

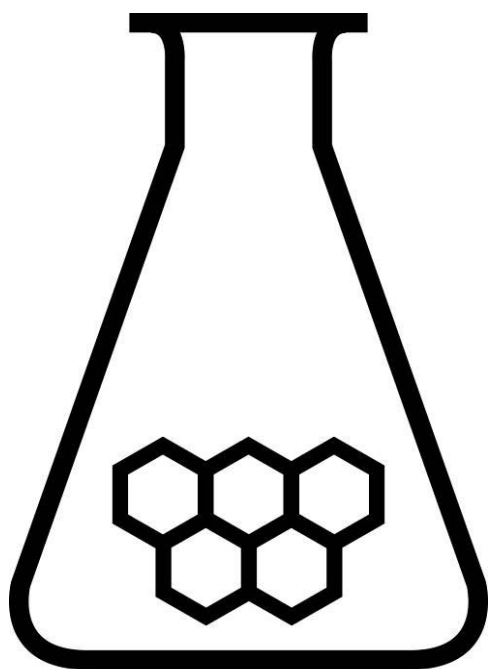
DUTCH NATIONAL CHEMISTRY OLYMPIAD

SELECTION ROUND 2

PROBLEMS

(the week of)

Wednesday 8 April 2009



SCHEIKUNDE OLYMPIADE



UNIVERSITY OF
CAMBRIDGE

800 Years 1209 - 2009



Specialising in Chemical Translations

- This selection round consists of 30 multiple choice questions divided over 8 subjects and 4 open questions consisting of a total of 23 sub questions, as well as an answer sheet for the multiple choice questions.
- Use a different answer sheet, with your name on it, for each problem (open questions).
- The maximum score for this test is 111 points.
- This selection round will take 3 hours (180 minutes) maximum.
- Resources needed: calculator and BINAS 5th edition
- For each problem, the number of points obtained for correct answers, is indicated.

Problem 1 Multiple choice questions

(45 points total)

1½ points per correct answer (For each question, write your answer (letter) on the answer sheet).

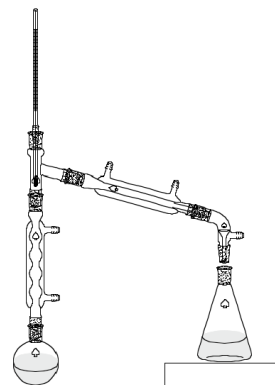
Please note: wrong answer $-\frac{1}{4}$ point; no answer: 0 points.

Phase changes

- 1 A mixture of pentane and hexane is separated with the setup shown, by means of fractional distillation.

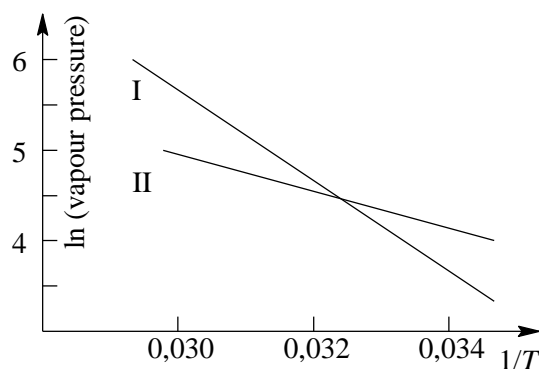
What temperature will the thermometer read when the first drop of condensation is forming on it?

boiling point	°C
pentane	36
hexane	69



- A less than 36 °C
- B 36 °C
- C between 36 °C and 69 °C
- D more than 69 °C

2



In the diagram, the natural logarithm is shown of the vapour pressure of two substances vs. $\frac{1}{T}$. Which conclusions would you draw with regard to the ΔH_{vapour} of substance I compared to substance II?

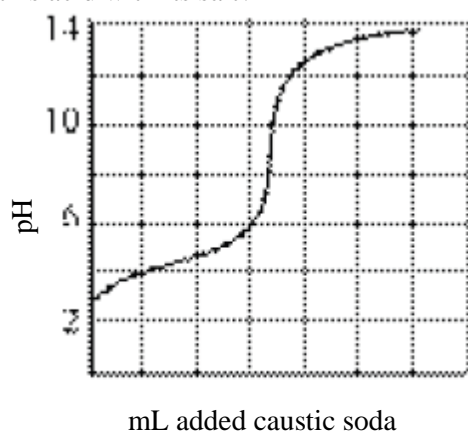
Hint: Use the equation in Binas table 37C and the fact that the liquid and gas phases are at equilibrium at the boiling point.

- A ΔH_{vapour} of I is larger than ΔH_{vapour} of II
 - B ΔH_{vapour} of I is smaller than ΔH_{vapour} of II
 - C ΔH_{vapour} of I equals ΔH_{vapour} of II
 - D No conclusion can be drawn from this information only.
- 3 The freezing point depression of a solution is proportional to the number of dissolved particles. Which solution will give the smallest freezing point depression?
A 0.1 M solution of:
- A AlCl_3
 - B CaCl_2
 - C CH_3COOH
 - D HCl

Acid-base

- 4 A standardised solution (i.e. the molarity is accurately known) of potassium hydrogen phthalate can be used to determine the molarity of a NaOH-solution (caustic soda) by means of titration. Which approach will give a molarity for the caustic soda which is too low?
- A** Weighing in half of the recommended amount of potassium hydrogen phthalate.
B Dissolving potassium hydrogen phthalate in more water than prescribed.
C Forgetting to rinse the tap of the burette with caustic soda before titration.
D Loss of a small amount of potassium hydrogen phthalate solution out of the Erlenmeyer flask before starting the titration.
- 5 For which equilibrium does the equilibrium constant equal K_z of NH_4^+ ?
- A** $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
B $\text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$
C $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
D $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

- 6 The diagram shows the titration of a weak monovalent acid. What is/are the pH range(s) of this acid with its salt?



