

BCHO [16]

Time for Chemistry!

16th Baltic States Chemistry Olympiad

Theoretical Examination
Solutions

English version

Secret compound

1. i) **A** is most probably some metal oxide, because it's insoluble in water (equation 4). Now let's say that **A** contains **x** oxygen atoms and **B** – **y**. If we count oxygen atoms in either equations 1 or 2, we would get the relationship

$$2y = x + 5.$$

It is clear from equations 1 and 4 that compound **C** does not contain sulphur. By counting oxygen atoms in equation 3, it is possible to deduce that **C** contains 4 oxygen atoms. Therefore using equation 4 we get another relationship

$$x + y = 7$$

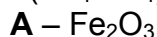
that is **x** = 3 and **y** = 4.

Now we know that **A** is of form **M**₂O₃, **B** is Na₂**MO**₄, **C** is Na₄**MO**₄ and **D** is **MSO**₄.

Using given data it is possible to count moles of NaOH present in the solution:

$$n(\text{NaOH}) = c \cdot V = 10^{(\text{pH}-14)} \cdot 0,1 = 0,00157 \text{ mol. Then}$$

$$n(\text{Na}_4\text{MO}_4) = 0,000472 \text{ mol and } M(\text{Na}_4\text{MO}_4) = 211.85 \text{ g/mol. } \mathbf{M} \text{ is Fe.}$$



- ii) Two Fe³⁺ ions are needed.

iii) $n(\text{Fe}^{3+}) = \mathbf{a}$

$$n(\text{Fe}^{2+}) = \mathbf{b}$$

$$\text{Then } 1 - \mathbf{x} = \mathbf{a} + \mathbf{b} \text{ and } 3\mathbf{a} + 2\mathbf{b} = 2.$$

Multiply first equation by -2 and sum with the second equation to obtain

$$\mathbf{a} = 2\mathbf{x}. \quad \text{Put this into first equation to obtain}$$

$$\mathbf{b} = 1 - 3\mathbf{x}. \quad \text{Then}$$

$$\mathbf{a/b} = 2\mathbf{x}/(1-3\mathbf{x}).$$

- iv) One elementary cube holds 4 Fe and 4 O atoms in perfect FeO. In Fe_{0.925}O however there are on average 3.7 Fe and 4 O atoms. Their weight is

$$(3.7 \cdot 55.85 + 4 \cdot 16)/6.02 \cdot 10^{23} = 4.49 \cdot 10^{-22} \text{ g}$$

Dividing this by density gives volume:

$$4.49 \cdot 10^{-22} \text{ g} / 6.02 \text{ g cm}^{-3} = 7.468 \cdot 10^{-23} \text{ cm}^3$$

The lattice constant is

$$(7.468 \cdot 10^{-23} \text{ cm}^3)^{1/3} = 4.21 \cdot 10^{-8} \text{ cm} = 4.21 \text{ \AA}$$

The distance between two closest Fe atoms is

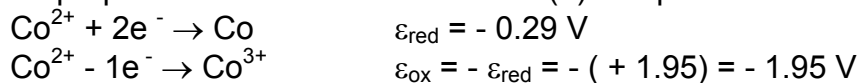
$$2^{1/2} \cdot 4.21 \text{ \AA} / 2 = \mathbf{2.98 \text{ \AA}}$$

- v) The distance between two oxygen atoms is the same **2.98 \AA**.

vi) $\rho = \frac{m}{V} = \frac{4(1-x) \cdot 55.85 + 4 \cdot 16}{6.02 \cdot 10^{23}} \cdot \frac{1}{7.468 \cdot 10^{-23}} = \frac{287.4 - 223.4x}{44.96} = \mathbf{6.40 - 4.97x}$

Chameleonic cobalt

2. i) Disproportionation reactions of cobalt (II) compounds:



