

# Analüütiline keemia ülesanded

## 1. Tugeva hape vesilahuse pH leidmine

### Solution 1. IChO 2003 – Ateena, Kreeka – Teooriavor Küsimus 2

$$[\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-]$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{H}^+] = [\text{Cl}^-] + \frac{K_w}{[\text{OH}^-]} \Rightarrow [\text{H}^+]^2 - [\text{Cl}^-][\text{H}^+] - K_w = 0 \Rightarrow [\text{H}^+] = \frac{[\text{Cl}^-] + \sqrt{[\text{Cl}^-]^2 + 4K_w}}{2}$$

## 2. Nõrkade hapete vesilahuse pH leidmine

### Solution 2. IChO 1993 – Perugia, Itaalia – Ettevalmistusülesanne 36

$$c(\text{H}_2\text{C}_2\text{O}_4) = [\text{H}_2\text{C}_2\text{O}_4] + [\text{HC}_2\text{O}_4^-] + [\text{C}_2\text{O}_4^{2-}]$$

$$K_1 = \frac{[\text{HC}_2\text{O}_4^-][\text{H}^+]}{[\text{H}_2\text{C}_2\text{O}_4]} \Rightarrow [\text{HC}_2\text{O}_4^-] = \frac{K_1[\text{H}_2\text{C}_2\text{O}_4]}{[\text{H}^+]}$$

$$K_2 = \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}^+]}{[\text{HC}_2\text{O}_4^-]} \Rightarrow [\text{C}_2\text{O}_4^{2-}] = \frac{K_1[\text{HC}_2\text{O}_4^-]}{[\text{H}^+]} = \frac{K_1K_2[\text{H}_2\text{C}_2\text{O}_4]}{[\text{H}^+]^2}$$

$$c(\text{H}_2\text{C}_2\text{O}_4) = [\text{H}_2\text{C}_2\text{O}_4] \left( 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1K_2}{[\text{H}^+]^2} \right) = [\text{H}_2\text{C}_2\text{O}_4] \left( \frac{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}{[\text{H}^+]^2} \right)$$

$$[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2 = 5.92 \cdot 10^{-6}$$

$$\alpha_0(\text{H}_2\text{C}_2\text{O}_4) = \frac{[\text{H}_2\text{C}_2\text{O}_4]}{c(\text{H}_2\text{C}_2\text{O}_4)} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2} = \frac{(10^{-4.25})^2}{5.92 \cdot 10^{-6}} = 5.33 \cdot 10^{-4}$$

$$\alpha_1(\text{HC}_2\text{O}_4^-) = \frac{[\text{HC}_2\text{O}_4^-]}{c(\text{HC}_2\text{O}_4^-)} = \frac{K_1[\text{H}^+]}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2} = \frac{5.36 \cdot 10^{-2} \cdot 10^{-4.25}}{5.92 \cdot 10^{-6}} = 5.08 \cdot 10^{-1}$$

$$\alpha_2(\text{C}_2\text{O}_4^{2-}) = \frac{[\text{C}_2\text{O}_4^{2-}]}{c(\text{C}_2\text{O}_4^{2-})} = \frac{K_1K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2} = \frac{5.36 \cdot 10^{-2} \cdot 5.42 \cdot 10^{-5}}{5.92 \cdot 10^{-6}} = 4.89 \cdot 10^{-1}$$

