

Obecná chemie

CHEMICKÁ ROVNOVÁHA A ELEKTROCHEMIE

① reakční Gibbsova energie $\Delta_r G$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q \quad Q = \prod_i a_i^{\nu_i}$$

$\Delta_r G^\circ$ $\uparrow$ $\Delta_r G^\circ$
std. aktivitní koef.

stech. koef.
 $\nu_i > 0$ P
 $\nu_i < 0$ R

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

$$\ln Q = \frac{1}{RT} (\Delta_r G - \Delta_r G^\circ)$$

$$Q = \exp\left\{\frac{1}{RT} (\Delta_r G - \Delta_r G^\circ)\right\}$$

$\uparrow$
 $= 0$ pro rovnováhu

$$\Rightarrow K = e^{-\frac{\Delta_r G^\circ}{RT}}$$

$\uparrow$
práva TD rovnovážná konst.

přzn.: $\Delta_r G = \Delta_r G^\circ + RT \ln Q$ odvodíme

$$dG = \sum \mu_i dn_i = \sum \mu_i \left(\frac{dn_i}{d\xi} \right) d\xi$$

$= \nu_i$

reakční
obrat

$$\Delta_r G = \frac{dG}{d\xi} = \sum \mu_i \nu_i = \sum \nu_i (\mu_i^\circ + RT \ln a_i)$$

$\Rightarrow \Delta_r G^\circ$ $\downarrow$
 $RT \ln Q$

$\rightarrow$ závislost na teplotě:

$$\left(\frac{\partial K}{\partial p}\right)_T = 0$$

→ závislost na teplotě:

$$\left(\frac{\partial K}{\partial T}\right)_p \rightarrow \left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{d}{dT}(\ln K) =$$

$$= \frac{d}{dT} \left(-\frac{1}{R} \frac{\Delta G^\circ}{T} \right) =$$

$$= -\frac{1}{R} \frac{d}{dT} \left(\frac{\Delta G^\circ}{T} \right)$$

$$G = H - TS$$

$$\left[\frac{\partial}{\partial T} \left(\frac{G}{T} \right) \right]_p = \frac{\left(\frac{\partial G}{\partial T} \right)_p T - G \cdot 1}{T^2}$$

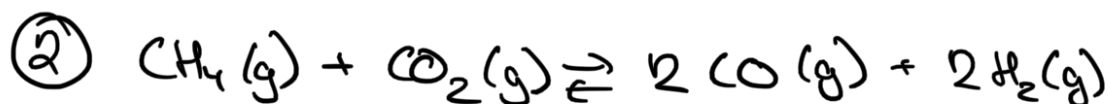
$$= \frac{-ST - H + ST}{T^2} = -\frac{H}{T^2}$$

$$\Rightarrow \frac{\partial \ln K}{\partial T} = + \frac{\Delta_r H}{RT^2}$$

van't Hoff

$$\left[\frac{\partial}{\partial T} \left(\frac{G}{T} \right) \right]_p = -\frac{H}{T^2}$$

Gibbs-Helmholtz



$$n_{\text{CH}_4}/n_{\text{CO}_2} = 1/3 \text{ ne poč.}$$

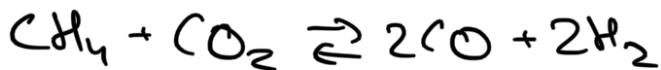
$$T = 1000 \text{ K rovnováha s } x_{\text{H}_2} = 0.29$$

(předpoklad IP)

$$\text{rovnovážná konst. } K = \sum_i a_i^{\nu_i} = \sum_i (f_i x_i)^{\nu_i} = \sum_i f_i^{\nu_i} x_i^{\nu_i}$$

$$a_i = x_i x_i$$

aktivitní koeficient $\gamma_i \rightarrow 1$ pro ideální chování



poc. n $3n$ 0 0

rovn. $n(1-d)$ $3n - nd$ $2dn$ $2dn$

celk. # částic v rovnováze:

$$n_{\text{tot}} = 2n(2+d)$$

$$x_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{tot}}} = \frac{2dn}{2n(2+d)} = \frac{d}{2+d} = 0,29 \Rightarrow \underline{\underline{d = 0,8169}}$$

d = stupeň konverze

reakce proběhla
≈ 81,69%

$$\Rightarrow x_{\text{CH}_4} = 0,0325$$

$$x_{\text{CO}_2} = 0,387$$

$$x_{\text{CO}} = x_{\text{H}_2} = 0,29$$

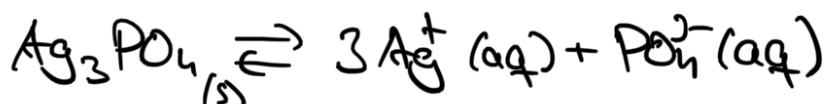
$$\Rightarrow \text{rovnovážná konstanta } K = \frac{x_{\text{H}_2}^2 x_{\text{CO}}^2}{x_{\text{CH}_4} x_{\text{CO}_2}} = \underline{\underline{0,5623}}$$

