$$\Delta U = q + w \qquad \text{q er \underline{tilført} varme, osv}$$

$$w = W_{vol} + W_{add}$$

$$\Delta H = q + W_{add} \qquad (P \text{ konstant})$$

$$\Delta H = q \qquad \text{når } W_{add} = 0 \qquad \left(\begin{array}{l} \Delta H < 0 \text{ exoterm} \\ q < 0, \text{ dvs varmeudvikling} \end{array} \right)$$

$$\Delta H(T_2) \simeq \Delta H(T_1) + \Delta C_p (T_2 - T_1)$$

$$\Delta S(T_2) \simeq \Delta S(T_1) + \Delta C_p \ln \frac{T_2}{T_1}$$

$$\Delta G = \Delta H - T \Delta S \qquad (P, T \text{ konst})$$

$$\Delta G = \Delta G^{\ominus} + RT \ln Q \qquad \begin{array}{l} \Delta G < 0 \text{ naturlig} \\ \quad\quad\quad \text{proces,} \\ \text{exergon.} \end{array}$$

$$0 = \Delta G^{\ominus} + RT \ln K \qquad (\text{ligevægt})$$

$$(-W_{add})_{max} = -\Delta G \qquad (P, T \text{ konst})$$

$$a = \gamma \cdot b \qquad \text{mest for 'ioner}$$

$$\log \gamma = -0,509 \cdot z^2 \cdot \sqrt{I}$$

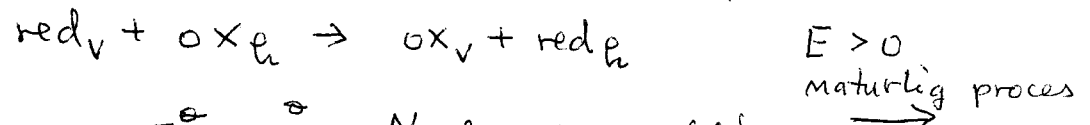$$I = \frac{1}{2} \{ z_1^2 \cdot b_1 + z_2^2 \cdot b_2 + z_3^2 \cdot b_3 + \dots \} / b^{\ominus}$$

$$ox + ze^- \rightarrow red \qquad (f, eks \; Fe^{3+} + e^- \rightarrow Fe^{2+})$$

$$\Delta G = -zFE$$

$$E_i^{\ominus} = \frac{\mu_{red}^{\ominus} - \mu_{ox}^{\ominus}}{-z_i F}$$

$$E_h = E_h^{\ominus} - \frac{N}{z} \log \frac{a(red)}{a(ox)}$$

$$E = E_h^{\ominus} - E_v^{\ominus} - \frac{RT}{zF} \ln Q$$

$$= E_h^{\ominus} - E_v^{\ominus} - \frac{N}{z} \log Q \qquad (25°c).$$

Q er massevirkningsbrøk for
den \underline{definitionsmæssige} celleproces:

$$red_v + ox_h \rightarrow ox_v + red_h \qquad \begin{array}{l} E > 0 \\ \text{naturlig proces} \end{array} \longrightarrow$$

$$0 = E_h^{\ominus} - E_v^{\ominus} - \frac{N}{z} \log K \qquad (\text{ligevægt}, 25°c)$$

$$E^{\ominus'} = E^{\ominus} + \frac{R-L}{z} \, 0,414 \qquad (25°c)$$

$$\Delta G^{\ominus'} = \Delta G^{\ominus} + (L-R) \cdot 39,93 \qquad (kJ/mol, \; 25°c)$$

$$\Delta G = \Delta G^{\ominus\,'} + RT \ln Q'$$

$$Q' \text{ er } Q \text{ uden } H^+ \text{ rev.}$$

$$0 = \Delta G^{\ominus\,'} + RT \ln K'$$

$$W_{add} = RT \ln \frac{a_2}{a_1} + z\, F\, (\phi_2 - \phi_1)$$

med fortegn.