### Solution 3. IChO 1993 – Perugia, Itaalia – Ettevalmistusülesanne 52

$$K_1 = \frac{[{}^+\text{H}_3\text{NCHR}\text{COO}^-][\text{H}^+]}{[{}^+\text{H}_3\text{NCHR}\text{COOH}]}, K_2 = \frac{[\text{H}_2\text{NCHR}\text{COO}^-][\text{H}^+]}{[{}^+\text{H}_3\text{NCHR}\text{COO}^-]}, K_1K_2 = \frac{[\text{H}_2\text{NCHR}\text{COO}^-][\text{H}^+]^2}{[{}^+\text{H}_3\text{NCHR}\text{COOH}]}$$

$$c_0 = [{}^+\text{H}_3\text{NCHR}\text{COOH}] + [{}^+\text{H}_3\text{NCHR}\text{COO}^-] + [\text{H}_2\text{NCHR}\text{COO}^-] \approx [{}^+\text{H}_3\text{NCHR}\text{COO}^-]$$

$$[{}^+\text{H}_3\text{NCHR}\text{COOH}] + [\text{H}^+] = [\text{H}_2\text{NCHR}\text{COO}^-] + [\text{OH}^-]$$

$$\frac{[\text{H}^+]}{K_1} [{}^+\text{H}_3\text{NCHR}\text{COO}^-] + [\text{H}^+] = \frac{K_2}{[\text{H}^+]} [{}^+\text{H}_3\text{NCHR}\text{COO}^-] + \frac{K_w}{[\text{H}^+]}$$

$$\frac{c_0[\text{H}^+]}{K_1} - \frac{c_0K_2}{[\text{H}^+]} - \frac{K_w}{[\text{H}^+]} + [\text{H}^+] \approx 0$$

$$[\text{H}^+]^2 \left( \frac{c_0}{K_1} + 1 \right) - c_0K_2 - K_w \approx 0 \Rightarrow [\text{H}^+] = \sqrt{K_1 \frac{c_0K_2 + K_w}{c_0 + K_1}} = \sqrt{10^{-2.348} \frac{0.200 \cdot 10^{-9.866} + 10^{-14}}{0.200 + 10^{-2.348}}} \Rightarrow \text{pH} = 6.11$$

### Solution 4. IChO 1994 – Oslo, Norra – Ettevalmistusülesanne 5

2.  $[H^+] \approx [H_2PO_3^-] + [Cl^-]$ ,  $K_1 = \frac{([H^+] - 3c_0)[H^+]}{c_0 - ([H^+] - 3c_0)} \Rightarrow [H^+]^2 + (K_1 - 3c_0)[H^+] - 4c_0K_1 = 0$
- $$[H^+] = \frac{-(K_1 - 3c_0) + \sqrt{(K_1 - 3c_0)^2 + 16c_0K_1}}{2}$$
- $$= \frac{0.3 - 1.6 \cdot 10^{-2} + \sqrt{(1.6 \cdot 10^{-2} - 0.3)^2 + 16 \cdot 0.1 \cdot 1.6 \cdot 10^{-2}}}{2} = 0.305 \text{ M} \Rightarrow \text{pH} = 0.516$$
3.  $n_0(\text{NaOH}) = 0.45 \text{ mol}$ ,  $n_0(\text{HCl}) = 0.30 \text{ mol}$ ,  $n_0(\text{H}_3\text{PO}_3) = 0.10 \text{ mol}$   
 $n(\text{Na}_2\text{HPO}_3) = 0.05 \text{ mol}$ ,  $n(\text{NaH}_2\text{PO}_3) = 0.05 \text{ mol}$
- $$K_2 = \frac{[\text{HPO}_3^{2-}][H^+]}{[\text{H}_2\text{PO}_3^-]} \Rightarrow [H^+] = K_2 \frac{[\text{H}_2\text{PO}_3^-]}{[\text{HPO}_3^{2-}]} = K_2 = 7 \cdot 10^{-7} \Rightarrow \text{pH} = 6.15$$

