

Analytical chemistry (5th Edition)

LuMg

March 2023

1 Chapter 7

1.

$$\delta_{Zn^{2+}} = \frac{1}{1 + \beta_{1,NH_3} * [NH_3] + \beta_{2,NH_3} * [NH_3]^2 + \beta_{3,NH_3} * [NH_3]^3 + \beta_{4,NH_3} * [NH_3]^4} = 3.23 * 10^{-6}$$

$$E_{Zn(NH_3)_4^{2+}/Zn}^{\phi} = E_{Zn^{2+}/Zn}^{\phi} + \frac{0.059}{2} \lg c_{Zn^{2+}}$$

$$= -0.763 + \frac{0.059}{2} * \lg(3.23 * 10^{-6} * c_{Zn(NH_3)_4^{2+}}) = -1.04V$$

(1)

2.

$$E_{Fe^{3+}/Fe^{2+}} = E_{Fe^{3+}/Fe^{2+}}^{\phi} + 0.059 * \lg \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$= E_{Fe^{3+}/Fe^{2+}}^{\phi} + 0.059 * \lg \frac{\frac{[FeR_3^{3+}]}{K_3 * [R]^3}}{\frac{[FeR_3^{2+}]}{K_2 * [R]^3}}$$

$$= E_{Fe^{3+}/Fe^{2+}}^{\phi} + 0.059 * \lg \frac{K_2}{K_3}$$

$$= 0.771 + 0.059 \lg 2.8 * 10^6 = 1.15V$$

(2)

3.

$$E_{Hg_2Cl_2/Hg}^{\phi} + \frac{0.059}{2} \lg \frac{1}{[Cl^-]^2} = E_{Hg_2^{2+}/Hg}^{\phi} + \frac{0.059}{2} \lg \frac{K_{sp}}{[Cl^-]^2} E_{Hg_2Cl_2/Hg}^{\phi} = E_{Hg_2^{2+}}^{\phi} + \frac{0.059}{2} \lg K_{sp}$$

$$= 0.265V$$

$$E_{Hg_2Cl_2/Hg} = E_{Hg_2Cl_2/Hg}^{\phi} + \frac{0.059}{2} * \lg \frac{1}{[Cl^-]^2} = 0.265 + \frac{0.059}{2} * \lg (0.01)^2 = 0.383V$$

(3)

4.

$$\begin{aligned}
[OH^-] &= 1 * 10^{-4} mol/L \\
[NH_3] &= \frac{[OH^-]}{[OH^-] + K_b} * c_{NH_3} = \frac{10^{-4}}{10^{-4} + 10^{-4.74}} * 0.1 = 0.085 mol/L \\
\delta_{Ag^+} &= \frac{1}{1 + \beta_1 * [NH_3] + \beta_2 * [NH_3]^2} E_{Ag^+/Ag} = E_{Ag^+/Ag}^{\phi} + 0.059 * lg \frac{1}{\delta_{Ag^+}} = 0.50V
\end{aligned}
\tag{4}$$

5.

Each :

$$\begin{aligned}
&KMnO_4 : \\
E_{MnO_4^-/Mn^{2+}} &= E_{MnO_4^-/Mn^{2+}}^{\phi} + \frac{0.059}{5} lg \frac{[MnO_4^-]}{[Mn^{2+}]} = E_{MnO_4^-/Mn^{2+}}^{\phi} = 1.45V \\
&K_2Cr_2O_7 : \\
E_{Cr_2O_7^{2-}/Cr^{3+}} &= E_{Cr_2O_7^{2-}/Cr^{3+}}^{\phi} + \frac{0.059}{6} lg \frac{[Cr_2O_7^{2-}]}{[Cr^{3+}]} = 1.01V
\end{aligned}
\tag{5}$$

6.

