 2Cl^-$ $\varphi^\ominus = 1.3582V$
电池反应
$H_2 + Cl_2 = 2H^+ + 2Cl^-$ $n=2$

$$\varphi_{阳} = 0 - \frac{RT}{2F}\ln\frac{P_{H_2}/P^\ominus}{(C_{H^+}/c^\ominus)^2}$$

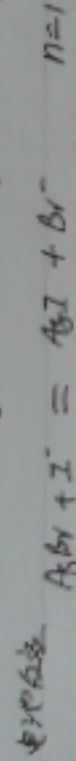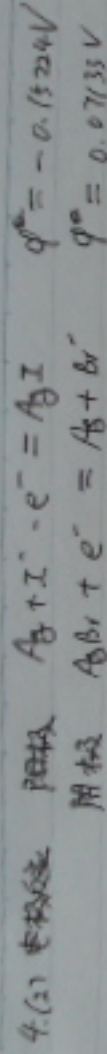$$= 0 - \frac{8.314 \times 293}{2 \times 96485}\ln\frac{10^5/101325}{(0.1/1)^2}$$

$$= -0.059V$$

$$\varphi_{阴} = 1.3582 - \frac{RT}{2F}\ln\frac{(C_{Cl^-}/c^\ominus)^2}{(P_{Cl_2}/P^\ominus)}$$

$$\varphi_{阴} = 1.3583 - \frac{8.314 \times 293}{2 \times 96485}\ln\frac{(0.1/1)^2}{10^5/101325}$$

$$= 1.3583 - \frac{8.314 \times 293}{2 \times 96485}\ln\frac{(0.1/1)^2}{10^5/101325}$$

$$= 1.417 V$$

$$E = \varphi_{阴} - \varphi_{阳} = 1.417 - (-0.059)$$

$$= 1.476 V$$

4.(2) 正极反应 阴极 $Ag + I^- - e^- = AgI$ $\varphi^{\Theta} = -0.15224V$

阴极 $AgBr + e^- = Ag + Br^-$ $\varphi^{\Theta} = 0.07133V$

电池反应 $AgBr + I^- = AgI + Br^-$ $n=1$

电动势 $\varphi_{正} = -0.15224 - \dfrac{RT}{F} \ln\left(\dfrac{C_{I^-}}{C^{\Theta}}\right)$

$= -0.15224 - \dfrac{8.314 \times 298}{96485} \ln 0.1 = -0.093V$

$\varphi_{负} = +0.07133V - \dfrac{RT}{F} \ln\left(\dfrac{C_{Br^-}}{C^{\Theta}}\right)$

$= 0.07133V - \dfrac{8.314 \times 298}{96485} \ln 0.1 = 0.130V$

电动势 $E = \varphi_{负} - \varphi_{正} = 0.130 - (-0.093) = 0.223V$

5. 求 $Hg_2Cl_2(s)$ 的 Ksp

正负各生 $Hg_2Cl_2(S) = Hg_2^{2+} + 2Cl^-$

设计电池

阳极 $2Hg - 2e^- = Hg_2^{2+}$ $\varphi_{Ag}^{\Theta} = 0.80V$

阴极 $Hg_2Cl_2(s) + 2e^- = 2Hg + 2Cl^-$ $\varphi_{M}^{\Theta} = 0.28V$

电池总反应主角生 m 化方程式 其中 $n=2$

$\ln k^{\Theta} = \dfrac{n E^{\Theta} F}{RT} = \dfrac{2 \times 9648}{8.314 \times 298} \left(\varphi_{M}^{\Theta} - \varphi_{Ag}^{\Theta}\right)$
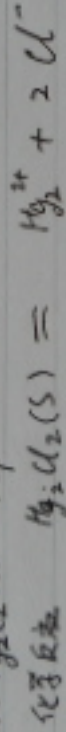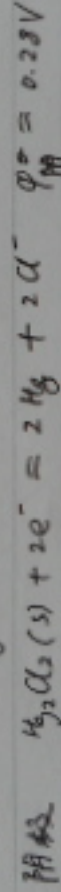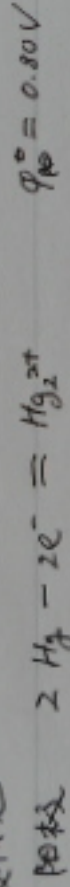
$= \dfrac{2 \times 9648}{3.314 \times 298} \times (-0.52) = -40.5$