- I** pH 4-6 **II** pH 7-9 **III** pH 12-13
- A** **I** only
B **II** only
C **I** and **III** only
D all ranges

Calculations

- 7 A number of melted chloride salts are electrolysed with an electric current of 3.00 A. Which amount of deposited metal would require the longest electrolysis time?
- A** 50 g Mg
B 75 g Al
C 100 g Ca
D 125 g Fe
- 8 Magnetite, Fe_3O_4 , can be reduced to iron by heating with carbon monoxide according to:
- $$\text{Fe}_3\text{O}_4 + 4 \text{CO} \rightarrow 3 \text{Fe} + 4 \text{CO}_2$$
- How much Fe_3O_4 (in kg) is needed to generate 5.0 kg iron with a yield of 88%?
- A** 6.1
B 6.9
C 7.9
D 18

- 9 What is the pH of the solution which is obtained when 45 mL 0.18 M KOH and 65 mL 0.15 M HCl are mixed together?
- A 1.07
 B 1.13
 C 1.82
 D 2.92

Physical chemistry: thermodynamics

- 10 Which standard formation enthalpy of ethyn, C_2H_2 (in kJ) follows from the information given below?

reaction equation	ΔH° kJ
$C_2H_2(g) + 2\frac{1}{2} O_2(g) \rightarrow 2 CO_2(g) + H_2O(l)$	-1299,5
$C(s) + O_2(g) \rightarrow CO_2(g)$	-393,5
$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	-285,8

- A -1978.8
 B -1121.4
 C -453.4
 D -226.7
 E 226.7
 F 453.4
 G 1121.4
 H 1978.8
- 11 Which statement is always true for a spontaneous reaction?
- A The enthalpy change of the system is negative.
 B The entropy change of the system is negative.
 C The total entropy change is positive.
 D The change in free energy of the system is positive.
- 12 Which value is NOT needed for the calculation of the lattice energy of NaCl by means of a Born-Haber cycle?
- A bond energy of $Cl_2(g)$
 B 1st ionisation energy of $Cl(g)$
 C formation enthalpy of $NaCl(s)$
 D sublimation enthalpy of $Na(s)$
- 13 Which value for the formation enthalpy in $kJ\ mole^{-1}$ of $Br_2(g)$ follows from the data below?
- | S° | $\frac{J}{mole\ K}$ |
|-----------|---------------------|
| $Br_2(g)$ | 245 |
| $Br_2(l)$ | 152 |
- A 7
 B 12
 C 31
 D 93
- 14 Which conclusions can be drawn with regard to the values of ΔG° and K_{eq} of a galvanic cell?
- A $\Delta G^\circ < 0$, $K_{ev} < 1$
 B $\Delta G^\circ < 0$, $K_{ev} > 1$
 C $\Delta G^\circ > 0$, $K_{ev} < 1$
 D $\Delta G^\circ > 0$, $K_{ev} > 1$

Physical chemistry: kinetics

- 15 Under certain circumstances, the velocity equation of the reaction between CO and NO₂, in which CO₂ and NO are formed, is:

$$s = k[\text{CO}][\text{NO}_2].$$

What is the unit of reaction constant k ?

- A $\frac{\text{mole}}{\text{L s}}$
B $\frac{\text{mole}^2}{\text{L}^2 \text{ min}}$
C $\frac{\text{mole s}}{\text{L}^2}$
D $\frac{\text{mole}^2}{\text{mol}^2 \text{ s}}$
- 16 The initial velocities of reaction $X + Y \rightarrow Z$ are given in the table.

[X] (mole L ⁻¹)	[Y] (mole L ⁻¹)	s (mole L ⁻¹ s ⁻¹)
0.10	0.10	0.020
0.10	0.20	0.080
0.30	0.30	0.54

The velocity equation is: $s =$

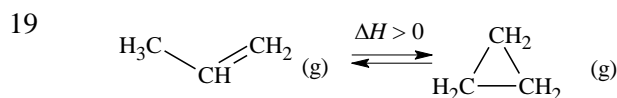
- A $k[\text{X}]^2$
B $k[\text{Y}]^2$
C $k[\text{X}][\text{Y}]$
D $k[\text{X}][\text{Y}]^2$
- 17 The velocity equation for reaction $A \rightarrow B$ is $s = k[A]$.
After 50.0 minutes, 40.0% of A has been converted.
From this, what can be concluded with regard to reaction constant k in min⁻¹?
- A $8.00 \cdot 10^{-3}$
B $1.02 \cdot 10^{-2}$
C $1.39 \cdot 10^{-2}$
D $1.83 \cdot 10^{-2}$

Equilibria

- 18 At a certain temperature, 2.00 mole H₂(g) and 2.00 mole I₂(g) are introduced into a vessel of 1.00 L. The following equilibrium is established: $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$. When the equilibrium has established, 3.50 mole HI is present.

What is the value of the equilibrium constant K_c ?

- A 3.7
B 14
C 49
D $2.0 \cdot 10^2$



Which of the changes below cause(s) of the amount of propene at equilibrium to increase?

- I increasing the temperature
II increasing the pressure

- A only I
B only II
C both I and II
D neither

- 20 A saturated solution of $\text{Fe}(\text{OH})_2$ has $\text{pH} = 8.67$.
What is the value of the solubility product K_s of $\text{Fe}(\text{OH})_2$?
- A** $5.1 \cdot 10^{-17}$
B $1.0 \cdot 10^{-16}$
C $2.3 \cdot 10^{-11}$
D $4.8 \cdot 10^{-6}$

Electrons

- 21 Which series of quantum numbers matches an electron in a 4d-orbit?
- | | n | l | m_l | m_s |
|----------|-----|-----|-------|----------------|
| A | 4 | 1 | -1 | $\frac{1}{2}$ |
| B | 4 | 2 | -2 | $-\frac{1}{2}$ |
| C | 4 | 3 | 3 | $\frac{1}{2}$ |
| D | 4 | 3 | -1 | $-\frac{1}{2}$ |
- 22 How many unpaired electrons does a $\text{Co}^{2+}(\text{g})$ -ion have in its ground state?
- A** 1
B 3
C 5
D 7