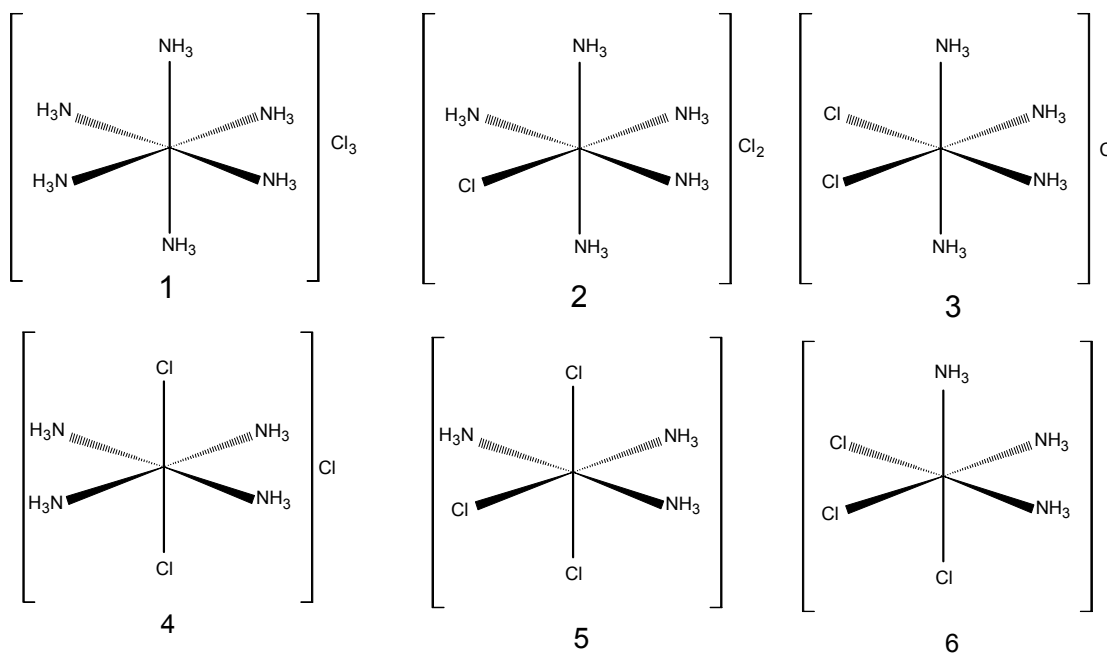
$$E_{\text{tot}} = \epsilon_{\text{red}} + \epsilon_{\text{ox}} = -0.29 - 1.95 < 0 \text{ V}$$

$\Rightarrow \Delta G = -z \cdot E \cdot F > 0 \dots$ **disproportionation is impossible**

Cobalt (II) classical compounds are more stable, than cobalt (III) compounds because it is hard to oxidize Co(II) to Co(III) (highly negative oxidation potential), but cobalt (III) compounds can easily be converted to Co(II) (highly positive potential, and reactions are fast, because 1 electron transition). Cobalt (III) compounds are very strong oxidants and they oxidize even water.

Cobalt (II) complexes get more easily oxidized (milder oxidants, including oxygen or air, are good enough), oxidation potential is not so negative (only -0.1 V) as it is for classical compounds. Reduction potential for Co (III) complexes is small.

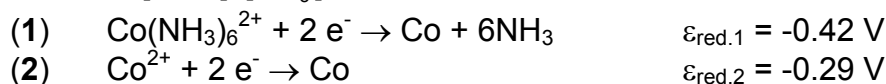
ii)



- 1 – hexaamminecobalt(III) chloride
- 2 – pentaamminechlorocobalt(III) chloride
- 3 – *cis*-tetraaminedichlorocobalt (III) chloride
- 4 – *trans*-tetraaminedichlorocobalt (III) chloride
- 5 – *mer*-triaminetrichlorocobalt(III)
- 6 – *fac*- triaminetrichlorocobalt (III)

iii) $\text{Co}^{2+} + 6\text{NH}_3 \rightarrow [\text{Co}(\text{NH}_3)_6]^{2+}$

$$K_{\text{stab. (II)}} = \frac{[\text{Co}(\text{NH}_3)_6^{2+}]}{[\text{Co}^{2+}] \cdot [\text{NH}_3]^6}$$



