LU Ķīmijas skola, kontroldarbs fizikālajā ķīmijā
28.03.2008. *Atrisinājumi*

a) The sulfur atoms are coordinated by one sulfur atom and three Fe^{2+} ions in a distorted tetrahedral arrangement.

b) The smallest unit cell with a lattice constant of a_0 contains 4 Fe and 8 S atoms. This leads to

$$\rho = \frac{4 \cdot M(\mathrm{Fe}) + 8 \cdot M(\mathrm{S})}{N_A a_0^3} = 5.011\,\mathrm{g/cm^3}$$

From this equation we obtain a_0 = 541.8 pm.

c) For varying iron content the calculations can be done as follows:

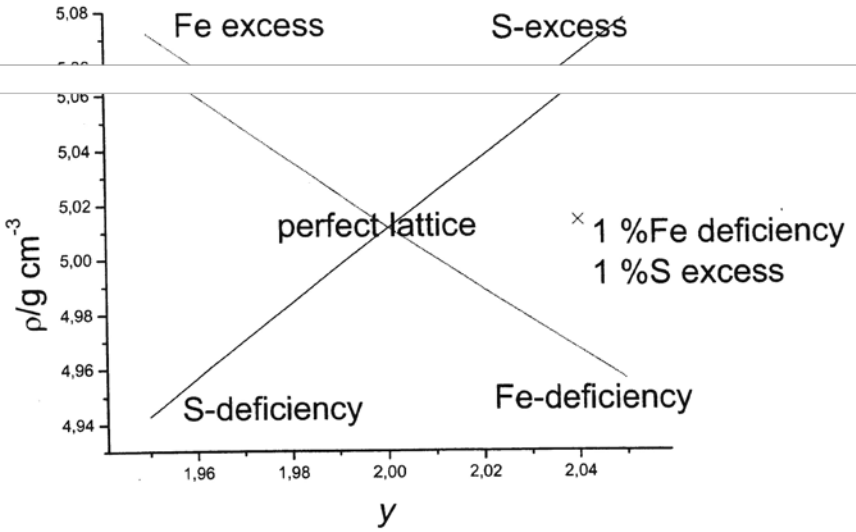
One mole of the crystal contains 8 mol S and 8/y mol Fe. Hence the relationship between the density of the crystal and the composition in the case of varying iron content is:

$$\rho = \frac{8 \cdot M(\mathrm{S}) + 8 \cdot M(\mathrm{Fe})/y}{N_A a_0^3} = \left(2.679 + \frac{4.667}{y}\right)\mathrm{g/cm^3}$$

For varying S content: one mole of the crystal contains 4 mol Fe and 4y mol S. Thus the dependence of density on y is:

$$\rho = \frac{4 \cdot M(\mathrm{Fe}) + 4y \cdot M(\mathrm{S})}{N_A a_0^3} = (2.332 + 1.339y)\,\mathrm{g/cm^3}$$

d)



e) In the unit cell of the natural pyrite sample, there is 4·0.99 = 3.96 mol Fe and 8·1.01 = 8.08 mol S. This gives y = 8.08/3.96 = 2.04. This is within the region where the unit cell parameter does not depend on the composition; therefore the density can be

6) $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2\uparrow$ (1)

$Fe_2O_3 + 3CO \rightarrow 3CO_2 + 2Fe$ (2)

(1) $\Delta H_f\ FeS_2 = -177,40\ \frac{kJ}{mol}$ $S^\circ = 52,99\ \frac{J}{mol \cdot K}$

$\Delta H_f\ Fe_2O_3 = -822,16\ \frac{kJ}{mol}$ $S^\circ = 87,45\ \frac{J}{mol \cdot K}$

$\Delta H_f\ SO_2 = -296,60\ \frac{kJ}{mol}$ $S^\circ = 248,07\ \frac{J}{mol \cdot K}$

$S^\circ_{O_2} = 205,04\ \frac{J}{mol \cdot K}$

$\Delta H_1 = -4 \cdot (-177,40) + 2 \cdot (-822,16) + 8 \cdot (-296,60) =$
$= -3307,52\ kJ$

