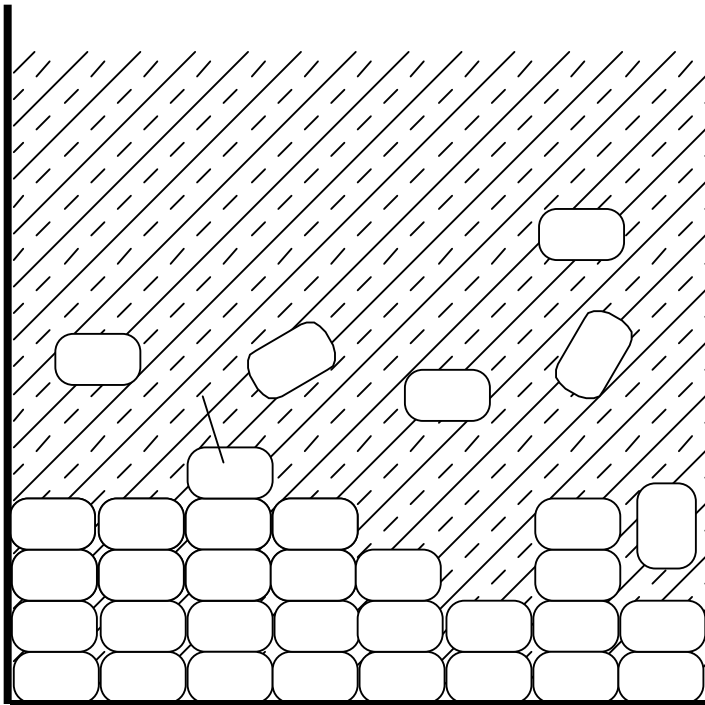
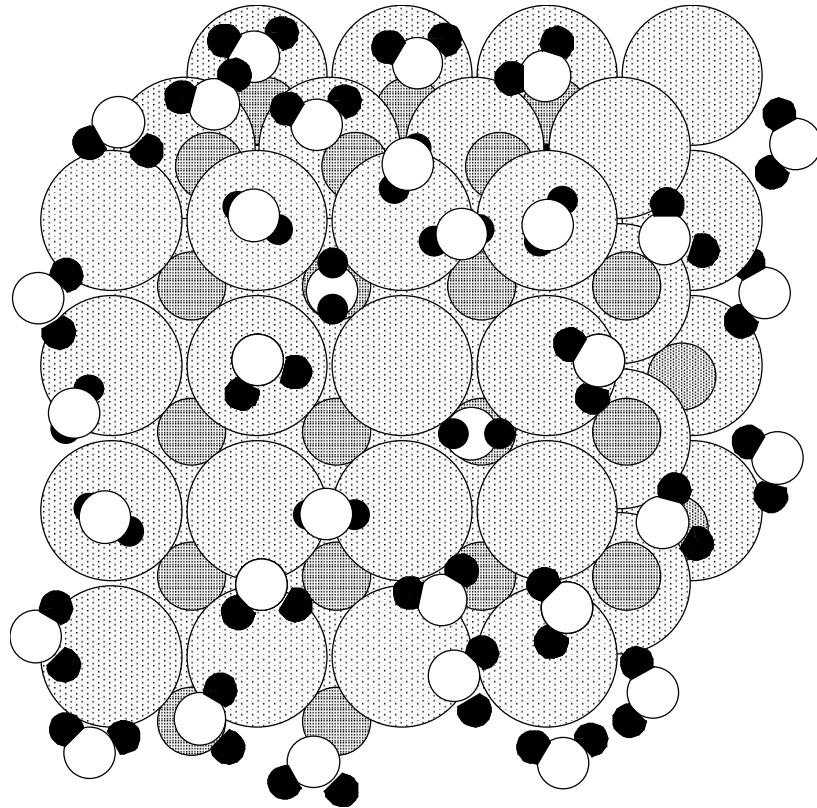


# Auflösung und Fällung

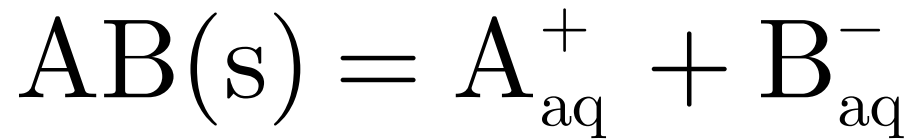


Gleichgewicht zwischen  
Festkörper und gelöstem  
Stoff (bzw. gelösten Ionen)

# Salzkristall AB in Wasser



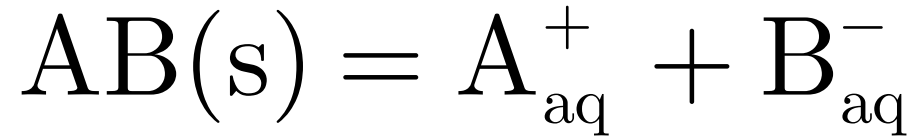
# Auflösen eines Salzes AB(s)



$$K = \frac{a_{\text{A}^{+}} \cdot a_{\text{B}^{-}}}{a_{\text{AB(s)}}}$$

Wir unterscheiden zwischen:

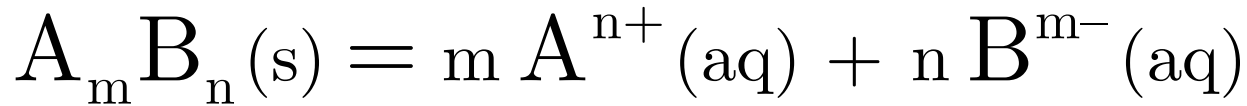
- Thermodynamische Konstante  $K$
- Löslichkeitskonstante  $K_{s0}$
- (Löslichkeitsprodukt  $L$ ,  $Lp$ ,  $K_{sp}$ )



$$K = \frac{a_{\text{A}^{+}} \cdot a_{\text{B}^{-}}}{a_{\text{AB(s)}}}$$

$$K_{\text{s0}} = a_{\text{A}^{+}} \cdot a_{\text{B}^{-}} \approx c_{\text{A}^{+}} \cdot c_{\text{B}^{-}}$$

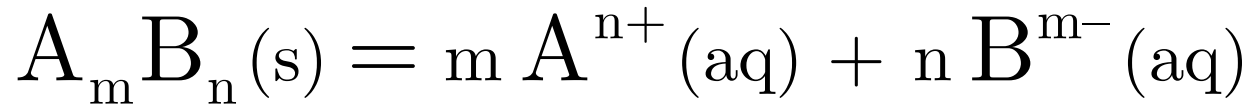
# Auflösen eines Salzes $A_m B_n(s)$



$$K = \frac{\left( a_{A^{n+}(aq)} \right)^m \cdot \left( a_{B^{m-}(aq)} \right)^n}{a_{A_m B_n (s)}}$$

$$K_{s0} = a_{A^{n+}(aq)}^m \cdot a_{B^{m-}(aq)}^n \equiv \left\{ A^{n+} (aq) \right\}^m \cdot \left\{ B^{m-} (aq) \right\}^n$$