$$\begin{aligned}
E_{Fe^{3+}/Fe^{2+}}^{\phi} &= E_{Fe^{3+}/Fe^{2+}}^{\phi} + lg \frac{\frac{c_{Fe^{3+}}}{\alpha_{FeY^{3+}}}}{\frac{c_{Fe^{2+}}}{\alpha_{FeY^{2+}}}} \\
\alpha_{FeY^{3+}} &= 1 + [Y] * \beta_{FeY^{3+}} \\
\alpha_{FeY^{2+}} &= 1 + [Y] * \beta_{FeY^{2+}} \\
&Given : \\
\alpha_{Y(H)} &= 10^{10.60} \\
[Y] &= \frac{c_Y}{\alpha_{Y(H)}} \\
c_Y &= 0.1 mol/L \\
E_{Fe^{3+}/Fe^{2+}}^{\phi} &= 0.134V
\end{aligned}
\tag{6}$$

7.

$$\begin{aligned}
E_{Ag^+/Ag}^\phi &= 0.8V \\
E_{Cu^{2+}/Cu}^\phi &= 0.337V \\
2Ag^+ &\sim Cu \\
lgK &= \frac{(E_{Ag^+/Ag}^\phi - E_{Cu^{2+}/Cu}^\phi) * 2}{0.059} = 15.7 \\
c_{Ag^+} &= 0.05mol/L \\
[Cu^{2+}] &= 0.025mol/L \\
[Ag^+] &= \sqrt{\frac{[Cu^{2+}]}{K}} = 2.2 * 10^{-9}mol/L
\end{aligned} \tag{7}$$

8.

$$\begin{aligned}
E_{Cr_2O_7^{2-}/Cr^{3+}}^\phi &= 1.33V \\
E_{Fe^{3+}/Fe^{2+}}^\phi &= 0.77V \\
lgK &= \frac{(1.33 - 0.77) * 6}{0.059} = 56.9 \\
[Fe^{3+}] &= 0.05mol/L \\
K &= \frac{[Fe^{3+}]^6 [Cr^{3+}]^2}{[Cr_2O_7^{2-}] [Fe^{2+}]^6 [H^+]^{14}} \\
&= \frac{[Fe^{3+}]^6 * (\frac{1}{3} * [Fe^{3+}])^2}{\frac{1}{6} [Fe^{2+}] * [Fe^{2+}]^6 * [H^+]^{14}} \text{ Given :} \\
[Fe^{2+}] &= 10^{-6}mol/L \\
[H^+] &= 0.015mol/L
\end{aligned} \tag{8}$$

9.

•

$$\begin{aligned}
\text{When } P &= 0.5 \\
[I_2] &= \frac{10 * 0.05}{30} \\
[I^-] &= \frac{10 * 0.05 * 2}{30} + \frac{20 * 1}{30} - \frac{0.05 * 10}{30} \\
E_{I_3^-/I_2}^\phi &= 0.545 + \frac{0.059}{2} lg \frac{[I_3^-]}{[I^-]^3} = 0.507V
\end{aligned} \tag{9}$$

•

When $P = 1.0$

$$\begin{aligned}
[S_4O_6^{2-}] &= 0.1 * 20/40 * 0.5 \\
[I^-] &= 0.5 + 0.05 * 2 * 20/40 \\
lgK &= \frac{(0.545 - 0.08) * 2}{0.059} = 15.8 \\
K &= \frac{[S_4O_6^{2-}][I^-]^3}{[S_2O_3^{2-}]^2[I_3^-]} \\
&= \frac{[S_4O_6^{2-}][I^-]^3}{[I_3^-] * (2[I_3^-])^2} E_{sp} = 0.545 + \frac{0.059}{2} * lg \frac{[I_3^-]}{[I^-]^3} = 0.384V
\end{aligned} \tag{10}$$

•

When $P = 1.5$

$$\begin{aligned}
[S_2O_3^{2-}] &= \frac{0.1 * 10}{50} \\
[S_4O_6^{2-}] &= \frac{0.05 * 20}{50} \\
E_{S_4O_6^{2-}/S_2O_3^{2-}}^{\phi} &= 0.08 + \frac{0.059}{2} lg \frac{[S_4O_6^{2-}]}{[S_2O_3^{2-}]^2} = 0.130V
\end{aligned} \tag{11}$$

10.

