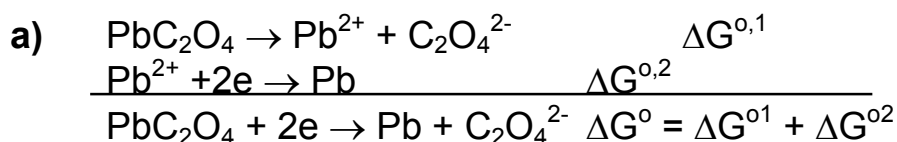


9th Baltic Chemistry Olympiad
April 25-27, 2001, Tartu

SOLUTIONS

PROBLEM 1



$$\Delta G^{0,1} = -RT \ln K_{\text{sol}} = -8,314 \cdot 298 \cdot 2,303 \cdot \log(8,50 \cdot 10^{-10}) = 51,75 \text{ kJ/mol} \approx 51,8 \text{ kJ/mol}$$

$$\Delta G^{0,2} = -nFE^0 = 2 \cdot 96485 \cdot 0,126 = 24,31 \text{ kJ/mol}$$

$$\Delta G^0 = 51,75 + 24,31 = 76,06 \text{ kJ/mol};$$

$$E^0_2 = -\Delta G^0/nF = -76060/(2 \cdot 96485) = -0,394 \text{ V}$$

$$\begin{aligned} \text{b)} \quad [\text{Pb}^{2+}][\text{C}_2\text{O}_4^{2-}] &= 8,50 \cdot 10^{-10}, \\ [\text{Pb}^{2+}] &= 8,50 \cdot 10^{-10}/0,025 = 3,4 \cdot 10^{-8} \text{ M} \end{aligned}$$

$$\begin{aligned} \text{c)} \quad 1. \text{ method from } [\text{Pb}^{2+}]: \\ E &= E^0_1 + (2,303RT/nF) \cdot \log[\text{Pb}^{2+}] = -0,126 - 0,221 = -0,347 \text{ V} \end{aligned}$$

$$\begin{aligned} 2. \text{ method from } [\text{C}_2\text{O}_4^{2-}]: \\ E &= E^0_2 - (2,303RT/nF) \cdot \log[\text{C}_2\text{O}_4^{2-}] = -0,394 + 0,047 = -0,347 \text{ V} \end{aligned}$$

PROBLEM 2

$$\text{a) General rate law is} \quad v = k[\text{NO}_2]^m[\text{CO}]^n$$

To calculate m we take experimental rate values from experiments 1 and 2

$$\frac{v_2}{v_1} = \frac{k[\text{NO}_2]_2^m[\text{CO}]_2^n}{k[\text{NO}_2]_1^m[\text{CO}]_1^n} = \left(\frac{[\text{NO}_2]_2}{[\text{NO}_2]_1} \right)^m$$

$$\begin{aligned} 0,080/0,005 &= (0,4/0,1)^m \\ 16 &= 4^m, m = 2 \end{aligned}$$

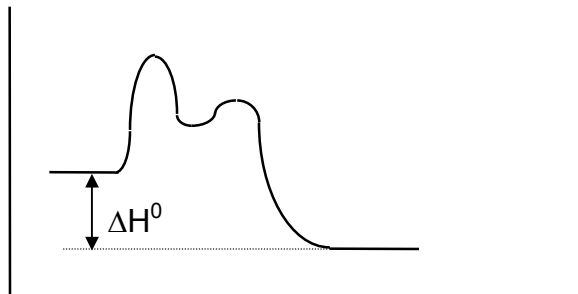
Similarly we obtain from experiments 1 and 3 for n the value 0 and the actual rate law is

$$v = k[\text{NO}_2]^2$$

b) The rate law corresponds to the slowest step of the overall reaction. For mechanism I (elementary reaction - only one step) the experimental rate law is not valid. For mechanisms II and III we can consider that rate-determining step is the first step and both mechanisms are consistent, but more reasonable is mechanism II because it involves only bimolecular steps.

Answer: **Mechanism II, first step.**

c)



PROBLEM 3

In oxide $w(\text{Me}) = 0,529$, $M_E = \frac{52,9 \cdot 8,0}{47,1} = 8,99 \text{ g/mol}$

$M(\text{I}) = 8,99 \text{ g/mol}$

$M(\text{II}) = 17,98$, $M(\text{III}) = 26,97$, $M(\text{IV}) = 35,97$, $M(\text{V}) = 44,95$, $M(\text{VI}) = 53,94$, $M(\text{VII}) = 62,93$.

