

11th BChO, 2003, Riga, Latvia

Problem 1 – CRYSTAL – Packing of peas and lupine

- a) Calculate the layer's thickness of 1 mol of peas (6 mm in diameter), covering the entire surface of the Earth ($5.10 \cdot 10^8 \text{ km}^2$) in the FCC arrangement. Assume that the surface is flat.
- b) Choose the correct answer that describes what would happen if these peas were mixed with 1 mol of lupine (2 mm in diameter). Fill in the gaps in your answer.
- ☐ With the particle size ratio smaller than 0.414, the FCC arrangement would transform into the ... arrangement and the layer's thickness would be ... m.
 - ☐ Lupine would fit into the ... holes of the FCC arrangement of peas, which can accommodate spherical particles with a diameter up to ... mm. The layer's thickness would not change.
 - ☐ Lupine would occupy the ... holes of the FCC arrangement, and it would expand slightly to increase the layer's thickness to ... m.
 - ☐ Lupine cannot fit into any holes of the FCC arrangement. It would form an independent layer on top of peas. The total thickness of both layers would be ... m.
 - ☐ Lupine would fit easily and indiscriminately into both ... and ... holes of the FCC arrangement. The layer's thickness would not change.

Problem 2 – STRUCT – Nitrogen hydrides

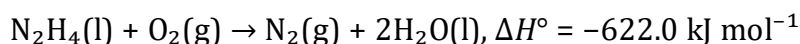
Nitrogen forms more than 20 binary compounds with hydrogen. The most important and well-known are ammonia NH_3 , hydrazine N_2H_4 , hydrogen azide (hydrazoic acid) HN_3 (a non-cyclic molecule), and cyclotriazene HN_3 .

- a) Draw possible Lewis dot structures for hydrogen azide HN_3 and cyclotriazene HN_3 .
- b) Show which two HN_3 structures have the largest contribution to the resonance structure.
- c) Predict the bond angles in a hydrogen azide molecule using VSEPR.
- d) Predict the hybridization of each nitrogen atom in a hydrogen azide molecule of the two structures giving the largest contribution to the hybrid resonance structure.

NH_3 is extremely explosive and even dilute solutions should be treated as potentially hazardous. When dissolved in water, it is a weak acid with $K_a = 1.80 \cdot 10^{-5}$.

- e) Calculate the pH of $5.00 \cdot 10^{-5} \text{ M}$ HN_3 solution.

Hydrazine N_2H_4 is used as a rocket fuel. The oxidation of hydrazine is strongly exothermic:



- f) Calculate the standard enthalpy of formation of N_2H_4 (l). $\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] = -285.8 \text{ kJ mol}^{-1}$.

Problem 3 – RADIO – Polonium

In 1898, Pierre and Marie Curie discovered a new chemical element, polonium, in uranium tar ore (Bohemia, Joachimsthal). One ton of this ore contains 0.14 grams of ^{226}Ra ($T_{1/2} = 1580$ years). The discovered polonium isotope ^{210}Po ($T_{1/2} = 138.4$ days) is formed from ^{226}Ra under α and β decay. ^{210}Po is extremely dangerous. When decaying to the stable ^{206}Pb isotope, it emits α particles, which are readily absorbed in tissues.

- a) Calculate the number of α and β disintegrations in the transformation $^{226}\text{Ra} \rightarrow ^{206}\text{Pb}$.
- b) Derive the relation between the ratio of half-lives and the ratio of equilibrium concen-

trations assuming that the decay rate of both isotopes is the same.