Suppose :

$$\begin{aligned}
c_{Fe^{3+}} &= c_{Sn^{2+}} = 1mol/L \\
V_{Fe^{3+}} &= V_{Sn^{2+}} = 1L \\
When P &= 99.9\%: [Sn^{2+}] = \frac{0.01}{3} \\
[Sn^{4+}] &= \frac{0.99}{3} \\
E &= E_{Sn^{4+}/Sn^{2+}}^{\phi} + \frac{0.059}{2} lg \frac{[Sn^{4+}]}{[Sn^{2+}]} \\
&= 0.14 + \frac{0.059}{2} lg \frac{0.99}{0.01} = 0.199V \\
When P &= 1.01: \\
[Fe^{3+}] &= \frac{0.02}{3} \\
[Fe^{2+}] &= \frac{1.98}{3} \\
E &= E_{Fe^{3+}/Fe^{2+}}^{\phi} + 0.059 lg \frac{0.02}{1.98} = 0.562V
\end{aligned} \tag{12}$$

11.

$$\begin{aligned}
E_{Ce^{4+}/Ce^{3+}}^{\phi} &= 1.44V \\
E_{Fe^{3+}/Fe^{2+}}^{\phi} &= 0.68V \\
E_{sp} &= \frac{1.44 + 0.68}{2} = 1.06V \\
E_{In}^{\phi} &= 0.94V \\
\Delta E &= -0.12V \\
Error &= \frac{10^{\Delta E/0.059} - 10^{-\Delta E/0.059}}{10^{(1.44-0.68)/(2*0.059)}} = -0.004\%
\end{aligned} \tag{13}$$

14.

$$\begin{aligned}
c_{I_2} &= \frac{500 * 10^{-3} * 0.051\%}{32 * 11.6 * 10^{-3}} = 6.87 * 10^{-4} mol/L \\
P_S &= \frac{7.00 * 10^{-3} * 6.87 * 10^{-4} * 32}{500 * 10^{-3}} = 0.003\%
\end{aligned} \tag{14}$$

15.

$$\begin{aligned}
5VO^{2+} &\sim MnO_4^- \\
4Mn^{2+} &\sim MnO_4^- \\
P_V &= \frac{5 * (0.02 * 2.5 * 10^{-3} * 51)}{1.000} = 1.27\% \\
P_{Mn} &= \frac{4 * (0.02 * 4 * 10^{-3} - 0.02 * 2.5 * 10^{-3}) * 55}{1.000} = 1.48\%
\end{aligned} \tag{15}$$

16.

$$\begin{aligned}
2Ce^{4+} + 2I^- &= 2Ce^{3+} + I_2 \\
I_2 + I^- &= I_3^- \\
n_{I_2} &= \frac{1}{2} * 0.005 * V - N_{I_3^-} \\
n_{I^-} &= 0.005 * 0.05 - 0.005 * V - n_{I_3^-} \\
c_{I_2} &= \frac{n_{I_2}}{0.05 + V} = 0.0133 \\
\frac{n_{I_3^-}}{n_{I_2} * n_{I^-}} &= 708 \\
V &= 26.69mL
\end{aligned} \tag{16}$$

17.

$$\begin{aligned}
n_{PbO_2} &= n_1 mmol \\
n_{PbO} &= n_2 mmol \\
2n_1 + n_2 &= 20 * 0.25 - 0.04 * 10 * \frac{5}{2} \\
n_1 + n_2 &= 30 * 0.04 * \frac{5}{2} \\
n_1 &= 1 mmol \\
n_2 &= 2 mmol \\
w_{PbO_2} &= 19.38\% \\
w_{PbO} &= 36.18\%
\end{aligned} \tag{17}$$

18.

