

$$pOH = pK_b + \lg \frac{[sals]}{[base]}$$

#12

$$4 = 4,755 + \lg \frac{0,1 \cdot V_{HCl}}{0,13 \cdot V_{NH_3} - 0,1 \cdot V_{HCl}} \quad / \quad V_{NH_3} \text{ ml}$$

$$-0,755 = \lg \frac{0,1 V_{HCl}}{1,3 - 0,1 V_{HCl}}$$

$$\frac{0,1 V_{HCl}}{1,3 - 0,1 V_{HCl}} = 0,175 \quad | \times 10$$

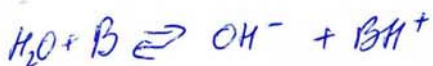
$$\frac{V_{HCl}}{1,3 - 0,1 V_{HCl}} = 1,75$$

$$V_{HCl} = 2,275 - 0,175 V_{HCl}$$

$$1,175 V_{HCl} = 2,275$$

$$V_{HCl} = \underline{\underline{1,93 \text{ ml}}}$$

#13



$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$10^{-6,2} = \frac{[BH^+] \cdot 10^{-7}}{[B]} \Rightarrow \frac{[BH^+]}{[B]} = 10^{0,8} = 6,3 \Rightarrow \left(\frac{[BH^+]}{[B]}\right)^{-1} = 0,158$$

$$\% = \frac{[BH^+]}{[B] + [BH^+]}$$

$$\frac{1}{\%} = \frac{[B]}{[BH^+]} + 1 = 0,158 + 1 = 1,158 \Rightarrow \% = \frac{1}{1,158} = \underline{\underline{86\%}}$$

#14

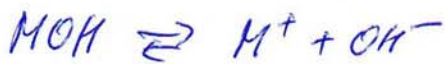


$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1,8 \cdot 10^{-11} = [\text{Mg}^{2+}] \cdot (10^{-4})^2$$

$$[\text{OH}^-] = 10^{-4} \text{ M}$$

$$[\text{Mg}^{2+}] = \underline{\underline{0,0018 \text{ M}}}$$

#15



$$K_{sp} = [\text{M}^+][\text{OH}^-] = 10^{-5}$$

$$[\text{H}^+][\text{OH}^-] = 10^{-14}$$

$$[\text{M}^+] + [\text{H}^+] = [\text{OH}^-]$$

$$\frac{K_{sp}}{[\text{OH}^-]} + \frac{K_w}{[\text{OH}^-]} = [\text{OH}^-] \quad | \times [\text{OH}^-]$$

$$K_{sp} + K_w = [\text{OH}^-]^2$$

$$K_{sp} + K_w \approx K_{sp} = [\text{OH}^-]^2$$

$$[\text{OH}^-] = 10^{-2,5} = 0,00316 \text{ M}$$

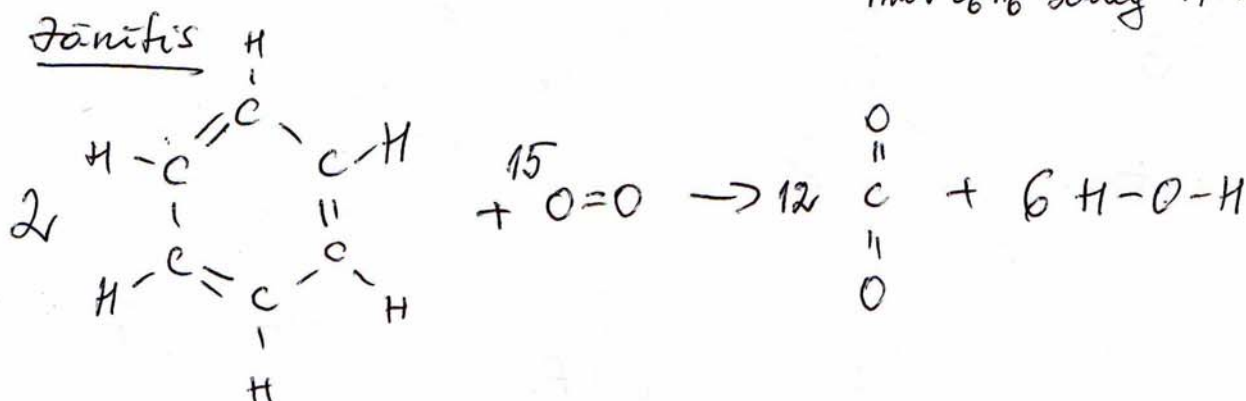
$$\text{pOH} = \underline{\underline{2,5}}$$

$$\text{pH} = 14 - \text{pOH} = 11,5$$



2 (Fiksāto ķīmija)

