

Analitička kemija

Preddiplomski studij kemijske
tehnologije

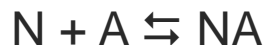
Preddiplomski studij

prehrambene tehnologije –
seminar, II. dio

Ak. godina 2018./19.

GRAVIMETRIJSKO ODREĐIVANJE

Gravimetrijski faktor ovisi o tome koji se taložni reagens koristi za taloženje analita. Gravimetrijski faktor je veličina koja je jednaka omjeru molarne mase tražene tvari i molarne mase oblika u kojem se nalazi ta tvar pomnožena s malim cijelim brojem koji izražava stehiometrijski odnos tražene tvari u traženom i vaganom obliku.




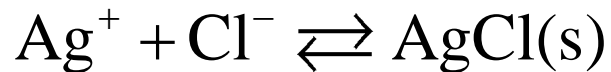
$$\text{gravimetrijski faktor} = \frac{a}{b} \cdot \frac{M_N}{M_{NA}}$$

- mali cijeli broj koji izražava stehiometrijski odnos komponente u traženom, a , i vaganom, b , obliku

N – analit

NA – analit u obliku koji se važe

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- A large black left square bracket and a large yellow right square bracket are positioned at the top of the slide, with a thin yellow horizontal line extending between them across the width of the page.
- Uzorak nečistog natrijevog klorida otopljen je u vodi i kloridi su istaloženi otopinom srebrovog nitrata. Nakon gravimetrijskog postupka, dobiveno je 1,2542 g srebrovog klorida. Kolika je masa klorida prisutnog u uzorku?



$$n(\text{Cl}^-) = n(\text{AgCl})$$


$$\frac{m(\text{Cl}^-)}{M(\text{Cl}^-)} = \frac{m(\text{AgCl})}{M(\text{AgCl})}$$

$$m(\text{Cl}^-) = m(\text{AgCl}) \cdot \frac{M(\text{Cl}^-)}{M(\text{AgCl})}$$

Gravimetrijski faktor

$$m(\text{Cl}^-) = 1,2542 \text{ g} \cdot \frac{35,45 \text{ g mol}^{-1}}{143,32 \text{ g mol}^{-1}}$$

$$m(\text{Cl}^-) = 0,3102 \text{ g}$$

- 
- Uzorak željezovog(III) fosfata koji sadrži određena inertna onečišćenja gravimetrijski je analiziran te je pronađeno 1,0855 g željezovog(III) oksida. Kolika je masa željezovog(III) fosfata te željezovih(III) i fosfatnih iona u uzorku?



$$n(\text{Fe}, \text{FePO}_4) = 2n(\text{Fe}, \text{Fe}_2\text{O}_3)$$

$$\frac{m(\text{FePO}_4)}{M(\text{FePO}_4)} = 2 \frac{m(\text{Fe}_2\text{O}_3)}{M(\text{Fe}_2\text{O}_3)}$$

$$m(\text{FePO}_4) = 2m(\text{Fe}_2\text{O}_3) \frac{M(\text{FePO}_4)}{M(\text{Fe}_2\text{O}_3)}$$

$$m(\text{FePO}_4) = 2 \cdot 1,0855 \frac{150,83 \text{ g mol}^{-1}}{159,70 \text{ g mol}^{-1}} = 2,0504 \text{ g}$$

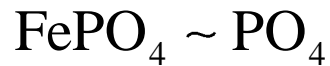
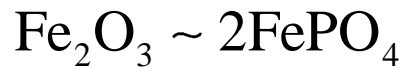


$$n(\text{Fe}^{3+}) = 2n(\text{Fe}, \text{Fe}_2\text{O}_3)$$

$$\frac{m(\text{Fe}^{3+})}{M(\text{Fe}^{3+})} = 2 \frac{m(\text{Fe}_2\text{O}_3)}{M(\text{Fe}_2\text{O}_3)}$$

$$m(\text{Fe}^{3+}) = 2m(\text{Fe}_2\text{O}_3) \frac{M(\text{Fe}^{3+})}{M(\text{Fe}_2\text{O}_3)}$$

$$m(\text{Fe}^{3+}) = 2 \cdot 1,0855 \frac{55,85 \text{ g mol}^{-1}}{159,70 \text{ g mol}^{-1}} = 0,7592 \text{ g}$$



$$n(\text{PO}_4^{3-}) = 2n(\text{Fe}_2\text{O}_3)$$

$$\frac{m(\text{PO}_4^{3-})}{M(\text{PO}_4^{3-})} = 2 \frac{m(\text{Fe}_2\text{O}_3)}{M(\text{Fe}_2\text{O}_3)}$$

$$m(\text{PO}_4^{3-}) = 2m(\text{Fe}_2\text{O}_3) \frac{M(\text{PO}_4^{3-})}{M(\text{Fe}_2\text{O}_3)}$$

$$m(\text{PO}_4^{3-}) = 2m(\text{Fe}_2\text{O}_3) \frac{M(\text{PO}_4^{3-})}{M(\text{Fe}_2\text{O}_3)}$$

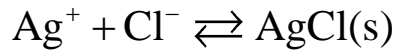
$$m(\text{PO}_4^{3-}) = 2 \cdot 1,0855 \frac{94,97 \text{ g mol}^{-1}}{159,70 \text{ g mol}^{-1}} = 1,2911 \text{ g}$$

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Analiziran je uzorak mase 0,8400 g koji se sastoji samo od natrijevog i kalijevog klorida. Pošto je uzorak otopljen, kloridi su istaloženi u obliku srebrovog klorida izmjerene mase 1,7021 g. Koliko iznose maseni udjeli NaCl i KCl u uzorku?

$x \equiv$ masa NaCl; $y \equiv$ masa KCl

$$x + y = 0,8400 \text{ g}$$



$$n(\text{Cl}^-)_{\text{ukupno}} = n(\text{Cl}^-)_{\text{NaCl}} + n(\text{Cl}^-)_{\text{KCl}} = n(\text{AgCl})$$

$$x \cdot \frac{M(\text{AgCl})}{M(\text{NaCl})} + y \cdot \frac{M(\text{AgCl})}{M(\text{KCl})} = 1,7021$$

$$x + y = 0,8400 \text{ g} \Rightarrow x = 0,8400 - y$$

$$(0,8400 - y) \cdot \frac{M(\text{AgCl})}{M(\text{NaCl})} + y \cdot \frac{M(\text{AgCl})}{M(\text{KCl})} = 1,7021$$

$$(0,8400 - y) \cdot \frac{143,34 \text{ g mol}^{-1}}{58,45 \text{ g mol}^{-1}} + y \cdot \frac{143,34 \text{ g mol}^{-1}}{74,56 \text{ g mol}^{-1}} = 1,7021$$

$$2,0598 - 2,4521y + 1,9225y = 1,7021$$

$$y = \frac{-2,0598 + 1,7021}{-2,4521 + 1,9225}$$

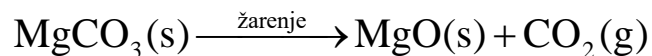
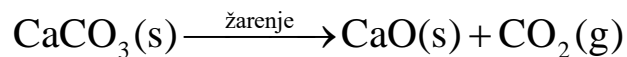
$$y = 0,6754 \text{ g}$$

$$x = 0,8400 - 0,6754 = 0,1646 \text{ g}$$

$$\omega(\text{NaCl}) = \frac{0,1646}{0,8400} \cdot 100 = 19,60\%$$

$$\omega(\text{KCl}) = \frac{0,6754}{0,8400} \cdot 100 = 80,40\%$$

1,0000 g uzorka koji sadrži samo kalcijev i magnezijev karbonat žarenjem je preveden u smjesu oksida mase 0,5000 g. Koliki su maseni udjeli kalcijevog i magnezijevog karbonata u uzorku?