- 23 Which particle is diamagnetic?
- A** NO
B N_2^+
C O_2
D O_2^{2-}

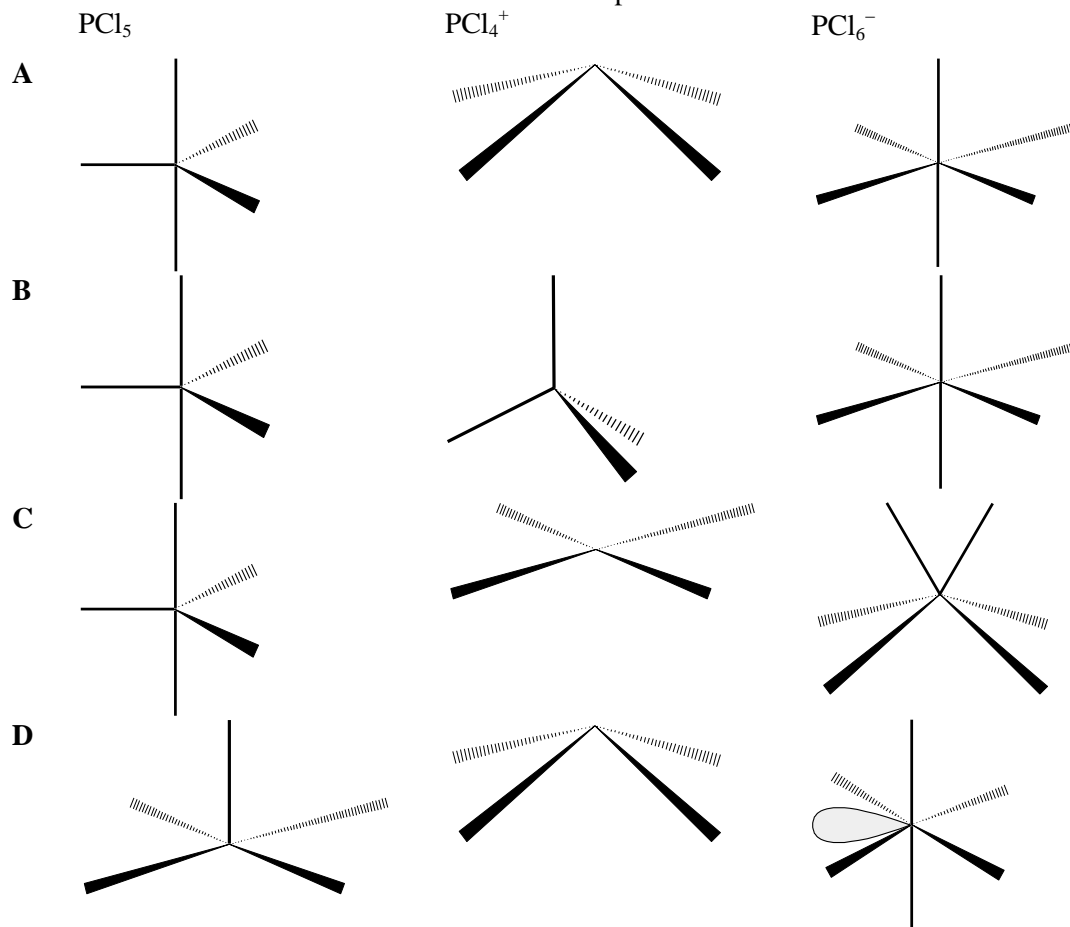
- 24 How many π -bonds does *trans*-butenedioic acid ($\text{C}_4\text{H}_4\text{O}_4$) contain?
- A** 1
B 2
C 3
D 4

Structure and properties

- 25 Which of these molecules have a dipole moment unequal to 0?
I $\text{H}_2\text{C}=\text{CHCl}$ **II** *cis*- $\text{ClHC}=\text{CHCl}$ **III** *trans*- $\text{ClHC}=\text{CHCl}$
- A** only **I**
B only **III**
C only **I** and **II**
D **I**, **II** and **III**
- 26 What is the bond angle of I-I-I in I_3^- ?
Hint: the negative charge is located on the centre I and mesomerism does not occur within the particle.
- A** 90°
B between 90 and 120°
C 120°
D 180°
- 27 Which particle has the shortest N-O bond?
- A** NO^+
B NO_2^+
C NO_2^-
D NO_3^-

28 In the gas phase, PCl_5 consists of individual molecules, but in the solid phase it has an ionic structure $\text{PCl}_4^+\text{PCl}_6^-$.

What are the 3 dimensional structures of these particles?



29 How many compounds have formula $\text{C}_2\text{H}_3\text{Cl}_3$?

- A 2
- B 3
- C 4
- D 5

30 Cellulose and starch are biopolymers. People can digest starch, but not cellulose. This difference is **mainly** due to a difference in

- A number of monomer units in both polymers
- B identity of the monomers in both polymers
- C bond orientation between the monomers
- D percentage of carbon in both polymers

Problem 2 NMR-SPECTROSCOPY**(24 points)**

(NOTE There are 2 NMR spectra with this problem. Below the ^1H spectrum, the integrals (= areas) of the signals are given as numbers ratios).

From the IR spectrum of an unknown substance X with $M = 102$, we know X to be an ester.

6p 1 Calculate the molecular formula of substance X.

Give all possible structural formulas of substance X.

The correct structural formula can be derived by NMR.

At the end of this problem, you'll find 2 NMR spectra:

- ^1H -NMR spectrum **I** of a solution of X in the solvent CDCl_3 , to which some TMS has been added, recorded at a frequency of 300 MHz.
- ^{13}C -NMR spectrum **II**, recorded in the same solution, at a frequency of 75 MHz. The three small signals in spectrum II around 77 ppm are originating from the solvent.

2p 2 Using the ^{13}C -NMR spectrum, explain how many different C-atoms (i.e. C-atoms with different surroundings) can be found in a molecule of substance X.

3p 3 Calculate the total integral.

You know from question 1 to how many H-atoms this corresponds.

Next, using the integral, calculate the number of H-atoms per σ -value.

1p 4 Why doesn't B show a split signal?

3p 5 For H's of the signal at 1.65 ppm, explain with how many neighbouring H's they are coupled.

At which σ -value(s) can these neighbouring H's be found?

2p 6 Explain why the H's resonating in signal A are the only ones with such a high σ -value.

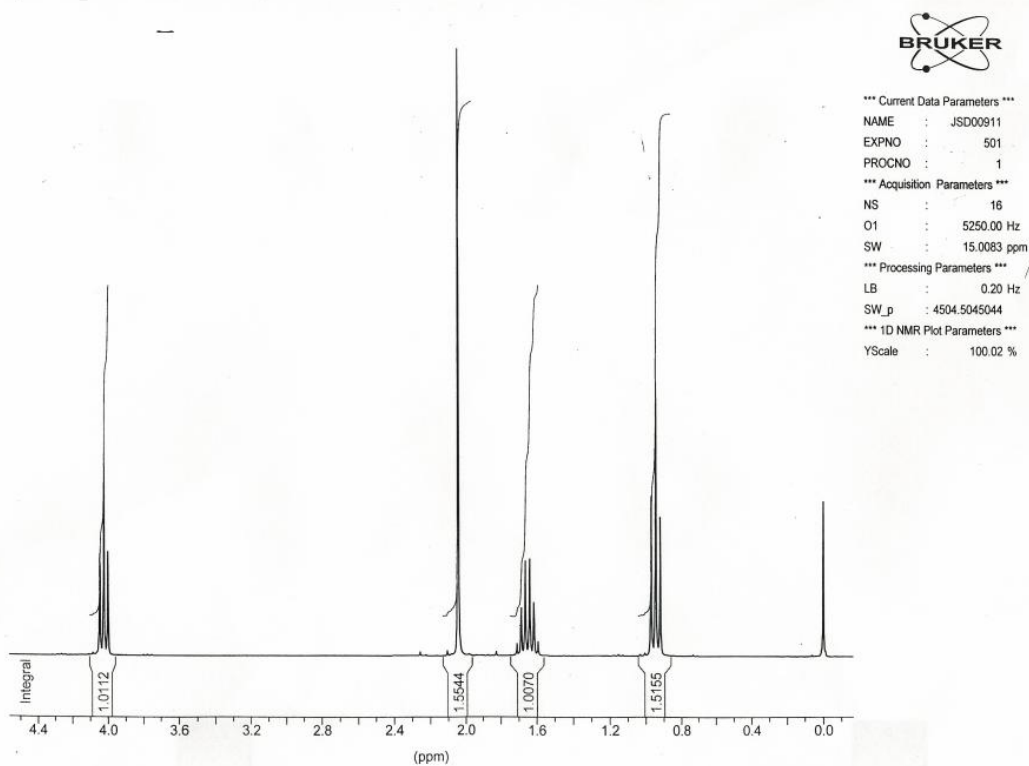
3p 7 Explain the structure of R_1 in substance X (the ester RCOOR_1).