$k^{\Theta} = 2.58 \times 10^{-18}$

6. 调解无变化 $Zn + Cu^{2+} = Cu + Zn^{2+}$ $E^{\Theta} = 1.1037V$

$E = E^{\Theta} - \dfrac{RT}{2F} \ln \dfrac{(C_{Zn^{2+}}/C^{\Theta})}{(C_{Cu^{2+}}/C^{\Theta})}$
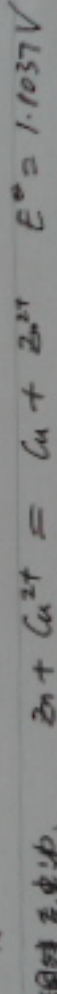
即 $1.10 = 1.1037 - \dfrac{8.314 \times 298.15}{2 \times 96485} \ln \dfrac{(C_{Zn^{2+}}/C^{\Theta})}{0.02}$

得 $C_{Zn^{2+}} = 0.0267 \ mol/L$

7. 电池反应 $Fe^{3+} + Ag(s) = Fe^{2+} + Ag^+$ $n=1$

负极 $Ag(s) - e^- = Ag^+$ $\varphi^{\ominus}_{Ag} = 0.7996$ V

正极 $Fe^{3+} + e^- = Fe^{2+}$ $\varphi^{\ominus}_{Fe} = 0.771$ V

$E^{\ominus} = \varphi^{\ominus}_{正} - \varphi^{\ominus}_{负} = 0.771 - 0.7996 = -0.0286$ V

$\ln K^{\ominus} = \dfrac{nFE^{\ominus}}{RT} = \dfrac{96485 \times (-0.0286)}{8.314 \times 298} = -1.114$

$K = 0.328$

3. 根据 $\varphi^{\ominus}$ 从大小比较可知还原型越强

Fe^{2+} 能被 O_2 氧化为 Fe^{3+}

Co^{2+} 不能被 O_2 氧化为 Co^{3+}

9. 化学反应 $Fe + 2Fe^{3+} = 3Fe^{2+}$

电池反应

负极 $Fe - 2e^- = Fe^{2+}$ $\varphi^{\ominus}_{Fe} = -0.44$ V

正极 $2Fe^{3+} + 2e^- = 2Fe^{2+}$ $\varphi^{\ominus}_{正} = 0.77$ V $n=2$

$E^{\ominus} = \varphi^{\ominus}_{正} - \varphi^{\ominus}_{负} = 0.77 - (-0.44) = 1.22$ V

$\ln K^{\ominus} = \dfrac{nE^{\ominus}F}{RT} = \dfrac{2 \times 1.22 \times 96485}{8.314 \times 298} = 95.02$

$K = 1.85 \times 10^{41}$

10. 反应 $Sn + Pb^{2+} \rightleftharpoons Sn^{2+} + Pb$

$E^{\ominus} = \varphi^{\ominus}_{(Pb^{2+}/Pb)} - \varphi^{\ominus}_{(Sn^{2+}/Sn)} = -0.1262 - (-0.1375) = 0.0113$ V

$K^{\ominus} = e^{\frac{nE^{\ominus}F}{RT}} = e^{\frac{2 \times 0.0113 \times 96485}{8.314 \times 298}} = 2.41$

$J = \dfrac{c_{Sn^{2+}}/c^{\ominus}}{c_{Pb^{2+}}/c^{\ominus}} = \dfrac{1\,mol/L}{0.1\,mol/L} = 10 > K = 2.41$

$E = \varphi^{\ominus}_{(Pb^{2+}/Pb)} - \varphi^{\ominus}_{(Sn^{2+}/Sn)} - \dfrac{RT}{nF} \ln\left[\dfrac{(c_{Sn^{2+}}/c^{\ominus})}{(c_{Pb^{2+}}/c^{\ominus})}\right] e$