Masa oslobođenog CO_2 :

$$m(\text{uzorka}) - m(\text{oksida}) = m(\text{CO}_2)$$

$$m(\text{CO}_2) = 1,0000 - 0,5000 = 0,5000 \text{ g}$$

$$x \equiv \text{masa CaCO}_3; y \equiv \text{masa MgCO}_3$$

$$x + y = 1,0000 \text{ g}$$

Masa CO_2 iz kalcijevog karbonata :

$$n(\text{CO}_2) = n(\text{CaCO}_3)$$

$$\frac{m(\text{CO}_2)}{M(\text{CO}_2)} = \frac{m(\text{CaCO}_3)}{M(\text{CaCO}_3)} \Rightarrow m(\text{CO}_2) = m(\text{CaCO}_3) \cdot \frac{M(\text{CO}_2)}{M(\text{CaCO}_3)}$$

Masa CO_2 iz magnezijevog karbonata :

$$n(\text{CO}_2) = n(\text{MgCO}_3)$$

$$\frac{m(\text{CO}_2)}{M(\text{CO}_2)} = \frac{m(\text{MgCO}_3)}{M(\text{MgCO}_3)} \Rightarrow m(\text{CO}_2) = m(\text{MgCO}_3) \cdot \frac{M(\text{CO}_2)}{M(\text{MgCO}_3)}$$

$$x \cdot \frac{M(\text{CO}_2)}{M(\text{CaCO}_3)} + y \cdot \frac{M(\text{CO}_2)}{M(\text{MgCO}_3)} = 0,5000$$

$$x + y = 1,0000 \text{ g} \Rightarrow y = 1,0000 - x$$

$$x \cdot \frac{M(\text{CO}_2)}{M(\text{CaCO}_3)} + (1,0000 - x) \cdot \frac{M(\text{CO}_2)}{M(\text{MgCO}_3)} = 0,5000$$

$$x \cdot \frac{44,01 \text{ g mol}^{-1}}{100,09 \text{ g mol}^{-1}} + (1,0000 - x) \cdot \frac{44,01 \text{ g mol}^{-1}}{84,33 \text{ g mol}^{-1}} = 0,5000$$

$$0,4397x + 0,5219 - 0,5219x = 0,5000$$

$$x = \frac{-0,5219 + 0,5000}{-0,5219 + 0,4397}$$

$$x = 0,2664 \text{ g}$$

$$y = 1,0000 - 0,2664 = 0,7336 \text{ g}$$

$$\omega(\text{CaCO}_3) = \frac{0,2664}{1,0000} \cdot 100 = 26,64\%$$

$$\omega(\text{MgCO}_3) = \frac{0,7336}{1,0000} \cdot 100 = 73,36\%$$

VOLUMETRIJSKO ODREĐIVANJE

- Taložne (argentometrijske) titracije
- Kiselo-bazne (neutralizacijske) titracije
- Kompleksometrijske titracije
- Redoks-titracije

Računanje u volumetrijskim titracijama

- Na početku titracije ($V = 0$ mL):
 - Kiselo-bazne titracije: ovisi o početnom pH kiseline i baze (složeniji izračun za slabe kiseline i baze)
 - Kompleksometrijske titracije: ovisi odvijaju li se paralelne reakcije između analita i pufera
 - Za taložne i redoks-titracije nije moguće

- Do točke ekvivalencije ($0 < V < V_{t.e.}$)
 - Ovisi o neizreagiranim analitu

$$c'_a = \frac{c_a \cdot V_a - c_t \cdot V_t}{V_a + V_t}$$

$$c'_a = [\text{neizreagirani analit}]$$

$$[\text{analit}] = \frac{V_{t.e.} - V_t}{V_{t.e.}} \cdot c_a \cdot \frac{V_a}{V_a + V_t}$$

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■ U točki ekvivalencije:

- Za kiselo-bazne titracije jakih kiselina i baze $\text{pH} = 7$
 - Taložne titracije: kao topljivost slabo topljivog taloga
 - Kiselo-bazne titracije slabih kiselina i baza i hidrolize nastale soli, odnosno konjugirane baze i kiseline
 - Kompleksometrijske titracije: kao disocijacija kompleksa
 - Redoks-titracije: iz elektrodnih potencijala analita i titranta vodeći računa o stehiometriji reakcije
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- Nakon točke ekvivalencije ($V > V_{t.e.}$)
 - Ovisi o suvišku titranta

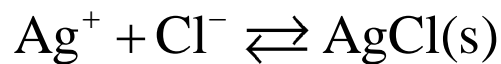
$$[\text{titrant}] = c_t \cdot \frac{V_t - V_{t.e.}}{V_a + V_t}$$

[INDIKATORI]

- Promjena boje mora biti što bliže vrijednosti u točki ekvivalencije.
 - Kiselo-bazne titracije: promjena boje indikatora ovisi o njegovoj K_a . Treba izabrati indikator čija se promjena odvija što bliže pH vrijednosti točke ekvivalencije

[TALOŽNE TITRACIJE]

- Izračunajte koncentraciju Ag^+ kationa i pAg prilikom titracije 50,0 mL otopine natrijevog klorida koncentracije 0,0100 M standardnom otopinom srebrovog nitrata koncentracije 0,0100 M i $F = 0,9901$, nakon dodatka 5,00; 25,25; 50,00; 50,50 i 55,00 mL.