Explain the structure of the R-group.

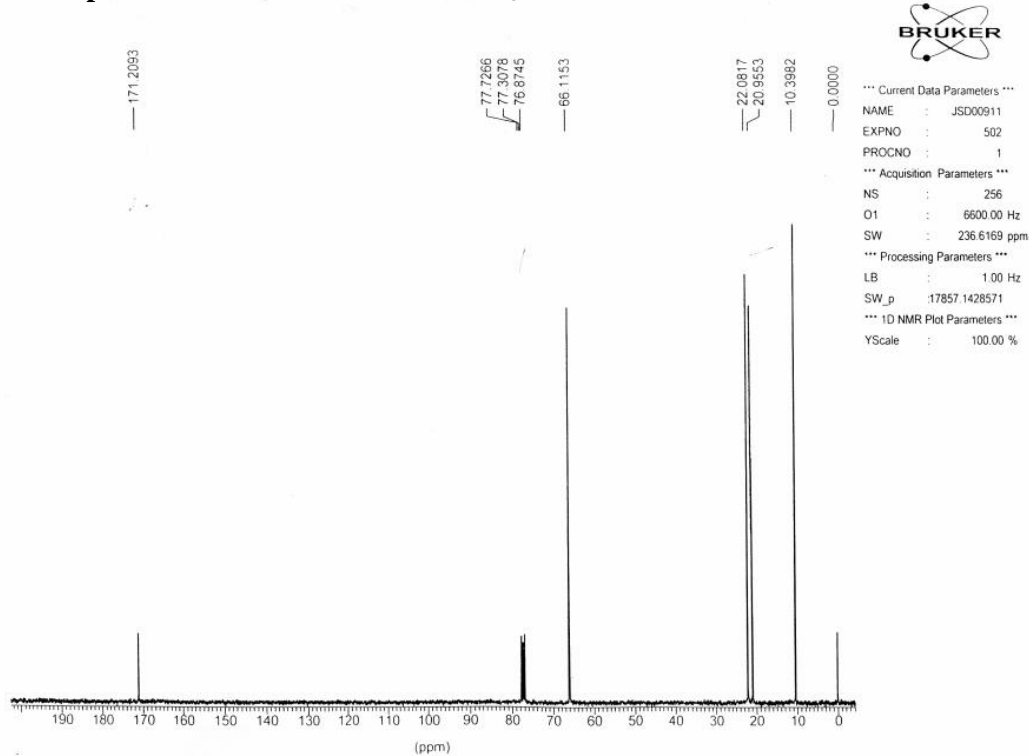
Give the structural formula of substance X.

4p 8 In the structural formula of substance X, put the correct signal position in ppm with each C-atom (^{13}C -NMR spectrum).

^1H NMR spectrum I of substance X in CDCl_3 at 300 MHz



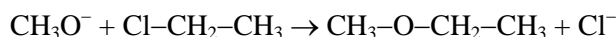
^{13}C NMR spectrum II of substance X in CDCl_3 at 75 MHz



Problem 3 Williamson reaction

(15 points)

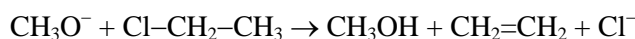
One application for solutions of sodium alkanolates in an alkanol solution is the so called Williamson reaction. A reaction in which an alkoxyalkane is obtained when a solution of an alkanolate reacts with a halogenalkane, is called a Williamson reaction. A solution of sodium methanolate in methanol contains, apart from CH_3OH molecules, also Na^+ ions and CH_3O^- ions. With the Williamson reaction occurring when this solution reacts with chloroethane, CH_3O^- ions will react with $\text{CH}_3\text{CH}_2\text{Cl}$ molecules, forming methoxyethane:



Methoxyethane can also be formed in a different way other than via a Williamson reaction. Different particles, other than CH_3O^- and $\text{CH}_3\text{CH}_2\text{Cl}$, will have to react with each other.

2p 9 Give the formulas of these other particles.

When a solution of sodium methanolate in methanol reacts with chloroethane, another reaction will take place apart from the Williamson reaction. With this other reaction, ethene is formed:



Alkene formation can occur if a solution of sodium methanolate in methanol reacts with a chloroalkane containing at least 2 C-atoms per molecule.

One could imagine the formation of an alkene from CH_3O^- and such a chloroalkane to proceed according to the following two partial reactions:

Partial reaction 1: a CH_3O^- -ion extracts a H^+ -ion from the chloroalkane. Only H-atoms bonded to a C-atom *next to* the C-atom to which the Cl-atom is bonded, are suitable for donation of the H^+ -ion.

Partial reaction 2: a Cl^- -ion separates from the ion formed in partial reaction 1, forming an alkene molecule.

2p 10 Give the electron formula of the ion formed in partial reaction 1, when a H^+ -ion is extracted from the chloroethane. In the electron formula, put the charge with the correct atom.

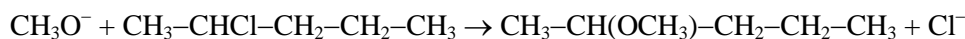
For some monochloroalkanes, with at least 2 C-atoms per molecule, no alkene formation will take place during a reaction with a solution of sodium methanolate in methanol.

2p 11 Give the structural formula of such a monochloroalkane.

Also during a reaction of 2-chloropentane, $\text{CH}_3-\text{CHCl}-\text{CH}_2-\text{CH}_2-\text{CH}_3$, with a solution of sodium methanolate in methanol, both the Williamson reaction and alkene formation take place. It has been shown that three alkenes are formed in this process.

2p 12 Give the names of these three alkenes.

The Williamson reaction, occurring when a solution of sodium methanolate in methanol reacts with 2-chloropentane, can be described by an equation in the following way:



There are 2 optical isomers of 2-chloropentane: a *R*-isomer and a *S*-isomer. There are also 2 optical isomers of 2-methoxypentane. If only (optical active) *R*-2-chloropentane reacts with a solution of sodium methanolate in methanol, both optical isomers of 2-methoxypentane are formed.

