Analitička kemija
Stručni preddiplomski studij Zaštita i oporaba materijala – seminar, II. dio

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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.

$$N + A \leftrightarrows NA$$

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

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

N – analit

NA – analit u obliku koji se važe

- 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?

$$Ag^+ + Cl^- \rightleftarrows AgCl(s)$$

$$n(Cl^-) = n(AgCl)$$

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

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

Gravimetrijski faktor

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

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

- 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?

$$2FePO_4 \sim Fe_2O_3$$

$$n(\text{Fe, } FePO_4) = 2n(\text{Fe, } Fe_2O_3)$$

$$\frac{m(FePO_4)}{M(FePO_4)} = 2\frac{m(Fe_2O_3)}{M(Fe_2O_3)}$$

$$m(FePO_4) = 2m(Fe_2O_3)\frac{M(FePO_4)}{M(Fe_2O_3)}$$

$$m(FePO_4) = 2 \cdot 1,0855 \frac{150,83 \text{ g mol}^{-1}}{159,70 \text{ g mol}^{-1}} = 2,0504 \text{ g}$$

$$2\mathrm{Fe}^{3+} \sim \mathrm{Fe_2O_3}$$

$$n(\mathrm{Fe}^{3+}) = 2n(\mathrm{Fe},\ \mathrm{Fe_2O_3})$$

$$\frac{m(\mathrm{Fe}^{3+})}{M(\mathrm{Fe}^{3+})} = 2\frac{m(\mathrm{Fe_2O_3})}{M(\mathrm{Fe_2O_3})}$$

$$m(\mathrm{Fe}^{3+}) = 2m(\mathrm{Fe_2O_3})\frac{M(\mathrm{Fe}^{3+})}{M(\mathrm{Fe_2O_3})}$$

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

$$Fe_2O_3 \sim 2FePO_4$$

$$FePO_4 \sim PO_4$$

$$Fe_2O_3 \sim 2PO_4^{3-}$$

$$n(PO_4^{3-}) = 2n(Fe_2O_3)$$

$$\frac{m(PO_4^{3-})}{M(PO_4^{3-})} = 2\frac{m(Fe_2O_3)}{M(Fe_2O_3)}$$

$$m(PO_4^{3-}) = 2m(Fe_2O_3)\frac{M(PO_4^{3-})}{M(Fe_2O_3)}$$

$$m(PO_4^{3-}) = 2m(Fe_2O_3)\frac{M(PO_4^{3-})}{M(Fe_2O_3)}$$

$$m(PO_4^{3-}) = 2 \cdot 1,0855\frac{94,97\ \text{g mol}^{-1}}{159,70\ \text{g mol}^{-1}} = 1,2911\ \text{g}$$

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

$x + y = 0,8400$ g

$Ag^+ + Cl^- \rightleftarrows AgCl(s)$

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

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

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

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

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

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

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

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

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

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

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

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?

$$CaCO_3(s) \xrightarrow{\text{žarenje}} CaO(s) + CO_2(g)$$

$$MgCO_3(s) \xrightarrow{\text{žarenje}} MgO(s) + CO_2(g)$$

Masa oslobođenog CO_2 :

$m(\text{uzorka}) - m(\text{oksida}) = m(CO_2)$

$m(CO_2) = 1,0000 - 0,5000 = 0,5000$ g

$x \equiv$ masa $CaCO_3$; $y \equiv$ masa $MgCO_3$

$x + y = 1,0000$ g

Masa CO_2 iz kalcijevog karbonata :

$n(CO_2) = n(CaCO_3)$

$$\frac{m(CO_2)}{M(CO_2)} = \frac{m(CaCO_3)}{M(CaCO_3)} \Rightarrow m(CO_2) = m(CaCO_3) \cdot \frac{M(CO_2)}{M(CaCO_3)}$$

Masa CO_2 iz magnezijevog karbonata :