Izračun volumena točke ekvivalencije:

$$n(\text{Cl}^-) = n(\text{Ag}^+)$$

$$c_a \cdot V_a = c_t \cdot V_t \cdot F$$

$$V_t = \frac{c_a \cdot V}{c_t \cdot F} = \frac{0,0100 \text{ mol L}^{-1} \cdot 50,00 \text{ mL}}{0,0100 \text{ mol L}^{-1} \cdot 0,9901} = 50,50 \text{ mL}$$

[Prije točke ekvivalencije]

- $0 < V < V_{t.e.}$

$V_t = 5; 25,25$ i 50 mL

$$c'_a = \frac{c_a \cdot V_a - c_t \cdot V_t}{V_a + V_t} = \frac{0,0100 \text{ mol L}^{-1} \cdot 50 \text{ mL} - 0,0100 \text{ mol L}^{-1} \cdot 0,9901 \cdot 5 \text{ mL}}{50 \text{ mL} + 5 \text{ mL}} = 0,0082 \text{ mol L}^{-1}$$

$$c'_a = [\text{Cl}^-] = 0,0082 \text{ mol L}^{-1}$$

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1,8 \cdot 10^{-10}}{0,0082} = 2,20 \cdot 10^{-8} \text{ mol L}^{-1}$$

$$pAg = -\log[\text{Ag}^+] = -\log(2,20 \cdot 10^{-8}) = 7,66$$



$$c'_a = \frac{c_a \cdot V_a - c_t \cdot V_t}{V_a + V_t} = \frac{0,0100 \text{ mol L}^{-1} \cdot 50 \text{ mL} - 0,0100 \text{ mol L}^{-1} \cdot 0,9901 \cdot 25,25 \text{ mL}}{50 \text{ mL} + 25,25 \text{ mL}} = 0,0033 \text{ mol L}^{-1}$$

$$c'_a = [\text{Cl}^-] = 0,0033 \text{ mol L}^{-1}$$

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1,8 \cdot 10^{-10}}{0,0033} = 5,45 \cdot 10^{-8} \text{ mol L}^{-1}$$

$$\text{pAg} = -\log[\text{Ag}^+] = -\log(5,45 \cdot 10^{-8}) = 7,26$$

$$c'_a = \frac{c_a \cdot V_a - c_t \cdot V_t}{V_a + V_t} = \frac{0,0100 \text{ mol L}^{-1} \cdot 50 \text{ mL} - 0,0100 \text{ mol L}^{-1} \cdot 0,9901 \cdot 50 \text{ mL}}{50 \text{ mL} + 50 \text{ mL}} = 0,00005 \text{ mol L}^{-1}$$

$$c'_a = [\text{Cl}^-] = 0,00005 \text{ mol L}^{-1}$$

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1,8 \cdot 10^{-10}}{0,00005} = 3,6 \cdot 10^{-6} \text{ mol L}^{-1}$$

$$\text{pAg} = -\log[\text{Ag}^+] = -\log(3,6 \cdot 10^{-6}) = 5,44$$

Drugi način računanja

$$[\text{Cl}^-] = \frac{V_{\text{t.e.}} - V_t}{V_{\text{t.e.}}} \cdot c_a \cdot \frac{V_a}{V_a + V_t}$$

$$[\text{Cl}^-] = \frac{50,50 \text{ mL} - 5 \text{ mL}}{50,50 \text{ mL}} \cdot 0,0100 \text{ mol L}^{-1} \cdot 0,9901 \cdot \frac{50 \text{ mL}}{50 \text{ mL} + 5 \text{ mL}}$$

$$[\text{Cl}^-] = 0,0082 \text{ mol L}^{-1}$$

$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} = \frac{1,8 \cdot 10^{-10}}{0,0082} = 2,20 \cdot 10^{-8} \text{ mol L}^{-1}$$

$$\text{pAg} = -\log[\text{Ag}^+] = -\log(2,20 \cdot 10^{-8}) = 7,66$$

[U točki ekvivalencije]

$$[\text{Cl}^-] = [\text{Ag}^+] = x$$

$$x^2 = K_{\text{sp}} \Rightarrow x = \sqrt{K_{\text{sp}}}$$

$$[\text{Ag}^+] = \sqrt{1,8 \cdot 10^{-10}} = 1,34 \cdot 10^{-5} \text{ mol L}^{-1}$$

$$\text{pAg} = -\log [\text{Ag}^+] = -\log(1,34 \cdot 10^{-5}) = 4,87$$

Nakon točke ekvivalencije

$$[\text{Ag}^+] = c_t \cdot \frac{V_t - V_{t.e.}}{V_a + V_t}$$

$$[\text{Ag}^+] = 0,0100 \text{ mol L}^{-1} \cdot 0,9901 \cdot \frac{55 \text{ mL} - 50,50 \text{ mL}}{50 \text{ mL} + 55 \text{ mL}}$$

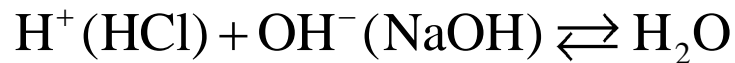
$$[\text{Ag}^+] = 4,24 \cdot 10^{-4} \text{ mol L}^{-1}$$

$$\text{pAg} = -\log[\text{Ag}^+] = -\log(4,24 \cdot 10^{-4}) = 3,37$$

KISELO-BAZNE TITRACIJE

Jaka kiselina

- Izračunajte koncentraciju H^+ kationa i pH prilikom titracije 25,0 mL otopine klorovodične kiseline koncentracije 0,0150 M standardnom otopinom natrijevog hidroksida (lužine) koncentracije 0,0200 M, nakon dodatka 5,00; 15,00; 18,70; 18,75; 18,80; 20,00 i 25,00 mL.



Izračun volumena točke ekvivalencije:

$$n(\text{H}^+) = n(\text{OH}^-)$$

$$c_a \cdot V_a = c_t \cdot V_t$$

$$V_t = \frac{c_a \cdot V_a}{c_t} = \frac{0,0150 \text{ mol L}^{-1} \cdot 25,00 \text{ mL}}{0,0200 \text{ mol L}^{-1}} = 18,75 \text{ mL}$$

[Na počtku titracije]

- $V = 0 \text{ mL}$

Budući da se radi o jakoj kiselini, pH se računa iz koncentracije kiseline:

$$c_a = [\text{H}^+] = 0,0150 \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(0,0150) = 1,82$$

[Prije točke ekvivalencije]

- $0 < V < V_{t.e.}$
 $V_t = 5; 15$ i $18,70$ mL

$$c'_a = \frac{c_a \cdot V_a - c_t \cdot V_t}{V_a + V_t} = \frac{0,0150 \text{ mol L}^{-1} \cdot 25 \text{ mL} - 0,0200 \text{ mol L}^{-1} \cdot 5 \text{ mL}}{25 \text{ mL} + 5 \text{ mL}} = 0,0092 \text{ mol L}^{-1}$$

$$c'_a = [\text{H}^+] = 0,0092 \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(0,0092) = 2,04$$



$$c'_a = \frac{c_a \cdot V_a - c_t \cdot V_t}{V_a + V_t} = \frac{0,0150 \text{ mol L}^{-1} \cdot 25 \text{ mL} - 0,0200 \text{ mol L}^{-1} \cdot 15 \text{ mL}}{25 \text{ mL} + 15 \text{ mL}} = 0,0019 \text{ mol L}^{-1}$$

$$c'_a = [\text{H}^+] = 0,0019 \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(0,0019) = 2,73$$

$$c'_a = \frac{c_a \cdot V_a - c_t \cdot V_t}{V_a + V_t} = \frac{0,0150 \text{ mol L}^{-1} \cdot 25 \text{ mL} - 0,0200 \text{ mol L}^{-1} \cdot 18,7 \text{ mL}}{25 \text{ mL} + 18,7 \text{ mL}} = 2,29 \cdot 10^{-5} \text{ mol L}^{-1}$$

$$c'_a = [\text{H}^+] = 2,29 \cdot 10^{-5} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(2,29 \cdot 10^{-5}) = 4,64$$

