V8

28.5.2019

Note Title

WDH / Ergänzung

* Bromierung mit Licht: $Br_2 \xrightarrow{I} Br\cdot + Br\cdot$

$[I] = \frac{\text{Einstein}}{L \cdot s}$

$\Rightarrow v_{Start} = \frac{1}{2}[Br\cdot]' = I$

thermisch: $[HBr]' \sim \sqrt{k_1 \cdot [Br_2]}^{1/2}$

photochemisch: $[HBr]' \sim \sqrt{\frac{I}{k_{-1}}}$

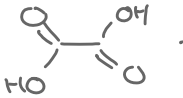
* Trauzsdorf - Norrish - Effekt

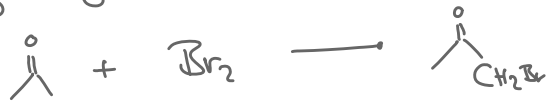
9. Katalyse

Rückblick: Autokatalyse / Inhibition

bspw. (1) $CH_3COH \xrightarrow{\Delta}$

(2) $[HBr]'$ $(t>0, [HBr]>0) \sim \frac{\nearrow}{[HBr]}$

(3)  + MnO_4^-, katalysiert durch Mn^{2+}

(4) 

$[\text{Keton}]' = k \cdot [\text{Keton}] \cdot [H^+]$

A. Lauszen (Metall/Halogenidionen)

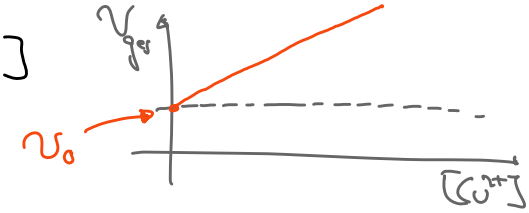
$V^{3+} + Fe^{3+} \xrightarrow[(aq)]{k_0} V^{4+} + Fe^{2+}$ $\quad v_0 = k_0 [V^{3+}][Fe^{3+}]$

Cu^{2+}-Katalyse: (i) $V^{3+} + Cu^{2+} \rightarrow V^{4+} + Cu^{+}$

(ii) $Fe^{3+} + Cu^{+} \rightarrow Fe^{2+} + Cu^{2+}$

$v_{Kat} = k_1 [V^{3+}][Cu^{2+}] \Rightarrow v_{Kat} = k_{Kat} \cdot [V^{3+}]$ / $[Cu^{2+}] = \text{const}$

gesamt: $v_{ges} = k_0 [Fe^{3+}][V^{3+}] + k_{Kat}[V^{3+}]$



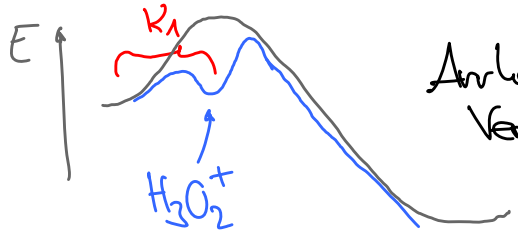
Bsp #2:

$H^+ + H_2O_2 \overset{K_1}{\rightleftharpoons} H_3O_2^+$ (1)

$H_3O_2^+ + Br^- \longrightarrow HO-Br + H_2O$ (2)

$HO-Br + H_2O_2 \longrightarrow H^+ + H_2O + Br^- + O_2$ (3)

$v_p \sim [H_2O_2][H^+][Br^-]$



Arrhenius-Verlauf

Säure/Base-Katalyse

$A \xrightarrow{k_0} P \qquad v_0 = k_0[A]$

$v_{pot} = v_0 + k_{H^+}[A][H^+]$

H^+-Katalyse: (OH^- — ") $\quad (k_{OH^-}[A][OH^-])$

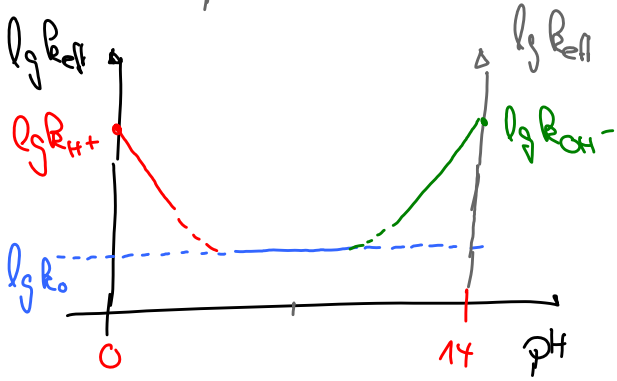
$K_W = [H^+][OH^-]$

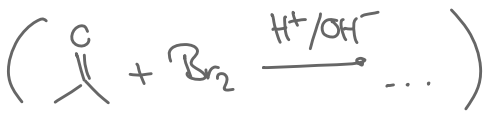
$\rightarrow v_p = \left(k_0 + k_{H^+}[H^+] + k_{OH^-}\cdot\frac{K_W}{[H^+]}\right)[A]$