$$\Delta\phi = \phi_2 - \phi_1 = -\frac{RT}{zF} \ln \frac{a_2}{a_1} = -\frac{N}{z} \log \frac{a_2}{a_1} \qquad (25°c)$$
ved ligevægt

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S \quad \Rightarrow \quad \left(\frac{\partial E}{\partial T}\right)_p = \frac{\Delta S}{zF}$$

$$\Delta H = -zFE + zFT\left(\frac{\partial E}{\partial T}\right)_p$$

$$\Delta C_p \equiv \left(\frac{\partial \Delta H}{\partial T}\right)_p = zFT\frac{\partial^2 E}{\partial T^2}$$

Donnan:
$$\Delta\phi \simeq \frac{RT}{2F}\frac{zc}{c_1} \qquad c, z: \text{protein} \quad c_1: Na^+, cl^-$$

$$\Pi \simeq RTc\left(1 + \frac{z^2}{4}\frac{c}{c_1}\right)$$

Gasser:
$$C \equiv \sqrt{\langle v^2\rangle} = \sqrt{\frac{3RT}{M}} \qquad \left(M \text{ i } \frac{kg}{mol}\right)$$

$$\bar{c} \equiv \langle v\rangle = \sqrt{\frac{8RT}{\pi M}}$$

$$\bar{C}_{rel} = \sqrt{2}\cdot\bar{c} = 4\cdot\sqrt{\frac{RT}{\pi M}}$$

kollisioner pr sec
for eet molekyle }
$$Z = \frac{\sigma \cdot \bar{C}_{rel} \cdot P \cdot N_A}{RT}$$

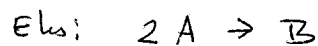$$\sigma \text{ i } m^2 ; \quad P \text{ i Pascal.}$$

middel fri vejlængde
$$\lambda \equiv \frac{\bar{c}}{Z} = \frac{RT}{N_A \cdot \sigma \sqrt{2} \cdot P}$$

kollisionstal med væg,
antal kollisioner pr m^2
pr sec }
$$Z_w = \frac{P \cdot N_a}{\sqrt{2\pi M R T}}$$

Kinetik:

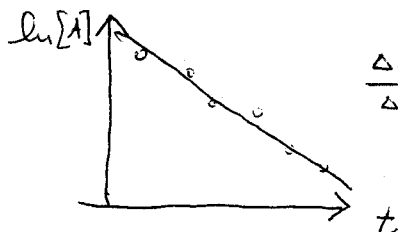$$V \equiv \frac{1}{\nu_i} \frac{d[i]}{dt}$$

Eks: $2A \rightarrow B$

$\nu_A = -2 \qquad \nu_B = +1$

1. ordens kinetik: $\frac{d[A]}{dt} = -k \cdot [A]$

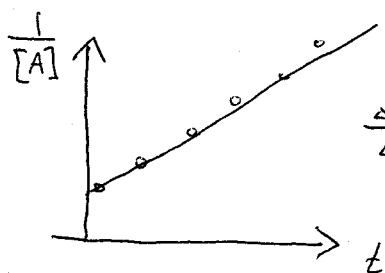$$\Rightarrow \quad \ln[A] = \ln[A_0] - kt \quad \Rightarrow [A] = [A_0]e^{-kt}$$

$$\frac{\Delta y}{\Delta x} = -k \qquad t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

2. ordens kinetik:

$$\frac{d[A]}{dt} = -k[A]^2$$

$$\Rightarrow \quad \frac{1}{[A]} = \frac{1}{[A_0]} + kt \quad \Rightarrow [A] = \frac{[A_0]}{1 + [A_0]kt}$$
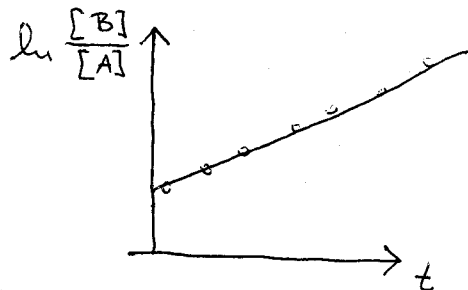