$\Rightarrow$ std. rx Gibbsova energie

$$\Delta_r G^\circ = -RT \ln K = \underline{\underline{6093 \text{ J}}}$$

③ součin rozpustnosti: $K_s = [\text{K}^+]^k [\text{A}^-]^a$

20 mg Ag_3PO_4 v $3 \text{ dm}^3 \text{ H}_2\text{O}$

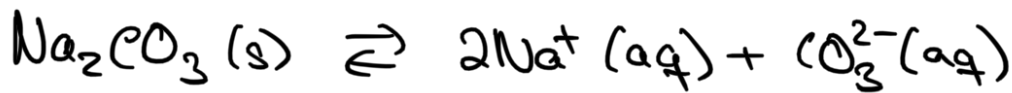


$$K_s = [\text{Ag}^+]^3 [\text{PO}_4^{3-}]^1 = (3c)^3 \cdot c = 27c^4 =$$

$$c_{Ag} = c_{PO_4} \\ c_{Ag} = 3c_{PO_4} = c \\ = 27 \cdot \left(\frac{m}{MV}\right)^4 = \underline{\underline{1,71 \cdot 10^{-18}}}$$

$$\textcircled{4} \quad pH = -\log a_{H^+}$$

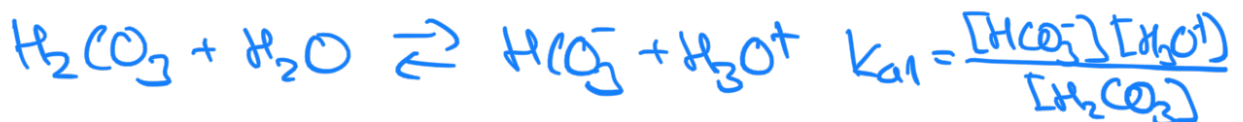
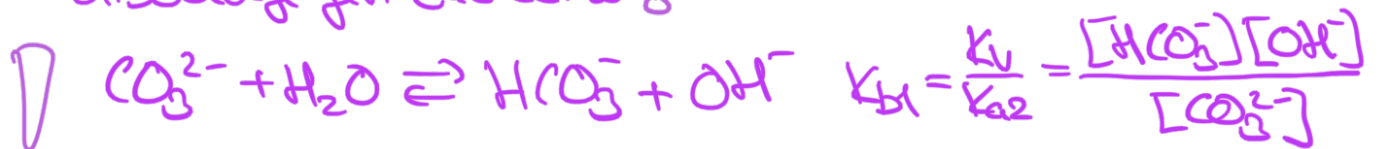
jeďla' soda Na_2CO_3 $c = 2 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$



Na_2CO_3 = sůl slabé kyseliny (H_2CO_3)
a silné zůsady ($NaOH$)

$NaOH \rightarrow Na^+ + OH^-$
disociuje úplně
 $\Rightarrow$ daleko nenúřejme

disociuje jen částečně!



$$K_v = [OH^-][H_3O^+]$$

$$K_{a1} = 4,45 \cdot 10^{-7} \Rightarrow K_{b2} = 2,247 \cdot 10^{-8}$$

$$K_{a2} = 4,69 \cdot 10^{-11} \Rightarrow K_{b1} = 2,132 \cdot 10^{-4}$$

$$K_{a1} \dots \dots \dots$$

$\frac{c_1}{K_{b2}} > 1000 \Rightarrow$ dvojsytnou zásadu budeme
uvážovat jako přibližně
jednotsytnou

$$\Rightarrow \text{pH} = -\log[\text{H}_3\text{O}^+] = 14 + \log[\text{OH}^-] = 14 - \text{pOH}$$

stupeň hydrolyzy γ :

$$[\text{CO}_3^{2-}] = c_r(1-\gamma)$$

$$[\text{HCO}_3^-] = \gamma c_r \Rightarrow [\text{OH}^-] = c_r \cdot \gamma$$

(zanedbáme ionty
vzniklé disociací vody)

$$K_{b1} = \frac{[\text{OH}^-][\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{c_r \gamma^2}{1-\gamma} \approx c_r \gamma^2$$