Formation of complex ion can combine following: reaction (2) minus reaction (1).
 Doing same with potentials we obtain:

$$E_{\text{tot}}^0 = \varepsilon_{\text{red},2} + \varepsilon_{\text{ox},1} = \varepsilon_{\text{red},2} - \varepsilon_{\text{red},1} = -0.29 - (-0.42) = 0.13 \text{ V}$$

$$E_{\text{tot}} = 0 = E_{\text{tot}}^0 - \frac{RT}{zF} \ln K$$

$$E_{\text{tot}}^0 = \frac{RT}{zF} \ln K$$

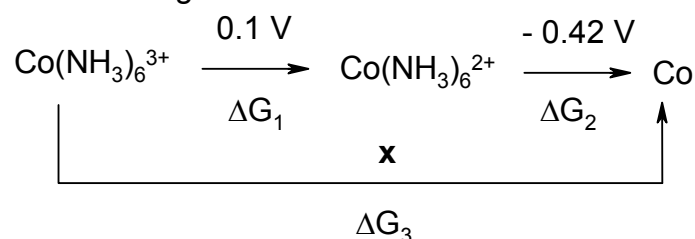
$$0.13 = \frac{8.314 \cdot 298}{2 \cdot 96500} \ln K$$

$$\ln K = 10.13$$

$$K_{\text{stab. (II)}} = 2,5 \cdot 10^4 \text{ M}^{-6}$$

$$\lg K_{\text{stab. (II)}} = 4,39$$

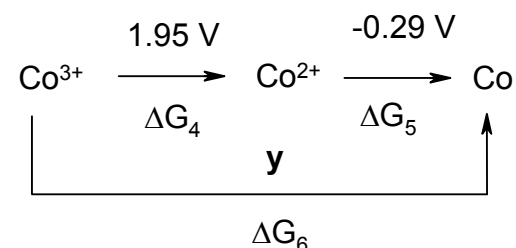
For cobalt (III) complexes we have to calculate corresponding potentials from Lattimer diagrams:



$$\Delta G_3 = \Delta G_1 + \Delta G_2$$

$$-3F \cdot x = -F \cdot 0.1 + (-(-0.42) \cdot 2F) = -0.1 F + 0.84 F = 0.74 F$$

$$x = \frac{0.74}{-3} = -0.277 \text{ V}$$

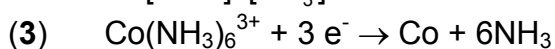


$$\Delta G_6 = \Delta G_4 + \Delta G_5$$

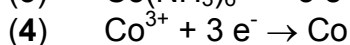
$$-3F \cdot y = -F \cdot 1.95 + (-(-0.29) \cdot 2F) = -1.95 F + 0.58 F = -1.37 F$$

$$y = \frac{-1.37}{-3} = 0.457 \text{ V}$$

$$K_{\text{stab. (III)}} = \frac{[\text{Co(NH}_3)_6^{3+}]}{[\text{Co}^{3+}] \cdot [\text{NH}_3]^6}$$



$$\varepsilon_{\text{red},1} = -0.277 \text{ V}$$



$$\varepsilon_{\text{red},2} = 0.457 \text{ V}$$

Formation of complex ion can combine following: reaction (4) minus reaction (3).
 Doing same with potentials we obtain:

$$E_{\text{tot}}^0 = \varepsilon_{\text{red.4}} + \varepsilon_{\text{ox.3}} = \varepsilon_{\text{red.4}} - \varepsilon_{\text{red.3}} = 0.457 - (-0.277) = 0.734 \text{ V}$$