∴ 反应向左 即 Pb^{2+} 和 Sn 都稳定。即 不会发生变化。

已知 298K 反电池的电动势 $E = 0.010$ V

1. 反电池构成

$$\underline{Pt, O_2(100kPa)|H^+(0.10\,mol\cdot L^{-1})}\,\|\,\underline{H^+(C)|O_2(100kPa),Pt}$$
$$\qquad\qquad 负极 \qquad\qquad\qquad\qquad\qquad 阳极$$

为浓差电池

(1) 电极反应

负极: $2H_2O - 4e = O_2 + 4H^+ (0.10\,mol/L)$

阳极: $O_2 + 4H^+(c) + 4e = 2H_2O$

(2) 电池反应

$2H_2O + O_2 + 4H^+(c) = 2H_2O + O_2 + 4H^+ (0.1\,mol/L)$

(3) 电池电动势
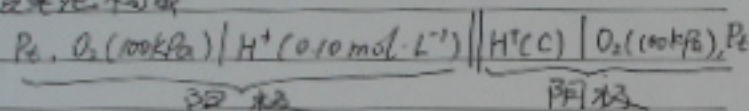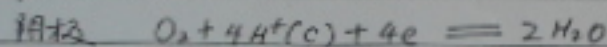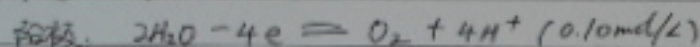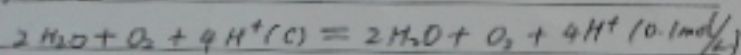
$$E = E^\ominus - \frac{RT}{nF} \ln \frac{(c_{H^+}/c^\ominus)^4}{(c_{H^+(c)}/c^\ominus)^4}$$

$$E^\ominus = \varphi^\ominus(阳) - \varphi^\ominus(阴) = 0$$

$$\begin{cases} E = 0.01\,V \\ n = 4 \\ c_{H^+} = 0.1\,mol/L \\ T = 298K \end{cases} \Rightarrow \boxed{c_{H^+(c)} = 0.148\,mol/L}$$

Data

$$\varphi^\ominus(Pt, O_2|H_2O) = 1.229\,V$$

$$\varphi = \varphi^\ominus - \frac{RT}{nF} \ln \frac{[还原态]}{[氧化态]}$$

$$\varphi_阳 = \varphi(O_2/H^+)$$
$$= \varphi^\ominus - \frac{RT}{4F} \ln \frac{1}{(c_{H^+}/c^\ominus)^4 \cdot (\frac{P_{O_2}}{p^\ominus})}$$

$$\varphi_阴 = \varphi(H^+/O_2)$$
$$= \varphi^\ominus - \frac{RT}{4F} \ln \frac{1}{(c_{H^+(c)}/c^\ominus)^4 \cdot \frac{P_{O_2}}{p^\ominus}}$$

$$E = \varphi_阳 - \varphi_阴$$
$$= -\frac{RT}{4F} \left[\ln \frac{1}{(c_{H^+(c)}/c^\ominus)^4} - \ln \frac{1}{(c_{H^+}/c^\ominus)^4} \right]$$

即 $0.010 = \frac{-8.314 \times 298}{4 \times 96485} \ln \left(\frac{c_{H^+(c)}}{c_{H^+}} \right)^{-4}$

即 $\ln \frac{c_{H^+(c)}}{c_{H^+}} = 0.389$

$$\frac{c_{H^+(c)}}{0.1\,mol/L} = 1.48$$

$$\therefore c_{H^+(c)} = 0.148\,mol/L$$

（四）判断氧化剂和还原剂相对强弱及氧化还原反应。

φ 越大，易发生还原反应，

该电对的氧化态为较强氧化剂，

φ 越小，易…氧化反应

浅…(不反去…块…还原反应)

$\varphi^\ominus$

(1) Fe^{3+}/Fe^{2+} $+0.771$ V

     I_2/I^- $+0.6355$ V

     Fe^{2+}/Fe -0.447 V

i. Fe^{3+} 是最强氧化剂，Fe 是最强还原剂

$\varphi^\ominus$

(2) MnO_4^-/Mn^{2+} $+1.507$ V

     Cl_2/Cl^- $+1.35827$ V

     H_2O_2/H_2O $+1.776$ V

ii. H_2O_2 是最强氧化剂，Cl^- 是最强还原剂

13. PH计 $E = k - \dfrac{2.303RT}{F} PH$　　　当电动势改变检测电势变化

$PH=10$　$\bar{E} = k - \dfrac{2.303RT}{F} \times 10$　　　　　　每升高 $0.118\ V$.

