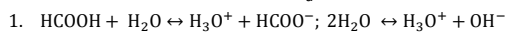


## Analizna kemija I

### 3. Porazdelitveni diagrami, topnost

Primer: Izračunaj koncentracijo  $\text{H}_3\text{O}^+$  ionov v 0,10 M  $\text{HCOOH}$  ( $K_a = 1,77 \times 10^{-4}$ )



2.  $K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1,77 \times 10^{-4}$ ,  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$

3. Mb:  $C = [\text{HCOOH}] + [\text{HCOO}^-]$

4. En:  $[\text{H}_3\text{O}^+] = [\text{HCOO}^-] + [\text{OH}^-]$

5. Nezn:  $[\text{HCOOH}]$ ,  $[\text{HCOO}^-]$ ,  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ ; enačbe:  $K_a$ ,  $K_w$ , Mb, En

6. 😊 Eksaktna rešitev:  $K_a = \frac{[\text{H}_3\text{O}^+]( [\text{H}_3\text{O}^+] - [\text{OH}^-] )}{c - ([\text{H}_3\text{O}^+] - [\text{OH}^-] )}$

$[\text{H}_3\text{O}^+]^3 + K_a[\text{H}_3\text{O}^+]^2 - (K_w + K_a C)[\text{H}_3\text{O}^+] - K_a K_w = 0$

$[\text{H}_3\text{O}^+] = 4,1195 \times 10^{-3} \text{ mol/L}$

### Poenostavitve 😊

- Poenostavljamo le masno bilanco in izraz za električno nevtralnost!

a) Raztopina bo **kisla**:  $[\text{H}_3\text{O}^+] \gg [\text{OH}^-]$

En:  $[\text{HCOO}^-] \approx [\text{H}_3\text{O}^+]$ ,  $[\text{HCOOH}] = C - [\text{H}_3\text{O}^+]$

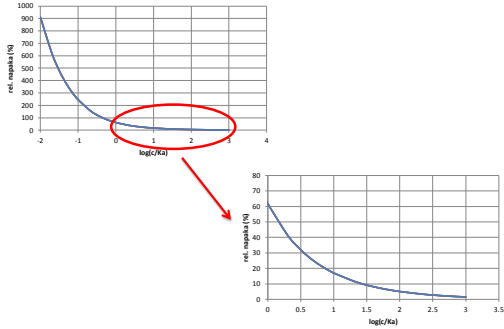
$K_a = \frac{[\text{H}_3\text{O}^+]^2}{c - [\text{H}_3\text{O}^+]}$   $\rightarrow [\text{H}_3\text{O}^+]^2 + K_a[\text{H}_3\text{O}^+] - K_a C = 0$

$[\text{H}_3\text{O}^+] = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a C}}{2} = 4,12 \times 10^{-3} \text{ mol/L}$

b)  $C \gg [\text{H}_3\text{O}^+] \rightarrow K_a = \frac{[\text{H}_3\text{O}^+]^2}{c}$

$[\text{H}_3\text{O}^+] = \sqrt{K_a C} = 4,21 \times 10^{-3} \text{ mol/L}$

Napaka zaradi približka  $C \approx C$




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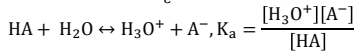
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Porazdelitveni diagram

- Prikaz deleža neke zvrsti  $\alpha_x$ , v odvisnosti od pH

$$\alpha_x = \frac{[X]}{C} = f(\text{pH})$$



$$\text{Mb: } C_{\text{HA}} = [\text{HA}] + [\text{A}^-] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{K_a} + [\text{A}^-] = [\text{A}^-] \left( 1 + \frac{[\text{H}_3\text{O}^+]}{K_a} \right)$$

$$[\text{HA}] = \frac{C[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+] + K_a},$$

$$[\text{A}^-] = \frac{CK_a}{[\text{H}_3\text{O}^+] + K_a}$$

$$a_{\text{HA}} = \frac{[\text{HA}]}{C} = \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+] + K_a},$$

$$a_{\text{A}^-} = \frac{[\text{A}^-]}{C} = \frac{K_a}{[\text{H}_3\text{O}^+] + K_a}$$

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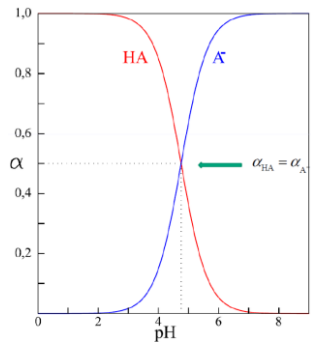
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Porazdelitveni diagram za  $\text{CH}_3\text{COOH}$




