



# **26th International Chemistry Olympiad**

**3 - 11 July 1994, Oslo Norway**

## **Theoretical Examination**

## **Problems**

According to the IChO rules the relative weights of the theoretical and practical problems has the ratio 40:60. It was decided by the jury that this could be accomplished by giving each problem a specified number of *red* points adding up to 40 and 60 in each category. The *blue* points were used to determine the relative weight of each sub-question within each problem.

### THEORETICAL PROBLEM No 1

(9 blue points, 8 red points)

Lactic acid is formed in the muscles during intense activity (anaerobic metabolism). In the blood, lactic acid is neutralized by reaction with hydrogen carbonate. This will be illustrated by the following calculations:

Lactic acid written HL is monoprotic, and the acid dissociation constant is  $K_{\text{HL}} = 1.4 \cdot 10^{-4}$ .

The acid dissociation constants for carbonic acid are:  $K_{\text{a1}} = 4.5 \cdot 10^{-7}$  and  $K_{\text{a2}} = 4.7 \cdot 10^{-11}$ .

All carbon dioxide remains dissolved during the reactions.

- a) Calculate pH in a  $3.00 \cdot 10^{-3}$  M solution of HL.
- b) Calculate the value of the equilibrium constant for the reaction between lactic acid and hydrogen carbonate.
- c)  $3.00 \cdot 10^{-3}$  mol lactic acid (HL) is added to 1.00 L of 0.024 M solution of  $\text{NaHCO}_3$  (no change in volume, HL completely neutralized).
  - i) Calculate the value of pH in the solution of  $\text{NaHCO}_3$  before HL is added.
  - ii) Calculate the value of pH in the solution after the addition of HL.
- d) pH in the blood of a person changed from 7.40 to 7.00 due to lactic acid formed during physical activity. Let an aqueous solution having pH = 7.40 and  $[\text{HCO}_3^-] = 0.022$  M represent blood in the following calculation. How many moles of lactic acid have been added to 1.00 L of this solution when its pH has become 7.00?
- e) In a saturated aqueous solution of  $\text{CaCO}_3(\text{s})$  pH is measured to 9.95. Calculate the solubility of calcium carbonate in water and show that the calculated value for the solubility product constant  $K_{\text{sp}}$  is  $5 \cdot 10^{-9}$ .
- f) Blood contains calcium. Determine the maximum concentration of "free" calcium ions in the solution (pH = 7.40,  $[\text{HCO}_3^-] = 0.022$  M) given in d).

**THEORETICAL PROBLEM No 2**

(7 blue points, 6 red points)

Nitrogen in agricultural materials is often determined by the Kjeldahl method. The method involves a treatment of the sample with hot concentrated sulphuric acid, to convert organically bound nitrogen to ammonium ion. Concentrated sodium hydroxide is then added, and the ammonia formed is distilled into hydrochloric acid of known volume and concentration. The excess hydrochloric acid is then back-titrated with a standard solution of sodium hydroxide, to determine nitrogen in the sample.

- a) 0.2515 g of a grain sample was treated with sulphuric acid, sodium hydroxide was then added and the ammonia distilled into 50.00 mL of 0.1010 M hydrochloric acid. The excess acid was back-titrated with 19.30 mL of 0.1050 M sodium hydroxide. Calculate the concentration of nitrogen in the sample, in percent by mass.
- b) Calculate the pH of the solution which is titrated in a), when 0 mL, 9.65 mL, 19.30 mL and 28.95 mL of sodium hydroxide has been added. Disregard any volume change during the reaction of ammonia gas with hydrochloric acid.  $K_a$  for ammonium ion is  $5.7 \cdot 10^{-10}$ .
- c) Draw the titration curve based on the calculations in b).
- d) What is the pH transition range of the indicator which could be used for the back titration.
- e) The Kjeldahl method can also be used to determine the molecular weight of amino acids. In a given experiment, the molecular weight of a naturally occurring amino acid was determined by digesting. 0.2345 g of the pure acid, and distilling the ammonia into 50.00 mL of 0.1010 M hydrochloric acid. A titration volume of 17.50 mL was obtained for the back titration with 0.1050 M sodium hydroxide. Calculate the molecular weight of the amino acid based on one and two nitrogen groups in the molecule, respectively.

**THEORETICAL PROBLEM No. 3**

(26.5 blue points, 9 red points)

Sulphur forms many different compounds with oxygen and halogens (sulphur as the central atom). These compounds are mainly molecular, and many are easily hydrolysed in water.

