FYSIKALISK KEMI

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Fysikalisk Kemi

Räkneövningar lp III 1996

Kemiska reaktioner:

$$\nu_A A + \nu_B B + \ldots \rightarrow \nu_X X + \nu_Y Y$$

Tillståndsfunktioner:

U, G, H

$\Delta U = \sum U(\text{prod}) - \sum U(\text{reakt.})$

Konst V : 1:a HS $dU = \delta q + \underbrace{\delta w}_{=0} = \delta q$

$\Delta U = q_v$ (Bombkalorimeter)

Hess lag

ΔH_f^θ (bildningsentalpi vid standardtryck = 1 bar)

$\Delta H^\theta = \sum \Delta H_f^\theta(\text{prod}) - \sum \Delta H_f^\theta(\text{reak})$

ΔH_f^θ grundämne $= 0$ (i det prefererade aggregationstillståndet)

T1. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ ①

Sök ΔH_1

$\left.\begin{array}{l} 1 = \text{start} \\ 2 = \text{slut} \end{array}\right\}$ 1 reaktionsenhet, konst T

$\left.\begin{array}{l} H_1 = U_1 + P_1 V \\ H_2 = U_2 + P_2 V \end{array}\right\}$ volymen konst i bombkalorimeter

$\left.\begin{array}{l} P_1 V = n_{g1} \cdot RT \\ P_2 V = n_{g2} \cdot RT \end{array}\right\}$ volymen av ämnen i flytande fas försummas

$$\Rightarrow \Delta H = \Delta U + \overbrace{(n_{g,2} - n_{g,1})}^{\Delta n_g} RT$$

$\Delta U_1 = -2195 \text{ kJ/mol} \ (= \text{kJ/r.e})$

$\Delta n_g = 3 - 6 = -3$

$\Delta H_1 = -2202 \text{ kJ/r.e.}$

T2 $C(NO_2)_4(l) + 6CO(g) \rightarrow 7CO_2(g) + 2N_2(g)$ ①

Sökt: ΔH_f^θ för $C(NO_2)_4(l)$

Givet: $\Delta H_f^\theta(CO_2) = -393,5 \text{ kJ/mol}$

$\Delta H_f^\theta(CO) = -110,5 \text{ kJ/mol}$

$$\Delta H_1^\theta = 7\Delta H_f^\theta(CO_2) + \underbrace{2\Delta H_f^\theta(N_2)}_{=0} - \Delta H_f^\theta(C(NO_2)_4) - 6\Delta H_f^\theta(CO)$$

(*) $\Delta H_f^\theta(C(NO_2)_4) = 7\Delta H_f^\theta(CO_2) - 6\Delta H_f^\theta(CO) - \Delta H_1^\theta$

Kalorimeterns värmekap = 2478 cal/°C

$\Delta T = 1,883\,°C$

T2 forts

Tillförd värme, glödtråd = 326 cal

Molmassa $C(NO_2)_4 = 196\ g/mol$

$$n_{C(NO_2)_4} = \frac{m}{M} = 9.1\cdot 10^{-3}\ mol = 9{,}1\cdot 10^{-3}\ r.e$$

Värmebalans

$$-\Delta U_1\,(\text{per r.e.})\cdot 9{,}1\cdot 10^{-3}\ r.e + \underbrace{326\ cal}_{\text{glödtråd}} = 1{,}883\,°C \cdot 2478\ cal/grad$$

$$\Delta U_1^\theta = -511{,}7\ kcal = -2141\ kJ/mol \quad (\approx \text{tryckoberoende})$$

$$\Delta H_1^\theta = \Delta U_1^\theta + RT\underbrace{\Delta n_g}_{=3} = -2133\ kJ/r.e.$$

$$\Delta H_f^\theta\,(C(NO_2)_4) = (\ast) = 42{,}2\ kJ/mol$$

T4. <u>Sublimationsvärme</u>

Sökt: $\lambda_{sub}\,(is, -25\,°C)$

$$1\,g\ \text{is}\ (-25\,°C) \xrightarrow{\Delta H_1} 1\,g\ \text{vattenånga}\ (-25°)$$

$$\swarrow \Delta H_2 \qquad\qquad\qquad\qquad \Delta H_3 \nearrow$$

$$\text{is}\ 0\,°C \xrightarrow{\Delta H_3} \text{vatten}\ 0\,°C \xrightarrow{\Delta H_4} \text{vatten}\ 100° \xrightarrow{\Delta H_5} \text{ånga}\ 100°$$

Hess lag: $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$

$$\left.\begin{aligned}
\Delta H_2 &= c_p(is)\cdot \underbrace{\Delta T_2}_{25°} \\
\Delta H_3 &= \lambda_m \\
\Delta H_4 &= c_p(l)\cdot \underbrace{\Delta T_4}_{100°} \\
\Delta H_5 &= \lambda_b \\
\Delta H_6 &= c_p(g)\,\underbrace{\Delta T_6}_{-125°}
\end{aligned}\right\}\ \lambda_{sub} = \Delta H_1 = 2{,}8\ kJ/g$$

T5 (T) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ (1)

$\Delta H_1(298K)$ ur ΔH_f°

Kirchoffs lag:

$$\Delta H_1(T) - \Delta H_1(298K) = \int_{298}^{T} \Delta C_p \, dT$$

$$\Delta C_p = C_p(CO_2) - \frac{1}{2}C_p(O_2) - C_p(CO)$$

Lös ut $\Delta H_1(T)$. Integrera.

T6 Jämvikt

$$\begin{cases} \Delta G = 0 & \text{jämvikt} \\ \Delta G < 0 & \text{spontan} \\ \Delta G > 0 & \text{ospontan} \end{cases}$$

S°_{298} (diamant) = 0,585 cal/Kmol

S°_{298} (grafit) = 1,365 cal/K mol

$CO_2(g) \rightarrow C(\text{diamant}) + O_2(g)$: $\Delta H_A = 94484$ cal/mol

$CO_2(g) \rightarrow C(\text{grafit}) + O_2(g)$: $\Delta H_B = 94030$ cal/mol

a) ΔG° grafit → diamant

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\left.\begin{aligned} \Delta S^\circ &= S^\circ_{dia} - S^\circ_{gra.} = -0{,}78 \text{ cal/K mol} \\ \Delta H^\circ &= \Delta H_A - \Delta H_B = 454 \text{ cal/mol} \end{aligned}\right\} \Delta G^\circ = 2{,}9 \text{ kJ}$$

b) $\Delta G > 0 \Rightarrow$ grafit stabil form

T6 c) Diamant stabil ?

$\Delta G < 0$ vid något tryck P.