### Solution 5. IChO 1994 – Oslo, Norra – Ettevalmistusülesanne 4

1.  $K_1 = \frac{[H^+]^2}{c_0 - [H^+]} \Rightarrow [H^+] = \frac{-K_1 + \sqrt{K_1^2 + 4c_0K_1}}{2} = \frac{-3.24 \cdot 10^{-4} + \sqrt{1.05 \cdot 10^{-7} + 4 \cdot \frac{3.55}{180} \cdot 3.24 \cdot 10^{-4}}}{2}$
- $$[H^+] = 0.00237 \text{ M} \Rightarrow \text{pH} = 2.63$$
2.  $n_{\text{tot}}(\text{aspiriin}) = 0.100 \cdot 180 = 18.0 \text{ g}$ ,  $n(\text{C}_9\text{H}_7\text{O}_4\text{Na}) = \frac{18.0 - 3.55}{180} = 0.0803 \text{ mol}$
- $$K_1 = \frac{[\text{C}_9\text{H}_7\text{O}_4^-][H^+]}{[\text{C}_9\text{H}_8\text{O}_4]} \Rightarrow [H^+] = K_1 \frac{[\text{C}_9\text{H}_8\text{O}_4]}{[\text{C}_9\text{H}_7\text{O}_4^-]} = 3.24 \cdot 10^{-4} \cdot \frac{3.55}{18.0 - 3.55} = 7.96 \cdot 10^{-5} \text{ M}$$
- $$\Rightarrow \text{pH} = 4.10$$

### Solution 6. IChO 1995 – Peking, Hiina – Ettevalmistusülesanne 10

1.  $K_1 = \frac{([\text{H}_3\text{NCHR}^+\text{COO}^-] + [\text{H}_2\text{NCHR}^+\text{COOH}])([H^+])}{[\text{H}_3\text{NCHR}^+\text{COOH}]} = K_{11} + K_{12} = 10^{-2.35} + 10^{-7.70} = 10^{-2.35}$
- $$K_{11} = 10^{-2.35}$$
- $$K_{11}K_{22} = K_{12}K_{21} \Rightarrow \frac{K_{22}}{K_{21}} = \frac{K_{12}}{K_{11}} = \frac{10^{-7.70}}{10^{-2.35}} = 10^{-5.35} \quad (K_{21} > K_{22})$$
- $$K_2 = \frac{[\text{H}_2\text{NCHR}^+\text{COO}^-][H^+]}{([\text{H}_3\text{NCHR}^+\text{COO}^-] + [\text{H}_2\text{NCHR}^+\text{COOH]})} = \frac{1}{\frac{1}{K_{22}} + \frac{1}{K_{21}}} = 10^{-9.78} \Rightarrow K_{22} = 10^{-9.78}$$
- $$K_{22} = 10^{-9.78}$$
- $$K_{21} = 10^{-9.78+5.35} = 10^{-4.43}$$
2.  $\text{pH} = \frac{\text{p}K_1 + \text{p}K_2}{2} = 6.06$

### Solution 7. IChO 2001 – Mumbai, India – Ettevalmistusülesanne 12

$$K = \frac{[\text{AcO}^-][\text{H}^+]}{[\text{AcOH}]} \Rightarrow \text{p}K = \text{pH} + \log \frac{[\text{AcOH}]}{[\text{AcO}^-]} \Rightarrow \frac{[\text{AcOH}]}{[\text{AcO}^-]} = 0.5715$$

$$[\text{AcOH}] + [\text{AcO}^-] = 0.500 \text{ M} \Rightarrow [\text{AcO}^-] = 0.3182 \text{ M}, [\text{AcOH}] = 0.1818 \text{ M}$$

$$n(\text{AcO}^-) = 0.3182 \cdot 0.300 + 4 \cdot 0.0100 \cdot 0.300 = 0.1075 \text{ mol}$$

$$n(\text{AcOH}) = 0.1818 \cdot 0.300 - 4 \cdot 0.0100 \cdot 0.300 = 0.0425 \text{ mol}$$

$$K = \frac{[\text{AcO}^-][\text{H}^+]}{[\text{AcOH}]} \Rightarrow \text{pH} = \text{p}K - \log \frac{[\text{AcOH}]}{[\text{AcO}^-]} = 4.76 - \log \frac{0.0425}{0.1075} = 5.16$$