$$\Rightarrow \underline{\underline{\gamma = \sqrt{\frac{K_{b1}}{c_r}}}}$$

malý stupeň
hydrolyzy

$$\Rightarrow [\text{OH}^-] = c_r \cdot \gamma = \sqrt{c_r \cdot K_{b1}}$$

$$\Rightarrow \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{K_v}{[\text{OH}^-]}\right) =$$

$$= -\log K_v + \log[\text{OH}^-] =$$

$$= -\log K_v + \log \sqrt{c_r \cdot K_{b1}}$$

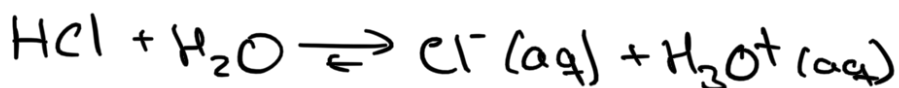
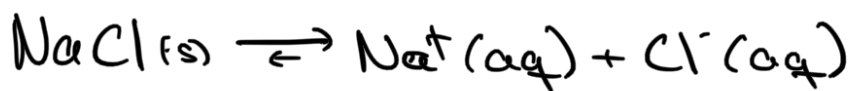
$$= \text{p}K_v - \frac{1}{2} \text{p}K_{b1} - \frac{1}{2} \log c_r = \underline{\underline{11,32}}$$

⑤ 1 dm³ 0,1 mol NaCl + 0,1 mol HCl

NaCl = silná K + silná Z

$\Rightarrow$ úplná disociace

HCl = silná K $\Rightarrow$ úplná disociace



Ⓐ iontovu sílu roztoku neuvažujeme

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (c_{\text{HCl}}) = -\log 0.01 = \underline{\underline{2}}$$

Ⓑ uvažujeme iontovu sílu roztoku

$$I = \frac{1}{2} \sum c_i z_i^2$$

$$I = \frac{1}{2} (\underset{\text{Na}^+}{0.01 \cdot 1^2} + \underset{\text{Cl}^-}{0.01 \cdot 1^2} + \underset{\text{Cl}^-}{0.01 \cdot 1^2}) = 0.01$$

(NaCl) (HCl)

$$\text{pH} = -\log a_{\text{H}_3\text{O}^+}$$

$$a_i = \gamma_i c_i$$

relativní konc.
 $c_r = \frac{c}{c_0}$

aktivitní koef

$$\begin{aligned} -\log \gamma_i &= A z_i \sqrt{I} && \text{pro } z \text{ oděné } \odot \\ -\log \gamma_i &= \frac{A z_i \sqrt{I}}{1 + \sqrt{I}} && \text{pro } I < 0.1 \text{ M} \end{aligned}$$

(I < 0.01 M)

Debye-Hückel

$$A = 0.509 \text{ mol}^{-1/2} \text{ dm}^{3/2} \text{ pro vodu}$$

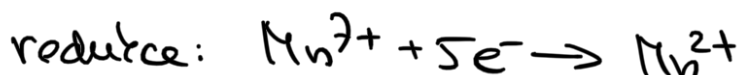
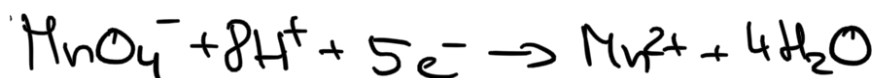
$$\Rightarrow -\log \gamma_{\text{H}_3\text{O}^+} = \frac{0.509 \cdot 1 \cdot \sqrt{0.01}}{1 + \sqrt{0.01}} = 0.1268$$

$$\Rightarrow \dots = 0.21 \dots$$

$$\frac{[\text{H}_3\text{O}^+] = 0,7468}{\text{---}}$$

$$\Rightarrow \text{pH} = -\log(0,7468 \cdot 0,01) = \underline{\underline{2,13}}$$

⑥ měrná Pt elektroda



Nernstova rovnice

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}}$$

↗

el. potenciál

stet. el. pot.

vynechaný el e⁻

definuje vztek mezi

potenciálem bukové elektrody

a aktivitou jejího iontu

v roztoku u jejího povrchu

$$\Rightarrow E = E^0 + \frac{RT}{nF} \ln \frac{[\text{MnO}_4^-][\text{H}_3\text{O}^+]^8}{[\text{Mn}^{2+}]}$$

$$\Rightarrow \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-]} = \exp \left\{ \frac{-nF}{RT} (E - E^0) \right\} \cdot [\text{H}_3\text{O}^+]^8$$

$$= \exp \left\{ -\frac{5 \cdot 96485}{8,314 \cdot 298} (1,32 - 1,51) \right\} \cdot 0,01$$

$$\doteq \underline{\underline{1,17}}$$