1 mol C_6H_6 sodeg 7,5 mol O_2



$$\Delta H_2 = \sum E_{\text{bonds broken}} - \sum E_{\text{bonds formed}} =$$

$$= \frac{(6 \cdot 413 + 3 \cdot 346 + 3 \cdot 602) - (24 \cdot 499 + 12 \cdot 463) + 15 \cdot 498}{2} =$$

$$= -5943 \frac{\text{kJ}}{\text{mol benzola}}$$

Pētītis

$$\Delta H_2 = \sum \Delta H_f \text{ produktam} \cdot z - \sum \Delta H_f \text{ izveidotam} \cdot z =$$

$$= \frac{12 \cdot (-393) + 6 \cdot (-285) - (2 \cdot (48,7))}{2} =$$

$$= \underline{\underline{-3262 \frac{\text{kJ}}{\text{mol}}}}$$

1 mol benzols sadegot rodas 3 mol H_2O

$$\Delta H_{deg. \text{Zānis}} = -5943 \text{ kJ}$$

$$\Delta H_{deg. \text{Pētens}} = -3262 \text{ kJ}$$

$$\Delta = 2682 \text{ kJ, kas atbilst 3 mol } H_2O \text{ iztvaikošanai}$$

tā kā pētens rodas šķidrā veidā, tad pētens
būtu jāizdalo ar šķidrā veidā dotajam daudzumam
(tā nos no aprēķinam!!)

$$\Delta H_{izt. H_2O} = \frac{-2682}{3} = -894 \frac{\text{kJ}}{\text{mol}}$$

negatīvs!! (neiespējami)
Zānim nav šķīdība

$$\ln \frac{p_1}{p_2} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{217,75}{1} = \frac{\Delta H}{8,314} \left(\frac{1}{\frac{39}{100+273}} - \frac{1}{\frac{100+373,99}{273}} \right)$$

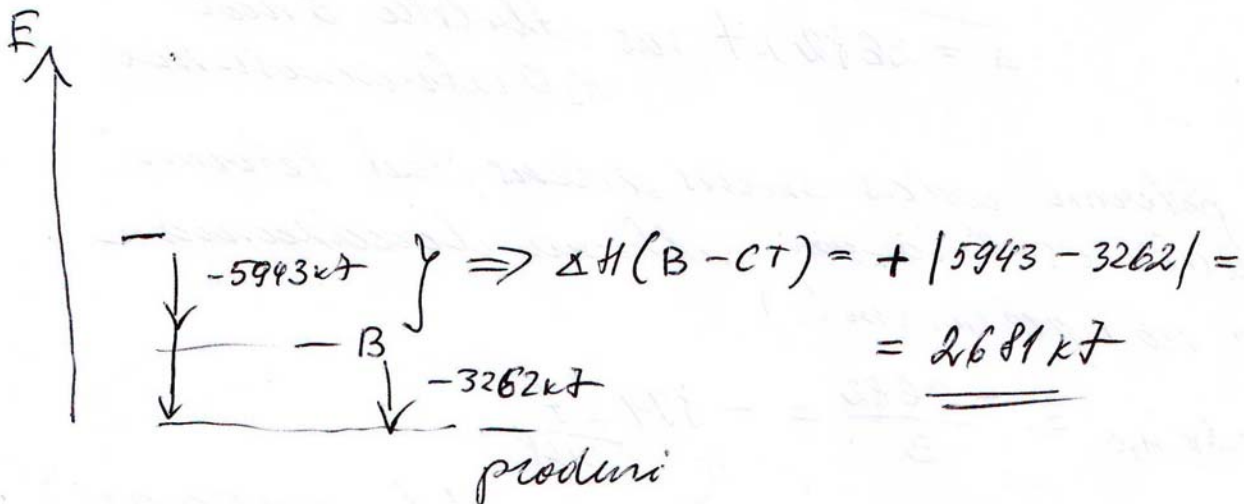
$$\Delta H = 39,4 \frac{\text{kJ}}{\text{mol}} \approx 39 \frac{\text{kJ}}{\text{mol}}$$

$$\text{rel. klūda} = \left| \frac{-894 - 39,4}{39,4} \times 100\% \right| = \underline{\underline{2370\%}}$$