# Stöchiometrie:



$$\rightarrow \frac{c_{B_{aq}^{m-}}}{c_{A_{aq}^{n+}}} = \frac{n}{m} \quad c_{B_{aq}^{m-}} = \frac{n}{m} \cdot c_{A_{aq}^{n+}}$$

$$K_{s0} \approx \left( c_{A^{n+}(aq)} \right)^m \cdot \left( c_{B^{m-}(aq)} \right)^n$$

$$\begin{aligned}
K_{s0} &= \left( c_{A_{\text{aq}}}^{\cdot n+} \right)^m \cdot \left( c_{B_{\text{aq}}}^{\cdot m-} \right)^n \\
&= \left( c_{A_{\text{aq}}}^{\cdot n+} \right)^m \cdot \left( \frac{n}{m} \cdot \left( c_{A_{\text{aq}}}^{\cdot n+} \right) \right)^n \\
&= \left( c_{A_{\text{aq}}}^{\cdot n+} \right)^m \cdot \left( c_{A_{\text{aq}}}^{\cdot n+} \right)^n \cdot \left( \frac{n}{m} \right)^n \\
&= \left( c_{A_{\text{aq}}}^{\cdot n+} \right)^{m+n} \cdot \left( \frac{n}{m} \right)^n
\end{aligned}$$

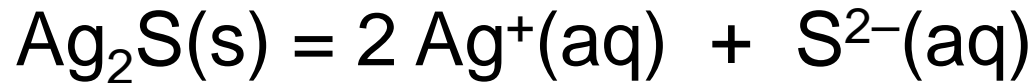
$$K_{s0} = \left( c_{A^{n+}}^{\bullet} \right)^{m+n} \cdot \left( \frac{n}{m} \right)^n$$

$$\left( c_{A^{n+}}^{\bullet} \right)^{m+n} = \frac{K_{s0}}{\left( \frac{n}{m} \right)^n} = K_{s0} \cdot \left( \frac{n}{m} \right)^{-n}$$

$$c_{A^{n+}}^{\bullet} = \sqrt[m+n]{\frac{K_{s0}}{\left( \frac{n}{m} \right)^n}} = \left( \frac{K_{s0}}{\left( \frac{n}{m} \right)^n} \right)^{\frac{1}{m+n}}$$

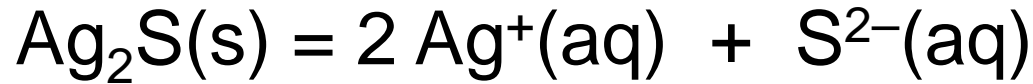
# Lösen von $\text{Ag}_2\text{S}$ in Wasser

Wie viele Silber- bzw. Sulfidionen gibt es in 1L Wasser im Gleichgewicht mit festem  $\text{Ag}_2\text{S}$ ?



$$K_{\text{s0}}(\text{Ag}_2\text{S}) = 5.5 \cdot 10^{-51}$$

$$K_{\text{s0}} = a_{\text{Ag}^+}^2 \cdot a_{\text{S}^{2-}}$$



$$K_{\text{s0}} = a_{\text{Ag}^+}^2 \cdot a_{\text{S}^{2-}} \approx \left( c_{\text{Ag}^+} \right)^2 \cdot c_{\text{S}^{2-}} = \left( c_{\text{Ag}^+} \right)^2 \cdot \frac{c_{\text{Ag}^+}}{2}$$

$$= \frac{\left( c_{\text{Ag}^+} \right)^3}{2}$$

$$\Rightarrow c_{\text{Ag}^+} = \sqrt[3]{2 \cdot K_{\text{s0}}}$$

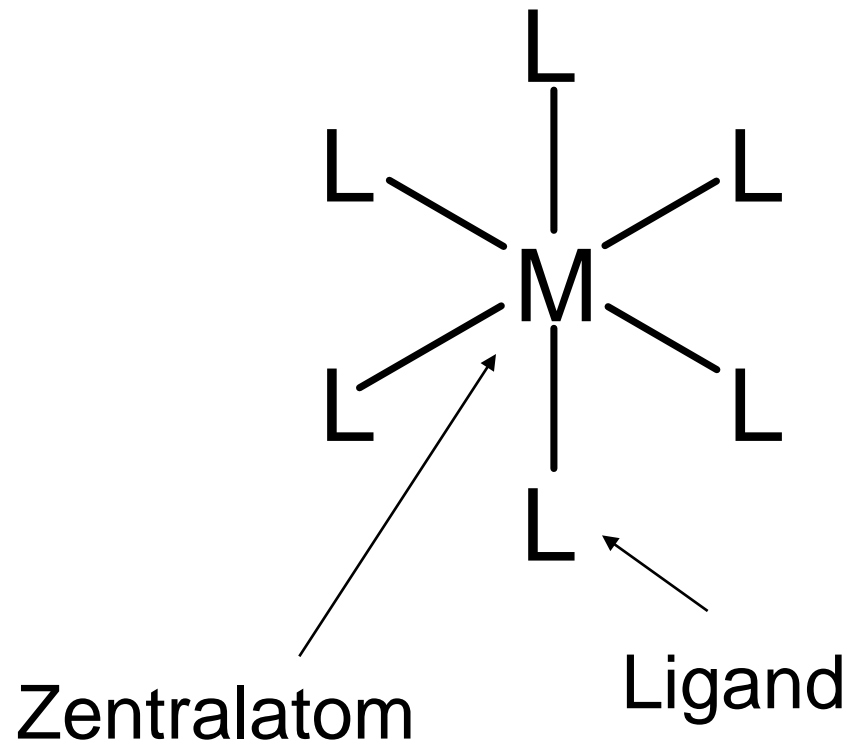
$$c_{\text{Ag}^+} = \sqrt[3]{2 \cdot K_{s0}} = 2.2 \cdot 10^{-17}$$