As it turns out, a reaction mixture is obtained in which *R*-2 methoxypentane and *S*-2-methoxypentane are present in molar ratio 2: 3.

3p 13 Explain whether this mixture will show optical activity.

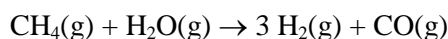
It is possible to prepare *R*-2-methoxypentane without formation of *S*-2-methoxypentane. This can be done via a Williamson reaction, but one would have to use a chloroalkane other than (*R*-)2-chloropentane and a solution of an alkanolate other than methanolate.

2p 14 Give the names of the alkanolate and the chloroalkane needed for the Williamson reaction which gives *R*-2-methoxypentane without the formation of *S*-2-methoxypentane.

2p 15 Explain why no *S*-2-methoxypentane is formed during the Williamson reaction between these two types of particles.

■ Problem 4 Industrial production of hydrogen (14 points)

In industry, hydrogen can be produced by heating hydrocarbons, like methane, with steam:



3p 16 Calculate the Gibbs change of energy $\Delta_r G^\circ$ of this reaction and, in doing so, the equilibrium constant K_p . Also indicate the unit of K_p .

2p 17 How does the value of equilibrium constant K_p change with temperature?

The industrial production can take place without a catalyst at atmospheric pressure and high temperature.

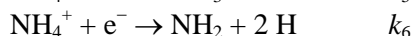
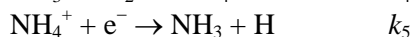
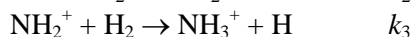
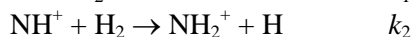
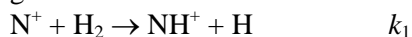
At equilibrium, usually 0.20 volume% methane gas remains.

7p 18 Calculate the value of K_p for this industrial process which gives 0.20 volume% methane gas at equilibrium. Assume that the reactions starts with equal amounts of methane and steam. Note: the conditions are far from standard.

2p 19 Estimate, using the Van 't Hoff-relation $\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ the temperature needed to produce hydrogen from methane in industry.

■ Problem 5 Interstellar chemistry (13 points)

A possible ion-molecule reaction mechanism for the synthesis of ammonia in interstellar gas clouds is given below:



5p 20 Show the relations between the concentrations of the intermediates NH^+ , NH_2^+ , NH_3^+ and NH_4^+ and the concentrations of the reactants: $[\text{N}^+]$, $[\text{H}_2]$ and $[\text{e}^-]$. Use the steady state approximation.

3p 21 Show that the overall production rate of NH_3 is given by: $\frac{d[\text{NH}_3]}{dt} = k_2 e [\text{N}^+][\text{H}_2]$.

In this equation, k_2 is the 2nd order reaction constant of the reaction. Express $k_2 e$ in the reaction rate constants of the partial steps k_1 , k_3 and k_6 .

2p 22 What is the cause of the activation energy in a chemical reaction?

The reaction rates of many ion-molecule reactions are almost independent of temperature.

3p 23 What can be concluded from this with regard to the activation energy?

Explain why this conclusion is important for reactions taking place in interstellar space.

naam:

Antwoordblad meerkeuzevragen van voorronde 2 van de Nationale Scheikundeolympiade 2009

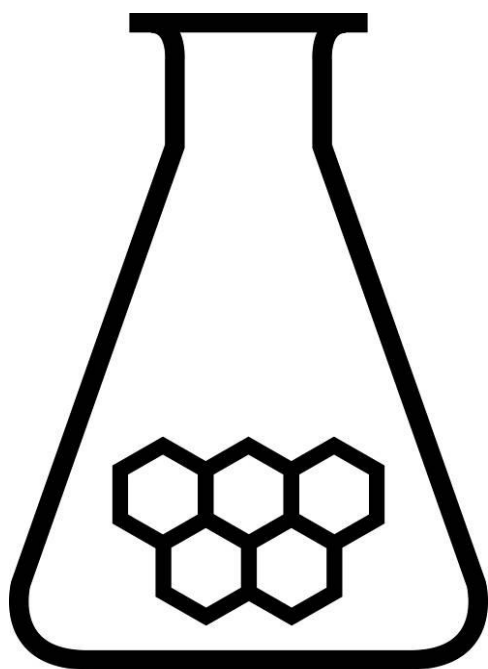
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DUTCH NATIONAL CHEMISTRY OLYMPIAD

SELECTION ROUND 2

CORRECTION MODEL

(the week of)
Wednesday 8 April 2009



**SCHEIKUNDE
OLYMPIADE**



UNIVERSITY OF
CAMBRIDGE

800 Years 1209 - 2009



Specialising in Chemical
Translations

- This selection round consists of 30 multiple choice questions divided over 6 subjects and 7 open questions consisting of a total of 23 subquestions
- The maximum score for this test is 111 points (no extra points)
- For each problem the number of points, obtained for correct answers, is indicated
- For correction of the work, the enclosed correction model must be used. Furthermore, the general rules, as provided by the correction regulations of the CSE¹, apply.

¹ CSE = National Final Exam for High School

Opgave 1 Multiple choice questions

(45 points total)

Per correct answer: 1½ points

Please note: wrong answer -¼ point; no answer: 0 points

Phase changes

1	B	Boiling point most volatile substance
2	A	At T_k the following applies: $\Delta G_{\text{vapour}} = 0 = \Delta H_{\text{vapour}} - T_k \Delta S_{\text{vapour}}$, therefore $T_k = \frac{\Delta H_{\text{vapour}}}{\Delta S_{\text{vapour}}}$; because the change in volume from liquid into gas is almost purely determined by the gas volume, ΔS_{vapour} is a constant for almost all liquids. At higher temperatures, substance I has a higher vapour pressure and therefore it also has the highest ΔH_{vapour} .
3	C	This is the only weak acid and therefore hardly separates into ions: few particles in solution.

Acid-base

4	C	In that case the titration liquid has a lower concentration, therefore the determined molarity is lower.
5	D	K_z values are determined relative to base/solvent H_2O
6	A	From $\text{pH} = 4 - 6$ the change in pH is small upon addition of base; this is the buffer zone.

