

Analytical chemistry (5th Edition)

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1 Chapter 5

1.

- $[NH_4^+] + [H^+] = [OH^-] + [NH_3]$
- $[H^+] = [H_2BO_3^-] + [OH^-]$
- $[H^+] = [H_2PO_4] + 2 * [HPO_4^{2-}] + 3 * [PO_4^{3-}] + [HCOO^-]$
- $[H^+] = [OH^-] + [Fe(OH)] + 2 * [Fe(OH)^{2-}] + 3 * [Fe(OH)^3]$

2.

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*For H_3BO_3 , $K_{a1} = 5.8 * 10^{-10}$*

*$K_{a2} = 4.0 * 10^{-13}$ can be neglected*

$$[H^+] = [OH^-] + [H_2BO_3^-]$$

where

$$[OH^-] = \frac{K_w}{[H^+]} \tag{1}$$

$$[H_2BO_3^-] = \frac{[H_3BO_3] * K_{a1}}{[H^+]}$$

$$[H^+] = \sqrt{K_{a1} * [H_3BO_3] + K_w} = 7.62 * 10^{-6} \text{ mol/L}$$

$$pH = 5.12$$

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For H_2SO_4 , $K_{a1} = 1.7 * 10^{-2}$

$K_{a2} = 6.4 * 10^{-8}$ which can be neglected

K_w can also be neglected

Same equation as above

$$[H^+] = \sqrt{K_{a1} * [H_2SO_4] + K_w}$$

$$\text{where } [H_2SO_4] = \frac{[H^+]}{[H^+] + K_{a1}} \quad (2)$$

$$[H^+]^3 + K_{a1} * [H^+]^2 - K_{a1} * c * [H^+] - K_{a1} * K_w = 0$$

$$[H^+] = \frac{-K_{a1} + \sqrt{K_{a1}^2 + 4 * K_{a1} * c}}{2}$$

$$= 0.0336 \text{ mol/L}$$

$$pH = 1.47$$

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$$K_b = 2.5 * 10^{-10}$$

$$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4 * K_b * c}}{2} = 5.0 * 10^{-6} \text{ mol/L} \quad (3)$$

$$pH = 8.7$$

• HCl can be redeemed as $K_a = \text{inf}$

$$[H^+] = [Cl^-] + [OH^-]$$

$$[H^+] = c_{HCl} + \frac{K_w}{[H^+]}$$

$$[H^+] = \frac{c + \sqrt{c^2 + 4 * K_w}}{2} = 1.28 * 10^{-7} \text{ mol/L} \quad (4)$$

$$pH = 6.89$$

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$$K_a = 7.52 * 10^{-3}$$

$$[H^+] = \sqrt{K_a * c} = 0.0388 \text{ mol/L} \quad (5)$$

$$pH = 1.41$$

3.

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$$k_b = 5.6 * 10^{-10}$$

$$[OH^-] = \sqrt{K_b * c} = 5.29 * 10^{-6} \text{ mol/L} \quad (6)$$

$$pH = 8.72$$

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$$k_{a_{NH_4^+}} = 5.5 * 10^{-10}$$

$$[H^+] = \sqrt{k_a * c} = 5.24 * 10^{-6} \quad (7)$$

$$pH = 5.28$$

- use PBE:

$$\begin{aligned}
[H^+] &= [OH^-] + [NH_3] - [HCN] \\
&\text{let :} \\
K_{a1} &= K_{a,NH_4^+} \\
K_{a2} &= K_{a,HCN} \\
&\text{then :} \\
[H^+] &= \sqrt{\frac{K_{a2}(K_w + K_{a1} * c)}{K_{a2} + c}} = 5.84 * 10^{-10} mol/L \\
pH &= 9.23
\end{aligned} \tag{8}$$

- The same equation as above:

$$\begin{aligned}
[H^+] &= \sqrt{\frac{K_{a2} * (K_w + K_{a3} * c)}{K_{a2} + c}} = 2.06 * 10^{-10} mol/L \\
pH &= 9.69
\end{aligned} \tag{9}$$

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$$\begin{aligned}
&[H_4N^+CH_2COOH] \\
&K_{a1} = 4.5 * 10^{-3} \\
&K_{a2} = 2.5 * 10^{-10} \\
[H^+] &= \sqrt{\frac{K_{a1} * (K_w + K_{a2} * c)}{K_{a1} + c}} = 1.02 * 10^{-6} mol/L \\
pH &= 5.99
\end{aligned} \tag{10}$$