$M(\text{Me(III)}) = 26,97 \text{ g/mol Al}$

$m(\text{Al}) = 0,510 \cdot 0,529 = 0,270$ $n(\text{Al}) = 0,010 \text{ mol}$

$\Delta m = 1,50 - 0,903 - 0,270 = 0,327 \text{ g}$

$v(\text{H}_2) = 0,448 - 0,336 = 0,112 \text{ L}$ it is $0,005 \text{ mol}$ or $0,010 M_E$

$M(\text{Me}) = \frac{0,327}{0,005} = 65,4 \text{ g/mol Zn}$ $n(\text{Zn}) = \frac{0,327}{65,4} = 0,005 \text{ mol}$

$\Delta m = 0,903 - 0,624 = 0,279 \text{ g}$ gained $n(\text{H}_2) = 0,005 \text{ mol}$

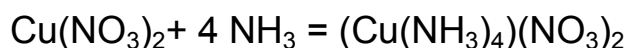
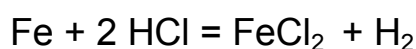
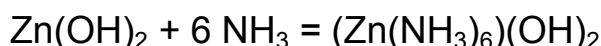
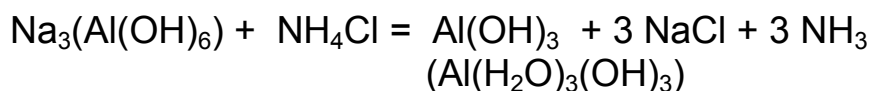
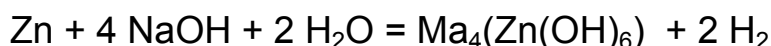
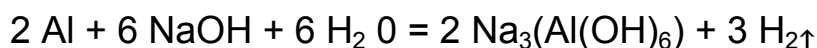
$M(\text{Me}) = \frac{0,279}{0,005} = 55,8 \text{ g/mol Fe}$ $n(\text{Fe}) = 0,005 \text{ mol}$

$\Delta m = 0,624 - 0,179 = 0,445 \text{ g}$. according properties **Cu**

$n(\text{Cu}) = \frac{0,445}{63,54} = 0,007 \text{ mol}$

$\rho = \frac{179}{9,27} = 19,3 \text{ g/cm}^3$ according density **Au**

$$n(\text{Au}) = \frac{0,179}{197,2} = 0,00091 \text{ mol}$$



PROBLEM 4

$$n(\text{HCl}) = \frac{100,0 \cdot 0,0300}{36,5} = 0,0822 \text{ mol}$$

$$n(\text{NaOH}) = 0,00696 \cdot 7,5 = 0,0522 \text{ mol}$$

$$n(\text{NH}_3) = 0,0822 - 0,0522 = 0,0300 \text{ mol}$$

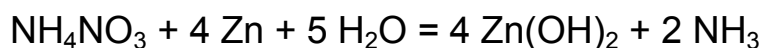
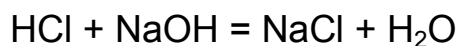
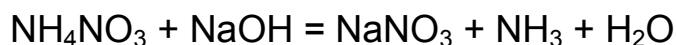
$$n'(\text{NaOH}) = 0,00562 \cdot 7,5 = 0,0422 \text{ mol}$$

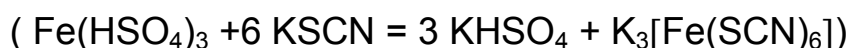
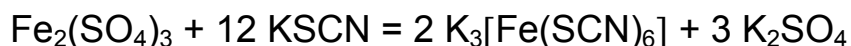
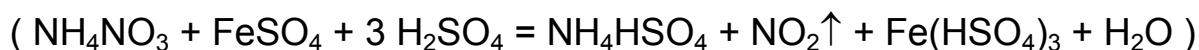
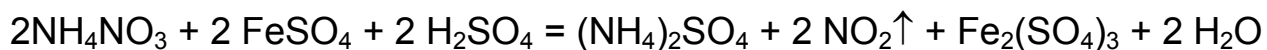
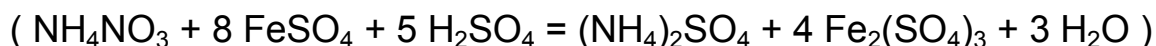
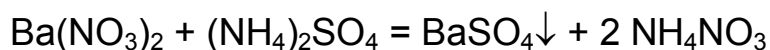
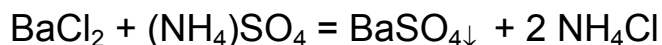
$$n'(\text{NH}_3) = 0,0822 - 0,0422 = 0,0400 \text{ mol}$$

$$n(\text{SO}_4^{2-}) = \frac{0,467}{233,4} \cdot 5 = 0,0100 \text{ mol}$$

Using $\text{Ba}(\text{NO}_3)_2$ instead of BaCl_2 did not change mass of the precipitate , solution did not contain SO_3^{2-} .