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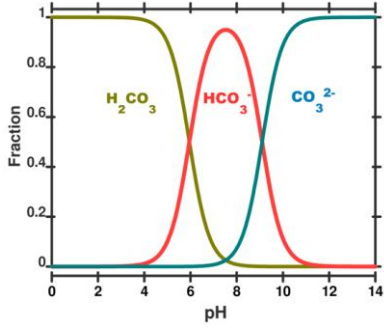
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Porazdelitveni diagram za H<sub>2</sub>CO<sub>3</sub>




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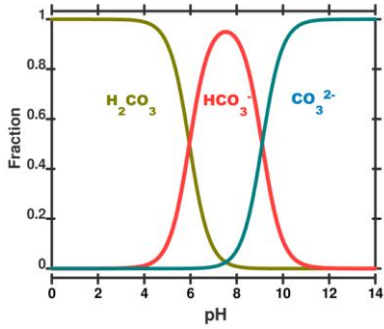
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Porazdelitveni diagram za H<sub>2</sub>CO<sub>3</sub>




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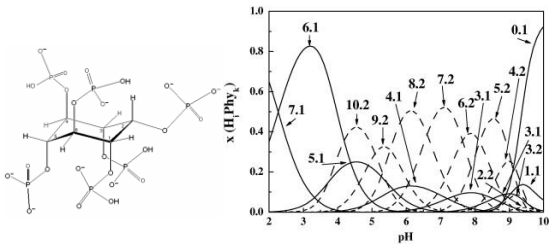
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Porazdelitveni diagram za fitat/fitinsko kislino




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## Logaritmski porazdelitveni diagram

- Prikaz logaritma ravnotežne koncentracije posamezne zvrsti  $\alpha_x$  v odvisnosti od pH

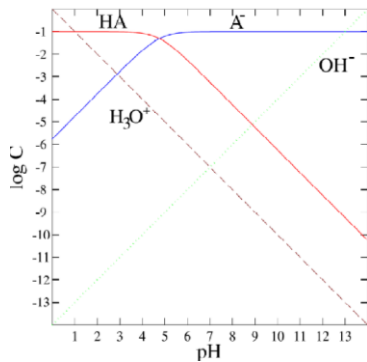
$$\log[X] = f(\text{H}_3\text{O}^+) = f(\text{pH})$$

$$\log[\text{HA}] = \log \frac{C}{[\text{H}_3\text{O}^+] + K_a} - \text{pH},$$

$$\log[\text{A}^-] = \log(CK_a) - \log([\text{H}_3\text{O}^+] + K_a)$$

$$[\text{H}_3\text{O}^+] \gg K_a; \log[\text{HA}] = \log C = \text{konst.}; \log[\text{A}^-] = \log(CK_a) + \text{pH}$$

$$[\text{H}_3\text{O}^+] \ll K_a; \log[\text{HA}] = \log \frac{C}{K_a} - \text{pH} = \text{konst.}; \log[\text{A}^-] = \log C = \text{konst.}$$

Logaritmski porazdelitveni diagram  $\text{CH}_3\text{COOH}$ 

## Analizna kemija I

## 3. Topnost oborin

## Ravnotežja trdno-tekoče

- Ravnotežja v heterogenih sistemih trdno tekoče, so v analizni kemiji pomembna za:
  - Separacijo posameznih komponent,
  - Gravimetrično analizo
  - Obarjalne titracije

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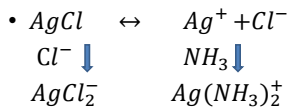
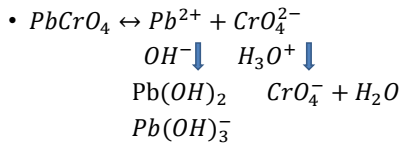
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## Kako raztopiti/oboriti?




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## Vplivi na topnost

- **pH** medija
- Prisotnost **ligandov**, ki tvorijo koordinacijske spojine
- Sestav in koncentracija ionov – **elektroliti**
- Narava **topila**
- **Temperatura**

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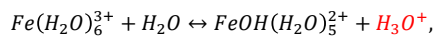
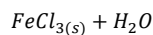
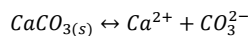
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## 1. Vpliv pH

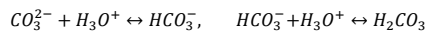
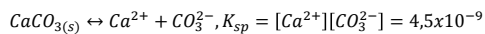
- Kdaj je topnost odvisna od pH?
- Interakcija med sestavinami oborine in  $H_3O^+$  ioni:
  - **Anioni z bazičnimi** lastnostmi (npr.:  $PO_4^{3-}$ ,  $CO_3^{2-}$ ,  $S^{2-}$ ,...)
  - **Kationi s kislimi** lastnostmi ( $Fe^{3+}$ ,  $Bi^{3+}$ ,  $Al^{3+}$ ,  $Zr^{4+}$ ,...)
  - **Hidroksidi** (zemeljskoalkalijske kovine, kovine prehoda,...)