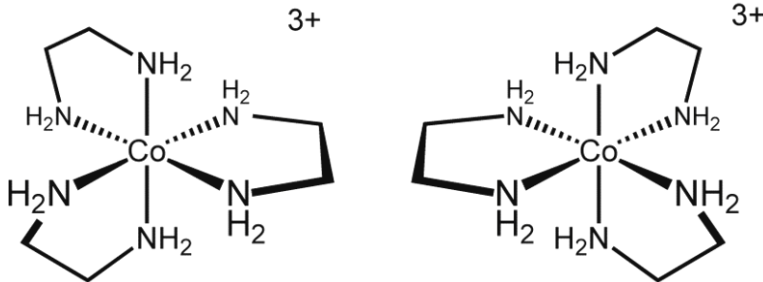
$$0.734 = \frac{8.314 \cdot 298}{3 \cdot 96500} \ln K$$

$$\ln K = 85.76$$

$$K_{\text{stab.(III)}} = 1.77 \cdot 10^{37} \text{ M}^{-6}$$

$$\lg K_{\text{stab.(III)}} = 37.2$$

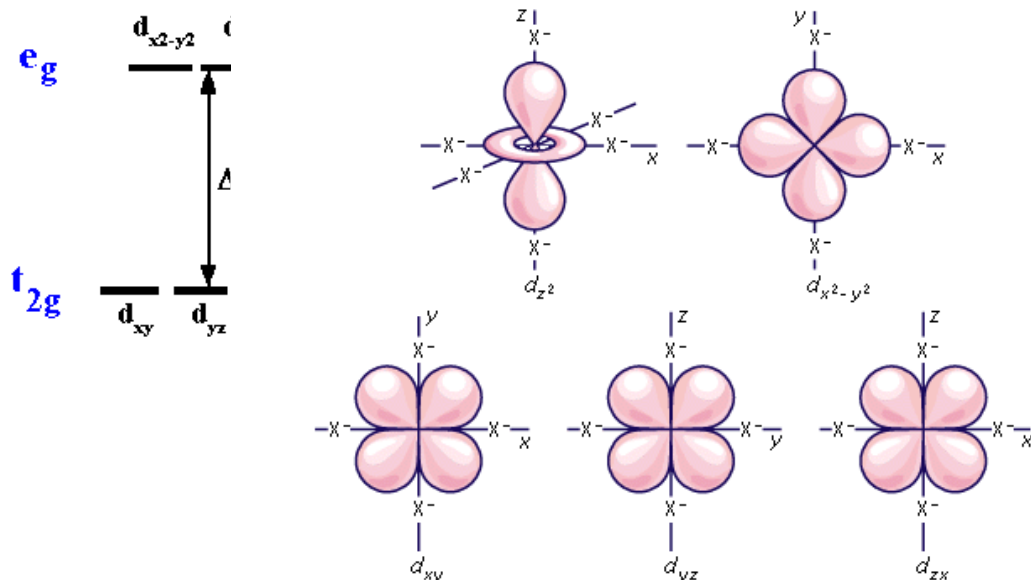
iv) Formula: $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_3]^{3+}$



Both isomers have the same physical properties excluding rotation of linearly polarized light. This parameter has the same magnitude, but is of different sign for different isomers.

Ethylenediamine is a **bidentate ligand**. It differs from ammonia and chloride ions by its ability to bind to central metal ion with its two nitrogen atoms forming a cyclic system.

v) In ligand field, orbitals split in two energy levels as it is shown in the picture below. Also it is shown from which starting orbitals each orbital is derived. In octaedral field the best describing is to bring nearer ligand by axis so with greater energy will be orbitals which are positioned on axes but with lower energy those who are in-between axes.



vi) Transition between t_{2g} and e_g orbitals is in visible region of spectrum, so it has a maximum at approximately 475 nm.

$$E = \frac{hc}{\lambda} = \frac{6.626 \cdot 10^{-34} \cdot 3.00 \cdot 10^8}{475 \cdot 10^{-9}} = 4.18 \cdot 10^{-19} \text{ J}$$

$$E_{\text{mol}} = E \cdot N_A = 4.18 \cdot 10^{-19} \cdot 6.022 \cdot 10^{23} = 252 \text{ kJ/mol}$$

Negative activation energy!?