- a) Write Lewis structures for the molecules  $\text{SCl}_2$ ,  $\text{SO}_3$ ,  $\text{SO}_2\text{ClF}$ ,  $\text{SF}_4$ , and  $\text{SBrF}_5$ .
- b) Carefully draw the geometries of the same 5 molecules. (Disregard small deviations from "ideal" angles.)
- c) A compound, consisting of sulphur (one atom per molecule), oxygen and one or more of the elements F, Cl, Br, and I, was examined. A small amount of the substance reacted with water. It was completely hydrolyzed without any oxidation or reduction, and all reaction products dissolved. 0.1 M solutions of a series of test reagents were added to separate, small portions of a diluted solution of the substance.

Which ions are being tested for in the following tests:

- i) Addition of  $\text{HNO}_3$  and  $\text{AgNO}_3$  .  
ii) Addition of  $\text{Ba}(\text{NO}_3)_2$ .  
iii) Adjustment to  $\text{pH} = 7$  with  $\text{NH}_3$  and addition of  $\text{Ca}(\text{NO}_3)_2$ .

Write the equations for the possible reactions in the tests:

- iv) Addition of  $\text{KMnO}_4$  followed by  $\text{Ba}(\text{NO}_3)_2$  to an acid solution of the substance.  
v) Addition of  $\text{Cu}(\text{NO}_3)_2$ .
- d) In practice, the tests in c) gave the following results:
- i) A yellowish precipitate  
ii) No precipitate  
iii) No visible reaction  
iv) The main features were that the characteristic colour of permanganate disappeared, and a white precipitate was formed upon addition of  $\text{Ba}(\text{NO}_3)_2$   
v) No precipitate

Write the formulas of the possible compounds, taking the results of these tests into account.

- e) Finally, a simple quantitative analysis was undertaken:  
7.190 g of the substance was weighed out and dissolved in water to give 250.0  $\text{cm}^3$  solution. To 25.00  $\text{cm}^3$  of this solution, nitric acid, and enough  $\text{AgNO}_3$  to secure complete precipitation, was added. The precipitate weighed 1.452 g after washing and drying.

Determine the formula of the compound.

- f) Write the equation describing the reaction of the substance with water.  
If you have not arrived at a formula for the compound, use  $\text{SOCIF}$ .

**THEORETICAL PROBLEM No. 4**

(21 blue points, 8 red points)

Platinum(IV) oxide is not found in the nature, but can be prepared in a laboratory. Solid platinum(IV) oxide is in equilibrium with platinum metal and oxygen gas of 1 atm ( $= 1.01325 \cdot 10^5$  Pa) at 650 °C.

- a) This suggests that the conditions on the Earth, when the minerals we know were formed, were:  
[ 1 ]  $p_{O_2} = 1$  atm,  $t = 650$  °C; [ 2 ]  $p_{O_2} < 1$  atm,  $t < 650$  °C; [ 3 ]  $p_{O_2} > 1$  atm,  $t < 650$  °C; [ 4 ]  $p_{O_2} < 1$  atm,  $t > 650$  °C; [ 5 ]  $p_{O_2} > 1$  atm,  $t > 650$  °C

Mark the most probable alternative [ 1 ] – [ 5 ] on the answer sheet. Please note, the marking of only one alternative will be accepted.

- b) What are  $\Delta G$  and  $K_p$  for the formation of platinum(IV) oxide at 1 atm oxygen pressure and 650 °C?

The preparation of platinum(IV) oxide involves boiling of a solution which contains hexachloroplatinate(IV) ions with sodium carbonate. In this process  $PtO_2 \cdot nH_2O$  is formed and this is in turn converted to platinum(IV) oxide upon subsequent filtering and heat treatment. In the following we assume  $n = 4$ .

$PtO_2 \cdot 4H_2O$  or  $Pt(OH)_4 \cdot 2H_2O$  can be dissolved in acids and strong bases.

- c) Write the balanced equations for the preparation of platinum(IV) oxide according to the procedure given above.
- d) Write the balanced equations for the dissolution of  $PtO_2 \cdot 4H_2O$  in both hydrochloric acid and sodium hydroxide.

Platinum is mainly found in the nature as the metal (in mixture or in alloying with other precious metals). Platinum is dissolved in aqua regia under the formation of hexachloroplatinate(IV) ions. Aqua regia is a mixture of concentrated hydrochloric and nitric acids in proportion 3 : 1, and of the nitrosylchloride (NOCl) and the atomic chlorine which are formed upon the mixing. The latter is believed to be the active dissolving component.

The hexachloroplatinate(IV) ions can be precipitated as diammonium hexachloroplatinate(IV) and by thermal decomposition of this compound, finely powdered platinum and gaseous products are formed.