$PH=8$　$E' = k - \dfrac{2.303RT}{F} \times 8$

$\therefore \Delta E = E' - \bar{E} = \dfrac{-2.303RT}{F} \times (8-10) = 0.118\ V$

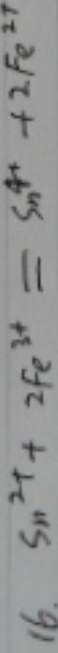15.　$ClO_3^- + 6H^+ + 5e^- = \tfrac{1}{2} Cl_2 + 3H_2O$
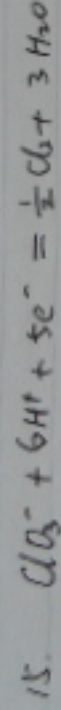
$\Delta_f G_m^\ominus$　　-3.3　　0　　　0　　　-237.19

$\Delta_r G_m^\ominus = + 3 \times (-237.18) - (-3.3) = -708.27\ kJ \cdot mol^{-1}$

$\varphi^\ominus = E = -\dfrac{\Delta_r G_m^\ominus}{nF} = \dfrac{708.27 \times 10^3}{5 \times 96485} = -1.47\ V$

受到抑制　$H_2 - 2e^- = 2H^+$　　$\varphi^\ominus = 0\ V$

16.　$Sn^{2+} + 2Fe^{3+} = Sn^{4+} + 2Fe^{2+}$　　$\varphi^\ominus(Sn^{4+}/Sn^{2+}) = 0.151V$

注意式中 Sn^{2+} 浓度为1，$\varphi(Sn^{2+}/\varphi_{Sn^{4+}})$ 的影响　$\varphi^\ominus(Fe^{3+}/Fe^{2+}) = 0.771V$.
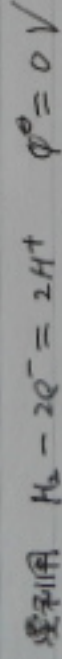
$E^\ominus = \varphi_{\text{正}}^\ominus - \varphi_{\text{负}}^\ominus = 0.771V - 0.151V = 0.62\ V$

(1) 所有离子浓度均为 $1\ mol/L$　　$E^\ominus > 0$　则 $\Delta G^\ominus < 0$　反应正向进行

(2)　$E = E^\ominus - \dfrac{RT}{nF} \ln \dfrac{1 \times 1}{0.001 \times 0.001} = 0.62 - \dfrac{8.314 \times 298}{2 \times 96485} \ln 10^4$
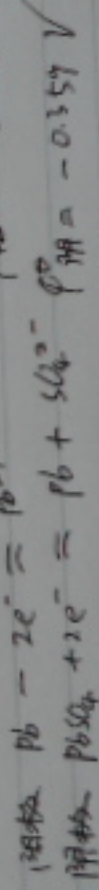
　　　　　　　　　　　$= 0.502\ V$

$E > 0,\ \Delta G < 0,\ $ 反应正向进行. 即 Sn^{2+} 能被还原为 Sn^{4+}.