- c) Calculate the amount of ore (in tons, which contains exactly 1 mg of ^{210}Po).
 - d) Calculate the mass defect (in Da) of the $^{226}\text{Ra} \rightarrow ^{210}\text{Po}$ transformation.
 - e) Calculate the energy released during the formation of exactly 1 mg of ^{210}Po .
- $m(^4\text{He}) = 4.00273 \text{ Da}$, $m(\beta) = 0.00055 \text{ Da}$, $m(^{226}\text{Ra}) = 226.02540 \text{ Da}$, $m(^{210}\text{Po}) = 209.98286 \text{ Da}$

Problem 4 – EQUIL – Slow reaction

An equilibrium is established in a solution of hydrogen iodide at the silver electrode, which can be expressed by the equations: (i) $\text{Ag(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{e}^-$ ($E^\circ = 0.799 \text{ V}$) and $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{AgI(s)}$ or using the total equation (ii) $\text{Ag(s)} + \text{I}^-(\text{aq}) \rightleftharpoons \text{AgI(s)} + \text{e}^-$ ($E^\circ = -0.152 \text{ V}$).

- a) Write expressions for electrode potentials corresponding to equations (i) and (ii), and calculate the solubility product of AgI at 25 °C.
- b) Show with calculations that hydrogen evaluation is theoretically possible at a silver electrode immersed into a 1 M solution of HI at 25 °C.
- c) Explain why hydrogen evaluation occurs so slowly that it is unnoticeable.

Problem 5 – EQUIL – Selenic acid

1.29 g of crystalline selenic acid H_2SeO_3 ($\text{p}K_{\text{a}1} = 2.62$, $\text{p}K_{\text{a}2} = 8.32$) was transferred into a measuring flask and distilled water was added up to 100 cm^3 mark. The solution was poured into a chemical beaker in which a glass electrode connected to a pH meter was placed.

- a) Estimate the number that appeared on the pH meter screen.

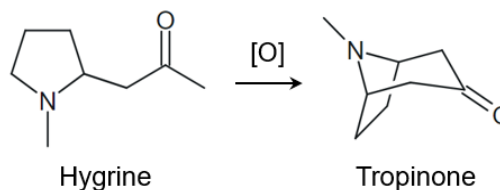
To the selenic acid solution, 5.00 cm^3 of sodium hydroxide solution ($c = 1.00 \text{ M}$) was added, it was stirred, and the pH was measured again. This procedure was repeated four more times, each time adding 5.00 cm^3 of sodium hydroxide and measuring the pH.

- b) Calculate the pH values of all six solutions. Neglect any changes in volume.

Problem 6 – ABC, BIO – Tropic acid

Tropic acid, $\text{C}_8\text{H}_{13}\text{O}_4\text{N}$, is a degradation product of atropine, an alkaloid of the deadly cherry *Atropa belladonna*. Tropic acid does not react with cold dilute KMnO_4 solution, Br_2/CCl_4 solution, and benzenesulfonyl chloride. Complete methylation gives the following results:

- i) Tropic acid + $\text{CH}_3\text{I} \rightarrow \text{A}$ ($\text{C}_9\text{H}_{16}\text{O}_4\text{NI}$)
- ii) $\text{A} + \text{Ag}_2\text{O} \rightarrow \text{B}$ ($\text{C}_9\text{H}_{15}\text{O}_9\text{N}$)
- iii) $\text{B} + \text{CH}_3\text{I} \rightarrow \text{C}$ ($\text{C}_{10}\text{H}_{18}\text{O}_4\text{NI}$)
- iv) $\text{C} + \text{Ag}_2\text{O} \rightarrow \text{D}$ ($\text{C}_7\text{H}_8\text{O}_4$) + $(\text{CH}_3)_3\text{N}$ + H_2O
- v) $\text{D} + \text{H}_2/\text{Ni} \rightarrow \text{Heptanedioic acid}$



Tropic acid is formed by oxidation of tropinone with CrO_3 . Reduction of tropinone gives tropine and pseudotropine (both $\text{C}_8\text{H}_{15}\text{ON}$). When heated with base, tropine is converted to pseudotropine.

- a) Draw the structural formulas of tropic acid and compounds A–D.
- b) Draw the structural formulas of tropine and pseudotropine.

Tropinone is produced by enzymatic oxidation of hygrine with NAD^+ or by chemical oxidation.

- c) Draw the mechanism for this cyclization.