↙ precīzā
ar sistematisko
klūdu

$$\Delta H_{\text{cirklohesrotiens}} = \Delta H_{\text{foms}} = -5943 \text{ kJ} \\ [\text{CT}]$$

$$\Delta H_{\text{ausols}} = \Delta H_{\text{pētuis}} = -3262 \text{ kJ} \\ [\text{B}]$$



3. Uzdevums - 15 punkti

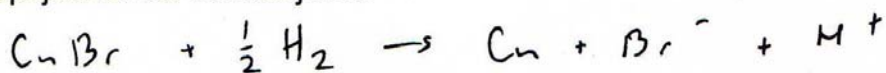
Dots galvaniskais elements (tā shēma): $\text{Pt(s)}|\text{H}_2(\text{g})|\text{HBr}(\text{aq})|\text{CuBr}(\text{s})|\text{Cu}(\text{s})$

(a) Uzrakstīt galvaniskā elementa reducēšanās pusreakcijas un kopējo šūnas vienādojumu.

reducēšanās pusreakciju vienādojumi:



kopējais šūnas vienādojums:



Ja $p(\text{H}_2) = 1 \text{ bar}$, $[\text{HBr}] = 0.1 \text{ mmol}$ tad pie 298 K galvaniskā elementa EDS ir $E_{\text{cell}} = 0.559 \text{ V}$

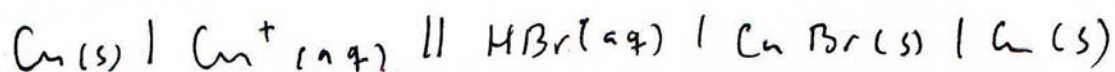
(b) Noteikt CuBr/Cu reducēšanās standartpotenciālu 298 K .

$$E = E^\ominus - \frac{RT}{F} \ln \frac{[\text{H}^+][\text{Br}^-]}{P(\text{H}_2)^{1/2}}$$

$$= 0.559 + \dots = 0.0860 \text{ V}$$

Lai izrēķinātu CuBr šķīdības reizinājumu tiek pētīts cits galvaniskais elements kura oks-red pāri ir Cu⁺/Cu[E° = 0.522 V] un CuBr/Cu.

(c) Uzrakstīt galvanisko elementa shēmu, ko veido šie pāri.



(d) Izrēķināt CuBr šķīšanas standart-Gibsa enerģiju 298 K un šķīdības reizinājumu

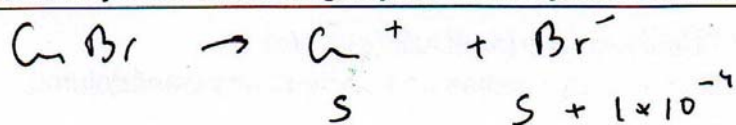
$K_{sp} = [\text{Cu}^+][\text{Br}^-]$.

$$E_{\text{cell}}^{\ominus} = 0.860 \text{ V} - 0.522 \text{ V} = -0.436 \text{ V}$$

$$\Delta G^{\ominus} = -nFE = 42.07 \frac{\text{kJ}}{\text{mol}}$$

$$K_{sp} = \exp\left(-\frac{\Delta G^{\ominus}}{RT}\right) = 4.22 \times 10^{-8}$$

(e) Izmantojot iegūto šķīdības reizinājumu, noteikt Cu⁺ jonu daudzumu otrajā aprakstā minētajā galvaniskajā elementā. Ja gadījumā nevarējāt atrisināt d. punktu, tad pieņemt, ka $K_{sp} = 2 \times 10^{-10}$.