### 3. Kahe hapete vesilahuse pH leidmine

#### Solution 8. IChO 1993 – Perugia, Itaalia – Ettevalmistusülesanne 33.1

$$K_{\text{prop}} = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}, K_{\text{prop}} = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-]([\text{CH}_3\text{CH}_2\text{COO}^-] + [\text{CH}_3\text{COO}^-])}{c_{\text{prop}} - [\text{CH}_3\text{CH}_2\text{COO}^-]}$$

$$K_{\text{et}} = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}, K_{\text{et}} = \frac{[\text{CH}_3\text{COO}^-]([\text{CH}_3\text{COO}^-] + [\text{CH}_3\text{CH}_2\text{COO}^-])}{c_{\text{et}} - [\text{CH}_3\text{COO}^-]}$$

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COO}^-]} \approx \frac{K_{\text{et}}}{K_{\text{prop}}} = 1.313 \Rightarrow [\text{CH}_3\text{COO}^-] = 1.28 \cdot 10^{-3}, [\text{CH}_3\text{CH}_2\text{COO}^-] = 7.8 \cdot 10^{-4}$$

$$[\text{H}^+] = [\text{CH}_3\text{COO}^-] + [\text{CH}_3\text{CH}_2\text{COO}^-] = 2.06 \cdot 10^{-3} \Rightarrow \text{pH} = 2.686$$

### 4. Nõrkade aluste vesilahuse pH leidmine

#### Solution 9. IChO 1994 – Oslo, Norra – Ettevalmistusülesanne 3

#### Solution 10. IChO 2000 – Kopenhage, Taani – Ettevalmistusülesanne 5

1.  $n_0(\text{Ba}(\text{OH})_2) = 3.17 \text{ mmol}$ ,  $n_0(\text{NH}_4\text{Cl}) = 18.7 \text{ mmol}$

$$n(\text{NH}_3) = 2 \cdot 3.17 = 6.34 \text{ mmol}, n(\text{NH}_4^+) = 18.7 - 2 \cdot 3.17 = 12.4 \text{ mmol}$$

$$K = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \Rightarrow [\text{H}^+] = K \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 10^{-9.24} \cdot \frac{12.4}{6.34} = 1.13 \cdot 10^{-9} \text{ M} \Rightarrow \text{pH} = 8.95$$

2.  $c(\text{Ba}^{2+}) = 0.0317 \text{ M}$ ,  $c(\text{NH}_4^+) = 0.124 \text{ M}$ ,  $c(\text{H}^+) = 1.13 \cdot 10^{-9} \text{ M}$ ,  $c(\text{OH}^-) = 8.85 \cdot 10^{-6} \text{ M}$ ,  
 $c(\text{Cl}^-) = 0.187 \text{ M}$

3.  $c(\text{H}^+) = \frac{(10.0 - 6.34) \text{ mmol}}{110 \text{ mL}} = 0.0333 \text{ M} \Rightarrow \text{pH} = 1.48$

4.  $c(\text{NH}_4^+) = \frac{18.7 \text{ mmol}}{110 \text{ mL}} = 0.170 \text{ M}$ ,  $[\text{NH}_3] = \frac{K[\text{NH}_4^+]}{[\text{H}^+]} = \frac{10^{-9.24} \cdot 0.170}{0.0333} = 2.9 \cdot 10^{-9} \text{ M}$

#### Solution 11. IChO 2000 – Kopenhage, Taani – Ettevalmistusülesanne 6

1.  $\text{pOH} = 14.0 - 10.5 = 3.5 \Rightarrow [\text{OH}^-] = 10^{-3.5} = 3.2 \cdot 10^{-4} \text{ M} \Rightarrow s = 1.6 \cdot 10^{-4} \text{ M} = 9.2 \cdot 10^{-4} \frac{\text{g}}{100 \text{ mL}}$