Reactions:

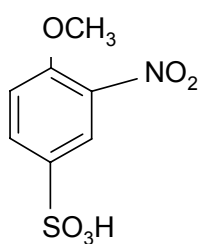




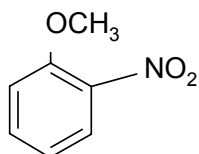
100 mL of solution A contains **0,010 mol $(\text{NH}_4)_2\text{SO}_4$ and 0,010 mol NH_4NO_3** .
its concentrations are 0,10 mol/L.

PROBLEM 5

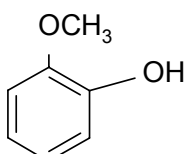
Structures of compounds **B** to **I** are as follow:



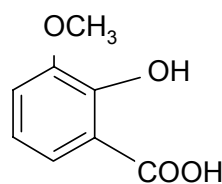
B



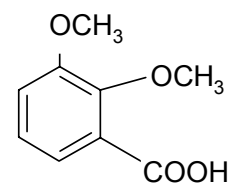
C



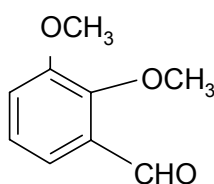
D



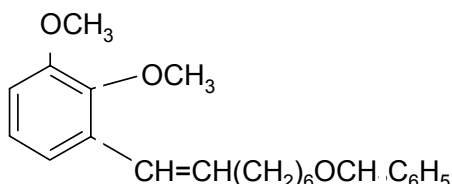
E



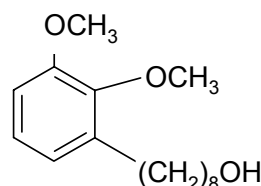
F



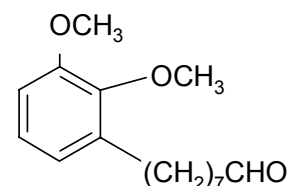
G



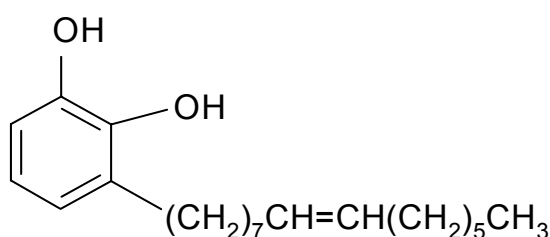
H



I

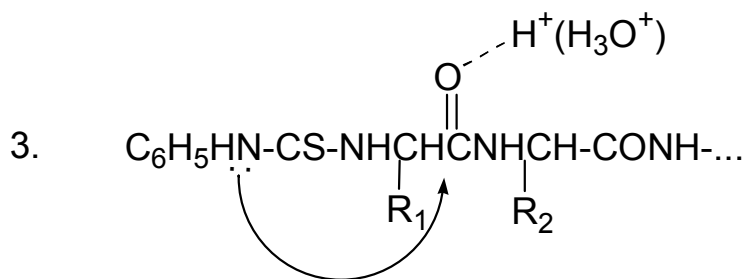
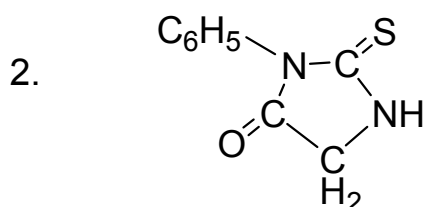
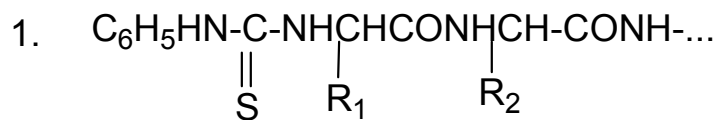


A



urushiol

PROBLEM 6



4. Widely used method for the determination of N-terminal amino acid is the reaction with 2,4-dinitrofluorobenzene in mild alkaline media followed by the hydrolysis of 2,4-dinitrophenylamide. This amide should be separated and identified.

C-terminus amino acid usually is determined by an enzyme carboxypeptidase. It cuts amino acids each by each from the C-terminal of peptide. It is necessary to separate amino acid and to identify it.

For longer polypeptides cleavage methods rely mostly on hydrolytic enzymes. For example, trypsin cleaves polypeptides only at the carboxy end of arginine and lysine. Other enzymes are chymotrypsin, pepsin, thermolysin.

5. Amino acid sequence of bradykinin is

Arg-Pro-Pro-Gly-Phe-Ser-Pro-Phe-Arg.