## Interakcija ionov s topilom



$$K_a = 9,3 \times 10^{-4}$$

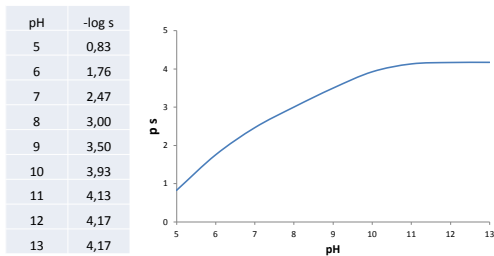
## Topnost pri znanem pH



$$s = [Ca^{2+}] = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$$

$$s = [Ca^{2+}] = \frac{K_{sp}}{[Ca^{2+}]} \left\{ 1 + \frac{H_3O^+}{K_{a2}} + \frac{[H_3O^+]^2}{K_{a1}K_{a2}} \right\}$$

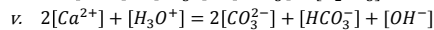
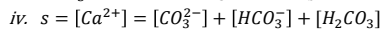
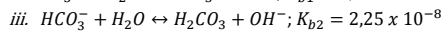
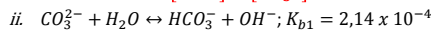
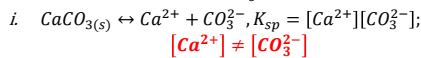
$$[Ca^{2+}] = \sqrt{K_{sp} \left( 1 + \frac{[H_3O^+]}{K_{a2}} + \frac{[H_3O^+]^2}{K_{a1}K_{a2}} \right)}$$

Topnost  $\text{CaCO}_3$  pri znanem pH

## Topnost v vodi – pH ni znan

- Protolitska reakcija lahko vpliva na pH, kar je odvisno od:
  - Bazičnosti aniona,
  - Topnosti oborine.

Primer: Kakšna je topnost  $\text{CaCO}_3$  v vodi?



6 neznank – 6 enačbe

## Poenostavitve – alkalna raztopina

- Raztopina bo zaradi protolize **alkalna**
  - $2[\text{Ca}^{2+}] \gg [\text{H}_3\text{O}^+]$ ;  $[\text{HCO}_3^-] \gg [\text{H}_2\text{CO}_3]$
  - Mb:  $[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^-]$ ;
  - En:  $2[\text{Ca}^{2+}] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-]$

– 4 enačbe – 4 neznanke

$$[\text{OH}^-] = \frac{K_{b1}[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (\approx [\text{HCO}_3^-]); [\text{HCO}_3^-] = [\text{Ca}^{2+}] - [\text{CO}_3^{2-}] \quad (\text{En-Mb})$$

$$[\text{Ca}^{2+}]^4 - 2K_{sp}[\text{Ca}^{2+}]^2 - K_{sp}K_{b1}[\text{Ca}^{2+}] + K_{sp}^2 = 0$$

$$s = [\text{Ca}^{2+}] = 1,24 \times 10^{-4} \frac{\text{mol}}{\text{L}}; s > (K_{sp})^{\frac{1}{2}} = 6,71 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

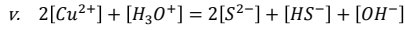
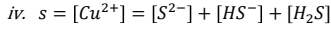
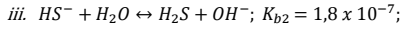
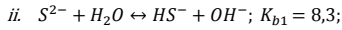
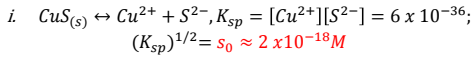
$$E_p = -46\%$$

$$[\text{CO}_3^{2-}] = 3,63 \times 10^{-5} \text{M}, [\text{HCO}_3^-] = 8,80 \times 10^{-5} \text{M}$$

$$[\text{H}_3\text{O}^+] = 1,14 \times 10^{-10} \text{M} \quad (\text{pH} = 9,94); [\text{H}_2\text{CO}_3] = 8,80 \times 10^{-5} \text{M}$$

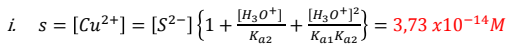
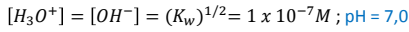
Poenostavitve – „netopna“ oborina

- Raztopina zaradi zelo nizke topnosti **ne bo alkalna** ( $s < 10^{-8} M$ )



**6 neznank – 6 enačb**

Poenostavitve:  $2[Cu^{2+}] \ll [H_3O^{+}]; 2[S^{2-}] + [HS^{-}] \ll [OH^{-}];$




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Topnost kovinskih hidroksidov

- Dve skupini  $M(OH)_x$ :

- Hidroksidi, ki v presežku **niso topni**,
- Hidroksidi, ki se v presežku reagenta raztopijo – **amfoterni hidroksidi**.