3. i) $v = k \cdot [\text{NO}]^x \cdot [\text{O}_2]^y$

Compare table rows 1 and 2:

When $[\text{NO}]$ increases 2 times, the reaction rate increases 4 times, $x = 2$

Compare table rows 1 and 3:

When $[\text{O}_2]$ increases 2 times, the reaction rate increases 2 times, $y = 1$

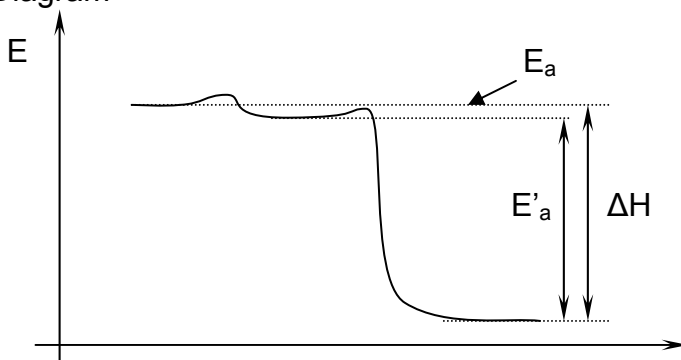
ii) $2,5 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1} = 2k \cdot (0,010 \text{ mol} \cdot \text{dm}^{-3})^2 \cdot (0,010 \text{ mol} \cdot \text{dm}^{-3})$

$k = 12,5 \text{ (dm}^3)^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$

iii) $E'_a = 8,3145 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot \frac{645 \text{ K} \cdot 600 \text{ K}}{645 \text{ K} - 600 \text{ K}} \ln \frac{407}{83,9} \cdot 1 \text{ mol} = 113 \text{ kJ}$

iv) $\Delta H_r = (2 \cdot 33,10 - 2 \cdot 90,29) \frac{\text{kJ}}{\text{mol}} = -114,38 \frac{\text{kJ}}{\text{mol}}$

v) Diagram



vi) $\frac{d[\text{NO}_3]}{dt} = k_1[\text{NO}][\text{O}_2] - k_{-1}[\text{NO}_3] - k_2[\text{NO}_3][\text{NO}] \Rightarrow [\text{NO}_3] = \frac{k_1[\text{NO}][\text{O}_2]}{k_{-1} + k_2[\text{NO}]}$