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$$\begin{aligned}
K_{b1} &= 1.41 \\
&K_{b2} = 7.69 * 10^{-8} \\
[OH^-] &= \sqrt{K_{b1} * [S^{2-}]} \\
[OH^-] &= \sqrt{K_{b1} * c * \frac{[OH^-]}{[OH^-] + K_{b1}}} \\
[OH^-] &= \frac{-K_{b1} + \sqrt{K_{b1}^2 + 4 * K_{b1} * c}}{2} = 0.0938 mol/L \\
pH &= 12.97
\end{aligned} \tag{11}$$

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$$\begin{aligned}
K_a &= 2.24 * 10^{-12} \\
[H^+] &= \sqrt{K_a * c + K_w} = 1.8 * 10^{-7} mol/L \\
pH &= 6.74
\end{aligned} \tag{12}$$

•

$$\begin{aligned}
& [CH_3CH_2NH_4^+] \\
& [NH_4Cl] \\
& K_{HA} = 1.8 * 10^{-11} \\
& K_{HB} = 5.5 * 10^{-10} \\
& [H^+] = \sqrt{K_{HA} * c + K_{HB} * c} = 5.33 * 10^{-6} mol/L \\
& pH = 5.27
\end{aligned} \tag{13}$$

• using PBE:

$$\begin{aligned}
& K_{a, ClCH_2COOH} = 1.4 * 10^{-3} \\
& [H^+] = [OH^-] - [ClCH_2COOH] + c_{Cl-} \\
& [H^+] = -[ClCH_2COOH] + c_{Cl-} \\
& \frac{K_w}{[OH^-]} = -\frac{K_b [ClCH_2COO^-]}{[OH^-]} + c_{Cl-} \\
& c_{Cl-} [OH^-]^2 + (c_{Cl-} * K_b - K_b * c_{Na+} - K_{w, right}) * [OH^-] - K_w * K_b = 0 \\
& [OH^-] = 6.93 * 10^{-13} mol/L \\
& pOH = 12.16 \\
& pH = 1.84
\end{aligned} \tag{14}$$

4.

$$\begin{aligned}
& pH = 7.40 \\
& K_{a1} = 4.0 * 10^{-7} \\
& K_{a2} = 7.0 * 10^{-11} \\
& [H_2CO_3] = \frac{[H^+]^2}{[H^+]^2 + K_{a1} * [H^+] + K_{a1} * K_{a2}} = 0.0904 \\
& [HCO_3^-] = \frac{K_{a1} * [H^+]}{[H^+]^2 + K_{a1} * [H^+] + K_{a1} * K_{a2}} = 0.908 \\
& [CO_3^{2-}] = \frac{K_{a1} * K_{a2}}{[H^+]^2 + K_{a1} * [H^+] + K_{a1} * K_{a2}} = 0.002
\end{aligned} \tag{15}$$

5.

$$\begin{aligned}
c_{HCl} &= 0.1 \text{ mol/L} \\
c_{HSO_4^-} &= 2.0 * 10^{-4} \text{ mol/L} \\
c_{Ac^-} &= 2.0 * 10^{-8} \text{ mol/L} \\
[H^+] &= 0.1 \text{ mol/L} \\
pH &= 1.00 \\
[H^+] &= [OH^-] + [Ac^-] + [HSO_4^-] \\
[H^+] &= [HSO_4^-] \\
[H^+] &= 2 * 10^{-4} \text{ mol/L} \\
pH &= 3.70
\end{aligned} \tag{16}$$

6.

$$\begin{aligned}
&0.02 \text{ mol/L Na}_2\text{CO}_3 \\
&0.08 \text{ mol/L NaHCO}_3 \\
&0.08 \text{ mol/L NaHC}_2\text{O}_4 \\
[OH^-] &= \sqrt{K_{b,CO_3^{2-}} * 0.02 + K_{b,HCO_3^-} * 0.08 + K_{b,HC_2O_4} * 0.08} = 1.78 * 10^{-3} \text{ mol/L} \\
pH &= 11.25
\end{aligned} \tag{17}$$

7.

$$\begin{aligned}
K_{a,Cr^{3+}} &= 10^{-3.8} \\
[H^+] &= \sqrt{K_{a,Cr^{3+}} * c} = 1.26 * 10^{-3} \text{ mol/L} \\
pH &= 2.9 \\
P_{Cr(OH)^{2+}} &= \frac{K_a}{K_a + [H^+]} = 0.11
\end{aligned} \tag{18}$$

8.