$n(CO_2) = n(MgCO_3)$

$$\frac{m(CO_2)}{M(CO_2)} = \frac{m(MgCO_3)}{M(MgCO_3)} \Rightarrow m(CO_2) = m(MgCO_3) \cdot \frac{M(CO_2)}{M(MgCO_3)}$$

$$x \cdot \frac{M(CO_2)}{M(CaCO_3)} + y \cdot \frac{M(CO_2)}{M(MgCO_3)} = 0,5000$$

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

$$x \cdot \frac{M(CO_2)}{M(CaCO_3)} + (1,0000 - x) \cdot \frac{M(CO_2)}{M(MgCO_3)} = 0,5000$$

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

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

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

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

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

$$\omega(CaCO_3) = \frac{0,2664}{1,0000} \cdot 100 = 26,64\%$$

$$\omega(MgCO_3) = \frac{0,7336}{1,0000} \cdot 100 = 73,36\%$$

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 ($0<V<V_{\text{t.e.}}$)
  - Ovisi o neizreagiranom analitu

$$c'_{\text{a}} = \frac{c_{\text{a}} \cdot V_{\text{a}} - c_{\text{t}} \cdot V_{\text{t}}}{V_{\text{a}} + V_{\text{t}}}$$

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

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

- U točki ekvivalencije:
  - Za kiselo-bazne titracije jakih kiselina i baze 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

- Nakon točke ekvivalencije ($V > V_{\text{t.e.}}$)
  - Ovisi o suvišku titranta

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

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.

$$\mathrm{Ag^+ + Cl^- \rightleftarrows AgCl(s)}$$

Izračun volumena točke ekvivalencije:

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

$$c_\mathrm{a} \cdot V_\mathrm{a} = c_\mathrm{t} \cdot V_\mathrm{t} \cdot F$$

$$V_\mathrm{t} = \frac{c_\mathrm{a} \cdot V}{c_\mathrm{t} \cdot F} = \frac{0{,}0100\ \mathrm{mol\ L^{-1}} \cdot 50{,}00\ \mathrm{mL}}{0{,}0100\ \mathrm{mol\ L^{-1}} \cdot 0{,}9901} = 50{,}50\ \mathrm{mL}$$

Prije točke ekvivalencije

- $0 < V < V_{t}$ .e.
  V_t= 5; 25,25 i 50 mL

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

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

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

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

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

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

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

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

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

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

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

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

Drugi način računanja

$$\left[\mathrm{Cl}^-\right] = \frac{V_{\mathrm{t.e.}} - V_{\mathrm{t}}}{V_{\mathrm{t.e.}}} \cdot c_{\mathrm{a}} \cdot \frac{V_{\mathrm{a}}}{V_{\mathrm{a}} + V_{\mathrm{t}}}$$

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

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

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

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

U točki ekvivalencije

$$\left[\mathrm{Cl}^-\right] = \left[\mathrm{Ag}^+\right] = x$$

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

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

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

Nakon točke ekvivalencije

$$\left[\mathrm{Ag}^{+}\right] = c_{\mathrm{t}} \cdot \frac{V_{\mathrm{t}} - V_{\mathrm{t.e.}}}{V_{\mathrm{a}} + V_{\mathrm{t}}}$$

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

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

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

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.

$$\mathrm{H^+(HCl) + OH^-(NaOH) \rightleftarrows H_2O}$$

Izračun volumena točke ekvivalencije:

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

$$c_\mathrm{a} \cdot V_\mathrm{a} = c_\mathrm{t} \cdot V_\mathrm{t}$$

$$V_\mathrm{t} = \frac{c_\mathrm{a} \cdot V_\mathrm{a}}{c_\mathrm{t}} = \frac{0,0150\ \mathrm{mol\ L^{-1}} \cdot 25,00\ \mathrm{mL}}{0,0200\ \mathrm{mol\ L^{-1}}} = 18,75\ \mathrm{mL}$$

