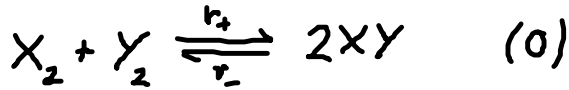


## 8.2 Chem. Reaktionen

• ...

• komplexe GG & Kinetik:

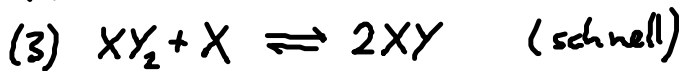
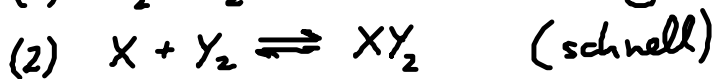
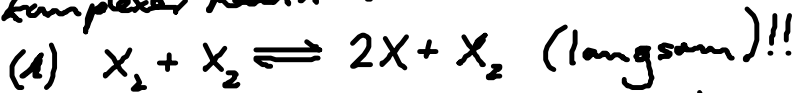


(i) naive Kinetik:

$$r_+ = k_+ c_{X_2} c_{Y_2} \stackrel{GG}{=} r_- = k_- (c_{XY})^2 \implies \frac{(c_{XY})^2}{c_{X_2} c_{Y_2}} = \frac{k_+}{k_-} \triangleq MWG$$

(ii) real:  $r_+ \sim (c_{X_2})^2 (c_{Y_2})^0$

Lsg: komplexer Reaktionsmechanismus



aber:  $MWG(0) = MWG(1) \times MWG(2) \times MWG(3) \dots$  im GG sind Details nicht wichtig

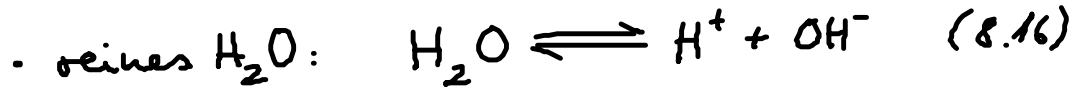
•  $c$  (Biomoleküle)  $\neq$  GG  $\rightarrow$  Kinetik ist wichtig  $\infty$

## 8.3 Dissoziation

• Elektro negativität:  $Cl + e^- \rightarrow Cl^-$ ,  $Na^+ Cl^- \hat{=} \text{Dipol}$ ,  $qU = \frac{e^2}{4\pi\epsilon_0 d}$   
in  $H_2O$ :  $\epsilon = 81 \rightarrow qU \approx \text{einige } k_B T \rightarrow \text{freie Ionen, wegen } d \gg 0$   
 $d \approx 0.3 \text{ nm}$   $200 k_B T$

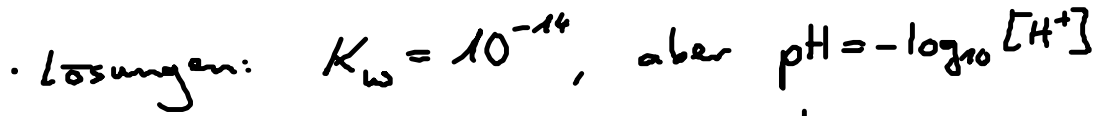
• polare Moleküle:  $-OH \dots$  Hydroxyl-Gruppe } gut löslich in  $H_2O$   
 $-NH_2 \dots$  Amino-Gruppe }

### 8.3.1 Säuren & Basen

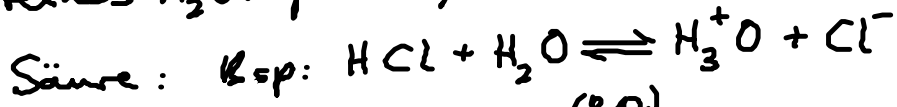


$$\left. \begin{array}{l} c_{H^+} = c_{OH^-} = 10^{-7} M \\ c_{H_2O} = 55 M = \text{const.} \end{array} \right\} \text{MWG: } K_w = [H^+][OH^-] = (10^{-7})^2 \text{ (8.17)}$$