$$\begin{aligned}
pH &= pKa + \lg \frac{c_{Ac^-}}{HAc} \\
4.44 &= 4.75 + \lg \frac{\frac{m_{NaAc}}{M_{NaAc}} - n_{HCl}}{n_{HCl}} \\
4.44 &= 4.75 + \lg \frac{\frac{m_{NaAc}}{82} - 0.01}{0.01} \\
m_{NaAc} &= 1.22g
\end{aligned} \tag{19}$$

9. Let the original c_{B-} :
In the previous equation:

$$pH = pKa + \lg \frac{c_{B^-}}{c_{HB}} \quad (20)$$

In the new solution:

$$\begin{aligned} pH &= 5.3 + \lg \frac{c_{B^-} * V + \frac{m_{NaOH}}{M_{NaOH}}}{c_{HB} * V - \frac{m_{NaOH}}{M_{NaOH}}} \\ pH &= 5.44 \end{aligned} \quad (21)$$

10.

$$\begin{aligned} K_{a,HCOOH} &= 1.8 * 10^{-4} \\ pH &= pKa + \lg \frac{c_{NaOH} * V_{NaOH}}{c_{HCOOH} * V_{HCOOH} - c_{NaOH} * V_{NaOH}} \end{aligned} \quad (22)$$

Given $pH = 3.0$, $V_{NaOH} = 6.0mL$

Given $pH = 4.0$, $V_{NaOH} = 25.7mL$

11.

$$\begin{aligned} m_{NH_2CH_2COOH} &= M_{NH_2CH_2COOH} * c * V = 0.75g \\ \beta &= 2.30 * [H^+] + 2.30 * \frac{c * K_a * [H^+]}{([H^+] + K_a)^2} = 0.072 \\ V_{add} &= \beta * V = 7.2mL \end{aligned} \quad (23)$$

12.

$$\begin{aligned} n_{(CH_2)_6N_4} &= \frac{m_{(CH_2)_6N_4}}{M_{(CH_2)_6N_4}} = 0.14mol \\ n_{HCl} &= c_{HCl} * V_{HCl} = 0.048mol \\ \frac{B^-}{HB} &= \frac{0.14 - 0.048}{0.048} < 10 \end{aligned} \quad (24)$$

13.

•

$$\begin{aligned}
K_{a1} &= 9.1 * 10^{-4} \\
K_{a2} &= 4.3 * 10^{-5} \\
I &= \frac{1}{2_i} * z_i^2 \\
&= \frac{1}{2} (0.034 * 1 + 0.034 * 1) = 0.034 \\
lg\gamma_i &= 0.0514 \\
[H^+] &= \sqrt{K_{a1} * K_{a2}} \\
&= \sqrt{K_{a1} * K_{a2} * \frac{1}{\gamma_B}} = 2.76 * 10^{-4} mol/L \\
pH &= 3.56
\end{aligned} \tag{25}$$

14.

$$\begin{aligned}
[OH^-] &= \sqrt{\frac{K_w}{K_a} * \frac{c}{1.25}} \\
pH &= 14 - pOH = 8.82
\end{aligned} \tag{26}$$

15.

$$\begin{aligned}
pH &= pK_{a1} = 1.92 \\
pH &= pK_{a2} = 6.22 \\
K_{a1} &= 1.2 * 10^{-2} \\
K_{a2} &= 6.0 * 10^{-7} \\
[H^+] &= \sqrt{\frac{K_{a1} * K_{a2} * c}{K_{a1} + c}} pH = 4.12 \\
[H^+]_2 &= \sqrt{\frac{K_w}{K_a} * c} = 2.35 * 10^{-5} mol/L \\
pH &= 9.37
\end{aligned} \tag{27}$$

16.

$$\begin{aligned}
[H^+] &= \sqrt{k_a * c} = 3.0 \\
K_a &= 10^{-5} \\
[OH^-] &= \sqrt{\frac{k_w}{k_a} * c} = 10^{-5} mol/L \\
pH &= 9.0
\end{aligned} \tag{28}$$

17. Let:

$$\begin{aligned}
n_{Na_2CO_3} &= n1 \\
n_{NaHCO_3} &= n2 \\
M_{Na_2CO_3} * n1 + M_{NaHCO_3} * n2 &= m_{sample} \\
2 * n1 + n2 &= c_{HCl} * V_{HCl} \\
n1 &= 2.5 * 10^{-3} mol \\
n2 &= 5.0 * 10^{-3} mol \\
V_{HCl, new} &= \frac{n1}{c_{HCl}} = 12.5 mL
\end{aligned} \tag{29}$$