$$c_{\text{Ag}^+} = 2.2 \cdot 10^{-17} \text{ mol dm}^{-3}$$

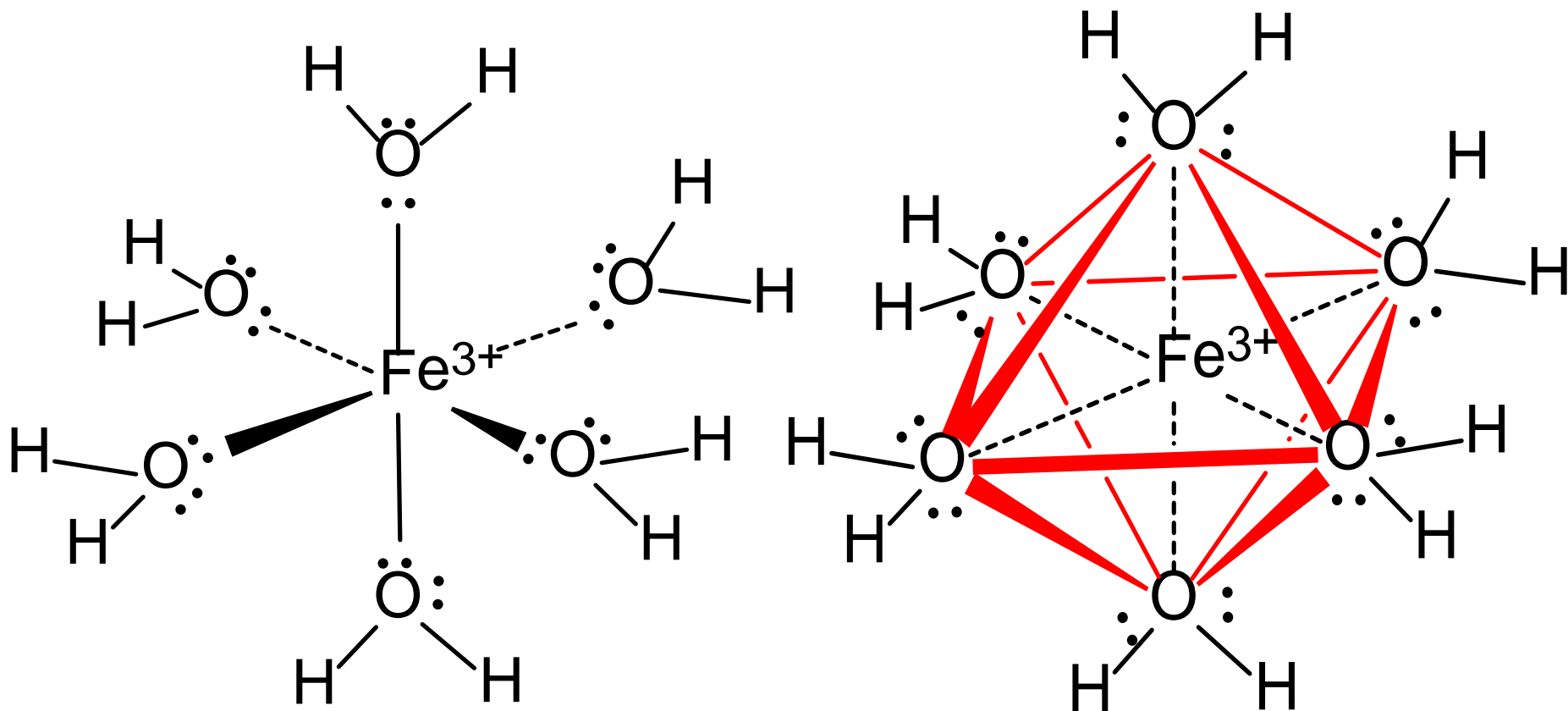
$$\begin{aligned} N_{\text{Ag}^+} &= c_{\text{Ag}^+} \cdot V \cdot N_A \\ &= 2.2 \cdot 10^{-17} \text{ mol dm}^{-3} \cdot 1 \text{ dm}^3 \cdot 6.0 \cdot 10^{23} \text{ mol}^{-1} \\ &= 1.3 \cdot 10^7 \end{aligned}$$

# Komplexgleichgewichte

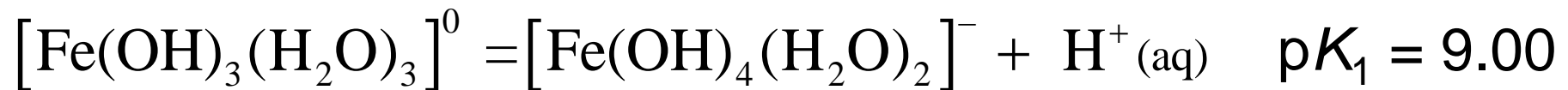
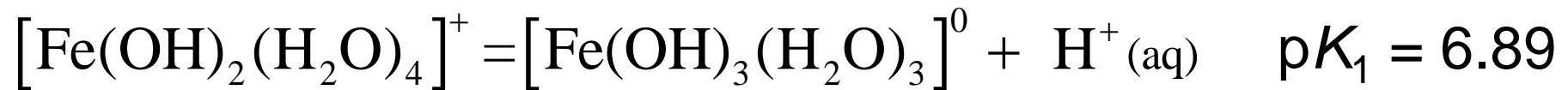
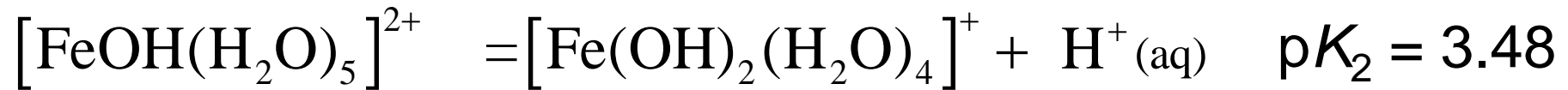
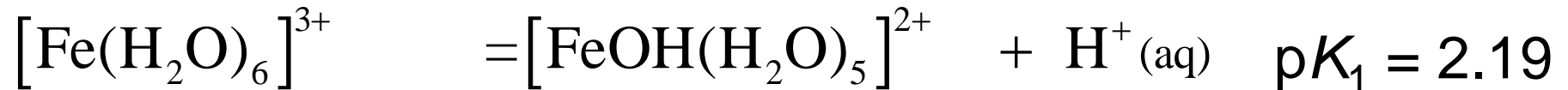
Komplex:



$\text{Fe}^{3+}(\text{aq})$

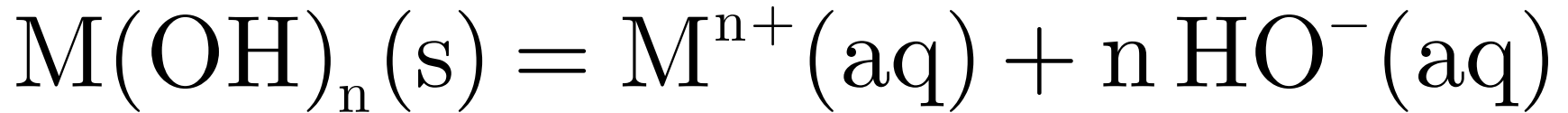


# An Metallionen koordinierte Wassermoleküle können sehr sauer sein



# pH – Abhängigkeit von Fällungen

## Hydroxide (S. 12-18 ff.)



$$K_{s0} = c_{\text{M}^{n+},\text{aq}} \cdot \left( c_{\text{HO}^{-},\text{aq}} \right)^n$$

$$K_{s0} = c_{M^+,aq} \cdot \left( c_{HO^-,aq} \right)^n$$

$$\log K_{s0} = \log c_{M^{n+},aq} + n \cdot \log \left( c_{HO^-,aq} \right)$$

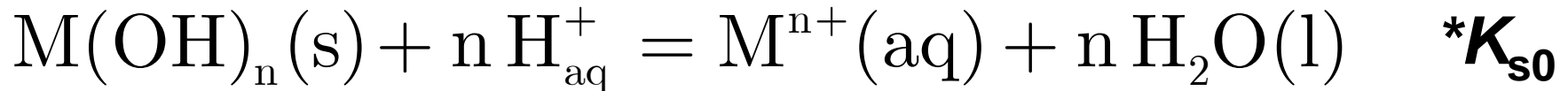
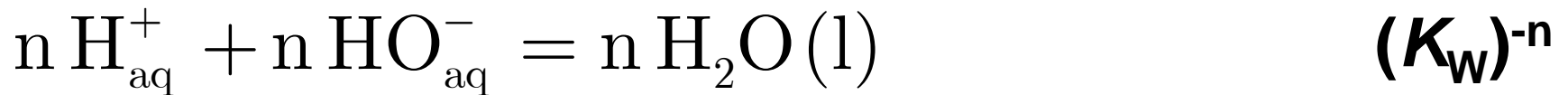
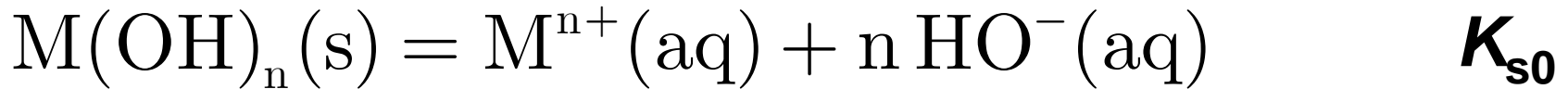
$$= \log c_{M^{n+},aq} + n \cdot \left( \log K_w - \log c_{H^+,aq} \right)$$

$$\log c_{M^{n+},aq} = \underbrace{\log K_{s0} - n \cdot \log K_w}_{\text{pH}} - n \cdot \text{pH}$$

$$:= \log \left( {}^* K_{s0} \right)$$

$$\log \left( {}^*K_{s0} \right) := \log K_{s0} - n \cdot \log K_W$$

$${}^*K_{s0} := \frac{K_{s0}}{\left( K_W \right)^n} \quad {}^*K: \text{Hydrolysekonstante}$$