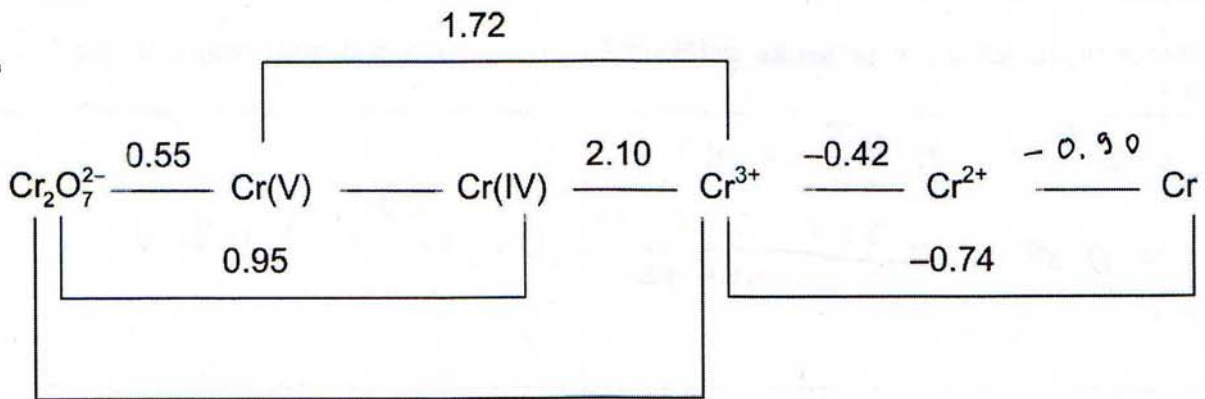


$$S \cdot (S + 1 \times 10^{-4}) = K_{sp} \Rightarrow S = 1.61 \times 10^{-4} \text{ M}$$

4. Uzdevums - 20 punkti

Dota hroma Latimēra diagramma skābā vidē (pH = 0):

(vērtības dotas voltos 298 K temperatūrā)



(a) Noteikt reducēšanās standartpotenciālu oks-red pārim Cr(V)/Cr(IV).

$\text{Cr}_2\text{O}_7^{2-} / \text{Cr(V)}$	$E_1^\ominus = 0.55 \text{ V} \Rightarrow \Delta_1 G^\ominus = -2 F \cdot 0.55$
$\text{Cr(V)} / \text{Cr(IV)}$	$E_2^\ominus = x \text{ V} \Rightarrow \Delta_2 G^\ominus = -2 F \cdot x$
$\text{Cr}_2\text{O}_7^{2-} / \text{Cr(IV)}$	$E_3^\ominus = 0.95 \text{ V} \Rightarrow \Delta_3 G^\ominus = -0.95 \cdot 4 F$
$\Delta_3 G^\ominus = \Delta_1 G^\ominus + \Delta_2 G^\ominus$	$j \quad -0.95 \cdot 4 F = -2 F (0.55 + x)$
	$x = 1.35 \text{ V}$

(b) Uzrakstīt Cr(V) disproporcionēšanās vienādojumu un noteikt standartpotenciālu.

$4 \text{Cr}^{5+} + 7 \text{H}_2\text{O} \rightarrow 2 \text{Cr}^{4+} + \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+$
$E^\ominus = E^\ominus_{\text{Cr(V)}/\text{Cr(IV)}} - E^\ominus_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr(V)}} = 1.35 - 0.55 = 0.8 \text{ V}$

(c) Izmantojot iegūto potenciālu noteikt Cr(V) jonu daudzumu līdzsvarā, ja sākotnēji eksistēja vienmolārs Cr(V) šķīdums.

$K = \exp\left(\frac{n E^\ominus F}{RT}\right) = \exp\left(\frac{4 \cdot 0.8 \cdot 96485}{8.3145 \cdot 298}\right) \approx 1.31 \cdot 10^{54}$											
$4 \text{Cr(V)} \rightarrow 2 \text{Cr(IV)} + \text{Cr}_2\text{O}_7^{2-}$	$K = \frac{2 \cdot x^2}{1 - 4x}$										
<table border="0" style="margin-left: auto; margin-right: auto;"> <tr><td style="text-align: center;">1</td><td style="text-align: center;">0</td><td style="text-align: center;">0</td></tr> <tr><td style="text-align: center;">-4x</td><td style="text-align: center;">+2x</td><td style="text-align: center;">+x</td></tr> <tr><td style="text-align: center;">1-4x</td><td style="text-align: center;">2x</td><td style="text-align: center;">x</td></tr> </table>	1	0	0	-4x	+2x	+x	1-4x	2x	x	$1 - 4x = x$	
1	0	0									
-4x	+2x	+x									
1-4x	2x	x									
	$x = \frac{1}{5} = \frac{1}{4}$										
$\Delta K = 2 \left(\frac{1}{4} - \frac{x}{4}\right)^2$											
$x = 9.52 \times 10^{-56} \text{ M}$											