Calculations

7	B	The electrolysis time depends only on the number of moles of electrons needed; $\frac{75}{27} \times 3 > \frac{50}{24.3} \times 2$ and $\frac{100}{40.1} \times 2$ and $\frac{125}{55.9} \times 2$ (or 3)
8	C	$5.0 \times \frac{100}{88} \times \frac{231.5}{3 \times 55.8} = 7.9 \text{ kg Fe}_3\text{O}_4$
9	C	$65 \text{ mL} \times 0.15 \frac{\text{mole}}{\text{L}} = 9.7(5) \text{ mmole H}_3\text{O}^+$; $45 \text{ mL} \times 0.18 \frac{\text{mole}}{\text{L}} = 8.1 \text{ mmole OH}^-$; remaining per 110 mL $1.65 \text{ mmole H}_3\text{O}^+$; $[\text{H}_3\text{O}^+] = \frac{1.65}{110} = 1.5 \cdot 10^{-2} \Rightarrow \text{pH} = 1.82$

Fysische chemie: thermo

10	E	$-\Delta_f H(\text{C}_2\text{H}_2) + 2 \times -393.5 + -285.8 = -1299.5$ $\Rightarrow \Delta_f H(\text{C}_2\text{H}_2) = 1299.5 - 2 \times 393.5 - 285.8 = 226.7$
11	C	A reaction proceeds spontaneously when the total entropy increases.
12	B	The electron affinity of $\text{Cl}(\text{g})$ is relevant to the Born Haber Cycle, but the ionisation energy isn't (no formation of Cl^+ particles)
13	C	The formation enthalpy is defined relative to the element/elements in their ground state. Therefore, the formation enthalpy of $\text{Br}_2(\text{g})$ equals the evaporation enthalpy of $\text{Br}_2(\text{l})$; boiling point of bromine is 332 K (Binas table 40A); at the boiling point, $\Delta_{\text{vapour}} H = T_{\text{bpt}} \Delta_{\text{vapour}} S = 332 \times 93 = 3.1 \cdot 10^4 \text{ J} = 31 \text{ kJ}$
14	B	The reaction in a galvanic cell proceeds spontaneously $\Rightarrow \Delta G^\circ < 0$ and therefore $(\Delta G^\circ = -RT \ln K)$ $K > 1$

Physical chemistry: thermodynamics

15	C	$\text{dim } k = \frac{\text{mole}}{\text{L s}} : \left(\frac{\text{mole}}{\text{L}}\right)^2$
16	D	With $[\text{X}]$ constant and $[\text{Y}]$ doubled, s increases by a factor of 4 $\Rightarrow s \div [\text{Y}]^2$; when both concentrations increase by a factor of 3, s increases by a factor of 27, the increase as a result of $[\text{Y}]$ would be a factor 9 $\Rightarrow s \div [\text{X}]$ or: with $s = k[\text{X}][\text{Y}]^2$, $k = 20$ in all three cases.
17	B	For a 1 st order reaction, $\ln \frac{[\text{A}]_0}{[\text{A}]} = kt \Rightarrow k = \frac{\ln\left(\frac{100}{60}\right)}{50.0 \text{ min}}$ applies.

		Equilibria
18	D	$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \left(\frac{3.50}{0.25}\right)^2 = 2.0 \cdot 10^2$
19	D	It is an endothermic equilibrium; this would shift to the right with increase of temperature, towards cyclopropane; the pressure does not affect the position of the equilibrium, since the number of gas particles left and right are equal.
20	A	$\text{pH} = 8.67 \Rightarrow \text{pOH} = 5.33;$ $K_s = [\text{Fe}^{2+}][\text{OH}^-]^2 = \frac{1}{2} \times (4.667 \cdot 10^{-6})^3 = 5.1 \cdot 10^{-17}$

		Electrons
21	B	$4 \Rightarrow n = 4; d \Rightarrow l = 2;$ with $l = 2$ correspond $m_l = -2, -1, 0, 1, 2$ and m_s can only have the values $\pm \frac{1}{2}$.
22	B	$\text{Co}^{2+}: ([\text{Ar}], 3d^7);$ the d -level is 5-fold degenerate $\Rightarrow 3$ (If: $\text{Co}^{2+}: [\text{Ar}], 4s^2, 3d^5$) and therefore 5 unpaired electrons \Rightarrow C 1 point
23	D	In a diamagnetic particle, all electrons are paired; NO and N_2^+ have an odd number of electrons and O_2 is a diradical $\Rightarrow \text{O}_2^{2-}$ is diamagnetic
24	C	three: $2 \times \text{C}=\text{O}$ and $1 \times \text{C}=\text{C}$ (it has $\frac{10-4}{2} = 3$ DBE (double bond equivalents))

		Structure and properties
25	C	The C–Cl bond is a polar atom bond; in the <i>trans</i> isomer, the individual dipole moments are compensated by symmetry; therefore, I and II have a dipole moment $\neq 0$
26	D	The centre I in I_3^- has a negative charge; as such, apart from 2 bonding pairs, this I-atom has 3 non-bonding electron pairs. This leads to a TBP structure, in which the non-bonding electron pairs are positioned as far apart as possible in the trigonal plane; the 2 bonding electron pairs are positioned perpendicular to this plane. Therefore, the particle has a linear structure.
27	A	NO^+ has a triple bond \Rightarrow shortest bond distance
28	B	central P in PCl_5 has 5 BP and no NBP, therefore TBP; PCl_4^+ has 4 BP and no NBP, therefore tetragonal; PCl_6^- has 6 BP and no NBP, therefore octahedral.
29	A	It is a saturated compound: 3 Cl on the same C-atom or 2 Cl on one C-atom and one on the neighbouring C-atom $\Rightarrow 2$
30	C	In both cases, the monomer is D-glucose (the α and β form can transform from one into the other) ; the difference is mainly in the glycosidic bond.

Open questions

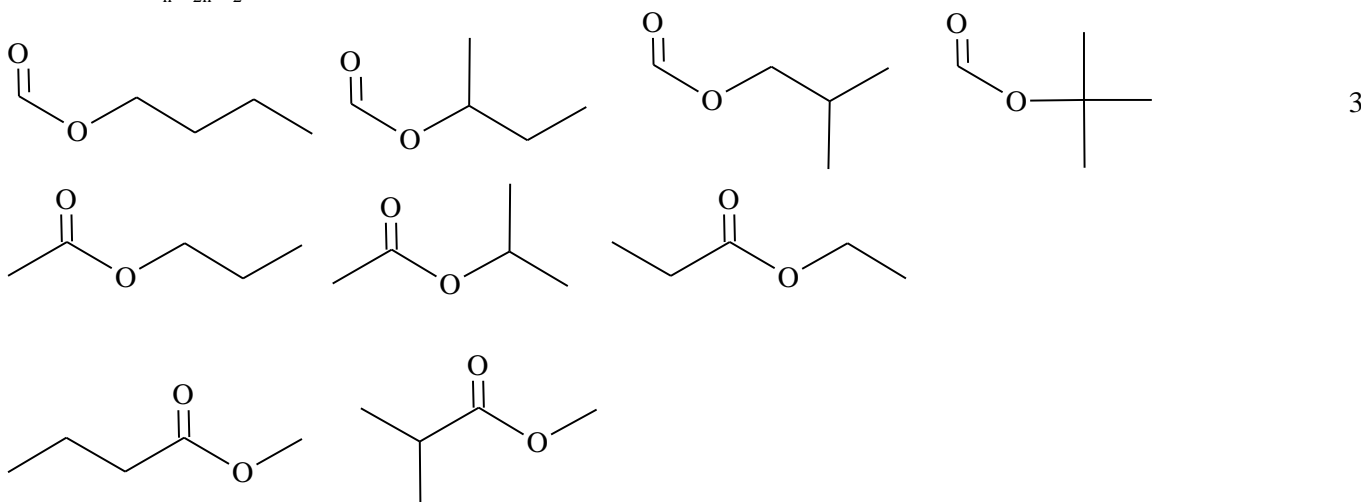
(66 points total)