- e) Write the balanced equations for the formation of aqua regia and its reaction with platinum.
- f) Write the balanced equation of the thermal decomposition of diammonium hexachloroplatinate(IV) at elevated temperature.

From diammonium hexachloroplatinate(IV) we can prepare  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  which occurs in *cis* ( $\Delta H_{\text{f}}^{\circ} = -467.4 \text{ kJ/mol}$ ,  $\Delta G_{\text{f}}^{\circ} = -228.7 \text{ kJ/mol}$ ) and *trans* ( $\Delta H_{\text{f}}^{\circ} = -480.3 \text{ kJ/mol}$ ,  $\Delta G_{\text{f}}^{\circ} = -222.8 \text{ kJ/mol}$ ) form.

- g) The occurrence of the isomers shows that  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  has  
 [ 1 ] linear [ 2 ] planar [ 3 ] tetrahedral [ 4 ] octahedral geometry.

Mark the correct alternative of [ 1 ] – [ 4 ] on the answer sheet.

- h) Is the [ 1 ] *cis* or [ 2 ] *trans* form the thermodynamic more stable?

Platinum is used as a catalyst in modern automobiles. In the catalyst carbon monoxide ( $\Delta H_{\text{f}}^{\circ} = -110.5 \text{ kJ/mol}$ ,  $\Delta G_{\text{f}}^{\circ} = -137.3 \text{ kJ/mol}$ ) reacts with oxygen to carbon dioxide ( $\Delta H_{\text{f}}^{\circ} = -393.5 \text{ kJ/mol}$ ,  $\Delta G_{\text{f}}^{\circ} = -394.4 \text{ kJ/mol}$ ).

- i) Is the reaction spontaneous at  $25 \text{ }^{\circ}\text{C}$ ? [ 1 ] yes or [ 2 ] no.

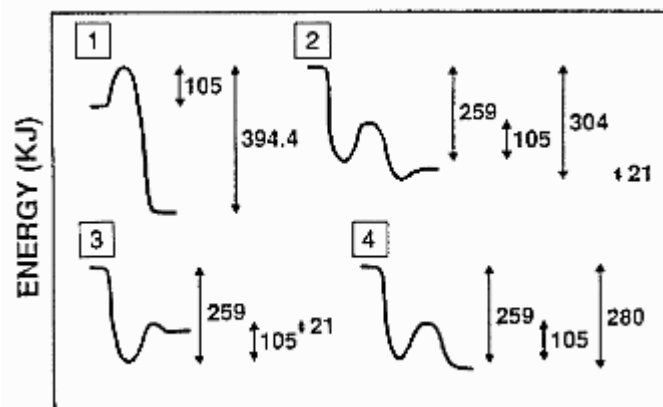
Is the reaction [ 1 ] endo- or [ 2 ] exothermic?

Calculate  $\Delta S^{\circ}$  for the reaction. Establish whether the entropy of the reaction system [ 1 ] increases or [ 2 ] decreases.

- j) Establish an expression for the temperature dependence of the equilibrium constant in this case.

The overall catalytic reaction is simple, whereas the reaction mechanism in the homogeneous phase is very complicated with a large number of reaction steps, and the course is difficult to control owing to a distinct chain character. With platinum as catalyst the significant reaction steps are: (i) Adsorption of CO and adsorption/dissociation of  $\text{O}_2$  ( $\Delta H = -259 \text{ kJ per mol CO} + \text{O}$ ), (ii) their activation ( $105 \text{ kJ per mol CO} + \text{O}$ ) and (iii) the reaction to and the desorption of  $\text{CO}_2$  ( $\Delta H = 21 \text{ kJ per mol CO}_2$ ).

A one-dimensional energy-diagram for the platinum catalyzed oxidation of carbon monoxide to dioxide can be represented as:



- k) Mark the correct alternative of [ 1 ] – [ 4 ] on the answer sheet.

**THEORETICAL PROBLEM No 6**

(18 blue points, 9 red points)

An optical active compound A ( $C_{12}H_{16}O$ ) shows amongst other a strong IR-absorption at  $3000-3500\text{ cm}^{-1}$ , and two medium signals at  $1580$  and  $1500\text{ cm}^{-1}$ . The compound does not react with 2,4-dinitrophenylhydrazine (2,4-D). Upon treatment with  $I_2/NaOH$ , A is oxidized and gives a positive iodoform reaction.