# Grafische Darstellung

$$\log c_{M^{n+},aq}^{\bullet} = \underbrace{\log K_{s0} - n \cdot \log K_w}_{:= \log \left( {}^*K_{s0} \right)} - n \cdot \text{pH}$$

$$\log c_{M^{n+},aq}^{\bullet} = \log {}^*K_{s0} - n \cdot \text{pH}$$

$$\log {}^*K_{s0} = \log K_{s0} + n \cdot \text{p}K_w$$

$$\log c_{M^{n+},aq}^{\bullet} = \log {}^*K_{s0} - n \cdot \text{pH}$$

$$\frac{d\left(\log c_{M^{n+},aq}^{\bullet}\right)}{d\text{pH}} = 0 - n = -n$$

Beispiel:

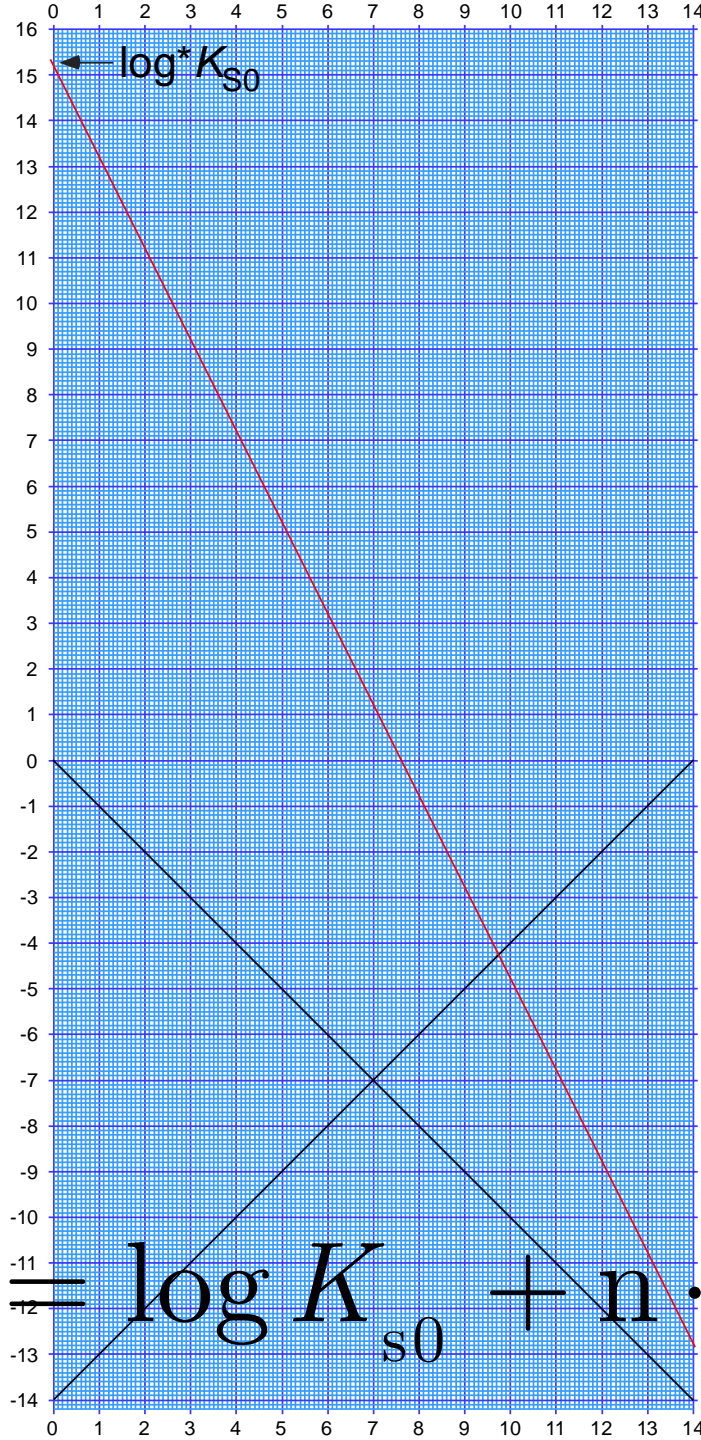


$$\log K_{s0} = -12.8$$

$$\log^* K_{s0} = 15.2$$

Steigung:  $-2$

$$\log^* K_{s0} = \log K_{s0} + n \cdot \text{p}K_w$$



**Schnittpunkt der Geraden  $\log c_{M^{n+}}^\bullet$  mit der Geraden  $\log c_{HO^-}^\bullet$ .**

$$\log c_{M^{n+}}^\bullet = \log c_{HO^-}^\bullet \quad \rightarrow \quad c_{M^{n+}}^\bullet = c_{HO^-}^\bullet$$

$$c_{M^{n+}}^\bullet \cdot \left( c_{HO^-}^\bullet \right)^n = K_{s0} \quad \left( c_{M^{n+}}^\bullet \right)^{n+1} = K_{s0}$$