$$\frac{\Delta y}{\Delta x} = +k$$

Bland 2 orden: $A + B \xrightarrow{k}$

$$\frac{d[A]}{dt} = -k[A][B]$$

$$\Rightarrow \quad \ln\frac{[B]}{[A]} = \ln\frac{[B_0]}{[A_0]} + (B_0 - A_0)kt$$
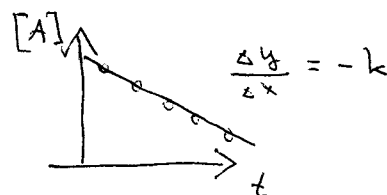

$$\frac{\Delta y}{\Delta x} = (B_0 - A_0)kt \qquad (\gtrless 0)$$

0'te orden: $\frac{d[A]}{dt} = -k$

$$\Rightarrow [A] = [A_0] - kt$$

$$\frac{\Delta y}{\Delta x} = -k$$

$$k(T) = \text{"}A\text{"} \, e^{-E_a/RT}$$

$$\ln \frac{k(T_2)}{k(T_1)} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\left(k(T) = Z \cdot e^{+\frac{\Delta S^\#}{R}} \cdot e^{-\frac{\Delta H^\#}{RT}} \quad ; \quad \text{ej pensum} \right)$$

$$B \rightleftharpoons C \qquad \text{elementær reaktioner}$$

$$K = \frac{[C]_{eq}}{[B]_{eq}} = \frac{k_F}{k_b}$$

relaxationstid
tæt ved ligevægt $\Big\}$ $\quad 1/\tau = k_f + k_b \qquad x \equiv [A]-[A]_{eq} = x_0 e^{-\frac{t}{\tau}}$

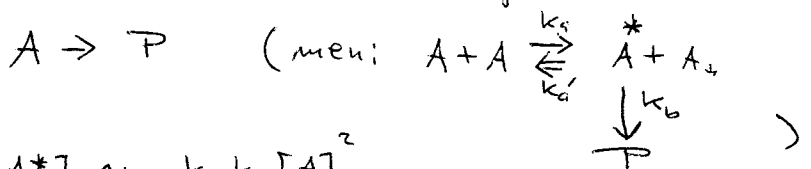Quasi steady state metoden! $\qquad$ For intermediater "x" og "y":

$$0 \approx \frac{d[x]}{dt} = a_1 x + b_1 y + c_1$$
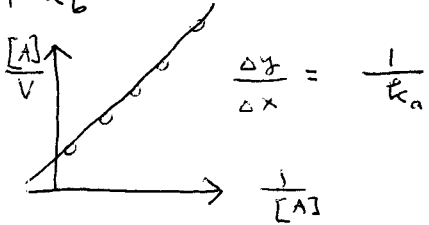
$$0 \approx \frac{d[y]}{dt} = a_2 x + b_2 y + c_2$$

Find x og y.

V sædvanligvis funktion af f.ex y: indsæt y.

Eks: Lindemann - Hinshelwood mek ("unimolekylær" reaktioner)

$$A \rightarrow P \qquad (\text{men:} \quad A + A \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} A^* + A \quad \downarrow k_b \quad)$$
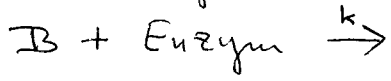$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad P$$

$$V = \frac{d[P]}{dt} = k_b[A^*] \approx \frac{k_a k_b [A]^2}{k_a'[A] + k_b}$$

$$\frac{[A]}{V} = \frac{1}{k_a}\frac{1}{[A]} + \frac{k_a'}{k_a k_b} \qquad \frac{\Delta y}{\Delta x} = \frac{1}{k_a}$$

Enzym kinetik

Diffusionsbegrænsning

$$B + \text{Enzym} \xrightarrow{k}$$

$$V = k \cdot [B][\text{Enzym}]$$

$$k_{max} = 4\pi \, a \, N_a \, D \qquad \frac{L}{mol \cdot s}$$

a typisk "diameter" i Enzymet