

CHEM-A2250 Fysikaalinen kemia Bio-IT:lle
2. välikoe 14.12.2016
Ratkaisut

1.

$$-\frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_3]}{dt} = k[\text{NO}] \cdot [\text{O}_3]$$

$$[\text{NO}]_0 = [\text{O}_3]_0 \Rightarrow \text{joka hetki } [\text{NO}] = [\text{O}_3] \Rightarrow -\frac{d[\text{O}_3]}{dt} = k[\text{O}_3]^2$$

$$\int_{[\text{O}_3]_0}^{[\text{O}_3]} \frac{d[\text{O}_3]}{[\text{O}_3]^2} = -\int_0^t k dt \Rightarrow \frac{1}{[\text{O}_3]} - \frac{1}{[\text{O}_3]_0} = kt$$

$$[\text{O}_3] = \left(kt + \frac{1}{[\text{O}_3]_0} \right)^{-1} = \left(1,3 \cdot 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \cdot 2,0 \text{ s} + \frac{1}{1 \cdot 10^{-6} \text{ mol dm}^{-3}} \right)^{-1} = 2,8 \cdot 10^{-7} \text{ mol dm}^{-3}$$

2.

K_b :n laskeminen difenyyliliuoksesta:

$$m_{\text{difenyyl}} = \frac{n_{\text{difenyyl}}}{w_{\text{tolueeni}}} = \frac{5,00 \text{ g} / 154 \text{ g mol}^{-1}}{0,100 \text{ kg}}$$

$$\Rightarrow K_b = \frac{\Delta T_{b,\text{difenyyl}}}{m_{\text{difenyyl}}} = \frac{(111,68 - 110,60) \text{ K} \cdot 0,100 \text{ kg}}{(5,00 \text{ g} / 154,21 \text{ g mol}^{-1})} = 3,331 \text{ K kg mol}^{-1}$$

Aineen X moolimassan laskeminen:

$$m_X = \frac{n_X}{w_{\text{tolueeni}}} = \frac{6,00 \text{ g} / M_X}{0,200 \text{ kg}} = \frac{\Delta T_{b,X}}{K_b}$$

$$M_X = \frac{6,00 \text{ g} \cdot K_b}{0,200 \text{ kg} \cdot \Delta T_{b,X}} = \frac{6,00 \text{ g} \cdot 3,331 \text{ K kg mol}^{-1}}{0,200 \text{ kg} \cdot (112,00 - 110,60) \text{ K}} = 71,4 \text{ g mol}^{-1}$$

3.

Tasapaino (Cd+Zn)-sula \Leftrightarrow (Cd+Zn)-höyry

Sulassa $x_{\text{Zn}} = 0,35$ ja $x_{\text{Cd}} = 0,65$

$$\log_{10} \gamma_{\text{Zn}} = 0,38 \cdot 0,65^2 - 0,13 \cdot 0,65^3 = 0,125 \Rightarrow \gamma_{\text{Zn}} = 1,3335$$

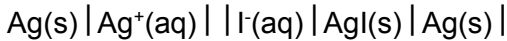
$$\text{Reaaliseos: } a_{\text{Zn}} = \frac{P_{\text{Zn}}}{P_{\text{Zn}}^*} = \gamma_{\text{Zn}} x_{\text{Zn}}$$

$$P_{\text{Zn}} = \gamma_{\text{Zn}} \cdot x_{\text{Zn}} \cdot P_{\text{Zn}}^* = 1,3335 \cdot 0,35 \cdot 3,25 \cdot 10^{-4} \text{ bar} = 1,52 \cdot 10^{-4} \text{ bar}$$

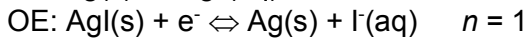
4.

a)

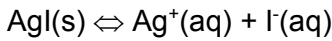
Kennokaavio:



Elektrodireaktiot:



Kennoreaktio:



b)

Kennoreaktiosta

$$\Delta G_{R,m} = \sum_i \nu_i \mu_i = \mu_{\text{Ag}^+}^\circ + RT \ln a_{\text{Ag}^+} + \mu_{\text{I}^-}^\circ + RT \ln a_{\text{I}^-} - \mu_{\text{AgI}}^\circ = \Delta G_{r,m}^\circ + RT \ln(a_{\text{Ag}^+} \cdot a_{\text{I}^-})$$

Sähkökem. tasapainossa $\Delta G_{R,m} = -nFE$ ja $\Delta G_{R,m}^\circ = -nFE^\circ$

\Rightarrow

$$E = E^\circ - \frac{RT}{nF} \ln(a_{\text{Ag}^+} \cdot a_{\text{I}^-})$$

c)

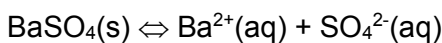
Kemiallisessa tasapainossa $\Delta G_{R,m} = 0$ ja $E = 0$, joten

$$E = E^\circ - \frac{RT}{nF} \ln(a_{\text{Ag}^+} \cdot a_{\text{I}^-})_{\text{eq}} = E^\circ - \frac{RT}{nF} \ln K_{\text{sp}} = 0$$

$$E = E_{\text{OE}}^\circ + (-E_{\text{VE}}^\circ) = -0,1522 \text{ V} + (-0,7991 \text{ V}) = -0,9513 \text{ V}$$

$$K_{\text{sp}} = \exp\left(\frac{nFE^\circ}{RT}\right) = \exp\left(\frac{1 \cdot 96485 \text{ C mol}^{-1} \cdot (-0,9513 \text{ V})}{8,314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K}}\right) = \exp(-37,05) = \mathbf{8,3 \cdot 10^{-17}}$$

5.



BaSO₄:n liukoisuus $c = c_{\text{Ba}^{2+}} = c_{\text{SO}_4^{2-}}$

$$K_{\text{sp}} = a_{\text{Ba}^{2+}} \cdot a_{\text{SO}_4^{2-}} = \left(\frac{\gamma_+ \cdot c_{\text{Ba}^{2+}}}{c^\circ}\right) \cdot \left(\frac{\gamma_- \cdot c_{\text{SO}_4^{2-}}}{c^\circ}\right) = \gamma_{\pm}^2 \cdot \left(\frac{c_{\text{Ba}^{2+}}}{c^\circ}\right) \cdot \left(\frac{c_{\text{SO}_4^{2-}}}{c^\circ}\right) \approx \left(\frac{c_{\text{Ba}^{2+}}}{c^\circ}\right) \cdot \left(\frac{c_{\text{SO}_4^{2-}}}{c^\circ}\right) = \left(\frac{c}{c^\circ}\right)^2$$

$$c = c^\circ \cdot \sqrt{K_{\text{sp}}} = 1 \text{ mol dm}^{-3} \cdot \sqrt{1,10 \cdot 10^{-10}} = 1,049 \cdot 10^{-5} \text{ mol dm}^{-3} = 1,049 \cdot 10^{-2} \text{ mol m}^{-3}$$

$$\Lambda_{m,\text{BaSO}_4}^\circ = (127,26 + 160,04) \text{ S cm}^2 \text{ mol}^{-1} = 287,30 \text{ S cm}^2 \text{ mol}^{-1} = 2,8730 \cdot 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$$

$\kappa = c \cdot \Lambda_m \approx c \cdot \Lambda_m^\circ$ koska liukoisuus pieni

$$\kappa = 1,049 \cdot 10^{-2} \text{ mol m}^{-3} \cdot 2,8730 \cdot 10^{-2} \text{ S m}^2 \text{ mol}^{-1} = \mathbf{3,014 \cdot 10^{-4} \text{ S m}^{-1}}$$