2.  $K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.6 \cdot 10^{-11}$

3.  $[\text{Mg}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} \approx \frac{1.6 \cdot 10^{-11}}{(0.010)^2} = 1.6 \cdot 10^{-7} \text{ M}$

$$4. [\text{OH}^-] = \sqrt{\frac{K_{sp}}{[\text{Mg}^{2+}]}} \approx \sqrt{\frac{1.6 \cdot 10^{-11}}{(0.050)^2}} = 1.8 \cdot 10^{-5} \text{ M} \Rightarrow \text{pOH} = -\log(1.8 \cdot 10^{-5}) = 4.7 \Rightarrow \text{pH} = 9.3$$

## 5. Puhverlahuse pH leidmine

### Solution 12. IChO 1994 – Oslo, Norra – Ettevalmistusülesanne 6

### Solution 13. IChO 1998 – Melbourne, Austraalia – Ettevalmistusülesanne 15

- $\text{CO}_{2(g)} \leftrightarrow \text{CO}_{2(aq)}$ ,  $\text{CO}_{2(aq)} + \text{H}_2\text{O}_l \leftrightarrow \text{HCO}_3^-(aq) + \text{H}^+$ ,  $\text{HCO}_3^-(aq) \leftrightarrow \text{CO}_3^{2-}(aq) + \text{H}^+$
- b) > a) > c)
- c) > a) > b)
- $[\text{CO}_{2(aq)}] = p(\text{CO}_2)K_H = 3.39 \cdot 10^{-2} \cdot 3.50 \cdot 10^{-4} = 1.19 \cdot 10^{-5} \text{ M}$   
 $[\text{H}^+] \approx \sqrt{K_a[\text{CO}_{2(aq)}]} = \sqrt{\frac{K_w}{K_b}[\text{CO}_{2(aq)}]} = \sqrt{4.46 \cdot 10^{-7} \cdot 1.19 \cdot 10^{-5}} = 2.30 \cdot 10^{-6} \text{ M} \Rightarrow \text{pH} = 5.64$
- $[\text{CO}_{2(aq)}] = p(\text{CO}_2)K_H = 3.39 \cdot 10^{-2} \cdot 1 = 3.39 \cdot 10^{-2} \text{ M}$   
 $[\text{H}^+] \approx \sqrt{K_a[\text{CO}_{2(aq)}]} = \sqrt{\frac{K_w}{K_b}[\text{CO}_{2(aq)}]} = \sqrt{4.46 \cdot 10^{-7} \cdot 3.39 \cdot 10^{-2}} = 1.23 \cdot 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.91$

### Solution 14. IChO 2003 – Ateena, Kreeka – Ettevalmistusülesanne 22

- $K = \frac{[\text{HCOO}^-][\text{H}^+]}{[\text{HCOOH}]} \Rightarrow \text{pH} = \text{p}K + \log \frac{[\text{AcO}^-]}{[\text{AcOH}]} = 3.68 + \log \frac{0.150}{0.200} = 3.55$
- $\Delta\text{pH} = 3.68 + \log \frac{0.150 + 0.0100}{0.200 - 0.0100} - 3.55 = 0.05$
- $[\text{CH}_3\text{COOH}] = \frac{15.00 - 0.200 \cdot V}{100.0 + V}$ ,  $[\text{CH}_3\text{COO}^-] = \frac{0.200 \cdot V}{100.0 + V}$   
 $K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{0.200 \cdot V \cdot [\text{H}^+]}{15.00 - 0.200 \cdot V} \Rightarrow V = 48.21 \text{ mL}$
- a
- a) c, b) b
- a) b, b) d
- a) c, b) c
- a) b, b) c