Drugi način računanja

$$[\text{H}^+] = \frac{V_{\text{t.e.}} - V_{\text{t}}}{V_{\text{t.e.}}} \cdot c_{\text{a}} \cdot \frac{V_{\text{a}}}{V_{\text{a}} + V_{\text{t}}}$$

$$[\text{H}^+] = \frac{18,75 \text{ mL} - 5 \text{ mL}}{18,75 \text{ mL}} \cdot 0,0150 \text{ mol L}^{-1} \cdot \frac{25 \text{ mL}}{25 \text{ mL} + 5 \text{ mL}}$$

$$[\text{H}^+] = 0,0092 \text{ mol L}^{-1}$$

$$\text{pH} = -\log [\text{H}^+] = -\log(0,0092) = 2,04$$

[U točki ekvivalencije]

$$V = V_{t.e.} = 18,75 \text{ mL}$$

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

$$x^2 = K_w \Rightarrow x = \sqrt{K_w}$$

$$[\text{H}^+] = \sqrt{1,0 \cdot 10^{-14}} = 1,0 \cdot 10^{-7} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1,0 \cdot 10^{-7}) = 7,0$$

Nakon točke ekvivalencije

$V > V_{t.e.}$
 $V_t = 18,75; 20,0 \text{ i } 25,0 \text{ mL}$

$$[\text{OH}^-] = c_t \cdot \frac{V_t - V_{t.e.}}{V_a + V_t}$$

$$[\text{OH}^-] = 0,0200 \text{ mol L}^{-1} \cdot \frac{18,80 \text{ mL} - 18,75 \text{ mL}}{25 \text{ mL} + 18,80 \text{ mL}}$$

$$[\text{OH}^-] = 2,28 \cdot 10^{-5} \text{ mol L}^{-1}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1,0 \cdot 10^{-14}}{2,28 \cdot 10^{-5}} = 4,38 \cdot 10^{-10} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(4,38 \cdot 10^{-10}) = 9,36$$

$$[\text{OH}^-] = c_t \cdot \frac{V_t - V_{\text{t.e.}}}{V_a + V_t}$$

$$[\text{OH}^-] = 0,0200 \text{ mol L}^{-1} \cdot \frac{20 \text{ mL} - 18,75 \text{ mL}}{25 \text{ mL} + 20 \text{ mL}}$$

$$[\text{OH}^-] = 5,56 \cdot 10^{-4} \text{ mol L}^{-1}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1,0 \cdot 10^{-14}}{5,56 \cdot 10^{-4}} = 1,82 \cdot 10^{-11} \text{ mol L}^{-1}$$

$$\text{pH} = -\log [\text{H}^+] = -\log(1,82 \cdot 10^{-11}) = 10,74$$

$$[\text{OH}^-] = c_t \cdot \frac{V_t - V_{t.e.}}{V_a + V_t}$$

$$[\text{OH}^-] = 0,0200 \text{ mol L}^{-1} \cdot \frac{25 \text{ mL} - 18,75 \text{ mL}}{25 \text{ mL} + 25 \text{ mL}}$$

$$[\text{OH}^-] = 0,0025 \text{ mol L}^{-1}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1,0 \cdot 10^{-14}}{0,0025} = 4,0 \cdot 10^{-12} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(4,0 \cdot 10^{-12}) = 11,40$$

KISELO-BAZNE TITRACIJE

Jaka baza

- Izračunajte koncentraciju H^+ kationa i pH prilikom titracije 20,0 mL otopine kalijeve lužine 0,1500 M standardnom otopinom klorovodične kiseline koncentracije 0,3000 M, nakon dodatka 2,00; 5,00; 9,95; 10,00; 10,05; i 15,00 mL.



Izračun volumena točke ekvivalencije:

$$n(\text{OH}^-) = n(\text{H}^+)$$

$$c_a \cdot V_a = c_t \cdot V_t$$

$$V_t = \frac{c_a \cdot V_a}{c_t} = \frac{0,1500 \text{ mol L}^{-1} \cdot 20,00 \text{ mL}}{0,3000 \text{ mol L}^{-1}} = 10,00 \text{ mL}$$

[Na počtku titracije]

- $V = 0 \text{ mL}$

Budući da se radi o jakoj bazi, pH (pOH) se računa iz koncentracije lužine:

$$c_a = [\text{OH}^-] = 0,1500 \text{ mol L}^{-1}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0,1500) = 0,82$$

$$\text{pH} = 14 - \text{pOH} = 14 - 0,82 = 13,18$$

[Prije točke ekvivalencije]

- $0 < V < V_{t.e.}$
 $V_t = 2; 5 \text{ i } 9,95 \text{ mL}$

$$c'_a = \frac{c_a \cdot V_a - c_t \cdot V_t}{V_a + V_t} = \frac{0,1500 \text{ mol L}^{-1} \cdot 20 \text{ mL} - 0,3000 \text{ mol L}^{-1} \cdot 2 \text{ mL}}{20 \text{ mL} + 2 \text{ mL}} = 0,1091 \text{ mol L}^{-1}$$

$$c'_a = [\text{OH}^-] = 0,1091 \text{ mol L}^{-1}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0,1091) = 0,96$$

$$\text{pH} = 14 - \text{pOH} = 14 - 0,96 = 13,04$$

$$c'_a = \frac{c_a \cdot V_a - c_t \cdot V_t}{V_a + V_t} = \frac{0,1500 \text{ mol L}^{-1} \cdot 20 \text{ mL} - 0,3000 \text{ mol L}^{-1} \cdot 5 \text{ mL}}{20 \text{ mL} + 5 \text{ mL}} = 0,0600 \text{ mol L}^{-1}$$

$$c'_a = [\text{OH}^-] = 0,0600 \text{ mol L}^{-1}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0,0600) = 1,22$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1,22 = 12,78$$

$$c'_a = \frac{c_a \cdot V_a - c_t \cdot V_t}{V_a + V_t} = \frac{0,1500 \text{ mol L}^{-1} \cdot 20 \text{ mL} - 0,3000 \text{ mol L}^{-1} \cdot 9,95 \text{ mL}}{20 \text{ mL} + 9,95 \text{ mL}} = 5,01 \cdot 10^{-4} \text{ mol L}^{-1}$$

$$c'_a = [\text{OH}^-] = 5,01 \cdot 10^{-4} \text{ mol L}^{-1}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(5,01 \cdot 10^{-4}) = 3,30$$