Na početku titracije

- V = 0 mL

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

$$c_{\mathrm{a}} = \left[\mathrm{H}^{+}\right] = 0,0150\ \mathrm{mol\ L^{-1}}$$

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

Prije točke ekvivalencije

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

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

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

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

$$c'_{\mathrm{a}} = \frac{c_{\mathrm{a}} \cdot V_{\mathrm{a}} - c_{\mathrm{t}} \cdot V_{\mathrm{t}}}{V_{\mathrm{a}} + V_{\mathrm{t}}} = \frac{0{,}0150\ \mathrm{mol\ L^{-1}} \cdot 25\ \mathrm{mL} - 0{,}0200\ \mathrm{mol\ L^{-1}} \cdot 15\ \mathrm{mL}}{25\ \mathrm{mL} + 15\ \mathrm{mL}} = 0{,}0019\ \mathrm{mol\ L^{-1}}$$

$$c'_{\mathrm{a}} = \left[\mathrm{H^+}\right] = 0{,}0019\ \mathrm{mol\ L^{-1}}$$

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

$$c'_{\mathrm{a}} = \frac{c_{\mathrm{a}} \cdot V_{\mathrm{a}} - c_{\mathrm{t}} \cdot V_{\mathrm{t}}}{V_{\mathrm{a}} + V_{\mathrm{t}}} = \frac{0{,}0150\ \mathrm{mol\ L^{-1}} \cdot 25\ \mathrm{mL} - 0{,}0200\ \mathrm{mol\ L^{-1}} \cdot 18{,}7\ \mathrm{mL}}{25\ \mathrm{mL} + 18{,}7\ \mathrm{mL}} = 2{,}29 \cdot 10^{-5}\ \mathrm{mol\ L^{-1}}$$

$$c'_{\mathrm{a}} = \left[\mathrm{H^+}\right] = 2{,}29 \cdot 10^{-5}\ \mathrm{mol\ L^{-1}}$$

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

Drugi način računanja

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

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

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

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

U točki ekvivalencije

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

$$\left[\mathrm{OH^-}\right] = \left[\mathrm{H^+}\right] = x$$

$$x^2 = K_\mathrm{w} \Rightarrow x = \sqrt{K_\mathrm{w}}$$

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

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

Nakon točke ekvivalencije

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

Vt= 18,75; 20,0 i 25,0 mL

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

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

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

$$\left[\mathrm{H^+}\right] = \frac{K_\mathrm{w}}{\left[\mathrm{OH^-}\right]} = \frac{1,0 \cdot 10^{-14}}{2,28 \cdot 10^{-5}} = 4,38 \cdot 10^{-10}\ \mathrm{mol\ L^{-1}}$$

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

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

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

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

$$\left[\mathrm{H^+}\right] = \frac{K_\mathrm{w}}{\left[\mathrm{OH^-}\right]} = \frac{1,0 \cdot 10^{-14}}{5,56 \cdot 10^{-4}} = 1,82 \cdot 10^{-11}\ \mathrm{mol\ L^{-1}}$$

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

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

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

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

$$\left[\mathrm{H}^+\right] = \frac{K_\mathrm{w}}{\left[\mathrm{OH}^-\right]} = \frac{1,0 \cdot 10^{-14}}{0,0025} = 4,0 \cdot 10^{-12}\ \mathrm{mol\ L^{-1}}$$

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

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.

$$OH^-(KOH) + H^+(HCl) \rightleftarrows H_2O$$

Izračun volumena točke ekvivalencije:

$$n(OH^-) = n(H^+)$$

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

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

Na početku titracije

- V = 0 mL

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

$$c_{\mathrm{a}} = \left[\mathrm{OH}^{-}\right] = 0{,}1500\ \mathrm{mol\ L^{-1}}$$