$$\log \left( c_{M^{n+}}^\bullet \right) = \frac{1}{n+1} \cdot \log K_{s0}$$

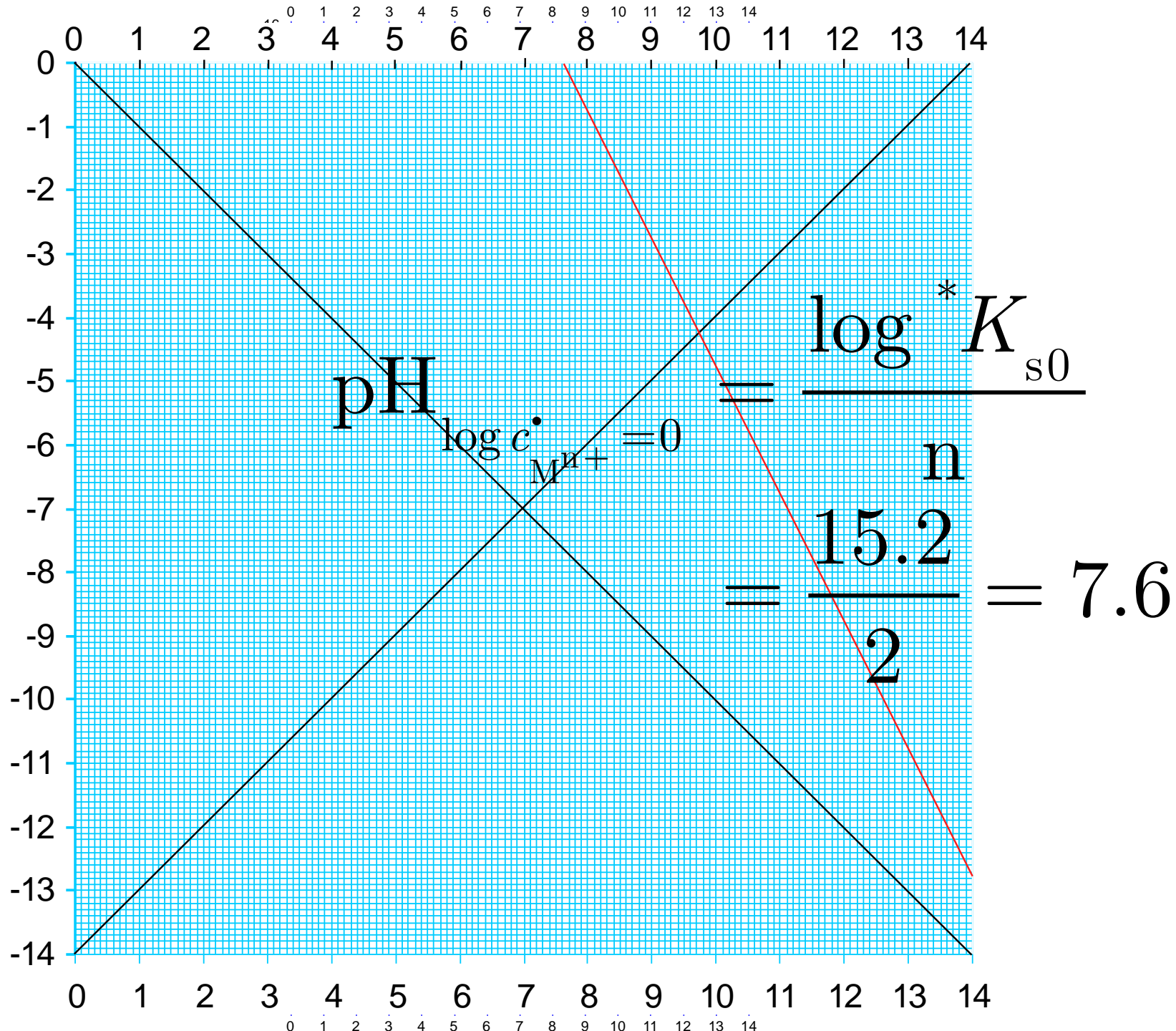
# pH bei $\log c_{M^{n+}}^{\bullet} = 0$

(Zeichnungshilfe für Grafik)

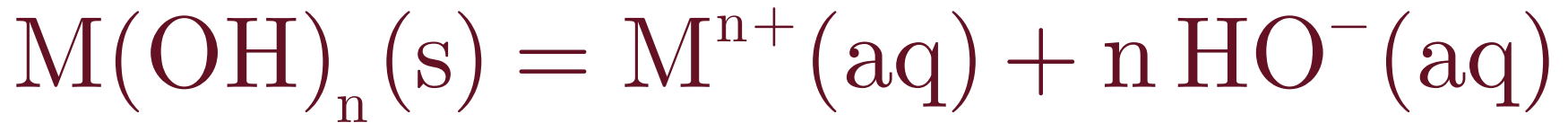
$$\log c_{M^{n+},aq}^{\bullet} = \log {}^*K_{s0} - n \cdot \text{pH}$$