- Glede na topnost, razdelimo hidrokside na:

- „netopni“ hidroksidi ( $s \ll 10^{-8} \text{ mol/L}$ ),
- Težko topni hidroksidi ( $10^{-8} \text{ mol/L} < s < 10^{-6} \text{ mol/L}$ ),
- Lahko topni hidroksidi ( $10^{-6} \text{ mol/L} < s$ )

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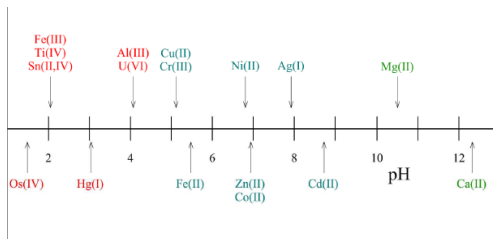
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Obarjanje  $M^{z+}$  ionov (0,1 M)




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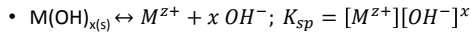
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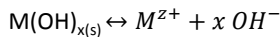


Topnost hidroksidov -  $M(OH)_{x(s)}$ 

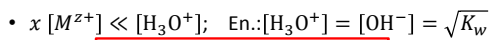
1.  $s = [M^{z+}]$ ;
2.  $K_w = [H_3O^{+}][OH^{-}]$ ;
3.  $x [M^{z+}] + [H_3O^{+}] = [OH^{-}]$

• Poenostavitve:

- i. „netopni hidroksidi:  $x [M^{z+}] \ll [H_3O^{+}]$ ;
- ii. Lahko topni hidroksidi:  $x [M^{z+}] \gg [H_3O^{+}]$ ;
- iii. Težko topni hidroksidi:  $x [M^{z+}] \approx [H_3O^{+}]$

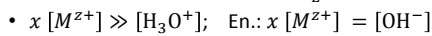


a) Netopni hidroksidi;  $s < 1 \times 10^{-8} \frac{mol}{L}$



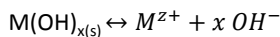
$$\text{Rešitev: } s = [M^{z+}] = \frac{K_{sp}}{[OH^{-}]^x} = K_{sp} 10^{7x}$$

b) Topni hidroksidi;  $s > 1 \times 10^{-6} \frac{mol}{L}$

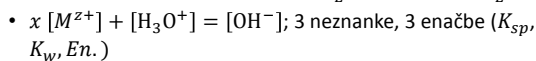


$$\text{Rešitev: } K_{sp} = [M^{z+}](x[M^{z+}])^x = x^x ([M^{z+}])^{(x+1)}$$

$$s = [M^{z+}] = \left( \frac{K_{sp}}{x^x} \right)^{1/(x+1)}$$



c) Težko topni hidroksidi;  $1 \times 10^{-6} \frac{mol}{L} < s < 1 \times 10^{-8} \frac{mol}{L}$



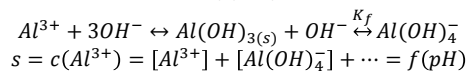
$$[M^{z+}] = \frac{K_{sp}}{[OH^{-}]^x}; [H_3O^{+}] = \frac{K_w}{[OH^{-}]}$$

$$x \frac{K_{sp}}{[OH^{-}]^x} + \frac{K_w}{[OH^{-}]} = [OH^{-}]; \text{ rešimo na } [OH^{-}]$$

$$s = [M^{z+}] = \frac{K_{sp}}{[OH^{-}]^x}$$

## Amfoterni hidroksidi

- Amfoterni hidroksidi se topijo v presežku  $\text{OH}^-$ :



$$s = \frac{K_{sp}}{[\text{OH}^-]^3} + K_f[\text{OH}^-]$$

Minimalna topnost  $\frac{\partial s}{\partial [\text{OH}^-]} = 0$

$$\frac{\partial s}{\partial [\text{OH}^-]} = -\frac{3K_{sp}}{[\text{OH}^-]^4} + K_f = 0$$

$$[\text{OH}^-]_{\min} = \left(\frac{3K_{sp}}{K_f}\right)^{1/4} = 8,8 \times 10^{-9} \frac{\text{mol}}{\text{L}} \quad (\text{pH} = 5,9)$$

$$s_{\min} = 1,2 \times 10^{-7} \frac{\text{mol}}{\text{L}}$$

$$s(\text{Al}(\text{OH})_3) = f(\text{pH})$$