$dG = VdP - SdT \rightarrow dG = Vdp$

$\Delta G = g(\text{diam}) - g(\text{grafit})$

$d(\Delta G) = \Delta V \cdot dp$

$\Delta v = v(\text{diam}) - v(\text{grafit})$

$$\int_1^P d(\Delta G) = \int_1^P \Delta V dp = \Delta V (P-1)$$

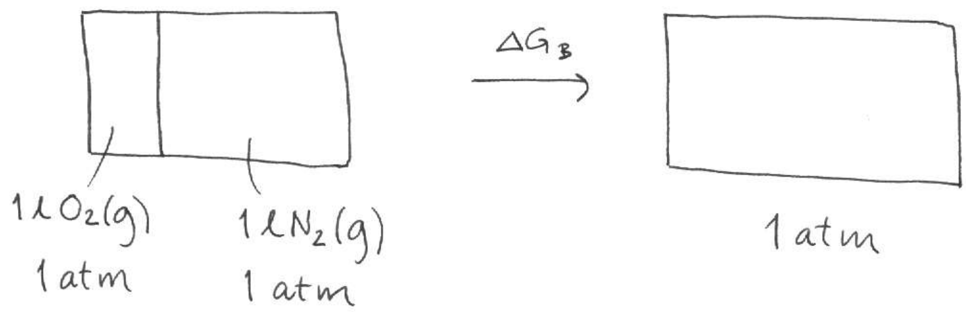
$\Delta G(P) - \Delta G(1\,\text{atm}) = \Delta V(P-1)$

$$\Delta V = \frac{12\,g/mol}{3{,}51\,g/cm^3} - \frac{12\,g/mol}{2.26\,g/cm^3} = -1{,}89 \cdot 10^{-3}\,dm^3/mol$$

$\Delta G(P) = \Delta G(1\,\text{atm}) + \Delta V(P-1) < 0$

$P > 15000$ atm

T7.



$$\Delta G_B = G_{bland} - G_{rena\ komp} = \sum n_i \mu_i - \sum n_i \mu_i^\ominus$$

Idealgasblandning: $\mu_i = \mu_i^\ominus + RT \ln \frac{P_i}{P^\ominus}$

T7 forts

Bevis: $$\mu_i(p_i) = \underbrace{\mu_i(p^\theta)}_{\mu_i^\theta} + \int_{p^\theta}^{p_i} \left(\frac{\partial \mu_i}{\partial p}\right) dp =$$

$$= \mu_i^\theta + \int_{p^\theta}^{p_i} V_i \, dp = \left\{ \text{i.g.} \Rightarrow V_i = \frac{RT}{p} \right\} =$$

$$= \mu_i^\theta + \int_{p^\theta}^{p_i} RT \frac{dp}{p} = \mu_i^\theta + RT \ln \frac{p_i}{p^\theta}$$

$$\Delta G_B = \sum n_i \left(\mu_i^\theta + RT \ln \frac{p_i}{p^\theta}\right) - \sum n_i \mu_i^\theta = RT \sum n_i \ln \frac{p_i}{p^\theta} =$$

$$= RT \left(n_{O_2} \cdot \ln \frac{p_{O_2}}{p^\theta} + n_{N_2} \cdot \ln \frac{p_{N_2}}{p^\theta} \right)$$

$$\begin{cases} n = \dfrac{pV}{RT} \Rightarrow \begin{cases} n_{O_2} = 4{,}461 \cdot 10^{-2} \text{ mol} \\ n_{N_2} = 0{,}1785 \text{ mol} \end{cases} \\[2ex] p_i = x_i P = \dfrac{n_i}{\sum n_i} \cdot P \Rightarrow \begin{cases} \dfrac{p_{O_2}}{p^\theta} = 0{,}20 \\[1ex] \dfrac{p_{N_2}}{p^\theta} = 0{,}80 \end{cases} \end{cases}$$

$$\Rightarrow \Delta G_B = -253 \text{ J}.$$

T8 (T)

Raoults lag: $p_i = x_i p_i^*$ – rent ämne. (ideal lösn.)

T9. Aktivitet & aktivitetsfaktor

Sökt: a_{Fe} och f_{Fe} för $X_{Fe} = 0{,}501$ vid 1600 K.

Givet:

$$\lg\left(\frac{P_{Fe}}{mmHg}\right) = -\frac{20087}{T} + 8{,}920 = -\frac{a}{T} + b \quad (1)$$

$$\lg\left(\frac{P^*_{Fe}}{mmHg}\right) = -\frac{20908}{T} + 10036 = -\frac{a^*}{T} + b^* \quad (2)$$

Ren Fe(s) i jämvikt med sin ånga:

$$\mu^*(s) = \mu^*(g) = \mu^\ominus(g) + RT\ln\frac{P^*_{Fe}}{P^\ominus} \quad (3)$$

Fe(s) löst i V(s) i jämvikt med sin ånga:

$$\mu(s) = \mu(g)$$

$$\mu^*(s) + RT\ln a_{Fe} = \mu^\ominus(g) + RT\ln\frac{P_{Fe}}{P^\ominus} \quad (4)$$

(4) - (3) $\Rightarrow$

$$RT\ln a_{Fe} = RT\ln\frac{P_{Fe}}{P^*_{Fe}}$$

$$\lg a_{Fe} = \lg\frac{P_{Fe}}{P^*_{Fe}} = \left\{(1),(2)\right\} = \frac{a^* - a}{T} + b - b^* = -0{,}6029$$

$$a_{Fe} = 0{,}250$$

$$f_{Fe} = \frac{a_{Fe}}{X_{Fe}} = 0{,}498 \quad (= 1 \text{ om idealt})$$

T10a)

Sökt: a (C i austenit) för 1,00 vikt-%, 1000 K

Ren grafit vid 1 atm stand. tillstånd

$$C\,(\text{i austenit}) + 2H_2\,(g) \rightleftharpoons CH_4\,(g)$$

Jämvikt: $0 = \Delta G = \mu_{CH_4} - 2\mu_{H_2} - \mu_{C\,i\,aust.}$

$$\begin{cases} \mu_{CH_4} = \mu^\theta_{CH_4} + RT\ln\dfrac{P_{CH_4}}{p^\theta} \\ \mu_{H_2} = \mu^\theta_{H_2} + RT\ln\dfrac{P_{H_2}}{p^\theta} \\ \mu_{C\,i\,aust} = \mu^*_{grafit} + RT\ln a \end{cases}$$