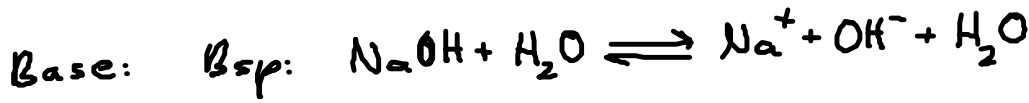
... Ionenprodukt von  $H_2O$



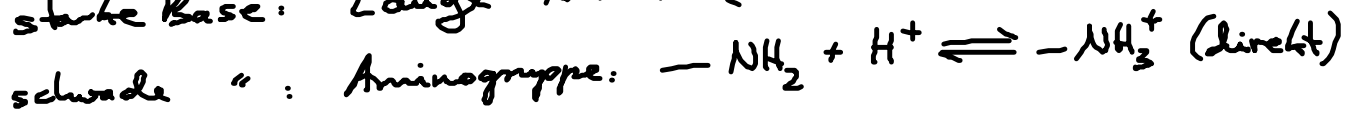
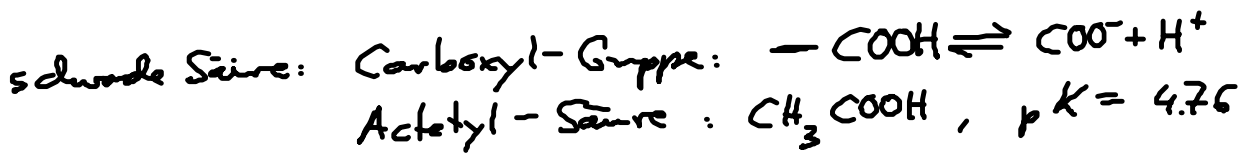
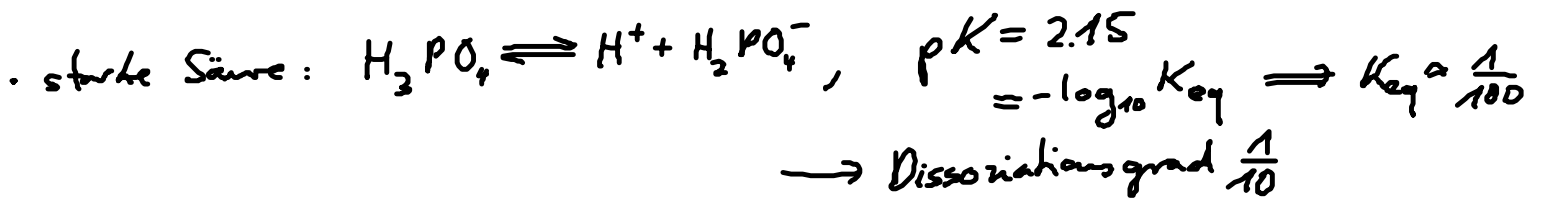
reines  $H_2O$ :  $pH = 7$ , neutral



$$[H^+] \uparrow \xrightarrow{(8.17)} [OH^-] \downarrow, \quad pH < 7$$



$$[OH^-] \uparrow \rightarrow [H^+] \downarrow, \quad pH > 7$$

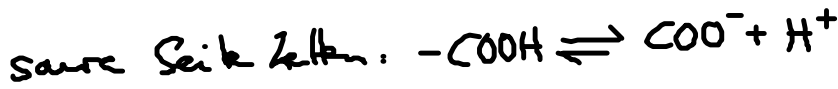


• Neutralisation

### 8.3.2 Proteinladung $\leftrightarrow$ pH

• Protein = Polypeptid: [Folien]

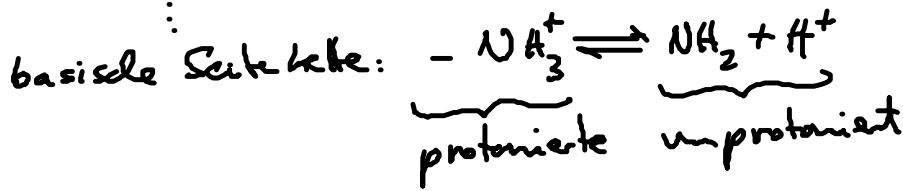
Aminosäuren - Seitenkette  $\alpha$ :  $\left. \begin{array}{l} - \text{Ww unbrecher} \\ - \text{mit } H_2O \end{array} \right\} \rightarrow \text{Protein-faltung}$



$$K_{eq, \alpha} = 10^{-4.4}$$

$$\vdots$$

$$10^{-12}$$



• Wahrscheinlichkeit für Protonierung: z.B.  $P_\alpha = \frac{[-COOH]}{[-COOH] + [-COO^-]}$

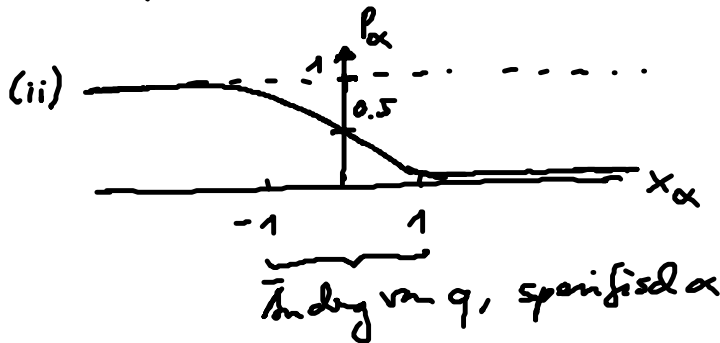
MWG:  $\frac{[-COO^-][H^+]}{[-COOH]} = K_{eq, \alpha}$

$$P_\alpha = \frac{1}{1 + K_{eq, \alpha} / [H^+]} + \frac{1}{1 + 10^{x_\alpha}} \quad , \quad x_\alpha = pH - pK_\alpha \quad (8.18)$$