(d) Pieņemot, ka nekas cits nemainās, aprēķināt Cr(V) disproporcionēšanās potenciālu pie pH = 3

$$E = E^{\ominus} - 14 \frac{RT}{zF} \ln H^+$$

$$= 0.80 - \frac{8.3145 \cdot 298 \cdot 14}{4 \cdot 96485} \ln 10^{-3} = 1.42 \text{ V}$$

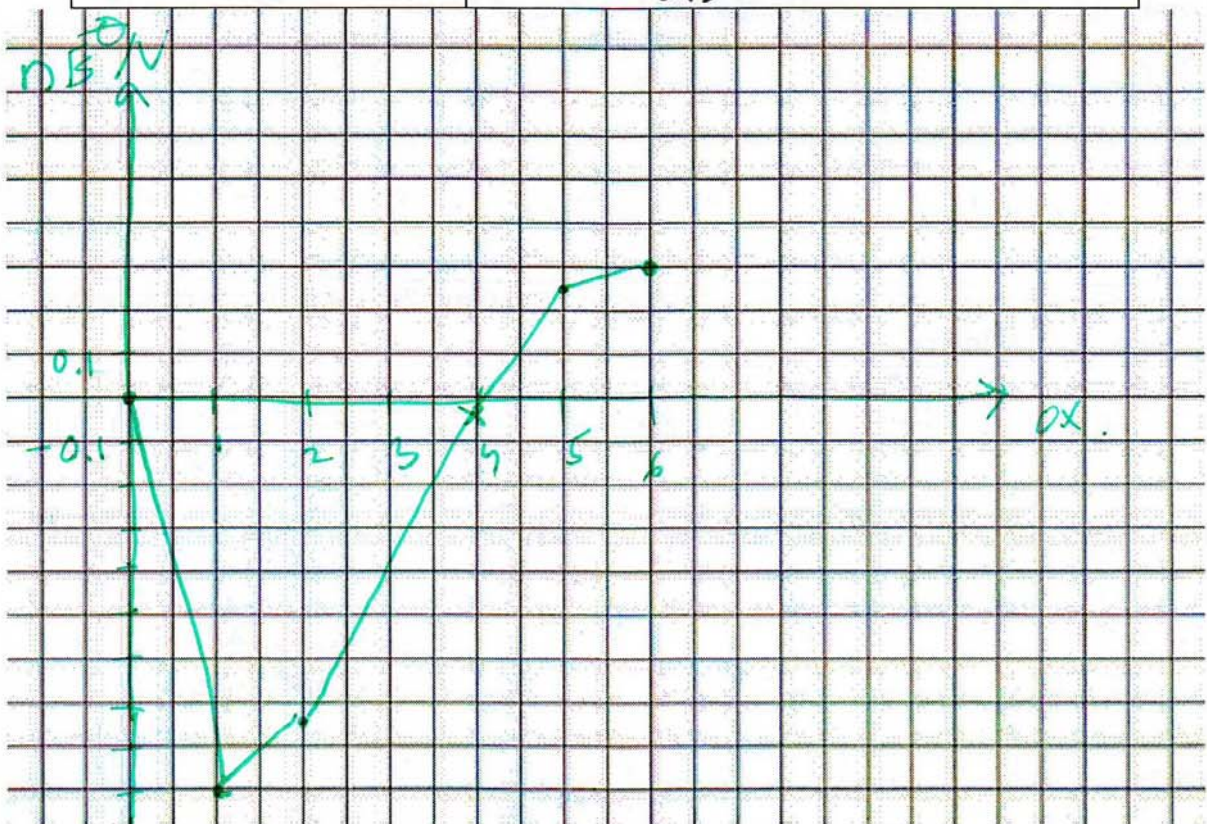
(e) Frosta diagramma parāda reducēšanās standartpotenciālu reakcijai

Jons ar oksidēšanās pakāpi $n + n e^- \rightarrow$ vienkārša viela,

kur standartpotenciāls reizināts ar elektronu skaitu n atkarībā no daļiņas oksidēšanās pakāpes.

