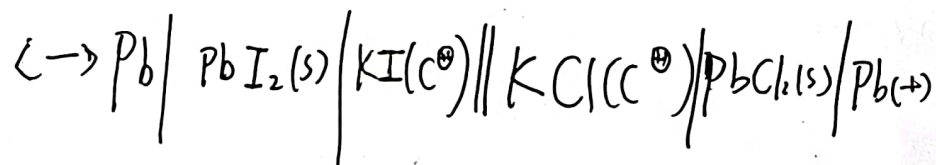
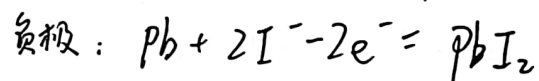
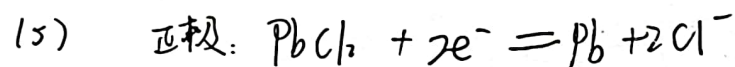
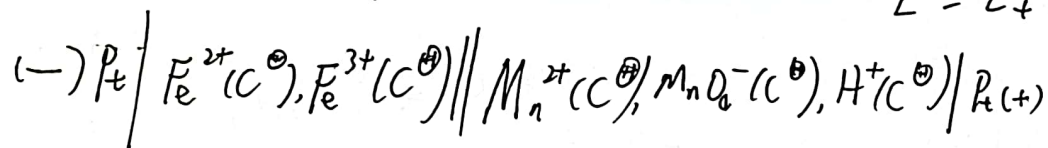
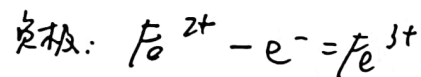
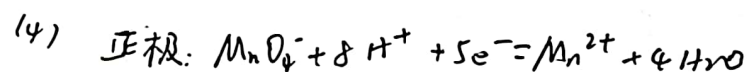
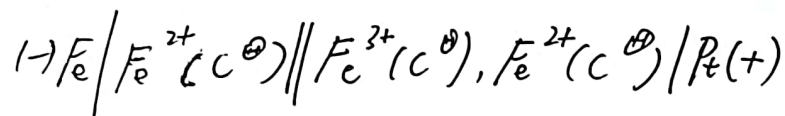
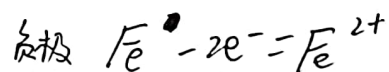
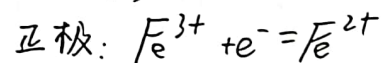
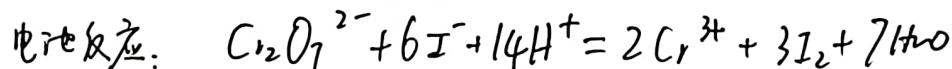
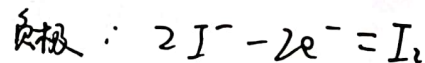
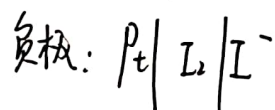
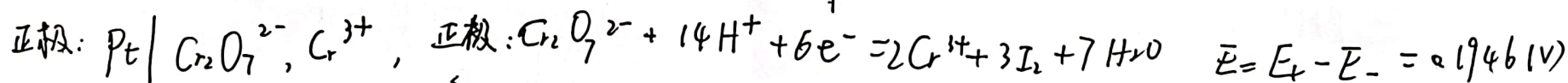


P220.1.(3)



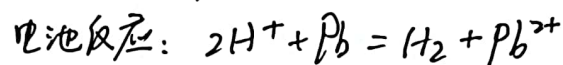
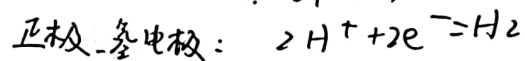
4. (1) $E(\text{I}_2/\text{I}^-) = 0.5355 - \frac{0.0592}{2} \lg \left(\frac{(\text{I}^-)}{\text{c}^\ominus} \right)^2 = 0.5947(\text{V})$

$E(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = E(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) + \frac{0.0592}{6} \lg \frac{0.1 \times (1 \times 10^{-4})^{14}}{1^2} = 0.7893(\text{V})$



4(2) $E(\text{Pb}^{2+}/\text{Pb}) = E^\ominus(\text{Pb}^{2+}/\text{Pb}) + \frac{0.0592}{2} \lg (\text{c}(\text{Pb}^{2+})/\text{c}^\ominus)$
 $= -0.1558(\text{V})$

$E(\text{H}^+/\text{H}_2) = E^\ominus(\text{H}^+/\text{H}_2) + \frac{0.0592}{2} \lg [\text{c}(\text{H}^+)/\text{c}^\ominus]^2$
 $= -0.0592(\text{V})$



$E = E_+ - E_- = E(\text{H}^+/\text{H}_2) - E(\text{Pb}^{2+}/\text{Pb}) = -0.0966(\text{V})$



$$7. \text{ (1) 正极: } \text{H}_3\text{AsO}_4 + 2\text{e}^- + 2\text{H}^+ = \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$$

$$\text{负极: } 2\text{I}^- - 2\text{e}^- = \text{I}_2$$

$$E^\ominus(\text{I}_2/\text{I}^-) = 0.5355 \text{ V}$$

$$E^\ominus(\text{H}_3\text{AsO}_4/\text{H}_3\text{AsO}_3) = 0.64 \text{ (V)}$$

$$E^\ominus = E_{\text{正}} - E_{\text{负}} = 0.64 - 0.5355 = 0.1045 \text{ (V)}$$

$$(2) \Delta_r G_m^\ominus = -nFE^\ominus = -2 \times 96500 \times 0.1045 \\ = -2.017 \times 10^4 \text{ (J/mol)}$$

$$(3) E(\text{H}_3\text{AsO}_4/\text{H}_3\text{AsO}_3) = E^\ominus(\text{H}_3\text{AsO}_4/\text{H}_3\text{AsO}_3) + \frac{0.0592}{2} \lg \left(\frac{c(\text{H}^+)}{c^\ominus} \right)^2 \\ = 0.2256 \text{ (V)}$$

$$E(\text{I}_2/\text{I}^-) = E^\ominus(\text{I}_2/\text{I}^-) = 0.5355 \text{ (V)}$$

$$\Delta_r G_m = -nFE = (-2) \times 96500 \times (0.2256 - 0.5355) \\ = 5.98 \times 10^4 \text{ (J/mol)} > 0$$