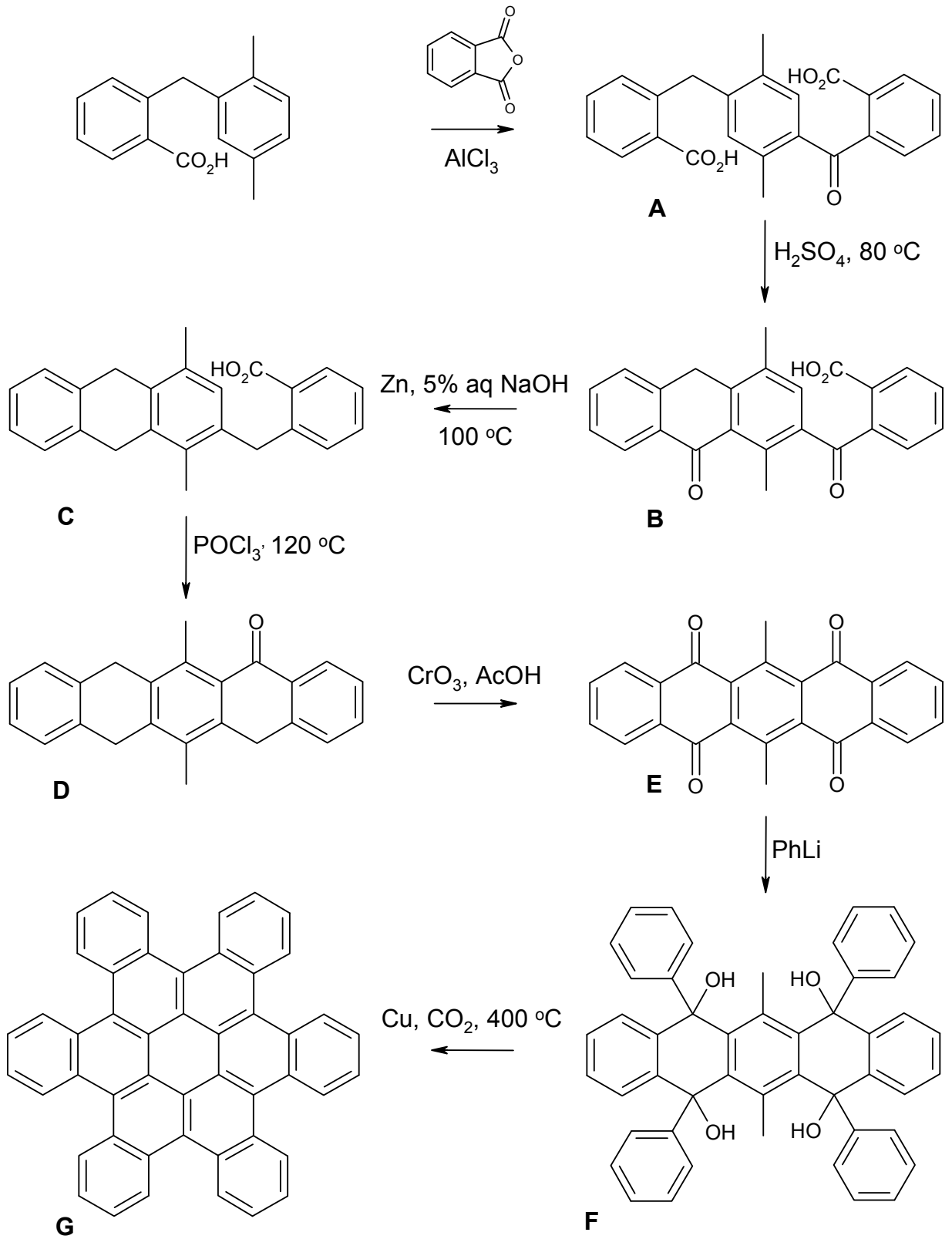
$\frac{d[\text{NO}_2]}{dt} = \frac{1}{2} k_2[\text{NO}_3][\text{NO}] = \frac{0,5k_1[\text{NO}][\text{O}_2]}{k_{-1} + k_2[\text{NO}]} \cdot k_2[\text{NO}] = \frac{0,5k_1k_2}{k_{-1} + k_2[\text{NO}]} [\text{NO}]^2[\text{O}_2]$

vii) The reaction mechanism supports the kinetic and thermodynamic experimental data.

From the derived equation, we may guess, that $k_{-1} > k_2[\text{NO}]$. The relationship means, that the equilibrium is fast and the concentration of intermediate NO_3 is noticeable. Also it means, that the experimental (seeming) activation energy equals entropy of the reaction $\text{NO}_2 + \text{O}_2 \rightarrow \text{NO}_3$ as the true activation energies are too small (≈ 0). Seeming activation energy equals -1.4 kJ ($113 - 114.4$). According to the Arrhenius equation, k should decrease, as temperature increases, when activation energy is negative.

Elegant structure

4.