$=: k_{eff}([H^+])$

$\rightarrow [H^+]\uparrow : \lg k_{eff} \sim \lg k_{H^+} - pH$

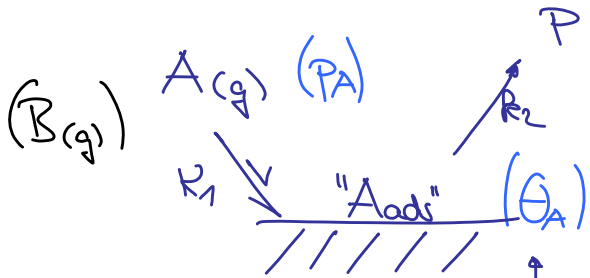
$\rightarrow [OH^-]\uparrow : \lg k_{eff} \sim \lg(k_{OH}\cdot K_W) + pH$





3. Heterogene Katalyse

$\theta_A = \frac{K_A p_A}{1 + K_A p_A}$



$p_A = \text{const}$

$\Rightarrow$ GG, $\theta_A' \approx 0$

Freundlich, Langmuir, BET

$\theta_A' = k_{ad}\cdot p_A\cdot \underbrace{N_{ges}\cdot(1-\theta_A)}_{\text{"frei"}} - k_{de}\underbrace{N_{ges}\cdot\theta_A}_{\text{"besetzt"}}$

$\left(K_A = k_{ad}/k_{des}\right)$

Ko-adsorption

$(p_A = \text{const}, p_B = \text{const})$

$\Rightarrow \theta_A' = 0, \theta_B' = 0$

$k_{de,A}\cdot(N_{ges}\cdot\theta_A) = k_{ad,A}\cdot p_A\cdot(N_{ges}\cdot(1-\theta_A-\theta_B))$

$\left(\text{mit } K_{ads,B} \cdot N_{ges} \Theta_B = \dots\right) \Longrightarrow \Theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B}$ | $\Theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}$

Dissoziation: $H_2 \longrightarrow H\cdot + \cdot H$

$k_{des,H} \cdot \Theta_H \cdot \Theta_H \longrightarrow k_{ad} p_{H_2} \cdot (1 - \Theta_H)^2$

bimolekular!

$\Longrightarrow \Theta_H = \frac{K \cdot p_{H_2}^{1/2}}{1 + K \cdot p_{H_2}^{1/2}}$

Unimolekularer Zerfall

$A_{(g)} \overset{K_A}{\rightleftharpoons} A_{ads} \xrightarrow{k_r} P$

$[P]' = k_r \cdot \Theta_A = k_r \left(\frac{K_A p_A}{1 + K_A p_A}\right)$

Bimolekulare Reaktion

Readsorption

$A_{(g)} + B_{(g)} \rightleftharpoons A_{ads} + B_{ads} \rightarrow P_{(g)}$

$v_p = k_r \cdot \frac{K_A p_A K_B p_B}{(1 + K_A p_A + K_B p_B)^2}$

Adsorption + Gasphase

$A_{(g)} \rightleftharpoons A_{ads} \xrightarrow{+B_{(g)}} P$

$v_p = k_r \cdot \Theta_A \cdot p_B = k_r \frac{K_A p_A}{1 + K_A p_A} \cdot p_B$

$p_A \uparrow (p_B \uparrow)$

$v_p \approx k_r \cdot K_A K_B \cdot p_A p_B$

$v_p \approx k_r \cdot \frac{K_B}{K_A} \cdot \frac{p_B}{p_A}$

$p_A \uparrow$

$v_p \approx k_r K_A p_A p_B$

$v_p = k_r \cdot p_B$

Lindemann, Hinshelwood, Langmuir

ELEY-RIDEAL-Mechanismus

$(v_{p,max})$

Bsp:

$CO + O_2 \xrightarrow{Pt, Pd} CO_2 + O$

exp.: $p\uparrow \sim$ 2. Ordnung

$p\uparrow \quad v_{CO_2} \sim 1/p_{CO} \quad \dots ?$