— sökt

$$0 = \mu^\theta_{CH_4} - 2\mu^\theta_{H_2} - \mu^*_{grafit} + RT\ln\frac{P_{CH_4}}{P^2_{H_2}\cdot a}$$

$$0 = \mu^\theta_{CH_4} - 2\mu^\theta_{H_2} - \mu^*_{grafit} + RT\ln\frac{r}{a}\ ,\quad r = \frac{P_{CH_4}}{P^2_{H_2}}\ (\text{given})$$

$$C\,(\text{grafit}) + 2H_2\,(g) \rightleftharpoons CH_4\,(g)$$

Pss erhålles vid jämvikt:

$$0 = \Delta G = \mu_{CH_4} - 2\mu_{H_2} - \mu^*_{grafit} =$$

$$= \mu^\theta_{CH_4} - 2\mu^\theta_{H_2} - \mu^*_{grafit} + RT\ln K_p\ ,\quad K_p = \frac{P_{CH_4}}{P^2_{H_2}}\ (\text{given})$$

$$\Longrightarrow\ 0 = RT\ln\frac{r}{aK_p}\ \Longrightarrow\ a = \frac{r}{K_p} = 0{,}546$$

T10b

Då austeniten är mättad med kol får vi en jämvikt mellan austenit & grafit.

$$C(\text{austenit}) \rightleftharpoons C(\text{grafit})$$

$$\Delta G = 0 = \mu^*_{grafit} - \underbrace{\mu_c}_{=\mu^*_{grafit} + RT\ln a} \Rightarrow 0 = -RT\ln a \Rightarrow a = 1$$

Mättad austenit : $\begin{cases} 1{,}49\,\%\ \text{kol} \\ 98{,}5\,\%\ \gamma\,\text{Fe} \end{cases} \Rightarrow x_c = \dfrac{\dfrac{1{,}49}{12\,g/mol}}{\dfrac{1{,}49}{12\,g/mol} + \dfrac{98{,}5}{56\,g/mol}} = 0{,}0657$

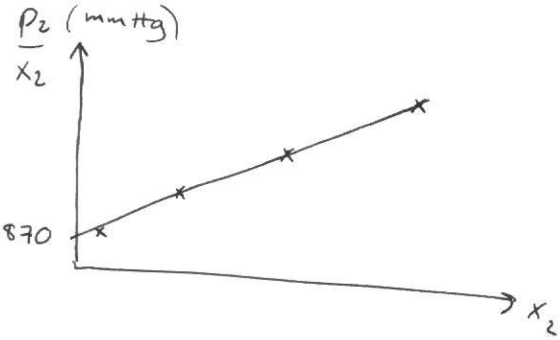
$f = \dfrac{a}{x} = 15{,}2$

T11 Henrys lag

a) K_2 är lutningen i $x_2 = 0$, hos den kurva som återger P_2:s beroende av x_2. $(2 = NH_3)$

$$K_2 = \left(\frac{\partial p_2}{\partial x_2}\right)_{x_2=0}$$

Plotta $\dfrac{P_2}{x_2}$ mot $x_2 \Rightarrow$



$K_2 = 870\,mmHg = 1{,}145\,atm$

b) γ_2

$$\mu_2(l) = \mu_2^\theta + RT\ln \gamma_2 x_2$$

Jämvikt: $\mu(l) = \mu(g)$

$$\mu_2^\theta + RT\ln\gamma_2 x_2 = \mu^\theta(g) + RT\ln\frac{P_2}{p^\theta} \quad (1) \Rightarrow$$

$$\exp\left(\left(\mu_2^\theta(l) - \mu^\theta(g)\right)/RT\right) = \frac{1}{\gamma_2}\cdot\frac{P_2}{x_2}\cdot\frac{1}{p^\theta}, \text{ för } x_2 \to 0$$

T11 forts

$$\exp\left(\left(\mu_2^\ominus(l)-\mu^\ominus(g)\right)/RT\right) = \frac{1}{P_\ominus}\underbrace{\lim_{x_2\to 0}\left(\frac{1}{\gamma_2}\right)}_{=1}\underbrace{\lim_{x_2\to 0}\left(\frac{P_2}{X_2}\right)}_{=K_2}$$

$$\mu^\ominus(l) = \mu^\ominus(g) + RT\ln\frac{K_2}{P^\ominus} \qquad (2)$$

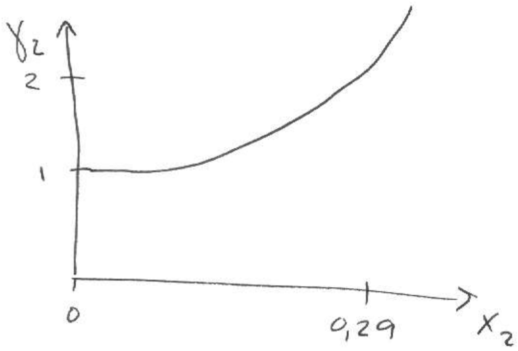
$(1)+(2) \Rightarrow$

$$RT\ln(K_2/P^\ominus) + RT\ln\gamma_2 x_2 = RT\ln(P_2/P^\ominus) \quad \Rightarrow$$

$$\frac{K_2\gamma_2 x_2}{P^\ominus} = \frac{P_2}{P^\ominus} \quad \Longrightarrow \quad \gamma_2 = \frac{P_2}{K_2 X_2} = f(P_2, x_2)$$

$x_2 = 0{,}29 \longrightarrow \gamma_2 = 2{,}78$

$x_2 = 0{,}016 \longrightarrow \gamma_2 = 1{,}06$



T12(T)

Gibbs-Helmholtz:

① $$\frac{\partial(\Delta G^\theta/T)}{\partial T} = -\frac{\Delta H^\theta}{T^2} \rightarrow \Delta H^\theta$$

$\Delta G^\theta (400°C)$

② $$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$$

$$A(s) + B(g) \rightarrow C(g) + \tfrac{1}{2}D(g)$$

$$\Delta G^\theta = -RT\ln K = -RT\ln\left(\frac{P_C \cdot P_D^{1/2}}{P_B}\right)$$

Uttryck P_B, P_C och P_D som funktion av P_{tot}, P_0

⇒ K vid 2 olika temp beräknas.

Integrera G-H ⇒ ΔH^θ

T14. Framställning av ren Ni.

Sökt: T då halten $Ni(CO)_4(g)$ är a) 90 mol%

b) 0.1 mol%

då jmv $P_{tot} = 1$ atm

$$Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(g)$$

a) $p(Ni(CO)_4) = X \cdot P = 0{,}9$ atm

$p(CO) = 0{,}1$ atm

$$K = \frac{P_{NiCO_4}}{(P_{CO})^4} = 9000\ atm^{-3}, \quad \ln K = 9{,}1$$

b) $p(NiCO_4) = x \cdot p = 0{,}001$ atm

$p(CO) = 0{,}999$ atm

$K = 10^{-3}\ atm^{-3}$ $\quad \ln K = -6{,}91$

Beräkna $\ln K$ vid 300, 400, 500 K.

(8/2)

Plotta mot $\frac{1}{T}$. $\Rightarrow$ Våra T kan avläsas, ty linjärt enl Gibbs-Helmholtz.