Aprēķināt visu punktu koordinātes un uzzīmēt hroma Forsta diagrammu:

Oksidēšanās pakāpe n	$n \cdot E^{\ominus}, \text{V}$
0	0
+2	-0.30
+3	-0.24
+4	-0.03 0.25
+5	0.25 0.30
+6	0.30



1. uzd

$$1) v = k [\text{HSO}_3^-]^a [\text{O}_2]^b$$

$$-\lg v = -\lg k [\text{HSO}_3^-]^a [\text{O}_2]^b$$

$$+\lg v = +\underbrace{a}_{\substack{\text{pārskaites} \\ \text{koeficients}}} \lg [\text{HSO}_3^-] + \underbrace{\lg k}_{\text{konstante}} [\text{O}_2]^b \quad 2 \text{ punkti}$$

$$a = \frac{5.8 - 4.0}{1.9 - 1.0} = 2 \Rightarrow 2. \text{ pakāpe pret } \text{HSO}_3^- \quad 1 \text{ punkts}$$

$$b = \frac{5.2 - 4.5}{1.9 - 1.0} = 1 \Rightarrow 1. \text{ pakāpe pret } \text{O}_2 \quad 1 \text{ punkts}$$

lai izrēķināt v pašam vienam punktu, piemēram $-\lg C_{\text{HSO}_3^-} = 1.0$ 1 punkts
 $C_{\text{HSO}_3^-} = 0.1 \text{ M}$

$$-\lg v = 4 \Rightarrow v = 10^{-4} \frac{\text{M}}{\text{s}}$$

$$10^{-4} = k \cdot 0.1^2 \cdot 0.05$$

$$k = \frac{10^{-4}}{0.1^2 \cdot 0.05} = 0.2 \text{ M}^{-2} \cdot \text{s}^{-1} \quad 1 \text{ punkts}$$

6 punkti

$$2) v = k \cdot [\text{HSO}_3^-]^2 [\text{O}_2]$$

$$v = 0.2 \cdot 0.1^2 \cdot 10^{-3} = 8 \cdot 10^{-6} \text{ M} \cdot \text{s}^{-1}$$

1 punkts

3) ~~visas~~ $[\text{HSO}_3^-] \gg [\text{O}_2]$ tāpat $[\text{HSO}_3^-] \approx \text{const}$ 1 punkts

$$\text{rate}(v) = \underbrace{(k [\text{HSO}_3^-]^2)}_{k'} [\text{O}_2] \quad 1 \text{ punkts}$$

pseudo first order in $[\text{O}_2]$
 $k' = 8 \cdot 10^{-3} \text{ s}^{-1}$ 2 punkti

$$T_{1/2} = \frac{\ln 2}{8 \cdot 10^{-3}} = 87 \text{ s} \quad 1 \text{ punkts}$$

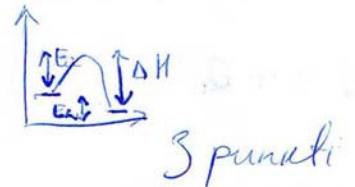
6 punkti

$$4) \ln \frac{k_2}{k_1} = \ln 1.5 = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad 1 \text{ punkt}$$

$$E_a = \frac{R \ln 1.5}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = 51.5 \text{ kJ/mol}$$

$$5) E_a(\text{reverse}) = E_a(\text{forward}) - \Delta H^\circ \quad \text{jo}$$