$\Delta S_1 = -4 \cdot (+52,99) - 11(+205,04) + 2 \cdot (87,45) + 8 \cdot (248,07) =$
$-307,94\ \frac{J}{K} =$
$= -0,30794\ \frac{kJ}{K}$

$T = \frac{\Delta H}{\Delta S} = \frac{-3307,52}{-0,30794} =$
$= 10\,740\ K \Rightarrow$

$\Rightarrow \Delta G < 0$, jo. $T < 10740\ K$

2-ja reakcija notiek visās temperatūrās līdz 10740 K, tikai zemā t° tās ātrums ir mazs

(2) $\Delta H_f\ CO = -110,53\ \frac{kJ}{mol}$ $S^\circ = 197,55\ \frac{J}{mol \cdot K}$

$\Delta H_f\ CO_2 = -393,51\ \frac{kJ}{mol}$ $S^\circ = 213,66\ \frac{J}{mol \cdot K}$

$S_0\ Fe = 27,15\ \frac{J}{mol \cdot K}$

$\Delta H_2 = 3 \cdot (-393,51) - 3 \cdot (-110,53) - (-822,16) = -26,78\ kJ$

$\Delta S_2 = 2 \cdot 27,15 + 3 \cdot 213,66 - 3 \cdot 197,55 - 87,45 = 15,18\ \frac{J}{K} =$
$= 0,01518\ \frac{kJ}{K}$

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

$-26,78 - T \cdot 0,01518 < 0$ T – jebkura

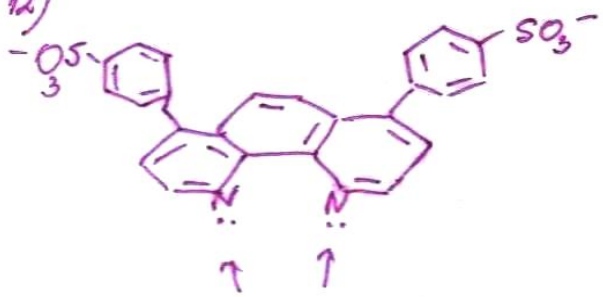
7) $\Delta G_1 = -1 \cdot F \cdot 0{,}771 = -0{,}771F$

$\Delta G_2 = -2 \cdot F \cdot (-0{,}44) = +0{,}88F$

$\Delta G_3 = 0{,}109F$

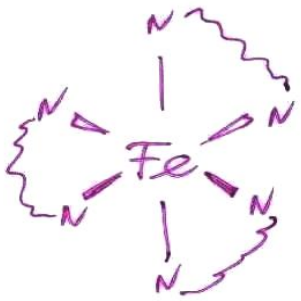
$E_{Fe^{3+}/Fe} = \frac{-0{,}109}{3} = -0{,}036V$

12)



bidentāts ligands

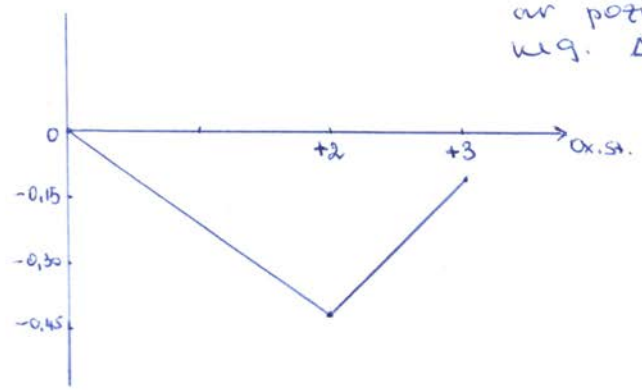
kompleks: FeL_3^{4-}



oktaedriska uzbūve (uzspējami d optiskie izomēri)

9)

Fe^{2+} ir stabilāks, jo gan oksidēšanai, gan reducēšai tas jāpievada elektriskā enerģijā (diagrammā atrodas zem taisnes, kas savieno $Fe - Fe^{3+}$)
Fe^{3+} ~~[illegible]~~ reducēšana uz Fe^{2+} notiek ar pozitīvu potenciālu, tātad ar kvg. ΔG un var notikt spontāni.