## 6. Kompleksimoodustumise reaktsioonid ja Tasakaaluliste kontsentratsioonid arvutamise

### Solution 15. IChO 2000 – Kopenhage, Taani – Ettevalmistusülesanne 9

- $K_{sp} = [\text{Cd}^{2+}][\text{OH}^-]^2 = s(2s)^2 = 4s^3 = 5.9 \cdot 10^{-15} \Rightarrow s = 1.14 \cdot 10^{-5} \text{ M}$
- $K_{sp} = [\text{Cd}^{2+}][\text{OH}^-]^2 = s(2s + 0.010)^2 \approx s(0.010)^2 = 5.9 \cdot 10^{-15} \Rightarrow s = 5.9 \cdot 10^{-11} \text{ M}$
- $s = 0.5[\text{OH}^-] = c(\text{Cd}) = [\text{Cd}^{2+}] + [\text{Cd}(\text{CN})^+] + [\text{Cd}(\text{CN})_2] + [\text{Cd}(\text{CN})_3^-] + [\text{Cd}(\text{CN})_4^{2-}]$   
 $0.5[\text{OH}^-] = [\text{Cd}^{2+}](1 + K_1[\text{CN}^-] + \beta_2[\text{CN}^-]^2 + \beta_3[\text{CN}^-]^3 + \beta_4[\text{CN}^-]^4)$

$$0.5[\text{OH}^-] = \frac{K_{sp}}{[\text{OH}^-]} \left( 1 + K_1[\text{CN}^-] + \beta_2[\text{CN}^-]^2 + \beta_3[\text{CN}^-]^3 + \beta_4[\text{CN}^-]^4 \right)$$

$$[\text{OH}^-] = \sqrt[3]{2K_{sp} \left( 1 + K_1[\text{CN}^-] + \beta_2[\text{CN}^-]^2 + \beta_3[\text{CN}^-]^3 + \beta_4[\text{CN}^-]^4 \right)}$$

$$[\text{OH}^-] = \sqrt[3]{2K_{sp} \left( 1 + K_1[\text{CN}^-] + K_1K_2[\text{CN}^-]^2 + K_1K_2K_3[\text{CN}^-]^3 + K_1K_2K_3K_4[\text{CN}^-]^4 \right)}$$

$$[\text{OH}^-] = \sqrt[3]{2 \cdot 5.9 \cdot 10^{-15} \left( 1 + 3.02 \cdot 10^2 + 3.99 \cdot 10^4 + 1.70 \cdot 10^6 + 7.59 \cdot 10^6 \right)} = 4.79 \cdot 10^{-3} \text{ M}$$

$$s = 2.4 \cdot 10^{-3} \text{ M}$$

$$4. [\text{OH}^-] = \sqrt[3]{2K_{sp} \left( 1 + K_1K_2K_3K_4[\text{CN}^-]^4 \right)}$$

$$[\text{OH}^-] = \sqrt[3]{2 \cdot 5.9 \cdot 10^{-15} \left( 1 + 7.59 \cdot 10^6 \right)} = 4.47 \cdot 10^{-3} \text{ M}$$

$$s = 2.24 \cdot 10^{-3} \text{ M}$$

$$\% = \frac{(2.40 - 2.24) \cdot 10^{-3}}{2.40 \cdot 10^{-3}} \cdot 100\% = 6.7\%$$

### Solution 16. IChO 1993 – Perugia, Italia – Ettevalmistusülesanne 33.3

$$[\text{Pb}^{2+}][\text{SO}_4^{2-}] = 1.1 \cdot 10^{-8}$$

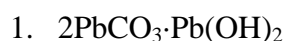
$$[\text{SO}_4^{2-}]/[\text{I}^-]^2 = 4.6 \cdot 10^{-1}$$

$$[\text{I}^-]^2/[\text{CrO}_4^{2-}] = 4.3 \cdot 10^{12}$$

$$[\text{S}^{2-}]/[\text{CrO}_4^{2-}] = 7.5 \cdot 10^{-8}$$

$$[\text{Pb}^{2+}][\text{S}^{2-}] = [\text{Pb}^{2+}][\text{SO}_4^{2-}] \frac{[\text{I}^-]^2}{[\text{SO}_4^{2-}]} \frac{[\text{CrO}_4^{2-}]}{[\text{I}^-]^2} \frac{[\text{S}^{2-}]}{[\text{CrO}_4^{2-}]} = \frac{1.1 \cdot 10^{-8}}{4.6 \cdot 10^{-1}} \frac{7.5 \cdot 10^{-8}}{4.3 \cdot 10^{12}} = 4.2 \cdot 10^{-28}$$