(i) Ladung  $q$  auf sauren  $\alpha$ :  $(-e)(1 - P_\alpha)$

    "    "    "    basische  $\alpha$ :  $e P_\alpha$

}  $q \downarrow$  für  $pH \uparrow$



• Titration von Proteinlösungen: ... spezifisch für jedes Protein

### 8.3.3 Elektrophorese $\leftrightarrow$ Protein-Komposition

• Salzlösung:  $v_\alpha = \frac{1}{\mu} q E$  , Mobilität:  $\mu = \frac{1}{\gamma} = \frac{1}{6\pi\eta a}$

• Makroion = globuläres Protein:  $q\mu < 0, 0, > 0$  je nach  $pH!$

→ keine Protein(varianten)

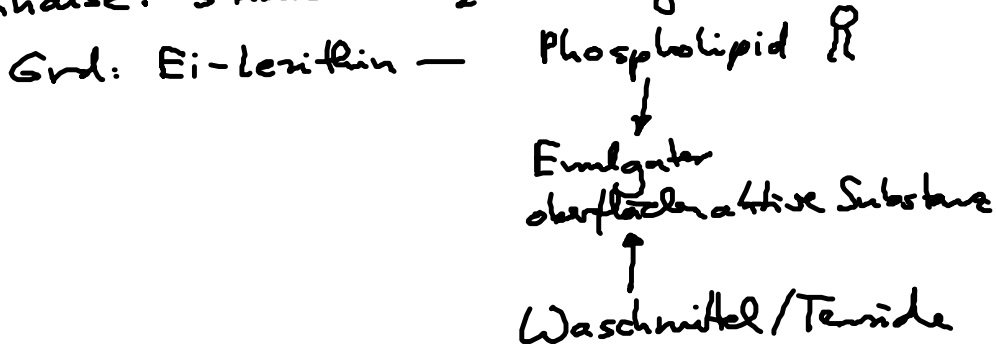
• Bsp: L. Pauling et al. 1949: Sichelzellen-Anämie

Folie

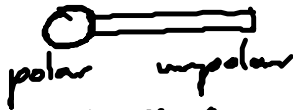
## 8.4 Selbstaggregation von Amphiphilen

- fundamentales Bauprinzip in Zelle
- hydrophober Effekt  $\leftrightarrow$  entropischer Natur
- Öl-H<sub>2</sub>O - Phasenseparation

Mayonnaise: stabile Öl-H<sub>2</sub>O-Mischung



$\Rightarrow$  amphiphile Moleküle:



$\rightarrow$  reduzieren Öl-H<sub>2</sub>O-Oberflächenspannung

$\rightarrow$  Mizelbildung  $\rightarrow$  Emulsionen

Anwendg: Reinigung

- Amphiphile in H<sub>2</sub>O  $\rightarrow$  monodisperse Mizellen
  - ↑
  - Geometrie
  - ↑
  - hydrophob. Effekt
- Mc Bain (1913): Mizellen existieren (session chair: „nonsense“)

• Theorie: Annahme: (1)  $K^+ \text{Oleat}^- \rightarrow K^+ + \text{Oleat}^-$

(2)  $N$  Monomere ( $\text{Oleat}^-$ )  $\rightleftharpoons$  1 Mizelle

$$\text{MWG: } \frac{c_N}{(c_1)^N} = \hat{K}_{eq} \quad (8.19)$$

$$c_{\text{tot}}(\text{Monomere}) = c_1 + N c_N \quad (8.20)$$

$\hat{=}$  2-Parameter-Modell ( $N, \hat{K}_{eq}$ )

$\xrightarrow{(8.19) \text{ in } (8.20)}$

$$c_{\text{tot}} = c_1 (1 + N \hat{K}_{eq} c_1^{N-1}) \quad (8.21)$$

führe ein: krit. Mizellenkonz.  $c_*$ :

$$c_* = c_{tot} \text{ so daß } c_{1*} = \frac{1}{2} c_* = N c_{N*} \xrightarrow{(8.19)} N K_{eq}^1 = \left(\frac{2}{c_*}\right)^{N-1}$$

$$\longrightarrow \boxed{c_{tot} = c_1 \left[ 1 + \left(\frac{2c_1}{c_*}\right)^{N-1} \right]} \quad (8.22)$$

$$c_1 \ll c_* : c_{tot} \approx c_1$$

$$c_1 \gg c_* : c_{tot} \approx N c_N$$

rel. osm. Druck:

$$\frac{p_{osm}}{2 c_{tot} k_B T} = \frac{c_{tot} + c_1 + c_N}{2 c_{tot}} \xrightarrow{(8.22)} \frac{1}{2} \left( 1 + \frac{1 + N^{-1} \left(\frac{2c_1}{c_*}\right)^{N-1}}{1 + \left(\frac{2c_1}{c_*}\right)^{N-1}} \right) \quad (8.23)$$

2 Fitparameter:  $N, c^*$

$$c = c_1 + N c_N \xrightarrow{(8.22)} c(c_1) \longrightarrow (8.23)$$

$\implies$  „scharfer“ Mizellen-Übergang  $\longleftrightarrow$  Kooperation: geometr. Packung bevorzugt ein  $N$

• weitere Verfeinerung nötig!