$$0 = \log {}^*K_{s0} - n \cdot \text{pH}$$

$$\text{pH}_{\log c_{M^{n+}}^{\bullet} = 0} = \frac{\log {}^*K_{s0}}{n}$$

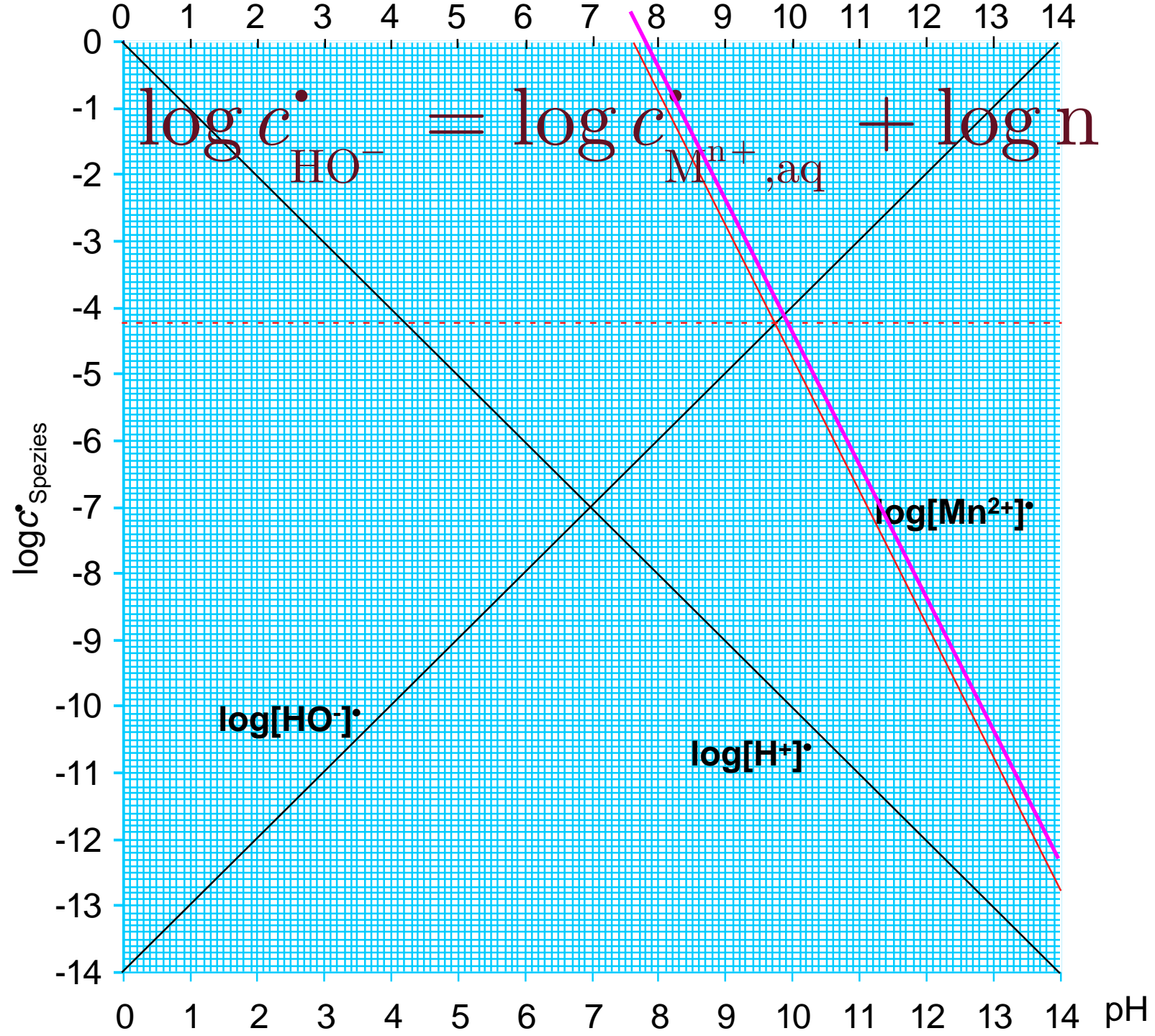


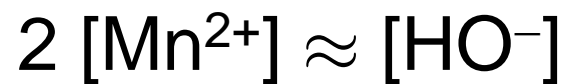
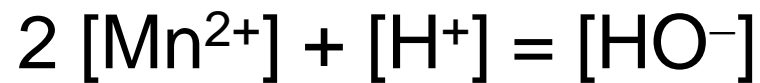
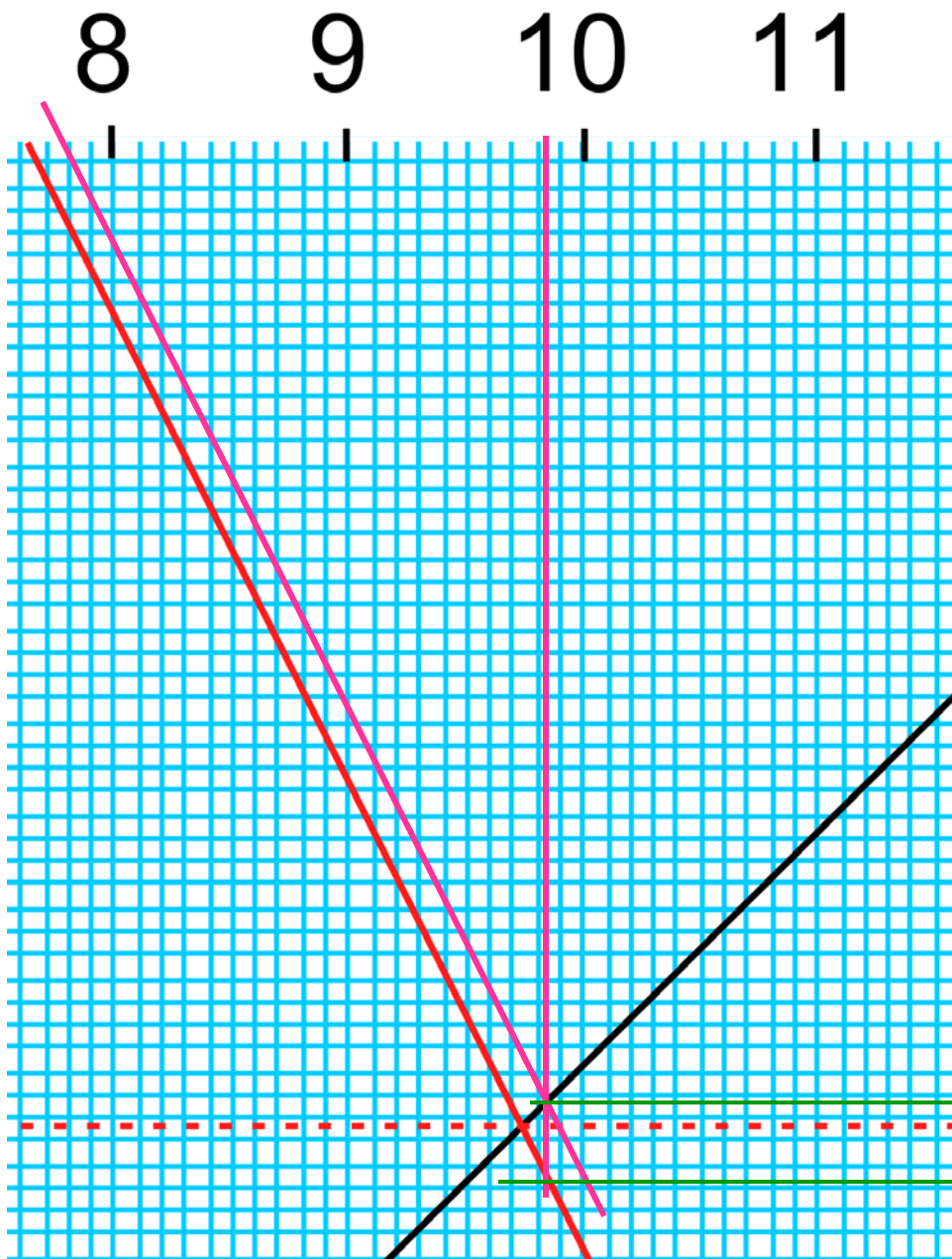
# Ermittlung des Gleichgewichtspunktes



$$c_{\text{HO}^-}^{\bullet} = n \cdot c_{\text{M}^{n+},\text{aq}}^{\bullet}$$

$$\log c_{\text{HO}^-}^{\bullet} = \log c_{\text{M}^{n+},\text{aq}}^{\bullet} + \log n$$