$$\text{pH} = 14 - \text{pOH} = 14 - 3,30 = 10,70$$

Drugi način računanja

$$[\text{OH}^-] = \frac{V_{\text{t.e.}} - V_{\text{t}}}{V_{\text{t.e.}}} \cdot c_{\text{a}} \cdot \frac{V_{\text{a}}}{V_{\text{a}} + V_{\text{t}}}$$

$$[\text{OH}^-] = \frac{10,00 \text{ mL} - 2 \text{ mL}}{10,00 \text{ mL}} \cdot 0,1500 \text{ mol L}^{-1} \cdot \frac{20 \text{ mL}}{20 \text{ mL} + 2 \text{ mL}}$$

$$[\text{OH}^-] = 0,1091 \text{ mol L}^{-1}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0,1091) = 0,96$$

$$\text{pH} = 14 - \text{pOH} = 14 - 0,96 = 13,04$$

[U točki ekvivalencije]

$$V = V_{t.e.} = 10,00 \text{ mL}$$

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

$$x^2 = K_w \Rightarrow x = \sqrt{K_w}$$

$$[\text{H}^+] = \sqrt{1,0 \cdot 10^{-14}} = 1,0 \cdot 10^{-7} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1,0 \cdot 10^{-7}) = 7,0$$

Nakon točke ekvivalencije

$V > V_{t.e.}$
 $V_t = 10,05$ i $15,00$ mL

$$[H^+] = c_t \cdot \frac{V_t - V_{t.e.}}{V_a + V_t}$$

$$[H^+] = 0,3000 \text{ mol L}^{-1} \cdot \frac{10,05 \text{ mL} - 10,00 \text{ mL}}{20 \text{ mL} + 10,05 \text{ mL}}$$

$$[H^+] = 4,99 \cdot 10^{-4} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[H^+] = -\log(4,99 \cdot 10^{-4}) = 3,30$$

$$[\text{H}^+] = c_t \cdot \frac{V_t - V_{\text{t.e.}}}{V_a + V_t}$$

$$[\text{H}^+] = 0,3000 \text{ mol L}^{-1} \cdot \frac{15,00 \text{ mL} - 10,00 \text{ mL}}{20 \text{ mL} + 15,00 \text{ mL}}$$

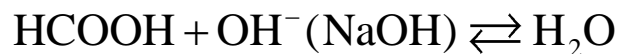
$$[\text{H}^+] = 0,0429 \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(0,0429) = 1,37$$

KISELO-BAZNE TITRACIJE

Slaba kiselina

- Izračunajte koncentraciju H^+ kationa i pH prilikom titracije 15,0 mL otopine mravlje kiseline ($HCOOH$, $K_a = 1,77 \times 10^{-4}$) koncentracije 0,1500 M standardnom otopinom natrijevog hidroksida (lužine) koncentracije 0,1500 M, nakon dodatka 5,00; 10,00; 14,95; 15,00; 15,05; i 20,00 mL.



Izračun volumena točke ekvivalencije:

$$\frac{n(\text{HCOOH})}{n(\text{OH}^-)} = \frac{1}{1}$$

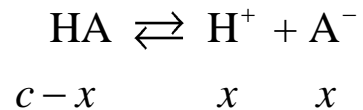
$$n(\text{HCOOH}) = n(\text{OH}^-)$$

$$c_a \cdot V_a = c_t \cdot V_t$$

$$V_t = \frac{c_a \cdot V_a}{c_t} = \frac{0,1500 \text{ mol L}^{-1} \cdot 15,00 \text{ mL}}{0,1500 \text{ mol L}^{-1}} = 15,00 \text{ mL}$$

Na početku titracije

• $V = 0 \text{ mL}$



$$K_a = \frac{x^2}{c - x} \Rightarrow x = \sqrt{K_a \cdot c}$$

$$[\text{H}^+] = x = \sqrt{1,77 \cdot 10^{-4} \cdot 0,1500} = 5,15 \cdot 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(5,15 \cdot 10^{-3}) = 2,29$$

[Prije točke ekvivalencije]

- $0 < V < V_{t.e.}$
 $V_t = 5; 10 \text{ i } 14,95 \text{ mL}$

$$\text{pH} = \text{p}K_a + \log \frac{V_t}{V_{t.e.} - V_t}$$

$$\text{pH} = 3,75 + \log \frac{5}{15-5} = 3,45$$

$$\text{pH} = \text{p}K_a + \log \frac{V_t}{V_{t.e.} - V_t}$$

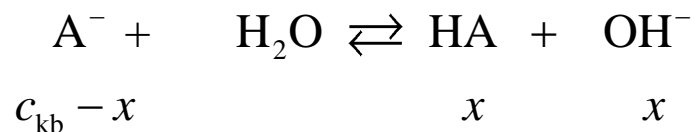
$$\text{pH} = 3,75 + \log \frac{10}{15-10} = 4,05$$

$$\text{pH} = \text{p}K_a + \log \frac{V_t}{V_{t.e.} - V_t}$$

$$\text{pH} = 3,75 + \log \frac{14,95}{15-14,95} = 6,23$$

[U točki ekvivalencije]

$$V = V_{t.e.} = 15,00 \text{ mL}$$



$$c_{\text{kb}} = c_a \cdot \frac{V_a}{V_a + V_{t.e.}} = 0,1500 \text{ mol L}^{-1} \cdot \frac{15 \text{ mL}}{15 \text{ mL} + 15 \text{ mL}} = 0,0750 \text{ mol L}^{-1}$$

$$K = \frac{K_w}{K_a} = K_b = \frac{1 \cdot 10^{-14}}{1,77 \cdot 10^{-4}} = 5,65 \cdot 10^{-11}$$

$$K_b = \frac{x^2}{c_{\text{kb}} - x} \Rightarrow x^2 = \sqrt{K_b \cdot c_{\text{kb}}} \Rightarrow x = \sqrt{5,65 \cdot 10^{-11} \cdot 0,0750} = 2,06 \cdot 10^{-6} \text{ mol L}^{-1}$$

$$[\text{OH}^-] = 2,06 \cdot 10^{-6} \text{ mol L}^{-1} \Rightarrow \text{pOH} = 5,69$$

$$\text{pH} = 14 - \text{pOH} = 14 - 5,69 = 8,31$$

Nakon točke ekvivalencije

$$V > V_{t.e.}$$

$$V_t = 15,05 \text{ i } 20,0 \text{ mL}$$

$$[\text{OH}^-] = c_t \cdot \frac{V_t - V_{t.e.}}{V_a + V_t}$$

$$[\text{OH}^-] = 0,1500 \text{ mol L}^{-1} \cdot \frac{15,05 \text{ mL} - 15,00 \text{ mL}}{15 \text{ mL} + 15,05 \text{ mL}}$$

$$[\text{OH}^-] = 2,50 \cdot 10^{-4} \text{ mol L}^{-1}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1,0 \cdot 10^{-14}}{2,50 \cdot 10^{-4}} = 4,01 \cdot 10^{-11} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(4,01 \cdot 10^{-11}) = 10,40$$

$$[\text{OH}^-] = c_t \cdot \frac{V_t - V_{\text{t.e.}}}{V_a + V_t}$$

$$[\text{OH}^-] = 0,1500 \text{ mol L}^{-1} \cdot \frac{20 \text{ mL} - 15,00 \text{ mL}}{15 \text{ mL} + 20 \text{ mL}}$$

$$[\text{OH}^-] = 0,0214 \text{ mol L}^{-1}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1,0 \cdot 10^{-14}}{0,0214} = 4,67 \cdot 10^{-13} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(4,67 \cdot 10^{-13}) = 12,33$$