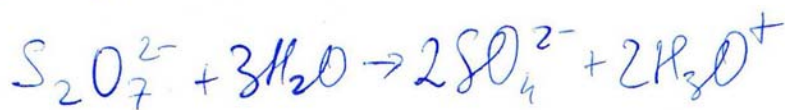
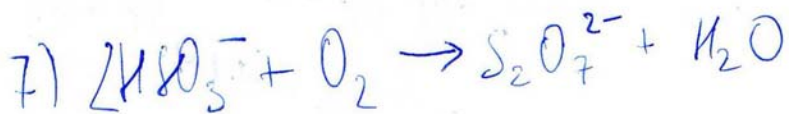
$$E_a(\text{preteška}) = 52 - (-96) = 148 \text{ kJ/mol}$$



$$6) \ln \frac{k_2}{k_1} = \ln 1000 = \frac{E_a - E_a(\text{katal})}{R} \left(\frac{1}{500} \right)$$

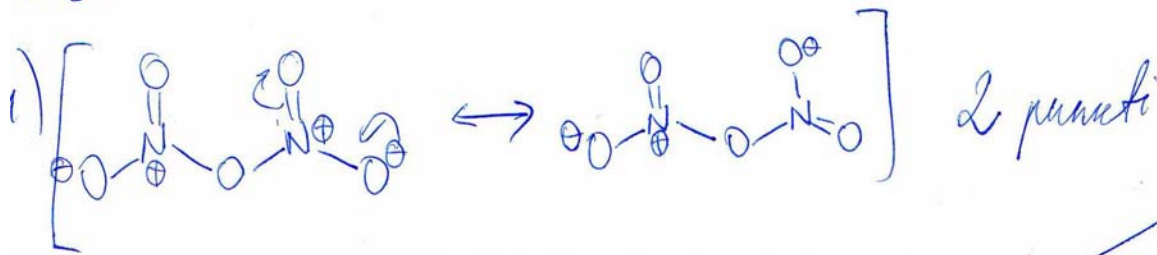
2 punkti

$$E_a(\text{katal}) = 38 \text{ kJ/mol}$$



2 punkti

N2



2) $v = \frac{d[\text{NO}_2]}{dt} = 9.6 \cdot 10^{-5} \text{ M/s}$ $-\frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{v}{2}$ jö $\frac{d[\text{NO}_2]}{4dt} = -\frac{d[\text{N}_2\text{O}_5]}{2dt}$

$\frac{v}{2} = k[\text{N}_2\text{O}_5]$ 1 punkts + 1 punkts

$\frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0} = \frac{\frac{v_t}{2}}{\frac{v_0}{2}} = \frac{v_t}{v_0} = \frac{1}{4}$ 1 punkts \rightarrow palika $\frac{1}{4}$ no sākuma vielas

tātad pagāja 2 pusperiodi \Rightarrow 1pusperiods = $1386/2 = 693 \text{ s}$ 1P

$k = \frac{\ln 2}{t_{1/2}} = 1 \cdot 10^{-3} \text{ s}^{-1}$ 1P

3) $[\text{N}_2\text{O}_5] = \frac{v/2}{k} = \frac{4.8 \cdot 10^{-5}}{1 \cdot 10^{-3}} = 0.048 \text{ M}$ jö $\frac{v}{2} = k[\text{N}_2\text{O}_5]$ 1P

$p_0 = \left(\frac{nRT}{V}\right)_{=c} = 0.048 \cdot 0.0821 \cdot 330 = 1.30 \text{ atm} = 1.32 \cdot 10^5 \text{ Pa}$ 1P

4) $Q = n\Delta H$

nizraģēja = $0.048 \cdot 5 \cdot \frac{3}{4} = 0.18 \text{ mol}$ $Q = 35.1 \text{ kJ}$ 2P

$$5) P_A = P_0 e^{-kt}$$

$$P = P_0 [e^{-kt} + 2(1 - e^{-kt}) + 0.5(1 - e^{-kt})] = P_0 (2.5 - 1.5e^{-kt}) \quad P_0 = 1.3 \text{ atm}$$

$$k = 1 \cdot 10^{-3} \text{ s}^{-1} \quad 4 \text{ p}$$

6) 4 mol N-O saišu šarauti 1 mols O=O saišu izvaidojās

$$4 \cdot E_{\text{N-O}} - E_{\text{O=O}} = 195.2 \quad E_{\text{N-O}} = 222 \text{ kJ/mol} \quad 4 \text{ p}$$