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

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

Prije točke ekvivalencije

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

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

$$c'_{a} = \left[\text{OH}^-\right] = 0{,}1091\ \text{mol L}^{-1}$$

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

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

$$c'_{\mathrm{a}} = \frac{c_{\mathrm{a}} \cdot V_{\mathrm{a}} - c_{\mathrm{t}} \cdot V_{\mathrm{t}}}{V_{\mathrm{a}} + V_{\mathrm{t}}} = \frac{0{,}1500\ \mathrm{mol\ L^{-1}} \cdot 20\ \mathrm{mL} - 0{,}3000\ \mathrm{mol\ L^{-1}} \cdot 5\ \mathrm{mL}}{20\ \mathrm{mL} + 5\ \mathrm{mL}} = 0{,}0600\ \mathrm{mol\ L^{-1}}$$

$$c'_{\mathrm{a}} = \left[\mathrm{OH^-}\right] = 0{,}0600\ \mathrm{mol\ L^{-1}}$$

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

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

$$c'_{\mathrm{a}} = \frac{c_{\mathrm{a}} \cdot V_{\mathrm{a}} - c_{\mathrm{t}} \cdot V_{\mathrm{t}}}{V_{\mathrm{a}} + V_{\mathrm{t}}} = \frac{0{,}1500\ \mathrm{mol\ L^{-1}} \cdot 20\ \mathrm{mL} - 0{,}3000\ \mathrm{mol\ L^{-1}} \cdot 9{,}95\ \mathrm{mL}}{20\ \mathrm{mL} + 9{,}95\ \mathrm{mL}} = 5{,}01 \cdot 10^{-4}\ \mathrm{mol\ L^{-1}}$$

$$c'_{\mathrm{a}} = \left[\mathrm{OH^-}\right] = 5{,}01 \cdot 10^{-4}\ \mathrm{mol\ L^{-1}}$$

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

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

Drugi način računanja

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

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

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

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

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

U točki ekvivalencije

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

$$\left[\mathrm{OH^-}\right] = \left[\mathrm{H^+}\right] = x$$

$$x^2 = K_\mathrm{w} \Rightarrow x = \sqrt{K_\mathrm{w}}$$

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

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

Nakon točke ekvivalencije

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

Vt= 10,05 i 15,00 mL

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

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

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

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

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

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

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

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

KISELO-BAZNE TITRACIJE
Slaba kiselina

- Izračunajte koncentraciju H^+ kationa i pH prilikom titracije 15,0 mL otopine mravlje kiseline (HCOOH, K_a = $1{,}77\times10^{-4}$) 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.

$$\mathrm{HCOOH} + \mathrm{OH^-(NaOH)} \rightleftarrows \mathrm{H_2O}$$

Izračun volumena točke ekvivalencije:

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

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

$$c_\mathrm{a} \cdot V_\mathrm{a} = c_\mathrm{t} \cdot V_\mathrm{t}$$

$$V_\mathrm{t} = \frac{c_\mathrm{a} \cdot V_\mathrm{a}}{c_\mathrm{t}} = \frac{0{,}1500\ \mathrm{mol\ L^{-1}} \cdot 15{,}00\ \mathrm{mL}}{0{,}1500\ \mathrm{mol\ L^{-1}}} = 15{,}00\ \mathrm{mL}$$

Na početku titracije

- V = 0 mL

$$\begin{array}{ccccc} \mathrm{HA} & \rightleftarrows & \mathrm{H^+} & + & \mathrm{A^-} \\ c-x & & x & & x \end{array}$$

$$K_\mathrm{a} = \frac{x^2}{c-x} \Rightarrow x = \sqrt{K_\mathrm{a} \cdot c}$$

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

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

Prije točke ekvivalencije

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

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

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

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

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

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

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

U točki ekvivalencije

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

$$\begin{array}{ccccccc} \mathrm{A^-} & + & \mathrm{H_2O} & \rightleftarrows & \mathrm{HA} & + & \mathrm{OH^-} \\ c_{\text{kb}} - x & & & & x & & x \end{array}$$

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

$$K = \frac{K_{\text{w}}}{K_{\text{a}}} = K_{\text{b}} = \frac{1 \cdot 10^{-14}}{1{,}77 \cdot 10^{-4}} = 5{,}65 \cdot 10^{-11}$$