Givet: $\Delta H_f^\ominus$, $\frac{g^\ominus - h_0^\ominus}{T}$

$$-RT\ln K = \Delta G^\ominus = T \cdot \frac{\Delta G^\ominus - \Delta H_0^\ominus}{T} + \Delta H_0^\ominus$$

$$\ln K = -\frac{1}{R} \frac{\Delta G^\ominus - \Delta H_0^\ominus}{T} - \frac{\Delta H_0^\ominus}{RT}$$

$$\Delta H_0^\ominus = \Delta H_f^\ominus (NiCO_4) - 4\Delta H_f^\ominus (CO) - \Delta H_f^\ominus (Ni) = -36680 \text{ cal/mol.}$$

$$\frac{\Delta G^\ominus - \Delta H_0^\ominus}{T} = \frac{g^\ominus - h_0^\ominus}{T}(NiCO_4) - 4\frac{g^\ominus - h_0^\ominus}{T}(CO) - \frac{g^\ominus - h^\ominus}{T}(Ni)$$

$$\left.\begin{array}{l} \ln K(300K) = 16.34 \\ \ln K(400K) = -0{,}05 \\ \ln K(500K) = -9{,}83 \end{array}\right\} \ln K \text{ plottas mot } 1000/T$$

$$\left.\begin{array}{l} \ln K = 9{,}1 \Rightarrow T = 337K \\ \ln K = -6{,}9 \Rightarrow T = 466K \end{array}\right\} \text{ur diagram.}$$

K1. Sönderfall: Oftast 1:a ordningen.

sökt: Reaktionsordning och hastighetskonst.

$$N_2O_5 \rightarrow N_2O_4 + \tfrac{1}{2}O_2$$

$$N_2O_4 \rightleftharpoons 2NO_2$$

Givet: Kvarvarande halt av N_2O_5.

K1 forts.

Vi antar 1:a ordningen.

$$\ln \frac{c_0}{c} = kt \iff \ln c = \ln c_0 - kt$$

Plotta → lutningen $= -k$ (om det blir en rät linje
annars inte 1:a ordningen)

$\Rightarrow k = 6{,}15 \cdot 10^{-4}\ s^{-1}$

$$k = \ln \frac{c_0}{c} \cdot \frac{1}{t}$$

K2. 1:a ordningen. Sök k.

c_0 = begynnelsekonc
$c_0 - x$ = konc vid tiden t
n_0 = antal mol gas (N_2), $t=0$
p = totaltryck, t
p_∞ = — " — då allt reagerat
v = reaktionslösn. volym
V = tillgänglig volym för gasen.

$$\ln \frac{c_0}{c_0 - x} = k \cdot t \iff x = c_0 \left(1 - e^{-kt}\right)$$

tot. ämnesmängd gas, tiden t: $n_{gas} = n_0 + x \cdot v = n_0 + c_0\left(1 - e^{-kt}\right)v$

$$p = \frac{RT}{V} n_{gas} = \frac{RT}{V}\left(n_0 + v c_0 \left(1 - e^{-kt}\right)\right)$$

$$t = \infty: \quad p_\infty = \frac{RT}{V}\left(n_0 + v c_0\right)$$

$$\Bigg\} \quad p_\infty - p = \frac{RT}{V} v \cdot c_0 e^{-kt}$$

$\ln(p_\infty - p) = \ln K - kt$: plottas $\Rightarrow k = 4{,}25 \cdot 10^{-4}\ s^{-1}$

K3. $A \rightarrow B$

Sökt: Visa 2:a ordningen. Beräkna k.

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

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k \cdot t \Leftrightarrow \frac{1}{[A]_0/2} - \frac{1}{[A]_0} = k t_{1/2}$$

Givet $t_{1/2}$ vid olika $[A]_0$

$$[A]_0 t_{1/2} = \frac{1}{k} = \text{konst.}$$

$[A]_0$	$t_{1/2}$	$[A]$
.	.	540
.	.	545
.	.	535
.	.	

$\Rightarrow$ 2:a ordn.

$k = 1.85 \cdot 10^{-3}\ M^{-1} min^{-1}$

$$2A + B \rightarrow C + D$$

$$r = k \cdot [A]^{\alpha} [B]^{\beta}$$

<u>sökt:</u> k, α, β

$$r_0 = k \cdot [A]_0^{\alpha} [B]_0^{\beta}$$

Om $[B]_0$ konst : $\quad r_0 = k'[A]_0^{\alpha}$

ur tabell: r_0 direkt prop. mot $[A]_0$ om $[B]_0$ konst. $\Rightarrow \alpha = 1$

Om $[A]_0$ konst : $\quad r_0 = k''[B]_0^{\beta}$

ur tabell : $r_0 \propto [B]_0^2$ om $[A]_0$ konst

$\Rightarrow \beta = 2$

$$k = \frac{r_0}{[A]_0^{\alpha} [B]_0^{\beta}} = 40\, M^{-2} s^{-1}$$

<u>Alt.</u> Logaritmera (1)

$$\ln r_0 = \ln k + \alpha \ln [A]_0 + \beta \ln [B]_0$$

om $[A]_0$ konst. $\Rightarrow \ln r_0 = \text{konst.} + \beta \ln [B]_0$

$\boxed{K7}$

$$2A + B \longrightarrow C + H_2O$$

<u>sökt:</u> K

$[A]_0 = 5.00 \text{ mM}$
$[B]_0 = 2.5 \text{ mM}$

<u>OBS!</u> A och B i stökiometriska mängder

$$\Rightarrow [A] = 2[B] \qquad (1)$$

$$r_A = -\frac{d[A]}{dt} = K \cdot [A][B] \overset{(1)}{=} \frac{1}{2}K[A]^2 \qquad (2)$$

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = \int_0^t \frac{1}{2} K\, dt$$

$$\Rightarrow \frac{1}{[A]} = \frac{1}{[A]_0} + \frac{1}{2} K t$$

$$[A] = [A]_0 - 2[C] = [A]_0 - 2\,\frac{m_c/M_c}{V}$$

$M_c = 292.4 \frac{g}{mol}$
$V = 203 \times 10^{-3}\ dm^3$

$$\Rightarrow [A] = \left(5.00 - 2\,\frac{\overset{\text{givet}}{m_c} \cdot 10^3}{282.4 \cdot 203 \times 10^{-3}}\right) \text{mM}$$