$$\begin{aligned}
Cr_2O_7^{2-} &\sim 6Fe^{2+} \\
p_{FeO} &= 0.03 mol/L * 25 mL * 6 * M_{FeO} / M_{sample} = 32.3\% \\
p_{Al_2O_3} &= (0.5 - 0.03 mol/L * 25 mL * 6 * \frac{M_{Fe_2O_3}}{2}) / M_{sample} = 14.09\%
\end{aligned} \tag{18}$$

19.

$$\begin{aligned}
2I_2 &\sim S_2O_3^{2-} \\
5I^- &\sim IO_3^- \\
c_{KI} &= \frac{5 * (10 * 0.05 - \frac{1}{2*3} * 0.1008 * 21.14)}{25.00} = 0.029 mol/L
\end{aligned} \tag{19}$$

20.

$$\begin{aligned}
n_{Mn} &= n_1 \\
n_{Cr} &= n_2 \\
n_{Fe^{2+}} &= 0.1 * 50 * 10^{-3} - 0.01 * 18.4 * 10^{-3} * 5 = 4.08 * 10^{-3} mol \\
3MnO_4^{2-} &\sim 2MnO_4^- + MnO_2 \\
\frac{2}{3} * n_1 * 5 + n_2 * 3 &= n_{Fe^{2+}} \\
\frac{1}{3} * n_1 &= \frac{1}{2} * (0.1 * 10 * 10^{-3} - 0.01 * 8.24 * 10^{-3} * 5) \\
n_1 &= 8.82 * 10^{-4} mol \\
n_2 &= 3.8 * 10^{-4} mol \\
w_{MnO} &= 3.13\% \\
w_{Cr_2O_3} &= 1.44\%
\end{aligned} \tag{20}$$

$$\begin{aligned}
21. \quad & 3NO_2 + H_2O = 2HNO_3 + NO \\
& P_{NH_3} = \frac{\frac{3}{2} * 0.01 * 0.02 * M_{NH_3}}{1.000} = 0.51\%
\end{aligned} \tag{21}$$

$$\begin{aligned}
22. \quad & P_{Fe_2O_3} = \frac{5 * 0.025 * 41.27 * 10^{-3} * \frac{1}{2} * M_{Fe_2O_3}}{0.4185} = 98.42\%
\end{aligned} \tag{22}$$

$$\begin{aligned}
23. \quad & 2KMNO_4^- \sim 3Mn^{2+} \\
& P_{Mn} = \frac{\frac{3}{2} * 0.03358 * 34.88 * 10^{-3} * M_{Mn}}{0.5165} = 18.69\%
\end{aligned} \tag{23}$$

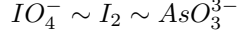
$$\begin{aligned}
24. \quad & U^{4+} + 2Fe^{3+} = 2Fe^{2+} + U^{6+} \\
& Cr_2O_7^{2-} \sim 6Fe^{2+} \\
& P_U = \frac{\frac{1}{2} * 6 * 0.00978 * 10.52 * 10^{-3} * 238.0}{0.315} = 23.32\%
\end{aligned} \tag{24}$$

$$\begin{aligned}
25. \quad & Cr \sim \frac{1}{2} Cr_2O_7^{2-} \sim 3Fe^{2+} \\
& d_{Cr} = \frac{\frac{1}{3} * (\frac{0.5}{M_{Fe(NH_4)(SO_4)2 \cdot 6H_2O}} - 6 * 0.00389 * 18.29 * 10^{-3}) * M_{Cr}}{7.20 * 30} \\
& = 7.3 * 10^{-5} cm
\end{aligned} \tag{25}$$

$$\begin{aligned}
26. \quad & 5CO \sim I_2O_5 \sim I_2 \\
& I_3^- \sim 2S_2O_3^{2-} \\
& w_{CO} = \frac{5 * \frac{1}{2} * 7.17 * 10^{-3} * 0.00329 * M_{CO} * 10^6}{4.79 * 1.23} = 280ug/g
\end{aligned} \tag{26}$$

$$\begin{aligned}
27. \quad & I^- \sim IO_3^- \sim 3I_2 \sim 6I^- \sim 6IO_3^- \sim 18I_2 \sim 36Na_2S_2O_3 \\
& w_{KI} = \frac{166 * \frac{1}{36} * 0.1 * 20.06 * 10^{-3}}{25 * 10^{-3}} = 0.37g/L
\end{aligned} \tag{27}$$