Lithium Batteries (Liitiumpatareid)



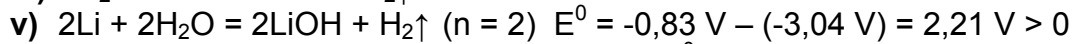
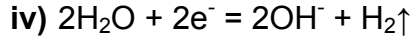
ii) $Q(\text{Li}/\text{Li}^+) = \frac{1}{1} \cdot 6,94 \text{ g} \cdot \frac{1 \text{ mol}}{6,94 \text{ g}} \cdot \frac{96490 \text{ C}}{1 \text{ mol}} \cdot \frac{1 \text{ h}}{3600 \text{ s}} \cdot \frac{1}{6,94 \text{ g}} = \frac{26,8 \text{ Ah}}{6,94 \text{ g}} = 3,86 \frac{\text{Ah}}{\text{g}}$

$Q(\text{Ca}/\text{Ca}^{2+}) = \frac{2}{1} \cdot \frac{26,8 \text{ Ah}}{40,08 \text{ g}} = 1,34 \frac{\text{Ah}}{\text{g}}$

$Q(\text{Al}/\text{Al}^{3+}) = \frac{3}{1} \cdot \frac{26,8 \text{ Ah}}{27,0 \text{ g}} = 2,98 \frac{\text{Ah}}{\text{g}}$

$Q(\text{Cd}/\text{Cd}^{2+}) = \frac{2}{1} \cdot \frac{26,8 \text{ Ah}}{112,4 \text{ g}} = 0,48 \frac{\text{Ah}}{\text{g}}$

iii) Li (a) $E^0(\text{Li}^+/\text{Li})$ is most negative (b) $Q(\text{Li}^+/\text{Li})$ is the largest



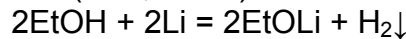
$E^0 = -0,83 \text{ V} - (-2,87 \text{ V}) = 2,04 \text{ V} > 0$

At $T=25^\circ\text{C}$ Al does not react with water, because it is covered with Al_2O_3 , although $E^0 > 0$.

vi) $\Delta G^0 = -2 \cdot \frac{96490 \text{ C}}{1 \text{ mol}} \cdot 2,21 \text{ V} = -426\,500 \text{ J/mol} < 0$ spontaneous process

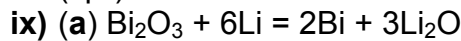
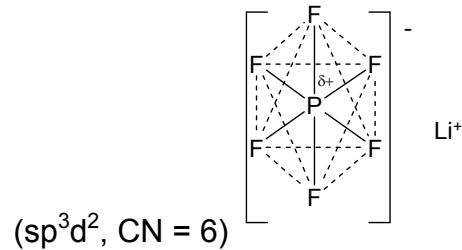
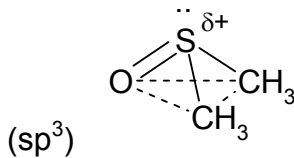
$\ln K = -\frac{\Delta G^0}{RT} = -\frac{-426\,500 \text{ J}}{8,314 \text{ J} \cdot 298 \text{ K}} = 172$ $K = e^{172} = 5,74 \cdot 10^{74}$

vii)(c) dimetüülsulfoksiid solvates ions, the electrical conductivity is good
Protonic solvents (H_2O , EtOH) do not fit because they react with metal



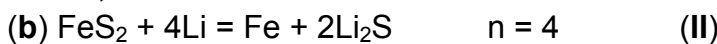
Hexane (C_6H_{14}) do not fit because it is nonpolar and does not solvate ions.

viii) dimethyl sulfoxide $\text{SO}(\text{CH}_3)_2$ lithium hexafluorophosphate(V) LiPF_6

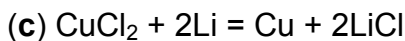


$\Delta G^0 = [3 \cdot (-562,11) - (-493,47)] \text{ kJ/mol} = -1192,9 \text{ kJ/mol}$