Plotta $\frac{1}{[A]}$ mot t $\Rightarrow$ rät linje med riktn. koeff. $= 5.81 \times 10^{-5}\ mM^{-1}\,s^{-1} = \frac{1}{2}K$

$$\Rightarrow \underline{K = 0.12\ M^{-1} s^{-1}}$$

OBS! K beror av hur hastighetsekv. skrivs

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

$$(1) \Rightarrow [B] = \tfrac{1}{2}[A] \Rightarrow r_B = -\frac{1}{2}\frac{d[A]}{dt} = \frac{1}{2}k'[A]^2$$

$$\Rightarrow -\frac{d[A]}{dt} = k'[A]^2 \qquad (3)$$

$$(2),(3) \Rightarrow \tfrac{1}{2}K = k'$$

$\boxed{K8}$

$$\underbrace{C_2H_5ONO_2}_{A} \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} C_2H_5O\cdot + NO_2 \qquad (1)$$

$$C_2H_5O\cdot + NO \xrightarrow{k_2} C_2H_5ONO \qquad (2)$$

Visa att
$$-\frac{d\ln[A]}{dt} = \frac{k_1}{1+\frac{K_{-1}[NO_2]}{K_2[NO]}} \qquad (3)$$

$$r = -\frac{d[A]}{dt} = K_1[A] - K_{-1}[C_2H_5O\cdot][NO_2] \quad (4)$$

Steady-State (SS) för $C_2H_5O\cdot$:

$$\frac{d[C_2H_5O\cdot]}{dt} = k_1[A] - K_{-1}[C_2H_5O\cdot]\cdot[NO_2] - K_2[C_2H_5O\cdot]\cdot[NO] = 0 \quad (5)$$

$$\Rightarrow [C_2H_5O\cdot] = \frac{K_1[A]}{K_{-1}[NO_2]+K_2[NO]}$$

Insättning i (4)

$$\Rightarrow -\frac{d[A]}{dt} = k_1[A] - \frac{K_1K_{-1}[A][NO_2]}{K_{-1}[NO_2]+K_2[NO]} = \longrightarrow$$

$$\Leftarrow = k_1 [A] \cdot \frac{k_2 [NO]}{k_{-1}[NO_2] + k_2 [NO]} = \frac{k_1 \; [A]}{1 + \frac{k_{-1}[NO_2]}{k_2 [NO]}}$$

$$-\frac{1}{[A]} \frac{d[A]}{dt} = \frac{k_1}{1 + \frac{k_{-1}[NO_2]}{k_2 [NO]}} = -\frac{d \ln [A]}{dt} \qquad \underline{\text{Vsb}}$$

Hur kan acetaldehyd utnyttjas för att bestämma k_1?

Acetaldehyd reagerar snabbt med NO_2

$\Rightarrow [NO_2]$ låg

$\Rightarrow \dfrac{k_{-1}[NO_2]}{k_2 [NO]} \ll 1$ om $[NO]$ tillr. hög

$\Rightarrow -\dfrac{d[A]}{dt} = k_1 [A]$

dvs. 1:a ordn. m.a.p. A

hast. konst. = k_1

$\boxed{K9}$ Termiskt sönderfall av väteperoxid

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2} O_2$$

$$H_2O_2 + H_2O \xrightarrow{k_1} 2OH\cdot + H_2O \qquad (1)$$

$$OH\cdot + H_2O_2 \xrightarrow{k_2} HO_2\cdot + H_2O \qquad (2)$$

$$OH\cdot + HO_2\cdot \xrightarrow{k_3} H_2O + O_2 \qquad (3)$$

$$HO_2\cdot + HO_2\cdot \xrightarrow{k_4} H_2O_2 + O_2 \qquad (4)$$

a) Mekanism A (1,2,3) :

$$-\frac{d[H_2O_2]}{dt} = k_1[H_2O_2][H_2O] + k_2[OH\cdot][H_2O_2] \quad (5)$$

SS-ant. för OH· :

$$\frac{d[OH\cdot]}{dt} = 2k_1[H_2O_2][H_2O] - k_2[OH\cdot][H_2O_2] - k_3[OH\cdot][HO_2\cdot] = 0 \quad (6)$$

↑ OBS!

SS-ant. för HO₂· :

$$\frac{d[HO_2\cdot]}{dt} = k_2[OH\cdot][H_2O_2] - k_3[OH\cdot][HO_2\cdot] = 0 \quad (7)$$

(6)-(7) :

$$2k_1[H_2O_2][H_2O] - 2k_2[OH\cdot][H_2O_2] = 0$$

$$(5) \Rightarrow \quad -\frac{d[H_2O_2]}{dt} = 2k_1[H_2O_2][H_2O] \quad (8)$$

Mekanism B (1,2,4) :

SS-ant. för OH· resp. HO₂· :

$$\frac{d[OH\cdot]}{dt} = 2k_1[H_2O_2][H_2O] - k_2[OH\cdot][H_2O_2] = 0 \quad (9)$$

$$\frac{d[HO_2\cdot]}{dt} = k_2[OH\cdot][H_2O_2] - 2k_4[HO_2\cdot]^2 = 0 \quad (10)$$

OBS!

-

⟶

$$-\frac{d[H_2O_2]}{dt} = k_1[H_2O_2][H_2O] + k_2[OH\cdot][H_2O_2] - $$
$$- k_4[HO_2\cdot]^2 \quad (11)$$

$$(9)+(10) \Rightarrow \quad k_1[H_2O_2][H_2O] = k_4[HO_2\cdot]^2$$

$$(11) \Rightarrow \quad -\frac{d[H_2O_2]}{dt} = 2k_1[H_2O_2][H_2O]$$

b) <u>givet:</u> $[H_2O_2]_0 = 3.2 \times 10^{-5}$ M
$[H_2O]_0 = 6.4 \times 10^{-4}$ M

k_1, k_2, k_3, k_4 givna

exp. $\Rightarrow$ $[HO_2\cdot] < 6 \times 10^{-7}$ M

<u>Mekanism A</u>:

$$(7) \Rightarrow [HO_2\cdot] = \frac{k_2}{k_3}[H_2O_2] \approx \frac{k_2}{k_3}[H_2O_2]_0 = \ldots = 4.8 \times 10^{-6}\,M$$

dvs. $[HO_2\cdot]$ ligger över detektionsgränsen
$\Rightarrow$ mekanism A kan förkastas

<u>Mekanism B</u>:

$$(9), (10) \quad [HO_2\cdot] = \left(\frac{k_1}{k_4}[H_2O_2][H_2O]\right)^{1/2} \approx$$
$$\approx \left(\frac{k_1}{k_4}[H_2O_2]_0[H_2O]_0\right)^{1/2} = \ldots = 1.3 \times 10^{-9}\,M$$

dvs under detektionsgränsen
$\Rightarrow$ mekanism B tänkbar

OBS! FEL!