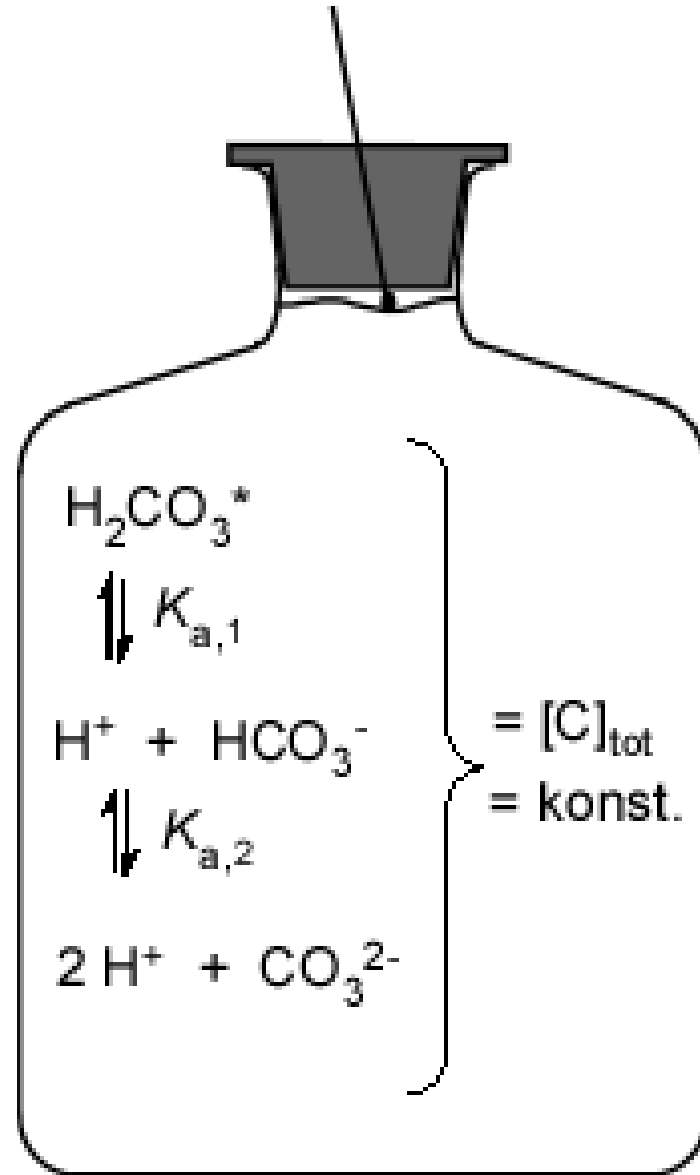


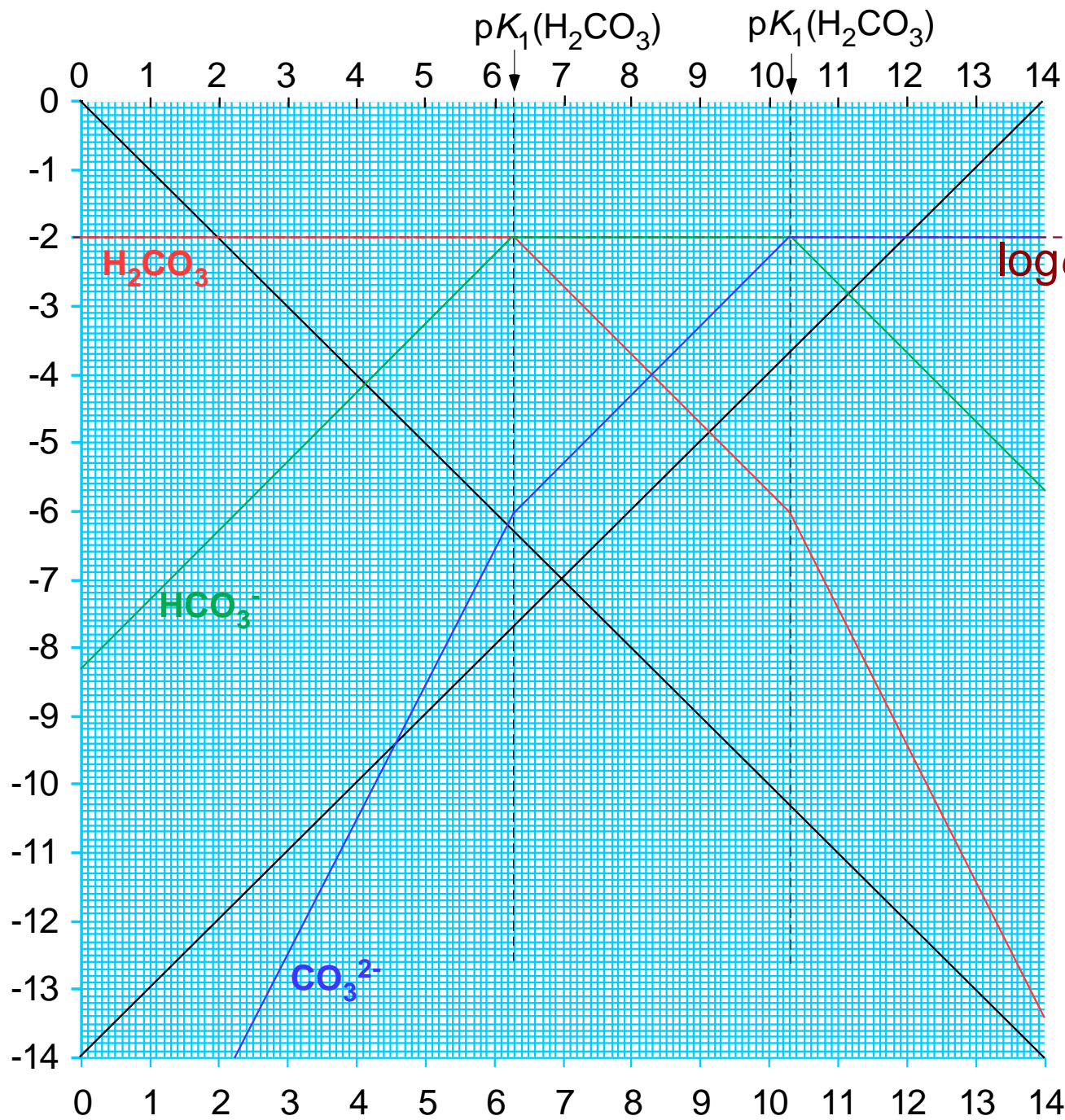


**pH  $\approx$  9.8**

0.3 (log 2)

Gasphase  
(wird vernachlässigt)





$c_T = 10^{-2} \text{ M}$

$\log c_T$

Geschlossenes Kohlen-säuresystem

$\text{H}_2\text{CO}_3^*$

$\text{HCO}_3^-$

$\text{CO}_3^{2-}$

# Löslichkeit von Carbonaten im geschlossenen System



$$K(T) = \frac{a_{\text{M}^{2+},aq} \cdot a_{\text{CO}_3^{2-}}}{a_{\text{CaCO}_3,s}}$$

$$K_{s0}(T) = c_{\text{M}^{2+}} \cdot c_{\text{CO}_3^{2-}}$$

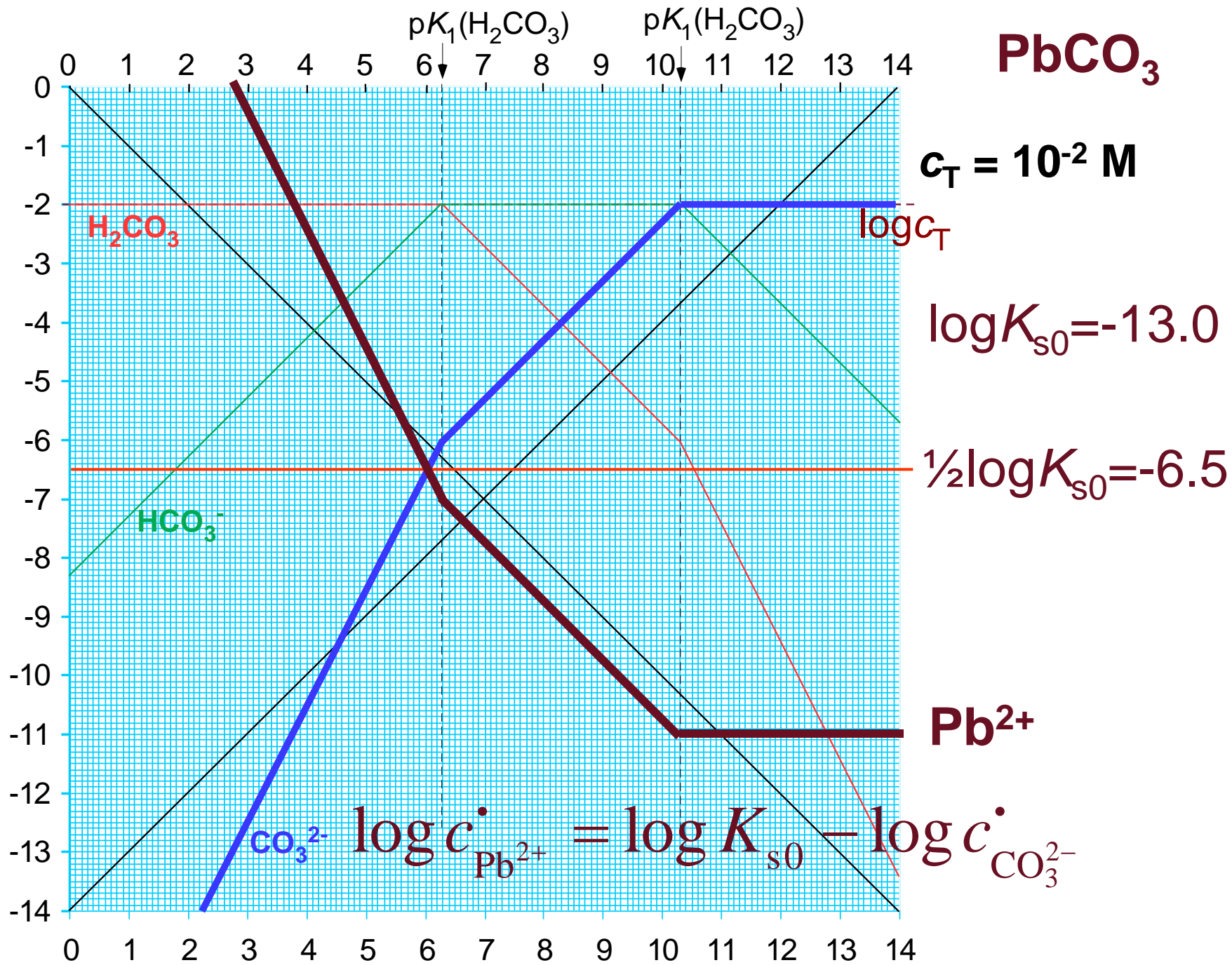
$$K_{s0}(T) = c_{M^{2+}}^{\cdot} \cdot c_{CO_3^{2-}}^{\cdot}$$