17.　$PbSO_4 = Pb^{2+} + SO_4^{2-}$

电极反应:　(阴极)　$Pb - 2e^- = Pb^{2+}$　　　　　$\varphi_{\text{负}}^\ominus = -0.126\ V$
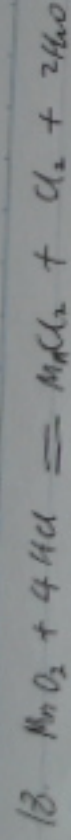
　　　　　(阳极)　$PbSO_4 + 2e^- = Pb + SO_4^{2-}$　　$\varphi_{\text{正}}^\ominus = -0.359\ V$
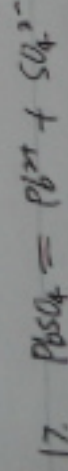
$E^\ominus = \varphi_{\text{正}}^\ominus - \varphi_{\text{负}}^\ominus = -0.359 - (-0.126) = -0.233\ V$

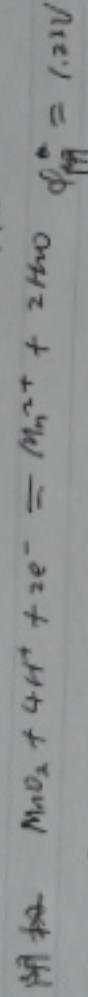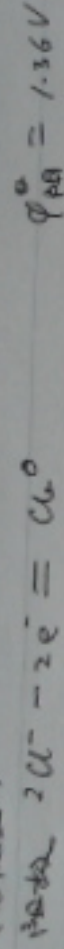$\dfrac{-2 \times 0.233 \times 96485}{8.314 \times 298} = -1.8 \times 10^{-8}$

$K_{sp} = K = e^{nEF/RT} = e^{\frac{-2 \times 0.233 \times 96485}{8.314 \times 298}} = 1.8 \times 10^{-8}$

13. $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$

设计电池反应。

正极 $2Cl^- - 2e^- = Cl_2^0$ $\varphi^\ominus_{正} = 1.36V$

负极 $MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$ $\varphi^\ominus_{负} = 1.21V$

$E^\ominus = \varphi^\ominus_{负} - \varphi^\ominus_{正} = 1.23 - 1.36V = -0.13V$

$$E = E^\ominus - \frac{RT}{2F} \ln \frac{(P_{Cl_2}/P^\ominus)(C_{Mn^{2+}}/C^\ominus)}{(C_{H^+}/C^\ominus)^4 (C_{Cl^-}/C^\ominus)^2}$$
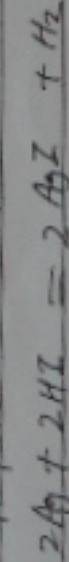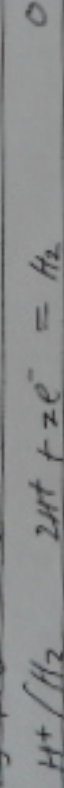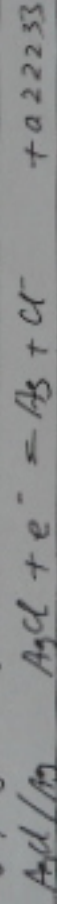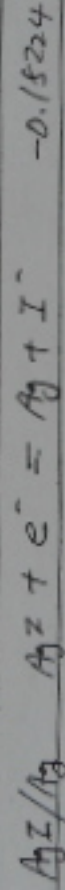
$$= -0.13 - \frac{8.314 \times 298}{2 \times 96485} \ln \frac{\frac{10^5}{101325} \times 0.2}{(0.01)^4 \times (0.21)^2}$$

$$= -0.13 - 0.256 = -0.39V. \quad <0$$

∴ 反应不能自发进行。

---

12. 解释 把Ag对应的置换 $1mol \cdot L^{-1}$ HCl 中的 Ag。

而 3··· 置换 $1mol \cdot L^{-1}$ HI 中的 Ag。

Ag^+/Ag $Ag^+ + e^- = Ag + I^-$ -0.1524

$AgCl/Ag$ $AgCl + e^- = Ag + Cl^-$ $+0.22233$

H^+/H_2 $2H^+ + 2e^- = H_2$ 0

$2Ag + 2HI = 2AgI + H_2$

$E = 0 - (-0.1524) = 0.1524 > 0$

∴ $\Delta G < 0$ 故该反应能进行。 $\Delta G^\ominus = -nFE^\ominus$

$2Ag + 2HCl = 2AgCl + H_2$

$E = 0 - (+0.22233) < 0$ ∴ $\Delta G > 0$

反应不能自发进行。