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

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

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

Nakon točke ekvivalencije

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

V_t= 15,05 i 20,0 mL

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

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

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

$$\left[\mathrm{H^+}\right] = \frac{K_\mathrm{w}}{\left[\mathrm{OH^-}\right]} = \frac{1{,}0 \cdot 10^{-14}}{2{,}50 \cdot 10^{-4}} = 4{,}01 \cdot 10^{-11}\ \mathrm{mol\ L^{-1}}$$

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

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

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

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

$$\left[\mathrm{H^+}\right] = \frac{K_\mathrm{w}}{\left[\mathrm{OH^-}\right]} = \frac{1{,}0 \cdot 10^{-14}}{0{,}0214} = 4{,}67 \cdot 10^{-13}\ \mathrm{mol\ L^{-1}}$$

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

KISELO-BAZNE TITRACIJE
Slaba baza

- Izračunajte koncentraciju H^+ kationa i pH prilikom titracije 15,0 mL otopine amonijaka (NH_3, $K_b = 1{,}76\times10^{-5}$; $K_a = 5{,}69\cdot10^{-10}$) 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.

$$NH_3 + H^+(HCl) \rightleftarrows NH_4^+$$

Izračun volumena točke ekvivalencije:

$$\frac{n(NH_3)}{n(H^+)} = \frac{1}{1}$$

$$n(NH_3) = n(H^+)$$

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

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

Na početku titracije

- V = 0 mL

$$\underset{}{\mathrm{B}} + \mathrm{H_2O} \rightleftarrows \mathrm{BH^+} + \mathrm{OH^-}$$

$$\underset{c-x}{} \qquad\qquad \underset{x}{} \qquad \underset{x}{}$$

$$K_\mathrm{b} = \frac{x^2}{c-x} \Rightarrow x = \sqrt{K_\mathrm{b} \cdot c}$$

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

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

Prije točke ekvivalencije

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

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

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

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

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

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

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

U točki ekvivalencije

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

$$\begin{array}{ccccc} \mathrm{BH^+} & \rightleftarrows & \mathrm{B} & + & \mathrm{H^+} \\ c_{\text{kk}} - x & & x & & x \end{array}$$

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

$$K = \frac{K_{\text{w}}}{K_{\text{b}}} = K_{\text{a}} = \frac{1 \cdot 10^{-14}}{1{,}76 \cdot 10^{-5}} = 5{,}69 \cdot 10^{-10}$$

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

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

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

Nakon točke ekvivalencije

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

V_t= 15,05 i 20,0 mL

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

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

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

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

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

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

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

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

KOMPLEKSOMETRIJSKE TITRACIJE

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

$$\mathrm{Mg^{2+} + Y^{4-} \rightleftarrows MgY^{2-}}$$

Izračun volumena točke ekvivalencije:

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

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

$$c_\mathrm{a} \cdot V_\mathrm{a} = c_\mathrm{t} \cdot V_\mathrm{t}$$

$$V_\mathrm{t} = \frac{c_\mathrm{a} \cdot V_\mathrm{a}}{c_\mathrm{t}} = \frac{0,2500\ \mathrm{mol\ L^{-1}} \cdot 15,00\ \mathrm{mL}}{0,2500\ \mathrm{mol\ L^{-1}}} = 15,00\ \mathrm{mL}$$

Računanje pMg tijekom titracije

- V_t= 0 mL

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

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

$$\left[\mathrm{Mg}^{2+}\right] = \frac{V_{\mathrm{t.e.}} - V_{\mathrm{t}}}{V_{\mathrm{t.e.}}} \cdot c_{\mathrm{a}} \cdot \frac{V_{\mathrm{a}}}{V_{\mathrm{a}} + V_{\mathrm{t}}}$$

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

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

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

$$\left[\mathrm{Mg}^{2+}\right] = \frac{V_{\text{t.e.}} - V_{\text{t}}}{V_{\text{t.e.}}} \cdot c_{\text{a}} \cdot \frac{V_{\text{a}}}{V_{\text{a}} + V_{\text{t}}}$$

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

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

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

$$\left[\mathrm{Mg}^{2+}\right] = \frac{V_{\text{t.e.}} - V_{\text{t}}}{V_{\text{t.e.}}} \cdot c_{\text{a}} \cdot \frac{V_{\text{a}}}{V_{\text{a}} + V_{\text{t}}}$$

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

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

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

- V_t = 15,0 mL (točka ekvivalencije)

$$\mathrm{MgY^{2-}} \rightleftarrows \mathrm{Mg^{2+}} + \mathrm{Y^{4-}}$$

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

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

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

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

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

Nakon točke ekvivalencije

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

V_t = 15,05 i 20,00 mL

Može se smatrati da je sav metal preveden u kompleks.