Opgave 2 NMR spectroscopy

(24 points)

□ 1 Maximum score 6

- the gross formula of an ester is $C_nH_{2n}O_2$ 1
- the molecular mass is 102, the mass of 2 O-atoms is 32 1
- the mass of $C_nH_{2n}O_2$ is 70 $\Rightarrow n = 2$ 1



- if 2 structural formulas are missing and rest correct 2
- if 3 structural formulas are missing and rest correct 1
- 5 or less structural formulas and rest correct 0

□ 2 Maximum score 2

- One signal of TMS, one of the solvent 1
- There are 7 signals, therefore there are 5 different C-atoms 1

□ 3 Maximum score 3

- The total integral is: $1.0112 + 1.5544 + 1.0070 + 1.5155 = 5.088$ 1
- This corresponds to 10 H-atoms, so approximately $\frac{1}{2}$ per atom 1
- This means the signals at 4.05; 2.05; 1.65 and 0.95 ppm correspond to 2, 3, 2 and 3 H-atoms respectively 1

□ 4 Maximum score 1

The H-atoms for this signal do not have direct neighbours.

□ 5 Maximum score 3

- The signal is split into 6 peaks 1
- Therefore, the number of H-neighbours must be 5. 1
- Signal B corresponds to a H without neighbours, as a result the neighbours must cause the signals at A (4.05 ppm) and D (0.95 ppm) 1

□ 6 Maximum score 2

These are the so-called enolic H's, as such extra acidic and no protective electron cloud.

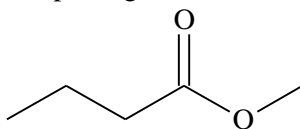
or

One can draw a structure (hyperconjugation) in which the double bonded O has a single bond and a negative charge and an α -H has no bond (H^+).

□ 7 Maximum score 3

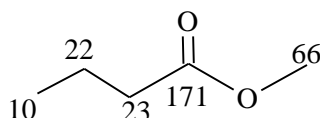
- Peak B (with a lower σ -value than peak A, singlet and standardised peak area of 3) has to be of a CH_3 -group attached to the alcohol side of the ester bond: R_1 is CH_3 . 1
- Of the 5 C-atoms in the ester, 3 remain for the alkyl group (on the acid side of the ester bond). These C-atoms all have different chemical surroundings: therefore, R has to be $-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (in accordance with the standardised peak areas 2, 2, 3 and splitting 3, 6, 3 and shifts 4.05; 1.65 and 0.95). 1

- The structural formula of X is therefore: 1



Note: An answer (with reasons) which leads to the structural formula of propylethanoate 2

□ 8 Maximum score 4



- oxo-carbon 171 1
- carbon atoms 23 and 22 1
- α -carbon 66 1
- ω -carbon 10 1

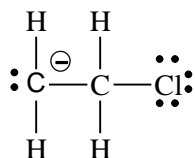
■ Opgave 3 Williamson Synthesis (15 points)

□ 9 Maximum score 2



Per correct formula 1

□ 10 Maximum score 2

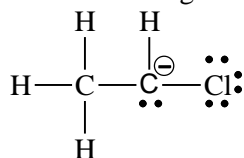


If the only mistake is omission of the charge or wrong charge on the C-atom or charge put in a wrong location 1

If the only mistake is not having drawn the non-bonded electron pair on the C-atom 1

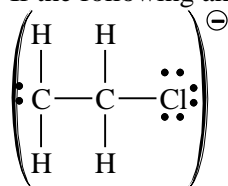
If the only mistake is not having drawn the three non-bonded electron pairs on the Cl-atom 1

If the following answer was given:



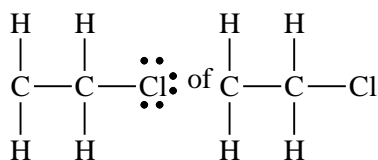
1

If the following answer was given:



1

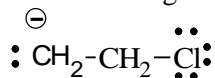
If only the following answer was given:



0

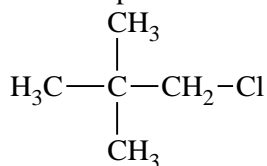
Note

The following answer may also be marked as correct:



□ 11 Maximum score 2

An example of a correct answer would be:



If the structural formula given is not of a chloroalkane, but it does not contain any H-atoms bonded to the C-atom next to the C-atom with the Cl-atom, e.g. the structural formula of chloropropanone

1

If the structural formula of chloromethane was given

0

If the structural formula given is of a chloroalkane containing a H-atom bonded to a C-atom next to the C-atom with the Cl-atom

0

□ 12 Maximum score 2

- 1-pentene and 2-pentene
- *cis-* en *trans-*

1

1

If, instead of names, an answer was given with the three correct structural formulas, showing the difference between *cis*-2-pentene and *trans*-2-pentene

1

Note

If the given answer is “1-pentene, *cis*-pentene and *trans*-pentene”, this is to be marked as correct.

□ 13 \ominus Maximum score 3

Examples of correct answers are:

A mixture is formed in which the molar ratio of the formed *R* and *S* types does not equal 1 : 1, therefore the mixture is optically active.

A non-racemic mixture is formed (of the *R* and *S* products), as such the mixture optically active.

- the molar ratio in which *R* and *S* are formed is not 1 : 1 / formation of a non-racemic mixture
- conclusion

2

1

Note

Answers such as ‘the mixture is left handed because of formation of more *R*-type than *S*-type’ are to be marked as correct.

□ 14 Maximum score 2

R-2-pentanolate and chloromethane

If the names “2-pentanolate and chloromethane” were given as answer

1

Note

A If the answer given is “*R*-pentanolate and chloromethane”, this is to be marked as correct.