18.

$$\begin{aligned}
pH = 4.80 &= pK_a + lg \frac{V_{NaOH}}{V_{ep, NaOH} - V_{NaOH}} \\
&= pK_a + lg \frac{11.00}{24.60 - 11.00} \\
pK_a &= 4.89
\end{aligned} \tag{30}$$

19.

$$\begin{aligned}
[OH^-] &= \sqrt{K_b * c} \\
&= \sqrt{\frac{K_w}{K_a} * 0.05} = 5.3 * 10^{-6} mol/L \\
pH_{ep} &= 8.72 \\
E_t &= \frac{10^{\Delta pH} - 10^{-\Delta pH}}{\sqrt{c * K_t}} \\
&= \frac{10^{-0.72} - 10^{0.72}}{\sqrt{0.05 * 10^{9.26}}} = -0.05\%
\end{aligned} \tag{31}$$

20.

$$E_t = \frac{10^{\Delta pH} - 10^{-\Delta pH}}{\sqrt{\frac{K_{a1}}{K_{a2}}}} = 0.82\% \tag{32}$$

21.

$$\begin{aligned}
C_9H_8O_4 &\sim 2NaOH \\
2NaOH &\sim H_2SO_4 \\
P &= \frac{\frac{1}{2} * (c_{NaOH} * V_{NaOH} - 2 * c_{H_2SO_4} * V_{H_2SO_4}) * M}{m_{sample}} = 92.8\%
\end{aligned} \tag{33}$$

22.

$$\begin{aligned}
K_{a,NH_2OH} &= 10^{-9.24} = K_{a1} \\
K_{a,NH_4Cl} &= 10^{-5.94} = K_{a2} \\
[H^+] &= \sqrt{K_{a1} * K_{a2}} = 2.57 * 10^{-8} mol/L \\
pH &= 7.59 \\
\delta &= \frac{K_{a1}}{K_{a1} + [H^+]} = 2.2\%
\end{aligned} \tag{34}$$

23.

$$\begin{aligned}
pH &= 5.0 = pK_a \\
pOH &= 5.0 = p \sqrt{\frac{k_w}{K_a} * c_A} \\
c_A &= 0.1 mol/L \\
c_A * \left(V_{HA} + \frac{n_A}{c_{NaOH}} \right) &= n_A \\
n_A &= 0.01 mol/L \\
P &= \frac{n_A * M_A}{m_{sample}} = 82.0\%
\end{aligned} \tag{35}$$

24.

$$\begin{aligned}
n_{KCl} + n_{NaCl} &= c_{HCl} * V_{HCl} \\
M_{KCl} * n_{KCl} + M_{NaCl} * n_{NaCl} &= 0.18 \\
\delta &= \frac{M_{KCl} * n_{KCl}}{0.18} = 48.0\%
\end{aligned} \tag{36}$$

25.

$$\begin{aligned}
&(NH_4)_3 PMo_{12}O_{40} \sigma 25 NaOH \\
P_P &= \frac{(c_{NaOH} * V_{NaOH} - c_{HNO_3} * V_{HNO_3}) / 25 * M_P}{m_{sample}} = 0.62\% \\
P_{P_2O_5} &= 1.44\%
\end{aligned} \tag{37}$$

26.

$$P_{protein} = \frac{5.7 * M_N (c_{HCl} * V_{HCl} - c_{NaOH} * V_{NaOH})}{m_{sample}} = 2.93\% \tag{38}$$

27.

$$\begin{aligned}
 I &= \frac{1}{2} \Sigma C_i Z_i^2 = 0.1 \\
 \gamma I n^- &= 0.6948 \\
 pH &= pKa + lg \gamma I n^- = 3.24
 \end{aligned}
 \tag{39}$$

28.

$$c_{C_2H_5ONa} = \frac{c_{HA} * V_{HA}}{V_{C_2H_5ONa}} = 0.150 mol/L \tag{40}$$

29.

$$\begin{aligned}
 HgO + 4KI + H_2O &= K_2HgI_4 + 2KOH \\
 HgO &\sim 2KOH \\
 P_{HgO} &= \frac{M_{HgO} * (c_{HCl} * V_{HCl}/2)}{m_{sample}} = 85.7\%
 \end{aligned}
 \tag{41}$$

30.

$$c_{HCHO} = \frac{c_{NaOH} * V_{NaOH}}{V_{HCHO}} = 0.313 mol/L \tag{42}$$