28.



$$c_{IO_4^-} = \frac{40.10 * 0.05}{50 * 10^{-3}} = 40.1 \text{ mmol/L}$$

$$M_{CH_2OHCH_2OH} = (50 - \frac{0.05 * 14.3}{40.1} * 10^3) * 10^{-3} * 40.1 * M_{CH_2OHCH_2OH} = 80.0 \text{ mg}$$

(28)

29.

Suppose :

$$n_{HCOOH} = n_1$$

$$n_{HAc} = n_2$$

$$HCOO^- \sim 2MnO_4^{2-} \sim \frac{4}{3}MnO_4^- \sim \frac{2}{3}MnO_2$$

$$n_{KMnO_4, \text{remaining}} = 0.025 * 50 * 10^{-3} - 2n_1$$

$$n_{Fe^{2+}} = (n_{KMnO_4, \text{remaining}} + \frac{4}{3} * n_1) * 5 + \frac{2}{3} * n_1 * 2$$

$$n_{Fe^{2+}} = 0.2 * 40 * 10^{-3} - 0.025 * 24 * 10^{-3} * 5 \quad (29)$$

$$n_1 = 6.25 * 10^{-4} \text{ mol}$$

Given :

$$n_1 + n_2 = 0.1 * 25 * 10^{-3}$$

$$n_2 = 1.875 * 10^{-3} \text{ mol}$$

$$c_{HCOOH} = 0.03125 \text{ mol/L}$$

$$c_{HAc} = 0.09375 \text{ mol/L}$$

30.

$$n_{Cr_2O_7^{2-}} = 25 * 10^{-3} * 0.01667 - 15 * 10^{-3} * 0.1 * \frac{1}{6}$$

$$3O_2 \sim 2Cr_2O_7^{2-}$$

$$COD = \frac{3}{2} * n_{Cr_2O_7^{2-}} * M_{O_2} / 0.100 = 80.04 \text{ mg/L} \quad (30)$$

31.



$$I_2 \sim 2S_2O_3^{2-}$$

$$w_{CH_3COCH_3} = \frac{10 * M_{CH_3COCH_3} * \frac{1}{3} * (50 * 10^{-3} * 0.05 - \frac{1}{2} * 0.1 * 10 * 10^{-3})}{1} = 38.67\%$$

(31)

33.

$$\begin{aligned}
 PbO_2 &\sim I_2 \sim 2NaS_2O_3 \\
 n_{PbO_2} &= \frac{1}{2} * c_{NaS_2O_3} * V_{NaS_2O_3} \\
 n_{PbO} &= c_Y * V_Y - n_{PbO_2}
 \end{aligned} \tag{32}$$

36.

$$\begin{aligned}
 n_{H_2O_2} &= \frac{1.023}{153.86} * \frac{1}{10} = 6.65 * 10^{-4} mol \\
 2MnO_4^- &\sim 5H_2O_2 : \\
 V_{MnO_4^-} &= \frac{2}{5} * n_{H_2O_2} / c_{MnO_4^-} = 25.4 mL \\
 V_{MnO_4^-} &= \frac{2}{3} * n_{H_2O_2} / c_{MnO_4^-} = 42.4 mL
 \end{aligned} \tag{33}$$

37.

$$\begin{aligned}
 C_3H_8O_3 &\sim 8Ce^{4+} \\
 w_{C_3H_8O_3} &= \frac{M_{C_3H_8O_3} * \frac{1}{8} * (50 * 10^{-3} * 0.0837 - 12.11 * 10^{-3} * 0.0448)}{0.1} = 41.89\%
 \end{aligned} \tag{34}$$