### Solution 17. IChO 1993 – Perugia, Italia – Ettevalmistusülesanne 48



3.  $s = [\text{Pb}^{2+}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^-]$

$$K_{b2} = \frac{K_w}{K_{a2}} = 2.32 \cdot 10^{-4} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} \approx \frac{[\text{HCO}_3^-]^2}{[\text{Pb}^{2+}] - [\text{HCO}_3^-]} = \frac{\left([\text{Pb}^{2+}] - [\text{CO}_3^{2-}]\right)^2}{[\text{CO}_3^{2-}]}$$

$$[\text{Pb}^{2+}][\text{CO}_3^{2-}] = 1.6 \cdot 10^{-13} \Rightarrow [\text{CO}_3^{2-}] = \frac{1.6 \cdot 10^{-13}}{[\text{Pb}^{2+}]}$$

$$K_{b2}[\text{CO}_3^{2-}] = [\text{Pb}^{2+}]^2 - 2[\text{Pb}^{2+}][\text{CO}_3^{2-}] + [\text{CO}_3^{2-}]^2$$

$$2.32 \cdot 10^{-4} \cdot \frac{1.6 \cdot 10^{-13}}{[\text{Pb}^{2+}]} = [\text{Pb}^{2+}]^2 - 2[\text{Pb}^{2+}] \frac{1.6 \cdot 10^{-13}}{[\text{Pb}^{2+}]} + \left(\frac{1.6 \cdot 10^{-13}}{[\text{Pb}^{2+}]}\right)^2$$

$$[\text{Pb}^{2+}]^4 - 3.2 \cdot 10^{-13}[\text{Pb}^{2+}]^2 - 3.7 \cdot 10^{-17}[\text{Pb}^{2+}] + 2.56 \cdot 10^{-26} = 0$$

$$[\text{Pb}^{2+}]^4 - 3.7 \cdot 10^{-17}[\text{Pb}^{2+}] \approx 0 \Rightarrow [\text{Pb}^{2+}] = \sqrt[3]{3.7 \cdot 10^{-17}} = 3.33 \cdot 10^{-6} \text{ M}$$

### Solution 18. IChO 1994 – Oslo, Norra – Ettevalmistusülesanne 2

$$1. [\text{SO}_4^{2-}]_{\text{Ag}^+} = \frac{K_{sp}(\text{Ag}_2\text{SO}_4)}{[\text{Ag}^+]^2} = 0.2 \text{ M}, [\text{SO}_4^{2-}]_{\text{Ba}^{2+}} = \frac{K_{sp}(\text{BaSO}_4)}{[\text{Ba}^{2+}]} = 1.1 \cdot 10^{-8} \text{ M}$$

$$2. [\text{SO}_4^{2-}]_{\text{Ba}^{2+}} = \frac{K_{sp}(\text{BaSO}_4)}{[\text{Ba}^{2+}]} = 1.1 \cdot 10^{-8} \text{ M}, [\text{Na}^+] = 1.1 \cdot 10^{-8} \cdot 2 = 2.2 \cdot 10^{-8} \text{ M}$$

$$3. [\text{SO}_4^{2-}]_{\text{Ag}^+} = \frac{K_{sp}(\text{Ag}_2\text{SO}_4)}{[\text{Ag}^+]^2} = 0.2 \text{ M}, [\text{Na}^+] = 0.2 \cdot 2 + 0.01 \cdot 2 = 0.42 \text{ M}$$

$$4. K_2 = \frac{[\text{SO}_4^{2-}][\text{H}^+]}{[\text{HSO}_4^-]} \Rightarrow \frac{[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{K_2}{[\text{H}^+]} = 0.5$$