10) $3Fe^{2+} \rightarrow 2Fe^{3+} + Fe$

$E = \varepsilon_0 Fe^{4}/Fe - \varepsilon_0 Fe^{3+}/Fe^{2+} < 0$ $\quad \Delta G = -EzF > 0$ reakcija nav iespējama

$= -1{,}211V$

(+)

8) a) Fe + 1 M HCl

$Fe + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow$

$\varepsilon^\circ_{Fe^{2+}/Fe} = -0{,}44\,V \quad \varepsilon^\circ_{H^+/H_2} = 0\,V$

$E = \varepsilon^\circ_{H^+/H_2} - \varepsilon^\circ_{Fe^{2+}/Fe} = 0{,}44\,V$ – reakcija notiek

$Fe + 3H^+ \rightarrow Fe^{3+} + 1{,}5H_2\uparrow$

$E = \varepsilon^\circ_{H^+/H_2} - \varepsilon^\circ_{Fe^{3+}/Fe} = 0{,}036\,V$

Teorētiski reakcija iespējama (praktiski Fe^{3+} gandrīz nerodas, jo lielā Fe^{3+}/Fe^{2+} potenciāla dēļ tas viegli oksidē Fe un H_2 un reducējas par Fe^{2+})

Tomēr dominē Fe oksidēšanās par Fe^{2+}

b) Fe + 0,1 M HCl

$\varepsilon_{H^+/H_2} = 0 + \frac{RT}{2F}\ln[H^+] = -0{,}059\,V$

$\varepsilon^\circ_{Fe^{2+}/Fe} = -0{,}44\,V$

$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$

$E = \varepsilon_{H^+/H_2} - \varepsilon^\circ_{Fe^{2+}/Fe} = 0{,}38\,V$ – reakcija notiek

$Fe + 3H^+ \rightarrow Fe^{3+} + 1{,}5H_2$

$E = \varepsilon_{H^+/H_2} - \varepsilon_{Fe^{3+}/Fe} = -0{,}023\,V$ – reakcija nenotiek

Notiek tikai Fe^{2+} jonu rašanās

11) $Fe + 6CN^- - 2e^- = [Fe(CN)_6]^{4-}, \quad \varphi^\circ = +1.16\,V \quad (1)$

$Fe^{2+} + 2e^- = Fe^\circ, \quad \varphi^\circ = -0.44\,V \quad (2)$

$Fe^{2+} + 6CN^- = [Fe(CN)_6]^{4-} \quad (3)$

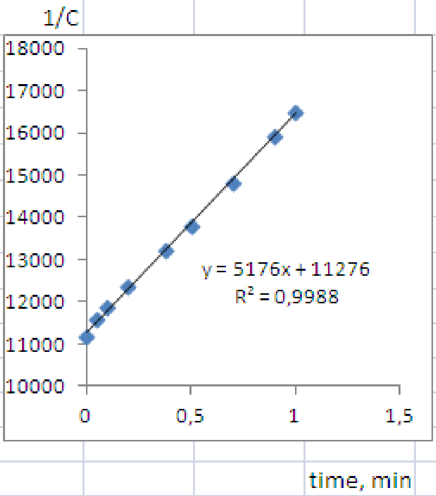
$\Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2 = -2 \times 96485\,C \cdot mol^{-1}\,(1.16\,V - 0.44\,V) = -1{,}39 \times 10^5\,J\,mol^{-1}$

$\Delta G^\circ = -RT \ln K$

$K = \exp(\Delta G^\circ / RT) = 2{,}19 \times 10^{24} = \beta \quad [M^{-6}]$

13)

t, min	A	C, M	ln C	1/C
0	0,9939	8,95405E-05	-9,32082	11168,13
0,05	0,9592	8,64144E-05	-9,35636	11572,14
0,1	0,9348	8,42162E-05	-9,38212	11874,2
0,2	0,8968	8,07928E-05	-9,42362	12377,34
0,38	0,8384	7,55315E-05	-9,49096	13239,5
0,5	0,804	7,24324E-05	-9,53286	13805,97
0,7	0,7485	6,74324E-05	-9,60438	14829,66
0,9	0,6967	6,27658E-05	-9,6761	15932,25
1	0,6723	6,05676E-05	-9,71175	16510,49



Reakcija ir otrās pakāpes. (sanāk vislabākais R^2).