反应逆向进行。

$$(4) E_{\text{正}} > E_{\text{负}}$$

$$\therefore 0.64 - 0.0592 \times \text{pH} > 0.5355$$

$$\therefore \text{pH} < 1.77$$

$$8. E^\ominus(\text{PbCl}_2/\text{Pb}) = E^\ominus(\text{Pb}^{2+}/\text{Pb}) + \frac{0.0592}{2} \lg \left(\frac{c(\text{Pb}^{2+})}{c^\ominus} \right)$$

$$= E^\ominus(\text{Pb}^{2+}/\text{Pb}) + \frac{0.0592}{2} \lg \left(\frac{K_{\text{sp}}^\ominus(\text{PbCl}_2)}{c(\text{Cl}^-)^2} \right)$$

$$c(\text{Cl}^-) = 1 \text{ mol/L}$$

$$E^\ominus(\text{PbCl}_2/\text{Pb}) = -0.2681 \text{ (V)}$$

$$10. \text{ (1) } \text{Ag} | \text{AgI(s)} | \text{I}^- (1 \text{ mol/L}) || \text{Ag}^+ (1 \text{ mol/L}) | \text{Ag}$$

$$(2) \text{电池反应式: } \text{Ag}^+ + \text{I}^- = \text{AgI}$$

$$(3) E^\ominus = E_{\text{正}} - E_{\text{负}} \\ = E^\ominus(\text{Ag}^+/\text{Ag}) - E^\ominus(\text{AgI}/\text{Ag}) \\ = 0.9518 \text{ (V)}$$

$$(4) \Delta_r G_m^\ominus = -nFE = -1 \times 96500 \times 0.9518 \\ = -91.848 \text{ (kJ/mol)}$$

$$(5) \Delta_r G^\ominus = -RT \ln K^\ominus \\ = RT \ln K_{\text{sp}} \\ \Rightarrow \ln K_{\text{sp}} = -37.074 \\ \Rightarrow K_{\text{sp}} = 7.94 \times 10^{-17}$$



$$11. E(H_2/H^+) = E^\ominus(H_2/H^+) + 0.0592 \lg \frac{a(H^+)}{C^\ominus}$$

$$= 0.0592 \lg x$$

$$E(Cd^{2+}/Cd) = E^\ominus(Cd^{2+}/Cd) + \frac{0.0592}{2} \lg \left[\frac{C(Cd^{2+})}{C^\ominus} \right]$$

$$= -0.436 V.$$

$$E = E_+ - E_- = 0.0592 \lg x - (-0.436) = 0.15 V$$

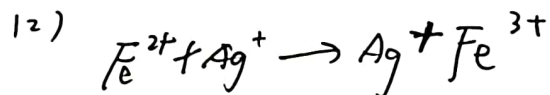
$$\Rightarrow PH = 4.77$$

$$C(H^+) = 1.7 \times 10^{-5} \text{ mol/L.}$$

$$13. (1) E^\ominus = E_+ - E_- = 0.0286 (V)$$

$$RT \ln K^\ominus = nFE^\ominus$$

$$K^\ominus = 3.046$$



$$\text{平衡: } x \quad x \quad 0.1-x$$

$$K^\ominus = \frac{0.1-x}{x^2} = 3.046$$

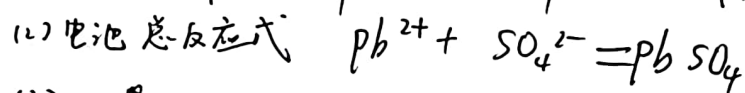
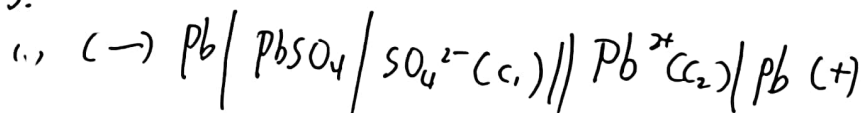
$$\Rightarrow C(Ag^+) = 0.0803 \text{ mol/L.}$$

$$14. \Delta_r G_m(3) = \Delta_r G_m^\ominus(1) + \Delta_r G_m^\ominus(2)$$

$$\therefore -n_3 F E_3^\ominus = -n_1 F E_1^\ominus - n_2 F E_2^\ominus$$

$$\therefore E_3^\ominus = -0.041 (V)$$

15.



$$(3) E = E_+ - E_- = \frac{0.0592}{2}$$

$$= -0.126 - (-0.356) - \frac{0.0592}{2} = 0.2004 (V)$$

$$(4) \Delta_r G_m^\ominus = -nFE^\ominus$$

$$= -44390 (J/mol)$$

$$RT \ln K^\ominus = nFE^\ominus$$

$$K_{sp}^\ominus = \frac{1}{K^\ominus}$$

$$\therefore K_{sp}^\ominus = 1.66 \times 10^{-8}$$