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

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

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

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

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

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

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

$$\left[\mathrm{MgY}^{2-}\right] \cong c(\mathrm{Mg}^{2+}) = c_{\mathrm{a}} \cdot \frac{V_{\mathrm{a}}}{V_{\mathrm{a}} + V_{\mathrm{t}}}$$

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

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

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

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

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

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

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 pH = 0, nakon dodatka 5,00; 10,00; 15,00 i 20,00 mL.
- $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ $\quad E^f = + 0{,}767$ V
- $Ce^{4+} + e^- \rightleftarrows Ce^{3+}$ $\quad E^f = + 1{,}700$ V

$$Fe^{2+} + Ce^{4+} \rightleftarrows Fe^{3+} + Ce^{3+}$$

Izračun volumena točke ekvivalencije:

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\frac{\left[\mathrm{Fe}^{2+}\right]}{\left[\mathrm{Fe}^{3+}\right]} = \frac{V_\mathrm{a} \cdot c_\mathrm{a} - V_\mathrm{t} \cdot c_\mathrm{t} \cdot \frac{\mathrm{b}}{\mathrm{a}}}{V_\mathrm{t} \cdot c_\mathrm{t} \cdot \frac{\mathrm{b}}{\mathrm{a}}} = \frac{15\ \mathrm{mL} \cdot 0,2500\ \mathrm{mol\ L^{-1}} - 10\ \mathrm{mL} \cdot 0,2500\ \mathrm{mol\ L^{-1}} \cdot \frac{1}{1}}{10\ \mathrm{mL} \cdot 0,2500\ \mathrm{mol\ L^{-1}} \cdot \frac{1}{1}}$$

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

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

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

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

- V_t = 15,0 mL (točka ekvivalencije)

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

$[Fe^{3+}] = [Ce^{3+}]$; $[Fe^{2+}] = [Ce^{4+}]$

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

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

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

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

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

Obje je jednadžbe potrebno zbrojiti jer nisu poznate: $\left[\text{Fe}^{2+}\right] = \left[\text{Ce}^{3+}\right] = ?$

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

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

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

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

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

Općenito vrijedi za redoks reakcije jednostavne stehiometrije

Nakon točke ekvivalencije

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

  $V_t = 20$ mL

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

$$[\mathrm{B}_{\text{oksidirani}}] = \frac{(V_\mathrm{t} - V_{\text{t.e.}}) \cdot c_\mathrm{t}}{V_\mathrm{a} + V_\mathrm{t}} \qquad [\mathrm{B}_{\text{reducirani}}] = \frac{V_\mathrm{t} \cdot c_\mathrm{t}}{V_\mathrm{a} + V_\mathrm{t}}$$

$$\frac{[\mathrm{B}_{\text{reducirani}}]}{[\mathrm{B}_{\text{oksidirani}}]} = \frac{\dfrac{V_\mathrm{t} \cdot c_\mathrm{t}}{V_\mathrm{a} + V_\mathrm{t}}}{\dfrac{(V_\mathrm{t} - V_{\text{t.e.}}) \cdot c_\mathrm{t}}{V_\mathrm{a} + V_\mathrm{t}}} = \frac{V_\mathrm{t} \cdot c_\mathrm{t}}{(V_\mathrm{t} - V_{\text{t.e.}}) \cdot c_\mathrm{t}} = \frac{V_\mathrm{t}}{V_\mathrm{t} - V_{\text{t.e.}}}$$

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

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

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

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

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