Fys K. övn 22/2 Formelsamling ; Elektrokemisk transport:

$$\Lambda = (\kappa - \kappa_0) / (C \Sigma z_+)$$

fattas

$$R = \frac{1}{\cancel{\lambda}} \cdot \frac{l}{A} = \frac{1}{\cancel{\lambda}} \cdot k_{cell}$$

κ $\quad$ κ

$\boxed{K10}$

$$(CH_3)_3COH \longrightarrow (CH_3)_2C{=}CH_2 + H_2O$$

givet: $t_{1/2}(1000\,K) = 1\,s$

$E_A = 258\ kJ/mol$

sökt: T som ger $t_{1/2} = 1\,ms$

Arrhenius:

$$k = \underbrace{A}_{\text{Kollision/tid}} \cdot e^{\left(-\frac{E_A}{RT}\right)} \quad (1)$$

= "lyckade" kollisioner / tot

andel med $E > E_A$

A = pre-exponentiell faktor

E_A = aktiveringsenergi

1:a ordn. : $-\frac{d[A]}{dt} = k[A]$

$$\Rightarrow t_{1/2} = \frac{\ln 2}{k} \quad (2)$$

$$(1), (2) \Rightarrow -\ln t_{1/2}(T) = \ln A' - \frac{E_A}{RT}$$

$$\ln \frac{t_{1/2}(T_2)}{t_{1/2}(T_1)} = \frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow T_2 = 1286\ K$$

$\boxed{K\,11}$

$$BrO_3^- + Br^- \xrightarrow{k_1} BrO_2^- + BrO^- \qquad (1)$$

$$BrO_2^- \xrightarrow{k_2} Br^- + O_2 \qquad (2)$$

$$BrO_3^- + BrO^- \xrightarrow{k_3} 2BrO_2^- \qquad (3)$$

a) Visa att $-\dfrac{d[BrO_3^-]}{dt} = 2k_1[BrO_3^-][Br^-]$

$$-\frac{d[BrO_3^-]}{dt} = k_1[BrO_3^-][Br^-] + k_3[BrO_3^-][BrO^-] \qquad (4)$$

SS-ant. för BrO^-:

$$\frac{d[BrO^-]}{dt} = k_1[BrO_3^-][Br^-] - k_3[BrO_3^-][BrO^-] \qquad (5)$$

$$(4),(5) \Rightarrow -\frac{d[BrO_3^-]}{dt} = 2k_1[BrO_3^-][Br^-] \qquad (6)$$

$$(6) \Rightarrow k_1(350\,°C) = 7.00 \times 10^{-3}\ M^{-1}\,min^{-1}$$

$$k_1(370\,°C) = 19.49 \times 10^{-3}\ M^{-1}\,min^{-1}$$

Arrhenius: $k = A \cdot e^{-E_A/RT}$

$$\ln\frac{k_1(T_1)}{k_1(T_2)} = \frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Rightarrow \underline{E_A = 171\ kJ}$$

$\boxed{K12}$

$$\underbrace{C_6H_5CH_3}_{A} \rightarrow C_6H_5CH_2\cdot + H\cdot \quad (1)$$

sökt: K vid olika T

E_A

1:a ordn. m.a.p. A: $-\frac{d[A]}{dt} = k[A] \quad (2)$

Mycket liten andel av A sönderdelas ($p \leq 0.52\%$)

$$[A] = [A]_0 - \underbrace{\frac{p}{100}[A]_0}_{\text{försummas}} \approx [A]_0 \quad (3)$$

$$-\frac{d[A]}{dt} \approx \frac{\Delta A}{\Delta t} = \frac{\frac{p}{100}[A]_0}{t} \quad (4)$$

$$(2),(3),(4) \Rightarrow \frac{\frac{p}{100}[A]_0}{t} = k[A]_0$$

$$\Rightarrow k = \frac{p}{100 \cdot t} \quad (5)$$

$T/°C$	$k \times 10^4/s^{-1}$
742	5.33
796	37.4
852	211

Arrhenius: $k = A \cdot e^{-E_A/RT}$

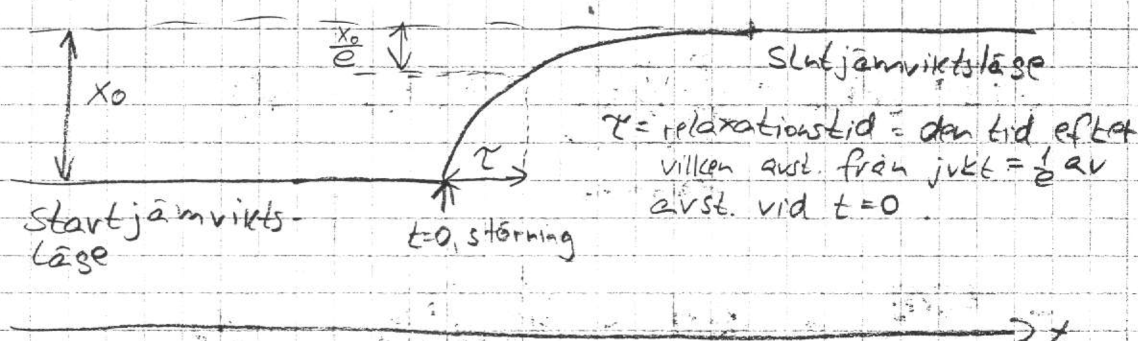
$$\ln k = \ln A - \frac{E_A}{R} \cdot \frac{1}{T}$$

Plotta $\ln k$ mot $\frac{1}{T}$ ⇒ rät linje

med lutn. $= -3.824 \times 10^4\ K = -\frac{E_A}{R}$

$\Rightarrow \underline{E_A = 318\ kJ/mol}$

Relaxationsmetoden



K13

$$Ni^{2+} + M^- \rightleftarrows NiM^+$$

$$A + B \underset{k_-}{\overset{k_+}{\rightleftarrows}} C$$

$$-\frac{d[A]}{dt} = k_+[A][B] - k_-[C] \quad (1)$$

Vid slutjämviktsläget: $-\frac{d[A]_e}{dt} = k_+[A]_e[B]_e - k_-[C]_e = 0$ (2)

På väg mot slutjämviktsläget: $[A] = [A]_e - x$

$[B] = [B]_e - x$

$[C] = [C]_e + x$

$$\left[\begin{array}{lll} \text{vid} & t=0 \text{ är} & x = x_0 \\ & t=\tau & x = \frac{x_0}{e} \\ & t=\infty & x = 0 \end{array}\right]$$

⟶

$\rightarrow$ ins. i (1) $\Rightarrow$ $-\frac{d([A]_e - x)}{dt} = k_+([A]_e - x)([B]_e - x) - k_-([C]_e + x)$

$$\frac{dx}{dt} = \underbrace{k_+[A]_e[B]_e - k_-[C]_e}_{=0 \text{ ekv.}(2)} - \underbrace{\{k_+([A]_e + [B]_e) + k_-\}}_{a = \text{konst.}} \cdot x + \underbrace{k_+ \cdot x^2}_{\text{försumma, ty } x \text{ litet}}$$

$$\frac{dx}{dt} = -a \cdot x \Rightarrow x = x_0 e^{-at}$$

För $t = \frac{1}{a}$ är $x = \frac{x_0}{e}$ $\Rightarrow$ $\frac{1}{a} = \tau$

$$\frac{1}{\tau} = k_+ ([A]_e + [B]_e) + k_-$$

Plotta $\frac{1}{\tau}$ mot $([A]_e + [B]_e)$

$\Rightarrow$ rät linje med lutningen $= 0.9556\ s^{-1}mM^{-1}$
och avskärning $= 0.39 s^{-1}$

$$\left(K = \frac{k_+}{k_-}\right)$$

$$\therefore \begin{cases} k_+ = 956\ s^{-1}M^{-1} \\ k_- = 0.39 s^{-1} \end{cases}$$