□ 15 Maximum score 2

The essence of a correct answer should be that the positioning of the groups around the asymmetric carbon atom in *R*-2-pentanolate won’t change (because the reaction doesn’t take place at that carbon atom).

Opgave 4 Industrial production of hydrogen

(14 points)

□ 16 Maximum score 3

- $\Delta_r H^\circ = -(-76) - (-242) + (-110.5) = 208 \text{ kJ mole}^{-1}$ and
 $\Delta_r S^\circ = -187 - 189 + 3 \times 131 + 198 = 215 \text{ J mole}^{-1} \text{ K}^{-1}$ 1
- $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = 2.08 \cdot 10^3 - 298 \times 215 = 1.44 \cdot 10^5 \text{ J mole}^{-1} = 144 \text{ kJ mole}^{-1}$ 1
- $\Delta_r G^\circ = -RT \ln K_p$
and
 $K_p = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left(-\frac{1.44 \cdot 10^5}{8.314 \times 298}\right) = 5.7 \cdot 10^{-26}$ 1

□ 17 Maximum score 2

- The reaction is endothermic 1
- With increase of temperature, the equilibrium will shift towards the products, the value of the equilibrium constant will increase. 1

Note: the answer can also be deduced from the formula $\Delta_r G^\circ = -RT \ln K_p$.

□ 18 Maximum score 7

- For ideal gases, the volume percentage is equal to the mole fraction. 1
- If 0.20 vol% CH_4 remains, there will also be 0.20 vol% H_2O remaining. 1
- The remaining 99.6% corresponds to the products H_2 and CO in the ratio 3 : 1. 1
- Therefore, there is 24.9% CO and 74.7% H_2 . 1
- $K_p = \frac{a(\text{H}_2)^3 a(\text{CO})}{a(\text{H}_2\text{O}) a(\text{CH}_4)} = \frac{\left(\frac{p(\text{H}_2)}{p^\circ}\right)^3 \left(\frac{p(\text{CO})}{p^\circ}\right)}{\left(\frac{p(\text{H}_2\text{O})}{p^\circ}\right) \left(\frac{p(\text{CH}_4)}{p^\circ}\right)}$ 1
- $K_p = \frac{\left(x(\text{H}_2) \frac{p_{\text{tot}}}{p^\circ}\right)^3 \left(x(\text{CO}) \frac{p_{\text{tot}}}{p^\circ}\right)}{\left(x(\text{H}_2\text{O}) \frac{p_{\text{tot}}}{p^\circ}\right) \left(x(\text{CH}_4) \frac{p_{\text{tot}}}{p^\circ}\right)} = \frac{x(\text{H}_2)^3 x(\text{CO})}{x(\text{H}_2\text{O}) x(\text{CH}_4)} \times \left(\frac{p_{\text{tot}}}{p^\circ}\right)^2$ 1
- $K_p = \frac{0.747^3 \times 0.294}{(2.0 \cdot 10^{-3})^2} \times \left(\frac{1.013}{1.000}\right)^2 = 3.2 \cdot 10^4$ 1

□ 19 Maximum score 2

$$\text{Van 't Hoff isochore: } \ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$T_2 = \left(-\frac{R}{\Delta_r H^\circ} \ln \frac{K_2}{K_1} + \frac{1}{T_1}\right)^{-1} = 1580 \text{ K.}$$

- correct substitution of $\Delta_r H^\circ$, K_1 and T_1 (following from question 16) as well as for K_2 (from question 17) 1
- rest of the calculation 1

Note: if an answer to question 19 is incorrect due to the consequential effect of incorrect answers at questions 16 and 18, this answer to question 19 is to be marked as correct.

Opgave 5 Interstellar chemistry

(13 points)

□ 20 Maximum score 5

In this problem, we will always use the steady state approximation SSA

$$\cdot \frac{d[\text{NH}^+]}{dt} = 0 = k_1[\text{N}^+][\text{H}_2] - k_2[\text{NH}^+][\text{H}_2]$$

$$\cdot \frac{d[\text{NH}_2^+]}{dt} = 0 = k_2[\text{NH}^+][\text{H}_2] - k_3[\text{NH}_2^+][\text{H}_2]$$

$$\cdot \frac{d[\text{NH}_3^+]}{dt} = 0 = k_3[\text{NH}_2^+][\text{H}_2] - k_4[\text{NH}_3^+][\text{H}_2]$$

$$\cdot \frac{d[\text{NH}_4^+]}{dt} = 0 = k_4[\text{NH}_3^+][\text{H}_2] - k_5[\text{NH}_4^+][\text{e}^-] - k_6[\text{NH}_4^+][\text{e}^-]$$

$$\cdot [\text{NH}^+] = \frac{k_1[\text{N}^+]}{k_2}$$

$$\cdot [\text{NH}_2^+] = \frac{k_2[\text{NH}^+]}{k_3} = \frac{k_2 k_1}{k_3 k_2} [\text{N}^+] = \frac{k_1}{k_3} [\text{N}^+]$$

$$\cdot [\text{NH}_3^+] = \frac{k_3[\text{NH}_2^+]}{k_4} = \frac{k_1}{k_4} [\text{N}^+]$$

$$\cdot [\text{NH}_4^+] = \frac{k_4[\text{NH}_3^+][\text{H}_2]}{(k_5+k_6)[\text{e}^-]} = \frac{k_1[\text{N}^+][\text{H}_2]}{(k_5+k_6)[\text{e}^-]}$$

1

1

1

1

1

□ 21 Maximum score 3

$$\cdot \frac{d[\text{NH}_3]}{dt} = k_5 [\text{NH}_4^+][\text{e}^-] =$$

$$\cdot \frac{k_1 k_5 [\text{N}^+][\text{H}_2]}{(k_5+k_6)} =$$

$$\cdot k_2^e [\text{N}^+][\text{H}_2]; \text{ hierin is } k_2^e = \frac{k_1 k_5}{k_5+k_6}$$

1

1

1

Note: if an answer to question 21 is incorrect due to the consequential effect of an incorrect answer at question 20, this answer to question 21 is to be marked as correct.

□ 22 Maximum score 2

The activation energy: is related to the energy necessary to break the first bond,

or

leads to sufficient rearranging in the reactant's geometry to start a reaction.

□ 23 Maximum score 3

(The temperature dependence of a reaction constant k is given by the Arrhenius equation:

$k(T) = A \exp -\frac{E_a}{RT}$, in which A is the pre-exponential factor, E_a the activation energy, R the gas constant and T the temperature).

· If there is hardly any temperature dependence, this means that the activation energy is almost zero.

· The temperature in interstellar space is extremely low.

· Only reactions with a very low activation energy can occur.

1

1

1