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = s \left( \frac{0.5}{1.5} s \right) = \frac{1}{3} s^2 \Rightarrow s = 1.82 \cdot 10^{-5} \text{ M}$$

### Solution 19. IChO 1995 – Peking, Hiina – Ettevalmistusülesanne 31

$$E_{\text{cell}} = E_{\text{Ag}} - E_{\text{SCE}} \Rightarrow 0.439 = 0.799 + 0.059 \log(0.0100) - E_{\text{SCE}} \Rightarrow E_{\text{SCE}} = 0.242 \text{ V}$$

$$0.0824 = 0.799 + 0.059 \log([\text{Ag}^+]) - 0.242 \Rightarrow [\text{Ag}^+] = 9.04 \cdot 10^{-9} \text{ M}$$

$$K_{sp} = [\text{Ag}^+][\text{I}^-] = [\text{Ag}^+]^2 = 8.17 \cdot 10^{-7}$$

$$0.228 = 0.242 - (0.799 + 0.059 \log([\text{Ag}^+])) \Rightarrow [\text{Ag}^+] = 4.95 \cdot 10^{-14} \text{ M}, [\text{I}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = 1.65 \cdot 10^{-3} \text{ M}$$

$$[\text{Pb}^{2+}] = \frac{1}{2}[\text{I}^-] = \frac{1}{2}(1.65 \cdot 10^{-3} - 4.95 \cdot 10^{-14}) = 8.25 \cdot 10^{-4} \Rightarrow K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 = 2.25 \cdot 10^{-9}$$

### Solution 20. IChO 1996 – Moskva, Venemaa – Ettevalmistusülesanne 23

$$E_1 = E_1^\circ + 0.059 \log[\text{Ag}^+], E_2 = E_2^\circ + \frac{0.059}{4} \log \frac{p\text{O}_2}{[\text{OH}^-]^4}$$

$$[\text{OH}^-] = \sqrt{K_b c(\text{NH}_3)} = 1.32 \cdot 10^{-3} \text{ M} \Rightarrow E_2 = 0.401 + \frac{0.059}{4} \log \frac{0.2059}{(1.32 \cdot 10^{-3})^4} = 0.561 \text{ V}$$

$$\log[\text{Ag}^+] = \frac{E_2 - E_1^\circ}{0.059} = -4.04 \Rightarrow [\text{Ag}^+] = 9.12 \cdot 10^{-5} \text{ M}$$

$$s = [\text{Ag}^+] + [\text{Ag}(\text{NH}_3)^+] + [\text{Ag}(\text{NH}_3)_2^+] = [\text{Ag}^+] (1 + \beta_1[\text{NH}_3] + \beta_2[\text{NH}_3]^2) = 9.12 \cdot 10^{-5} (1 + 10^{2.32} + 10^{5.23}) = 15.5 \text{ M!!!}$$

### Solution 21. IChO 1997 – Montreal, Kanada – Ettevalmistusülesanne 41

$$1. s = \sqrt{K_{sp}} = 1.33 \cdot 10^{-7} \text{ M}$$

$$2. [\text{Pb}^{2+}] = \frac{K_{sp}}{[\text{CrO}_4^{2-}]} = 1.77 \cdot 10^{-13} \text{ M}$$

$$3. [\text{CrO}_4^{2-}] = \frac{K_{sp}}{[\text{Pb}^{2+}]_0 + [\text{CrO}_4^{2-}]} \Rightarrow [\text{CrO}_4^{2-}]^2 + 3.0 \cdot 10^{-7} \cdot [\text{CrO}_4^{2-}] - 1.77 \cdot 10^{-14} = 0$$

$$[\text{CrO}_4^{2-}] = \frac{-3.0 \cdot 10^{-7} + \sqrt{(3.0 \cdot 10^{-7})^2 + 4 \cdot 1.77 \cdot 10^{-14}}}{2} = 5.05 \cdot 10^{-8} \text{ M}$$