$\boxed{E1}$

1) 0.3370×10^{-3} M HA $R_1 = 3486\,\Omega$

2) 0.0100 M KCl $R_2 = 247.2\,\Omega$

$\varkappa_2 = 1.409 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$

$\Lambda^\circ(HA) = 361.1\ cm^2\,\Omega^{-1}\,ekv^{-1}$

$$\Lambda = \frac{\varkappa - \varkappa_0}{c \sum z_+}$$

sökt: stökiometriska syrakonst.

Svag syra: $HA \rightleftarrows H^+ + A^-$

Före jvikt	c	–	–
vid jvikt	$(1-\alpha)c$	αc	αc

α = syrans protolysgrad

$$K_A = \frac{c_{H^+} \cdot c_{A^-}}{c_{HA}} = \frac{\alpha^2 c}{1-\alpha} \quad (1)$$

$c = 0.3370 \times 10^{-3}$ M

Bestäm α: (FS:) $\varkappa = \sum c_i |z_i| \lambda_i$

$$\varkappa_1 = c_{H^+} \cdot 1 \cdot \lambda_{H^+} + c_{A^-} \cdot |-1| \cdot \lambda_{A^-} = \alpha c (\lambda_{H^+} + \lambda_{A^-}) \approx$$

$$\approx \alpha c \underbrace{(\lambda^\circ_{H^+} + \lambda^\circ_{A^-})}_{\Lambda^\circ(HA)} = \alpha c \Lambda^\circ(HA) \quad (2)$$

givna

→

$\rightarrow \quad \kappa_1$:

(FS:) $R = \frac{K_{cell}}{\kappa}$

$\Rightarrow \frac{R_1}{R_2} = \frac{\kappa_2}{\kappa_1} \Rightarrow \kappa_1 = 9.9915 \times 10^{-5}\ \Omega^{-1}\,cm^{-1}$

(2) $\Rightarrow \alpha = 0.821$

(1) $\underline{K_A} = \frac{\alpha^2 c}{1-\alpha} = \underline{1.27 \times 10^{-3} M}$

$\boxed{E3}$

givet: Λ för natriumpropionat (NaA) av olika koncentration.

$\Lambda^\circ(HCL)$

$\Lambda^\circ(NaCL)$

sökt: a) $\Lambda^\circ(NaA)$

b) $\Lambda^\circ(HA)$

a) Kohlrauschs lag:

$\Lambda = \Lambda^\circ - k\sqrt{c}$ (starka elektrolyter vid låga halter)

Plotta Λ mot $\sqrt{c}$. Extrapolera till $\sqrt{c} = 0$

$\Rightarrow \Lambda^\circ(NaA) = 85.8\ cm^2\,\Omega^{-1}\,ekv^{-1}$

b) $\Lambda^{\circ}(HA)$:

$$\Lambda^{\circ} = \lambda_{+}^{\circ} + \lambda_{-}^{\circ} \qquad (FS)$$

$$\Lambda^{\circ}(HA) = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{A^-} = \underbrace{\lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-}}_{\Lambda^{\circ}(HCl)} - \underbrace{(\lambda^{\circ}_{Cl^-} + \lambda^{\circ}_{Na^+})}_{\Lambda^{\circ}(NaCl)} + \underbrace{\lambda^{\circ}_{Na^+} + \lambda^{\circ}_{A^-}}_{\Lambda^{\circ}(NaA)} =$$

$$\Rightarrow \underline{\Lambda^{\circ}(HA) = 385.5 \ cm^2 \, \Omega^{-1} \, ekv^{-1}}$$

28/2/96 P.W.

29

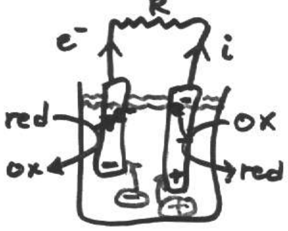
ELEKTROKEMISKA CELLER:

VARFÖR?

Batterier; rost/korrosion; framställning av metaller i industrin; bidrar till transportmekanismer i levande celler; ger termodynamisk information om kemiska reaktioner.

OFTA BILLIGT & ENKELT!

ELEKTROKEMISK CELL = GALVANISKT ELEMENT (batteri) är en strömkälla, ger energi, spontana processer.



⊕ POL $ox + n \cdot e^- \longrightarrow red$ (reduktion)

⊖ POL $red \longrightarrow ox + n \cdot e^-$ (oxidation)

I ledningen transporteras e^-, i lösningen joner.

- ALLMÄNT SKRIVSÄTT: ← saltbro tex.

⊖ elektrod 1 | lösning 1 || lösning 2 | elektrod 2 ⊕

- Teckna halvcellsförlopp
- Addera dessa till totala cellförloppet
- Teckna ΔG för cellförloppet:

$$\Delta G = \sum_i \nu_i \mu_i = \sum_i \nu_i \mu_i^{\ominus} + RT\sum \nu_i \ln a_i = \Delta G^{\ominus} + RT \ln \prod a_i^{\nu_i}$$

- Vid konstant T & P:

$$\begin{cases} \Delta G = -n \cdot F \cdot E \\ \Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P = n \cdot F \cdot \left(\frac{\partial E}{\partial T}\right)_P \\ \Delta H = \Delta G + T \cdot \Delta S = -n F \cdot E + n \cdot F \cdot T \cdot \left(\frac{\partial E}{\partial T}\right)_P \end{cases}$$

$F = e \cdot N_A$ = Faradays konstant = 96485 As/mol

E = potentialskillnad mellan elektroderna

n = antal e^- inblandade i cellförloppet

E6. $AgCl(s) + \frac{1}{2} H_2(g) \rightarrow Ag(s) + HCl(g)$ (1) (29/2)

Sök ΔG° för ovanstående reaktion

Givet: $\ominus$ $Pt, H_2 \,(1\,atm) \,|\, 9\,molal\; HCl \,|\, AgCl(s), Ag(s)$ $\oplus$