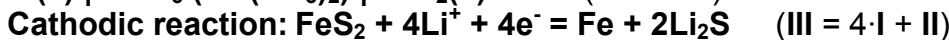
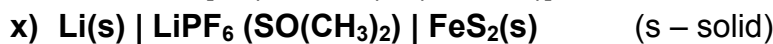
$w_{e, \text{max}} = \Delta G^0 = -1192,9 \text{ kJ/mol}$



$\Delta G^0 = [2 \cdot (-439,08) - (-160,07)] \text{ kJ/mol} = -718,09 \text{ kJ/mol}$



$\Delta G^0 = [2 \cdot (-384,02) - (-173,81)] \text{ kJ/mol} = -594,23 \text{ kJ/mol}$

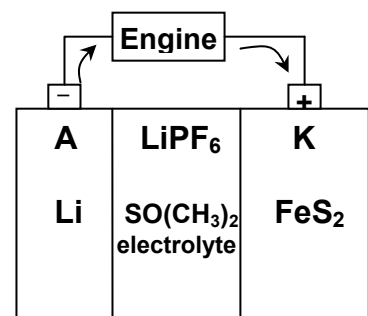


$E^0(\text{II}) = -\frac{\Delta G^0}{nF} = -\frac{-718090 \text{ J}}{4 \cdot 96490 \text{ C}} = 1,86 \text{ V}$

$E^0(\text{III}) = -3,04 \text{ V} + 1,86 \text{ V} = -1,18 \text{ V}$

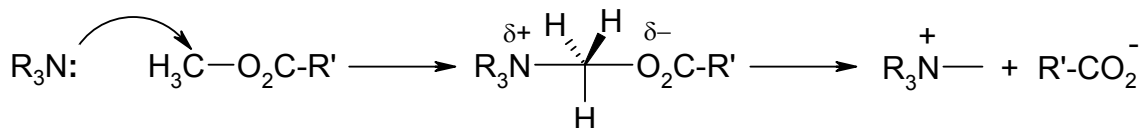
xi)

xii) FeS_2 . Otherwise the residual lithium might react very energetically with water and cause explosion.



Supramolecular basket

6. i) S_N2 mechanism



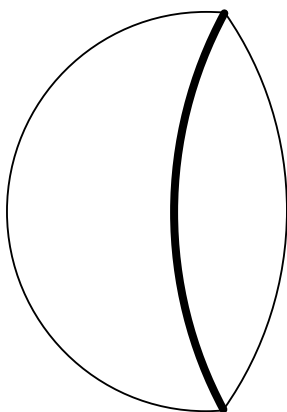
ii) Polar solvents solvate charged particles. The intermediate complex is partially charged on N and C atoms, so it is stabilized by the polar solvent and the activation energy is decreased. Similarly stabilized are charged products.

iii) (Explanation)

iv)

(scheme of the reaction mechanism)

v)



(structure)

vi) (beginning of the solution is absent)

is in interval 3.5-4.5 Å. Adding twice the hydrogen radius we get the diameter of quinuclidine (5.9-6.9 Å), so there is enough space in the bucket for only one molecule.

$$\text{vii) } c = \frac{N}{N_A} \cdot \frac{1}{V} = \frac{1 \text{ mol}}{6.022 \cdot 10^{23}} \cdot \frac{1}{160 \text{ \AA}^3} \cdot \frac{10^{27} \text{ \AA}^3}{1 \text{ dm}^3} = 10.4 \frac{\text{mol}}{\text{dm}^3} = \mathbf{10,4 \text{ M}}$$

viii) Mesitylene molecule is larger than quinuclidine, therefore it can not fit into the ester bucket which is left empty for quinuclidine molecules only. Chloroform molecules are small enough and they compete with quinuclidine molecules for space in the bucket. Since chloroform concentration is considerably larger than quinuclidine, chloroform molecules fill all the buckets, blocking the formation of reactive supramolecular complex.