KISELO-BAZNE TITRACIJE

Slaba baza

- Izračunajte koncentraciju H^+ kationa i pH prilikom titracije 15,0 mL otopine amonijaka (NH_3 , $K_b = 1,76 \times 10^{-5}$; $K_a = 5,69 \cdot 10^{-10}$) koncentracije 0,2500 M standardnom otopinom klorovodične kiseline koncentracije 0,2500 M, nakon dodatka 5,00; 10,00; 14,95; 15,00; 15,05; i 20,00 mL.



Izračun volumena točke ekvivalencije:

$$\frac{n(\text{NH}_3)}{n(\text{H}^+)} = \frac{1}{1}$$

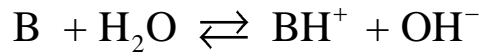
$$n(\text{NH}_3) = n(\text{H}^+)$$

$$c_a \cdot V_a = c_t \cdot V_t$$

$$V_t = \frac{c_a \cdot V_a}{c_t} = \frac{0,2500 \text{ mol L}^{-1} \cdot 15,00 \text{ mL}}{0,2500 \text{ mol L}^{-1}} = 15,00 \text{ mL}$$

Na počtku titracije

- $V = 0 \text{ mL}$



$$c - x \qquad \qquad \qquad x \qquad \qquad x$$

$$K_b = \frac{x^2}{c - x} \Rightarrow x = \sqrt{K_b \cdot c}$$

$$[\text{OH}^-] = x = \sqrt{1,76 \cdot 10^{-5} \cdot 0,2500} = 2,1 \cdot 10^{-3} \text{ mol L}^{-1} \Rightarrow \text{pOH} = -\log(2,1 \cdot 10^{-3}) = 2,69$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2,69 = 11,31$$

[Prije točke ekvivalencije]

- $0 < V < V_{t.e.}$
 $V_t = 5; 10 \text{ i } 14,95 \text{ mL}$

$$\text{pH} = \text{p}K_a + \log \frac{V_{t.e.} - V_t}{V_t}$$

$$\text{pH} = 9,25 + \log \frac{15 - 5}{5} = 9,55$$

$$\text{pH} = \text{p}K_a + \log \frac{V_{t.e.} - V_t}{V_t}$$

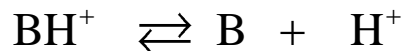
$$\text{pH} = 9,25 + \log \frac{15 - 10}{10} = 8,95$$

$$\text{pH} = \text{p}K_a + \log \frac{V_{t.e.} - V_t}{V_t}$$

$$\text{pH} = 9,25 + \log \frac{15 - 14,95}{14,95} = 6,77$$

[U točki ekvivalencije]

$$V = V_{t.e.} = 15,00 \text{ mL}$$



$$c_{\text{kk}} - x \qquad x \qquad x$$

$$c_{\text{kk}} = c_a \cdot \frac{V_a}{V_a + V_{t.e.}} = 0,2500 \text{ mol L}^{-1} \cdot \frac{15 \text{ mL}}{15 \text{ mL} + 15 \text{ mL}} = 0,1250 \text{ mol L}^{-1}$$

$$K = \frac{K_w}{K_b} = K_a = \frac{1 \cdot 10^{-14}}{1,76 \cdot 10^{-5}} = 5,69 \cdot 10^{-10}$$

$$K_a = \frac{x^2}{c_{\text{kk}} - x} \Rightarrow x^2 = \sqrt{K_a \cdot c_{\text{kk}}} \Rightarrow x = \sqrt{0,1250 \cdot 5,69 \cdot 10^{-10}} = 8,43 \cdot 10^{-6} \text{ mol L}^{-1}$$

$$[\text{H}^+] = 8,43 \cdot 10^{-6} \text{ mol L}^{-1}$$

$$\text{pH} = 5,07$$

Nakon točke ekvivalencije

$$V > V_{t.e.}$$
$$V_t = 15,05 \text{ i } 20,0 \text{ mL}$$

$$[\text{H}^+] = c_t \cdot \frac{V_t - V_{t.e.}}{V_a + V_t}$$

$$[\text{H}^+] = 0,2500 \text{ mol L}^{-1} \cdot \frac{15,05 \text{ mL} - 15,00 \text{ mL}}{15 \text{ mL} + 15,05 \text{ mL}}$$

$$[\text{H}^+] = 4,16 \cdot 10^{-4} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(4,16 \cdot 10^{-4}) = 3,38$$

$$[\text{H}^+] = c_t \cdot \frac{V_t - V_{t.e.}}{V_a + V_t}$$

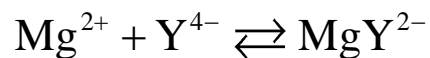
$$[\text{H}^+] = 0,2500 \text{ mol L}^{-1} \cdot \frac{20 \text{ mL} - 15,00 \text{ mL}}{15 \text{ mL} + 20 \text{ mL}}$$

$$[\text{H}^+] = 3,57 \cdot 10^{-2} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(3,57 \cdot 10^{-2}) = 1,45$$

KOMPLEKSOMETRIJSKE TITRACIJE

- Izračunajte koncentraciju Mg^{2+} kationa i pMg prilikom titracije 15,0 mL otopine magnezijevih kationa koncentracije 0,2500 M standardnom otopinom EDTA koncentracije 0,2500 M u amonijakalnom puferu $\text{pH} = 10$, nakon dodatka 5,00; 10,00; 14,95; 15,00; 15,05; i 20,00 mL.
- $K_f(\text{MgY}^{2-}) = 4,37 \cdot 10^8$; $\alpha(\text{Y}^{4-}) = 0,36$
- $K_f'(\text{MgY}^{2-}) = 1,57 \cdot 10^8$



Izračun volumena točke ekvivalencije:

$$\frac{n(\text{Mg}^{2+})}{n(\text{Y}^{4-})} = \frac{1}{1}$$

$$n(\text{Mg}^{2+}) = n(\text{Y}^{4-})$$

$$c_a \cdot V_a = c_t \cdot V_t$$

$$V_t = \frac{c_a \cdot V_a}{c_t} = \frac{0,2500 \text{ mol L}^{-1} \cdot 15,00 \text{ mL}}{0,2500 \text{ mol L}^{-1}} = 15,00 \text{ mL}$$