$\ominus$ pol: $\frac{1}{2} H_2(g) \rightarrow H^+ + e^-$

$\oplus$ pol: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$

(2) Totalt: $\frac{1}{2} H_2(g) + AgCl(s) \rightarrow Ag(s) + H^+ + Cl^-$ för 1F

$$\Delta G_2 = \mu^\circ_{Ag} + \mu^\circ_{H^+} + RT \ln a_H + \mu^\circ_{Cl^-} + RT \ln a_{Cl}$$

$$- \frac{1}{2} \mu^\circ_{H_2} - \frac{1}{2} RT \ln \frac{P_{H_2}}{P^\circ} - \mu^\circ_{AgCl}$$

$$= \Delta G^\circ_2 + RT \ln (a_H \cdot a_{Cl^-})$$

$$\Delta G_2 = -1 \cdot F \cdot E$$

$$\Delta G^\circ_2 = -FE - RT \ln (a_{H^+} a_{Cl^-}) \quad (2b)$$

Jämvikt: $HCl(g) \rightleftharpoons H^+ + Cl^-$ (3)

$$\Delta G_3 = \mu^\circ_{H^+} + RT \ln a_{H^+} + \mu^\circ_{Cl^-} + \ln a_{Cl^-} - \mu^\circ_{HCl(g)} - RT \ln \frac{P_{HCl}}{P^\circ}$$

$$\Delta G^\circ_3 = -RT \ln a_{H^+} a_{Cl^-} + RT \ln \frac{P_{HCl}}{P^\circ} \quad (3b)$$

$$\Delta G^\circ_2 - \Delta G^\circ_3 = -FE - RT \ln \frac{P_{HCl}}{P^\circ} = 14{,}52\, kJ$$

$$\Delta G_2^\theta - \Delta G_3^\theta = \mu^\theta_{Ag} + \mu^\theta_{H+} + \mu^\theta_{Cl} - \frac{1}{2}\mu^\theta_{H_2} - \mu^\theta_{AgCl} -$$

$$- \mu^\theta_{H+} - \mu^\theta_{Cl} + \mu^\theta_{HCl} = \Delta G_1^\theta = 14{,}52\,kJ$$

(29/2)

E7 $2Ag(s) + S(l) \longrightarrow Ag_2S(s)$ för 2F

cellförlopp

$$\Delta G^\theta_{573K} = -2F\,E_{573K}$$

$$\Delta S^\theta_{573K} = 2F\left(\frac{\partial E}{\partial T}\right)_{P,573K}$$

$$\Delta H^\theta_{573K} = \Delta G^\theta + 573 \cdot \Delta S^\theta$$

$$\Delta H^\theta = \sum_i \nu_i \Delta H_f^\theta = \Delta H_f^\theta(Ag_2S) = -29{,}3\,kJ/mol$$

E8 $Fe(s) + PdO(s) \longrightarrow FeO(s) + Pd(s)$ för 2F

Rena, fasta ämnen $\mu = \mu^\theta$

$$\Delta G = -2FE = \mu^\theta_{FeO} + \mu^\theta_{Pd} - \mu^\theta_{Fe} - \mu^\theta_{PdO} - \frac{1}{2}\mu^\theta_{O_2} + \frac{1}{2}\mu^\theta_{O_2}$$

$$= \left(\mu^\theta_{FeO} - \mu^\theta_{Fe} - \frac{1}{2}\mu^\theta_{O_2}\right) - \left(\mu^\theta_{PdO} - \mu^\theta_{Pd} - \frac{1}{2}\mu^\theta_{O_2}\right) =$$

$$= \Delta G_f^\theta(FeO) - \Delta G_f^\theta(PdO)$$

$$\Delta G_f^\theta(PdO) = \Delta G_f^\theta(FeO) + 2FE$$

$$\frac{\partial(\Delta G^\theta/T)}{\partial T} = \frac{-\Delta H^\theta}{T^2}$$

E8 forts

(29/2)

$$\frac{\partial(\Delta G_f^\ominus(PdO)/T)}{\partial T} = \frac{-\Delta H^\ominus(PdO)}{T^2}$$

$$\Rightarrow \frac{\Delta G_f^\ominus}{T} = \text{konst} + \frac{\Delta H_f^\ominus}{T}$$

Plotta ΔG_f° mot $\frac{1}{T}$ $\Rightarrow$ lutningen: $\Delta H_f^\circ(PdO) = -115\,kJ/mol$

E9.

$\ominus$pol: $Cd(l) \longrightarrow Cd^{2+} + 2e^-$

$\oplus$pol: $Cd^{2+} + 2e^- \longrightarrow Cd(Pb)$

Totalt: $Cd(l) \rightarrow Cd(Pb)$ för 2F

Standardtillstånd: ren Cd(l), 500°C, 1 atm.

$$\Delta G = -2FE = \mu_{Cd(Pb)} - \mu_{Cd(l)} = \mu^*_{Cd(l)} + RT\ln a_{Cd(Pb)} - \mu^*_{Cd(l)}$$

$$= RT\ln a_{Cd(Pb)}$$

$$E = \frac{RT\ln a_{Cd(Pb)}}{-2F}$$

Jämvikt: legering & ånga

partialtryck, Cd

$$\mu_{Cd(Pb)} = \mu_{Cd(g)}$$

$$\mu^*_{Cd(l)} + RT\ln a_{Cd(Pb)} = \mu^\ominus_{Cd(g)} + RT\ln\frac{P_{Cd}}{P^\ominus} \quad (1)$$

Jämvikt: ren Cd & ren ånga

$$\mu^*_{Cd(l)} = \mu^\ominus_{Cd(g)} + RT\ln\frac{P^*_{Cd}}{P^\ominus} \quad (2)$$

$$(1) - (2) \Rightarrow RT\ln a_{Cd(Pb)} = RT\ln\frac{P_{Cd}}{P^*_{Cd}} \Rightarrow a_{Cd(Pb)} = \frac{P_{Cd}}{P^*_{Cd}}$$

E9 forts: $P_{cd} = 5 \cdot 10^{-3}$ atm

E10.

$\ominus$ Na(l) | Na^+ i smälta | Na-am $\oplus$

$X_{Na} = 0{,}011$

Sökt: $f_{Na(am)}$

$\ominus$pol: $Na(l) \longrightarrow Na^+ + e^-$

$\oplus$pol: $Na^+ + e^- \longrightarrow Na(am)$

Tot: $Na(l) \longrightarrow Na(am)$ för 1F

$$\Delta G = -FE = \cancel{\mu}_{Na(am)} - \cancel{\mu}_{Na(l)} = \cancel{\mu}^*_{Na(l)} + RT \ln a_{Na(am)} - \cancel{\mu}^*_{Na(l)}$$

$$= RT \ln a_{Na(am)} = RT \ln x + RT \ln f_{(Na(am))}$$

$a = f \cdot x$

$$\ln f = \frac{-FE}{RT} - \ln x_{Na(am)} \Rightarrow f = 4{,}55 \cdot 10^{-6}$$