Ozonolysis of A (a.  $O_3$ ; b.  $Zn, H^+$ ) gives B ( $C_9H_{10}O$ ) and C ( $C_3H_6O_2$ ). Both B and C give precipitation when treated with 2,4-D, and only C gives positive reaction with Tollens reagent. Nitration of B ( $HNO_3/H_2SO_4$ ) may give two mono-nitro compounds D and E, but in practical work only D is formed.

Acidification followed by heating of the product formed by the Tollens reaction on C gives compound F ( $C_6H_8O_4$ ). The compound gives no absorption in IR above  $3100\text{ cm}^{-1}$ .

- a) Based on the above information draw the structure formula(e) for the compounds A–F and give the overall reaction scheme, including the (2,4-D) and the products of the Tollens and iodoform reactions.
- b) Draw C in an R-configuration. Transform this into a Fischer projection formula and state whether it is a D or L configuration.

**THEORETICAL PROBLEM No 7**

(5 blue points, 5 red points)

- a) When an ideal, monatomic gas expands reversibly from a volume  $V_1$  to a volume  $V_2$ , a work

$$w = - \int_{V_1}^{V_2} P_{\text{ext}} dV$$

$$(w = -\int_{V_1}^{V_2} P dV)$$

is performed on the system by the surroundings. In this equation,  $w$  is the work and  $P$  is the pressure of the gas.

Determine the performed work when one mole ideal gas expands isothermally from  $V_1 = 1.00 \text{ dm}^3$  to  $V_2 = 20.0 \text{ dm}^3$  at the temperature  $T = 300.0 \text{ K}$ .

Given: The gas constant  $R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$ .

- b) Determine how much heat must be added to the gas during the process given under a).
- c) The gas will perform less work in an adiabatic expansion than in an isothermal expansion. Is this because the adiabatic expansion is characterized by (check the square you think is most important).

- 1:        The volume of the gas is constant  
 2:        The expansion is always irreversible  
 3:        No heat is supplied to the gas

- d) The cyclic process shown schematically in Figure 1 shows the four steps in a refrigeration system with an ideal gas as working medium. Identify the isothermal and adiabatic steps in the process. Here,  $T_H$  and  $T_C$  represent high and low temperature, respectively. Specify for each step whether it is adiabatic or isothermal.

Fig. 1 (not reproduced in this report shows a Carnot cycle)



**THEORETICAL PROBLEM No 8**  
(9 blue points, 7 red points)

Avogadro's Number:  $6.022 \cdot 10^{23}$

**a)** An atom of  $^{238}\text{U}$  disintegrates by a series of  $\alpha$ -decays and  $\beta^-$ -decays until it becomes  $^{206}\text{Pb}$ , which is stable.

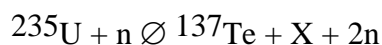
i) How many  $\alpha$ -decays and how many  $\beta^-$ -decays does an atom starting as  $^{238}\text{U}$  undergo before it becomes stable ?

ii) One of the following ten nuclides is formed from a series of disintegrations starting at  $^{238}\text{U}$ . Which one ?

$^{235}\text{U}$ ,  $^{234}\text{U}$ ,  $^{228}\text{Ac}$ ,  $^{224}\text{Ra}$ ,  $^{224}\text{Rn}$ ,  $^{220}\text{Rn}$ ,  $^{215}\text{Po}$ ,  $^{212}\text{Po}$ ,  $^{212}\text{Pb}$ ,  $^{211}\text{Pb}$ .

**b)** In a thermal neutron-induced fission process,  $^{235}\text{U}$  reacts with a neutron and breaks up into energetic fragments and (normally) 2-3 new neutrons.

We consider one single fission event:



Identify the fragment X.

**c)** The half-life of  $^{238}\text{U}$  is  $4.5 \cdot 10^9$  years, the half-life of  $^{235}\text{U}$  is  $7.0 \cdot 10^8$  years. Natural uranium consists of 99.28 %  $^{238}\text{U}$  and 0.72 %  $^{235}\text{U}$ .

i) Calculate the ratio in natural U between the disintegration rates of these two uranium isotopes.

ii) A mineral contains 50 weight percent uranium. Calculate the disintegration rate of  $^{238}\text{U}$  in 1.0 kg of this mineral.

**d)** We have the following radioactive sequence:



Halflives:  $^{97}\text{Ru}$ : 2.7 days ;  $^{97}\text{Tc}$ :  $2.6 \cdot 10^6$  years

At  $t = 0$ , a radioactive source containing only  $^{97}\text{Ru}$  has a disintegration rate of  $1.0 \cdot 10^9$  Bq.

i) What is the total disintegration rate of the source at  $t = 6.0$  days ?

ii) What is the total disintegration rate of the source at  $t = 6000$  years