Računanje pMg tijekom titracije

- $V_t = 0$ mL

$$\text{pMg} = -\log[\text{Mg}^{2+}] = -\log(0,2500) = 0,60$$

- $0 < V < V_{t.e.}$

$$V_t = 5; 10 \text{ i } 14,95 \text{ mL}$$

$$[\text{Mg}^{2+}] = \frac{V_{t.e.} - V_t}{V_{t.e.}} \cdot c_a \cdot \frac{V_a}{V_a + V_t}$$

$$[\text{Mg}^{2+}] = \frac{15 \text{ mL} - 5 \text{ mL}}{15 \text{ mL}} \cdot 0,2500 \text{ mol L}^{-1} \cdot \frac{15 \text{ mL}}{15 \text{ mL} + 5 \text{ mL}}$$

$$[\text{Mg}^{2+}] = 0,1250 \text{ mol L}^{-1}$$

$$\text{pMg} = -\log[\text{Mg}^{2+}] = -\log(0,1250) = 0,90$$

$$[\text{Mg}^{2+}] = \frac{V_{\text{t.e.}} - V_t}{V_{\text{t.e.}}} \cdot c_a \cdot \frac{V_a}{V_a + V_t}$$

$$[\text{Mg}^{2+}] = \frac{15 \text{ mL} - 10 \text{ mL}}{15 \text{ mL}} \cdot 0,2500 \text{ mol L}^{-1} \cdot \frac{15 \text{ mL}}{15 \text{ mL} + 10 \text{ mL}}$$

$$[\text{Mg}^{2+}] = 0,0500 \text{ mol L}^{-1}$$

$$\text{pMg} = -\log[\text{Mg}^{2+}] = -\log(0,0500) = 1,30$$

$$[\text{Mg}^{2+}] = \frac{V_{\text{t.e.}} - V_t}{V_{\text{t.e.}}} \cdot c_a \cdot \frac{V_a}{V_a + V_t}$$

$$[\text{Mg}^{2+}] = \frac{15 \text{ mL} - 14,95 \text{ mL}}{15 \text{ mL}} \cdot 0,2500 \text{ mol L}^{-1} \cdot \frac{15 \text{ mL}}{15 \text{ mL} + 14,95 \text{ mL}}$$

$$[\text{Mg}^{2+}] = 4,17 \cdot 10^{-4} \text{ mol L}^{-1}$$

$$\text{pMg} = -\log[\text{Mg}^{2+}] = -\log(4,17 \cdot 10^{-4}) = 3,38$$

• $V_t = 15,0 \text{ mL}$ (točka ekvivalencije)



$$c_k - x \qquad \qquad x \qquad \qquad x$$

$$c_k = c_a \cdot \frac{V_a}{V_a + V_{t.e.}} = 0,2500 \text{ mol L}^{-1} \cdot \frac{15 \text{ mL}}{15 \text{ mL} + 15 \text{ mL}} = 0,1250 \text{ mol L}^{-1}$$

$$K_f' = \frac{c_k - x}{x^2} \Rightarrow x^2 = \sqrt{\frac{c_k}{K_f'}} \Rightarrow x = \sqrt{\frac{0,1250}{1,57 \cdot 10^8}} = 2,82 \cdot 10^{-5} \text{ mol L}^{-1}$$

$$[\text{Mg}^{2+}] = 2,82 \cdot 10^{-5} \text{ mol L}^{-1}$$

$$\text{pMg} = 4,55$$

Nakon točke ekvivalencije

- $V > V_{t.e.}$

$$V_t = 15,05 \text{ i } 20,00 \text{ mL}$$

$$[\text{MgY}^{2-}] \cong c(\text{Mg}^{2+}) = c_a \cdot \frac{V_a}{V_a + V_t}$$

$$[\text{MgY}^{2-}] = 0,2500 \text{ mol L}^{-1} \cdot \frac{15 \text{ mL}}{15 \text{ mL} + 15,05 \text{ mL}}$$

$$[\text{MgY}^{2-}] = 0,1248 \text{ mol L}^{-1}$$

$$c(\text{EDTA}) = 0,2500 \left(\frac{V_t - V_{t.e.}}{V_a + V_t} \right) = 0,2500 \text{ mol L}^{-1} \cdot \left(\frac{15,05 - 15,00}{15,00 + 15,05} \right) = 4,16 \cdot 10^{-4} \text{ mol L}^{-1}$$

$$\frac{0,1248}{[\text{Mg}^{2+}] \cdot 4,16 \cdot 10^{-4}} = 1,57 \cdot 10^8$$

$$[\text{Mg}^{2+}] = 1,91 \cdot 10^{-6} \text{ mol L}^{-1}$$

$$\text{pMg} = 5,72$$

Može se smatrati da je sav metal preveden u kompleks.

$$[\text{MgY}^{2-}] \cong c(\text{Mg}^{2+}) = c_a \cdot \frac{V_a}{V_a + V_t}$$

$$[\text{MgY}^{2-}] = 0,2500 \text{ mol L}^{-1} \cdot \frac{15 \text{ mL}}{15 \text{ mL} + 20 \text{ mL}}$$

$$[\text{MgY}^{2-}] = 0,1071 \text{ mol L}^{-1}$$

$$c(\text{EDTA}) = 0,2500 \left(\frac{V_t - V_{\text{t.e.}}}{V_a + V_t} \right) = 0,2500 \text{ mol L}^{-1} \cdot \left(\frac{20,00 - 15,00}{15,00 + 20,00} \right) = 3,57 \cdot 10^{-2} \text{ mol L}^{-1}$$

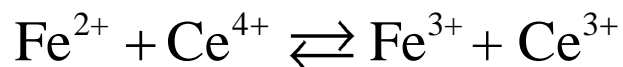
$$\frac{0,1071}{[\text{Mg}^{2+}] \cdot 3,57 \cdot 10^{-2}} = 1,57 \cdot 10^8$$

$$[\text{Mg}^{2+}] = 1,91 \cdot 10^{-8} \text{ mol L}^{-1}$$

$$\text{pMg} = 7,72$$

REDOKS TITRACIJE

- Izračunajte potencijal tijekom redoks titracije 15,0 mL otopine Fe^{2+} kationa 0,2500 M standardnom otopinom Ce^{4+} koncentracije 0,2500 M u perklorno kiselom mediju $\text{pH} = 0$, nakon dodatka 5,00; 10,00; 15,00 i 20,00 mL.
- $\text{Fe}^{3+} + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+} \quad E^{\text{f}} = + 0,767 \text{ V}$
- $\text{Ce}^{4+} + \text{e}^{-} \rightleftharpoons \text{Ce}^{3+} \quad E^{\text{f}} = + 1,700 \text{ V}$



Izračun volumena točke ekvivalencije:

$$\frac{n(\text{Fe}^{2+})}{n(\text{Ce}^{4+})} = \frac{1}{1}$$

$$n(\text{Fe}^{2+}) = n(\text{Ce}^{4+})$$

$$c_a \cdot V_a = c_t \cdot V_t$$

$$V_t = \frac{c_a \cdot V_a}{c_t} = \frac{0,2500 \text{ mol L}^{-1} \cdot 15,00 \text{ mL}}{0,2500 \text{ mol L}^{-1}} = 15,00 \text{ mL}$$