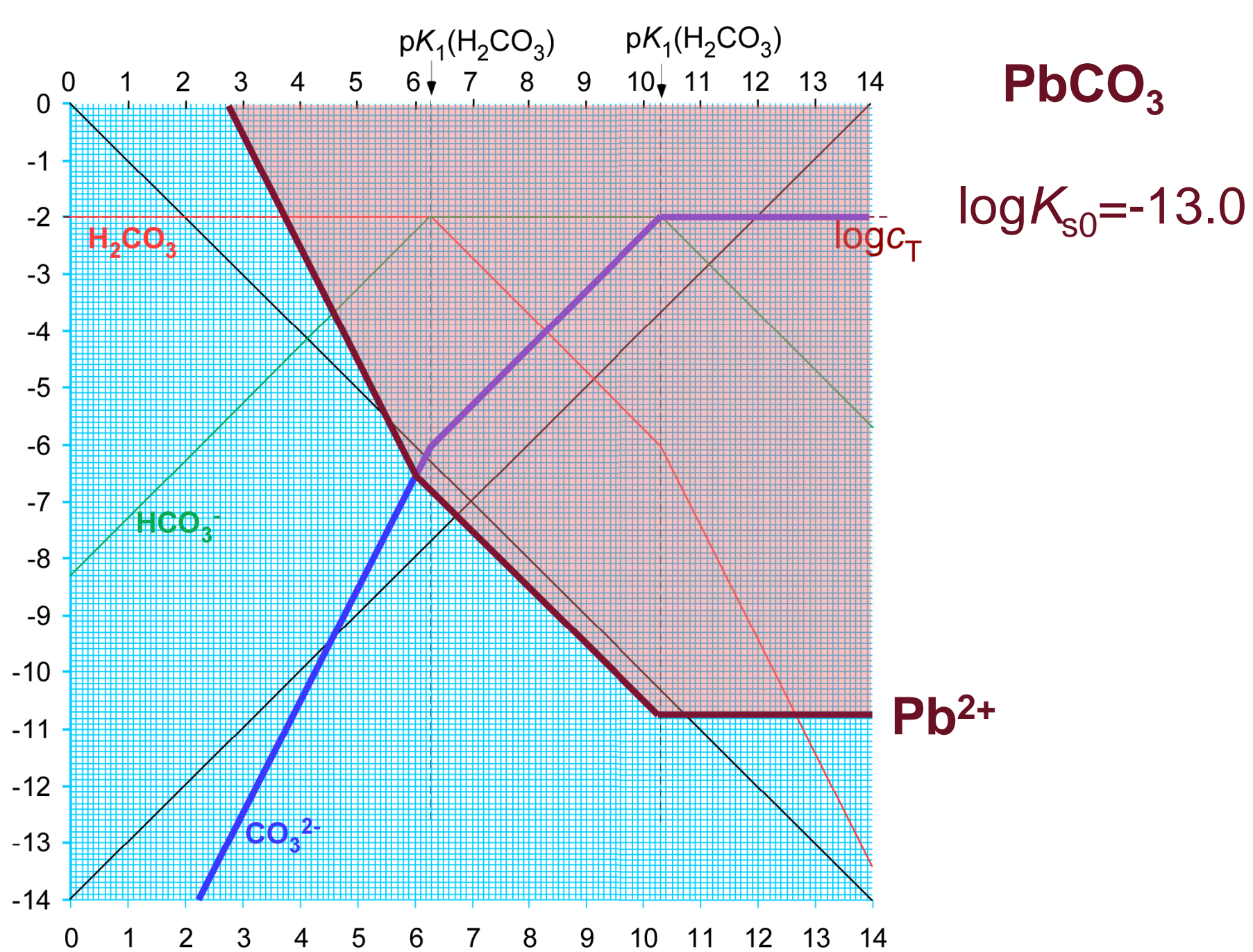
$$\log c_{M^{2+}}^{\cdot} = \log K_{s0} - \log c_{CO_3^{2-}}^{\cdot}$$


Beide Konzentrationen sind Funktionen des pH  
Die Steigungen sind immer entgegengesetzt gleich!

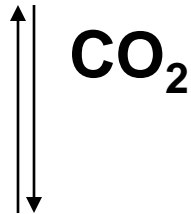
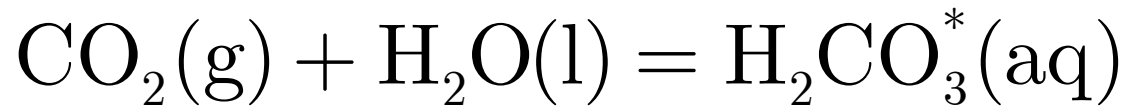
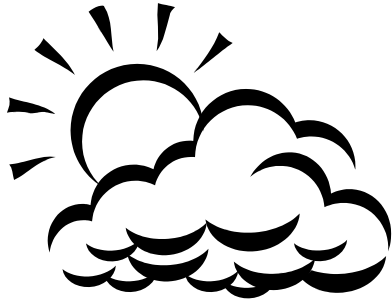
Der Schnittpunkt der beiden Funktionen liegt bei:

$$\log c_{M^{2+}}^{\cdot} = \log c_{CO_3^{2-}}^{\cdot} = \frac{1}{2} \log K_{s0}$$

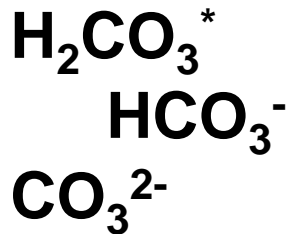




# Das offene Kohlensäure-System



$$K_{\text{H}} = \frac{c_{\text{H}_2\text{CO}_3^*, \text{aq}}}{p_{\text{CO}_2}}$$



$$\log K_{\text{H}} = -1.47$$

$p_{\text{CO}_2}$  beträgt ca.  $3.8 \cdot 10^{-4}$  bar

$$\begin{aligned} \rightarrow c_{\text{H}_2\text{CO}_3,\text{aq}} &= K_{\text{H}} \cdot p_{\text{CO}_2} \\ &= 10^{-1.47} \cdot 3.8 \cdot 10^{-4} = 1.3 \cdot 10^{-5} \end{aligned}$$

$$\log c_{\text{H}_2\text{CO}_3,\text{aq}} = -4.89$$

$\rightarrow c_{\text{H}_2\text{CO}_3,\text{aq}}$  ist konstant!