- [
- $0 < V < V_{t.e.}$
 $V_t = 5,00$ i $10,00$ mL

Za računanje potencijala članka koristi se reakcija članka s redoks parom Fe^{3+}/Fe^{2+}

]

$$[A_{\text{oksidirani}}] = \frac{(V_t \cdot c_t \cdot \frac{b}{a})^b}{(V_a + V_t)^b} \quad [A_{\text{reducirani}}] = \frac{(V_a \cdot c_a - V_t \cdot c_t \cdot \frac{b}{a})^b}{(V_a + V_t)^b}$$

$$\frac{[A_{\text{reducirani}}]}{[A_{\text{oksidirani}}]} = \frac{\frac{V_a \cdot c_a - V_t \cdot c_t \cdot \frac{b}{a}}{V_a + V_t}}{\frac{V_t \cdot c_t \cdot \frac{b}{a}}{V_a + V_t}} = \frac{V_a \cdot c_a - V_t \cdot c_t \cdot \frac{b}{a}}{V_t \cdot c_t \cdot \frac{b}{a}}$$

$$\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = \frac{V_a \cdot c_a - V_t \cdot c_t \cdot \frac{b}{a}}{V_t \cdot c_t \cdot \frac{b}{a}} = \frac{15 \text{ mL} \cdot 0,2500 \text{ mol L}^{-1} - 5 \text{ mL} \cdot 0,2500 \text{ mol L}^{-1} \cdot \frac{1}{1}}{5 \text{ mL} \cdot 0,2500 \text{ mol L}^{-1} \cdot \frac{1}{1}}$$

$$\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 2$$

$$E_{\text{katode}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^f - \frac{0,0592}{\underbrace{a \cdot b}_z} \log \frac{[\text{Fe}^{2+}]^b}{[\text{Fe}^{3+}]^b}$$

$$E_{\text{katode}} = 0,767 - \frac{0,0592}{1} \log(2)^{\frac{1}{b}}$$

$$E_{\text{katode}} = 0,749 \text{ V}$$

$$\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = \frac{V_a \cdot c_a - V_t \cdot c_t \cdot \frac{b}{a}}{V_t \cdot c_t \cdot \frac{b}{a}} = \frac{15 \text{ mL} \cdot 0,2500 \text{ mol L}^{-1} - 10 \text{ mL} \cdot 0,2500 \text{ mol L}^{-1} \cdot \frac{1}{1}}{10 \text{ mL} \cdot 0,2500 \text{ mol L}^{-1} \cdot \frac{1}{1}}$$

$$\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 0,5$$

$$E_{\text{katode}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^f - \frac{0,0592}{z \cdot a \cdot b} \log \frac{[\text{Fe}^{2+}]^b}{[\text{Fe}^{3+}]^b}$$

$$E_{\text{katode}} = 0,767 - \frac{0,0592}{1} \log(0,5)^{\frac{1}{b}}$$

$$E_{\text{katode}} = 0,785 \text{ V}$$

• $V_t = 15,0 \text{ mL}$ (točka ekvivalencije)

Ako mali dio Fe^{3+} prelazi u Fe^{2+} istodobno nastaje ista množina Ce^{4+} , stoga vrijedi:



U točki ekvivalencije obje reakcije članka su jednako pogodne (nepogodne) za računanje potencijala članka.



$$E_{\text{katode}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^f - \frac{0,0592}{a \cdot b} \log \frac{[\text{Fe}^{2+}]^b}{[\text{Fe}^{3+}]^b}$$

$$E_{\text{katode}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^f - \frac{0,0592}{a \cdot b} \log \frac{[\text{Ce}^{3+}]^a}{[\text{Ce}^{4+}]^a}$$

$$E_{\text{katode}} = 0,767 - \frac{0,0592}{1} \log \frac{[\text{Fe}^{2+}]^1}{[\text{Fe}^{3+}]^1}$$

$$E_{\text{katode}} = 1,700 - \frac{0,0592}{1} \log \frac{[\text{Ce}^{3+}]^1}{[\text{Ce}^{4+}]^1}$$

Objе je јednadžbe potrebno zbroјiti јer nisu poznate: $[\text{Fe}^{2+}] = [\text{Ce}^{3+}] = ?$

$$2E_{\text{katode}} = 0,767 - \frac{0,0592}{1} \log \frac{[\text{Fe}^{2+}]^1}{[\text{Fe}^{3+}]^1} + 1,700 - \frac{0,0592}{1} \log \frac{[\text{Ce}^{3+}]^1}{[\text{Ce}^{4+}]^1}$$

$$2E_{\text{katode}} = 2,467 - 0,0592 \log \frac{[\text{Fe}^{2+}][\text{Ce}^{3+}]}{[\text{Fe}^{3+}][\text{Ce}^{4+}]}$$

Budući da vrijedi: $[\text{Fe}^{2+}] = [\text{Ce}^{4+}]$ i $[\text{Fe}^{3+}] = [\text{Ce}^{3+}]$

$$2E_{\text{katode}} = 2,467$$

$$E_{\text{katode}} = \frac{2,467}{2} = 1,234 \text{ V}$$

Općenito vrijedi za redoks reakcije jednostavne stehiometrije

[Nakon točke ekvivalencije]

- $V > V_{t.e.}$

$$V_t = 20 \text{ mL}$$

Za računanje potencijala članka koristi se reakcija članka s redoks parom $\text{Ce}^{4+}/\text{Ce}^{3+}$

$$[B_{\text{oksidirani}}] = \frac{(V_t - V_{\text{t.e.}}) \cdot c_t}{V_a + V_t} \quad [B_{\text{reducirani}}] = \frac{V_t \cdot c_t}{V_a + V_t}$$

$$\frac{[B_{\text{reducirani}}]}{[B_{\text{oksidirani}}]} = \frac{\frac{V_t \cdot c_t}{V_a + V_t}}{\frac{(V_t - V_{\text{t.e.}}) \cdot c_t}{V_a + V_t}} = \frac{V_t \cdot c_t}{(V_t - V_{\text{t.e.}}) \cdot c_t} = \frac{V_t}{V_t - V_{\text{t.e.}}}$$

$$\frac{[Ce^{3+}]}{[Ce^{4+}]} = \frac{V_t}{V_t - V_{\text{t.e.}}} = \frac{20 \text{ mL}}{20 \text{ mL} - 15 \text{ mL}}$$

$$\frac{[Ce^{3+}]}{[Ce^{4+}]} = 4$$

$$E_{\text{katode}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^f - \frac{0,0592}{z} \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E_{\text{katode}} = 1,700 - \frac{0,0592}{1} \log 4$$

$$E_{\text{katode}} = 1,664 \text{ V}$$