

**20<sup>th</sup>**



**6 theoretical problems  
2 practical problems**

# THE TWENTIETH INTERNATIONAL CHEMISTRY OLYMPIAD

**ESPOO 1988  
FINLAND**

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## THEORETICAL PROBLEMS

### PROBLEM 1

The periodic system of the elements in our three-dimensional world is based on the four electron quantum numbers  $n = 1, 2, 3, \dots$ ;  $l = 0, 1, \dots, n - 1$ ,  $m = 0, \pm 1, \pm 2, \dots, \pm l$ ; and  $s = \pm 1/2$ . In Flatlandia, a two-dimensional world, the periodic system is thus based on three electron quantum numbers:  $n = 1, 2, 3, \dots$ ;  $m_l = 0, \pm 1, \pm 2, \dots, \pm (n-1)$ ; and  $s = \pm 1/2$  where  $m_l$  plays the combined role of  $l$  and  $m_l$  of the three dimensional world. The following tasks relate to this two-dimensional world, where the chemical and physical experience obtained from our world is supposed to be still applicable.

- Draw the first four periods of the Flatlandian periodic table of the elements. Number them according to their nuclear charge. Use the atomic numbers ( $Z$ ) as symbols of the specific element. Write the electron configuration for each element.
- Draw the hybrid orbitals of the elements with  $n = 2$ . Which element is the basis for the organic chemistry in Flatlandia? Find the Flatlandian analogous for ethane, ethene and cyclohexane. What kind of aromatic ring compounds are possible?
- Which rules in Flatlandia correspond to the octet and the 18-electron rules in the three dimensional world?
- Predict graphically the trends in the first ionization energies of the Flatlandian elements with  $n = 2$ . Show graphically how the electronegativities of the elements increase in the Flatlandian periodic table.
- Draw the molecular orbital energy diagrams of the neutral homonuclear diatomic molecules of the elements with  $n = 2$ . Which of these molecules are stable in Flatlandia?

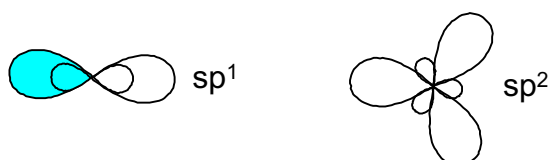
- f) Consider simple binary compounds of the elements ( $n = 2$ ) with  $Z = 1$ . Draw their Lewis structure, predict their geometries and propose analogues for them in the three dimensional world.
- g) Consider elements with  $n \leq 3$ . Propose an analogue and write the chemical symbol from our world for each of these Flatlandian elements. On the basis of this chemical and physical analogue predict which two-dimensional elements are solid, liquid or gaseous at normal pressure and temperature.

### SOLUTION

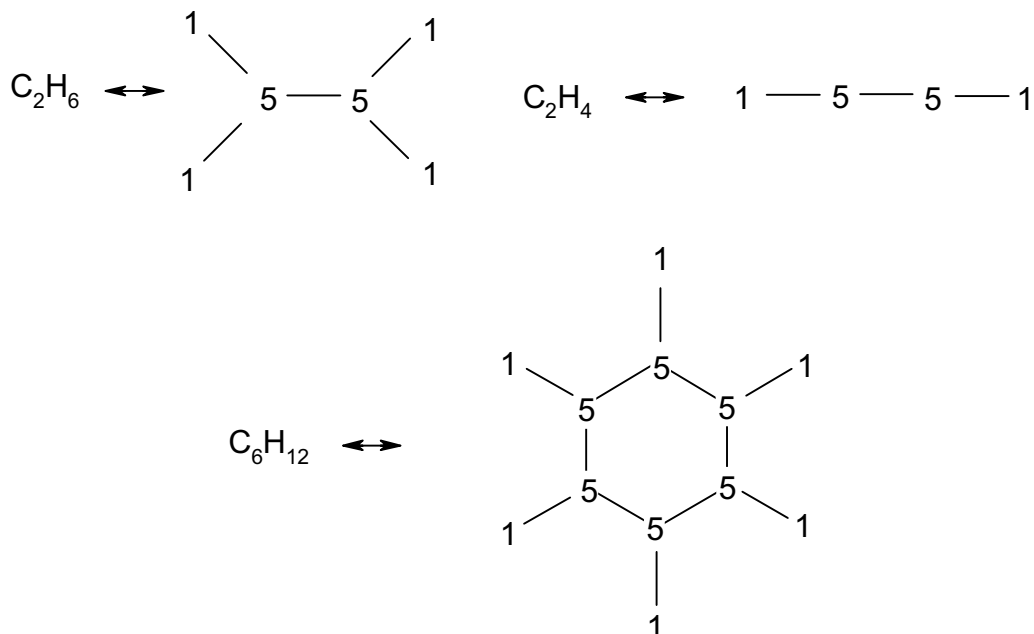
- a) In the two dimensional world and the electron quantum numbers given, we obtain the following Flatlandian periodic table:

<b>1</b> $1s^1$							<b>2</b> $1s^2$		
<b>3</b> $[ ]2s^1$	<b>4</b> $[ ]2s^2$					<b>5</b> $[ ]2s^2 2p^1$	<b>6</b> $[ ]2s^2 2p^2$	<b>7</b> $[ ]2s^2 2p^3$	<b>8</b> $[ ]2s^2 2p^4$
<b>9</b> $[ ]3s^1$	<b>10</b> $[ ]3s^2$					<b>11</b> $[ ]3s^2 3p^1$	<b>12</b> $[ ]3s^2 3p^2$	<b>13</b> $[ ]3s^2 3p^3$	<b>14</b> $[ ]3s^2 3p^4$
<b>15</b> $[ ]4s^1$	<b>16</b> $[ ]4s^2$	<b>17</b> $[ ]4s^2 3d^1$	<b>18</b> $[ ]4s^2 3d^2$	<b>19</b> $[ ]4s^2 3d^3$	<b>20</b> $[ ]4s^2 3d^4$	<b>21</b> $[ ]4s^2 3d^4 4p^1$	<b>22</b> $[ ]4s^2 3d^4 4p^2$	<b>23</b> $[ ]4s^2 3d^4 4p^3$	<b>24</b> $[ ]4s^2 3d^4 4p^4$

- b)  $sp^1$  and  $sp^2$  hybrid orbitals are possible:

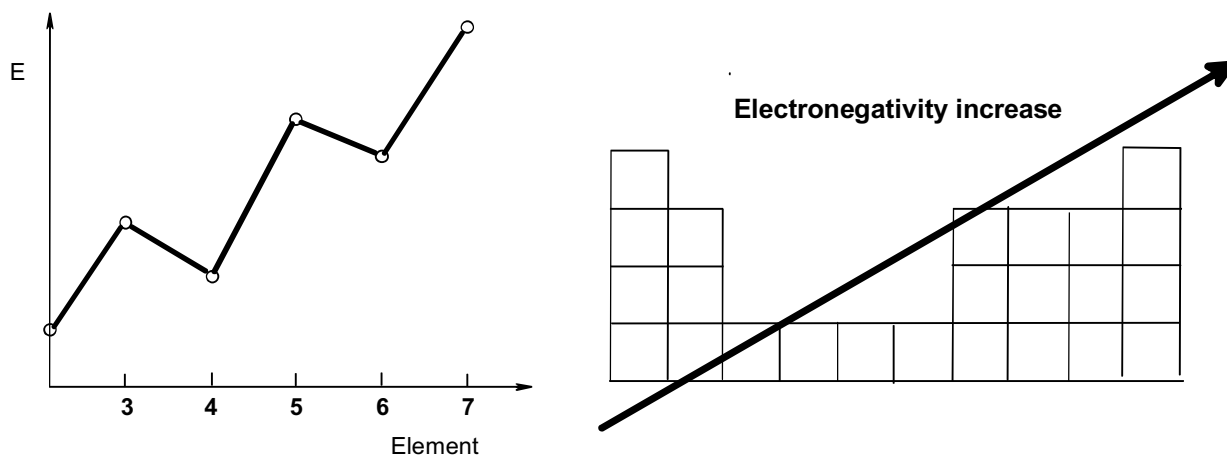


The element of life is the element with  $Z = 5$ . The corresponding compounds of ethane, ethene and cyclohexane are:

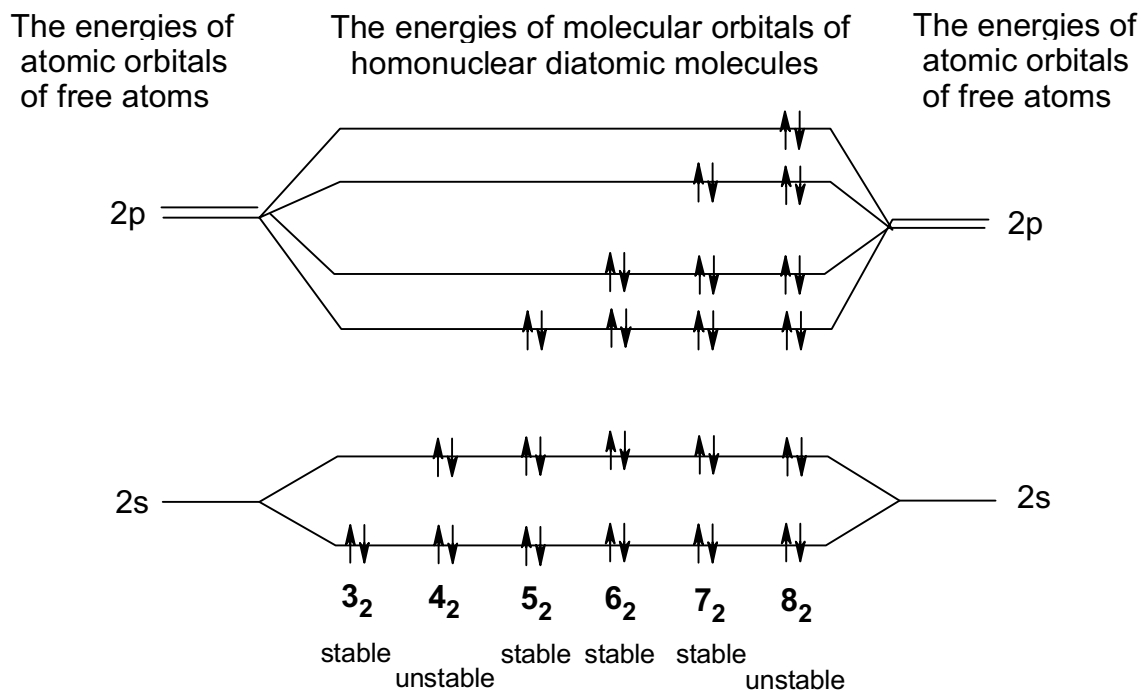


Aromatic ring compounds are not possible since there are no electron orbitals left that may overlap in the case of  $sp^2$ .

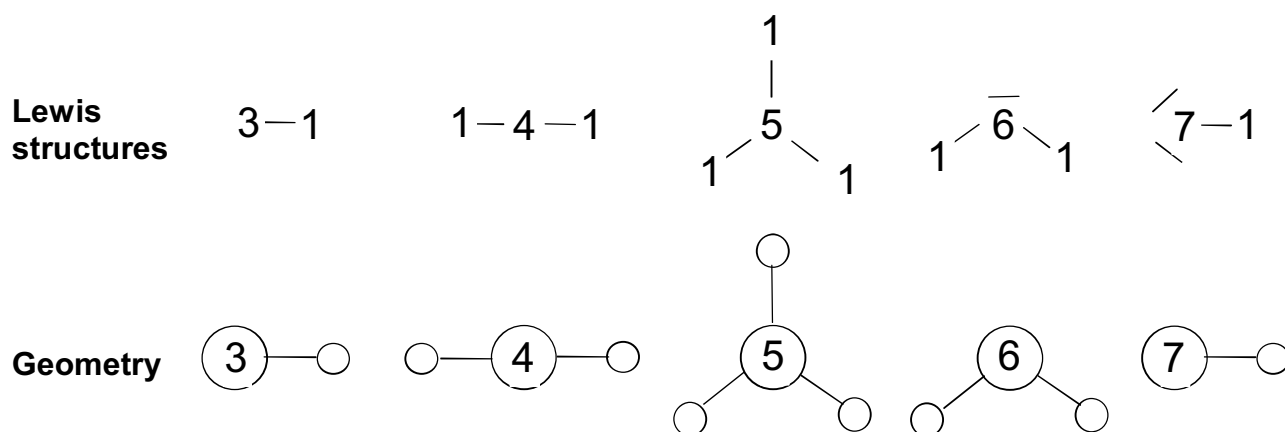
- c) The Octet rule is changed to a Sextet rule, the 18-electron rule corresponds to a 10-electron rule.
- d) The ionization energies and the trends in electronegativity



e) The molecular orbital diagram of the homonuclear  $X_2$  molecules:



f) The Lewis structures and geometries:

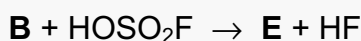


g) The three-dimensional analogues of Flatlandian elements are:

1: H, gas	5: B or C, solid	9: Na, solid	13: Cl, gas
2: He, gas	6: N or O, gas	10: Mg, solid	14: Ar, gas
3: Li, solid	7: F, gas	11: Al or Si, solid	
4: Be, solid	8: Ne, gas	12: P or S, solid	

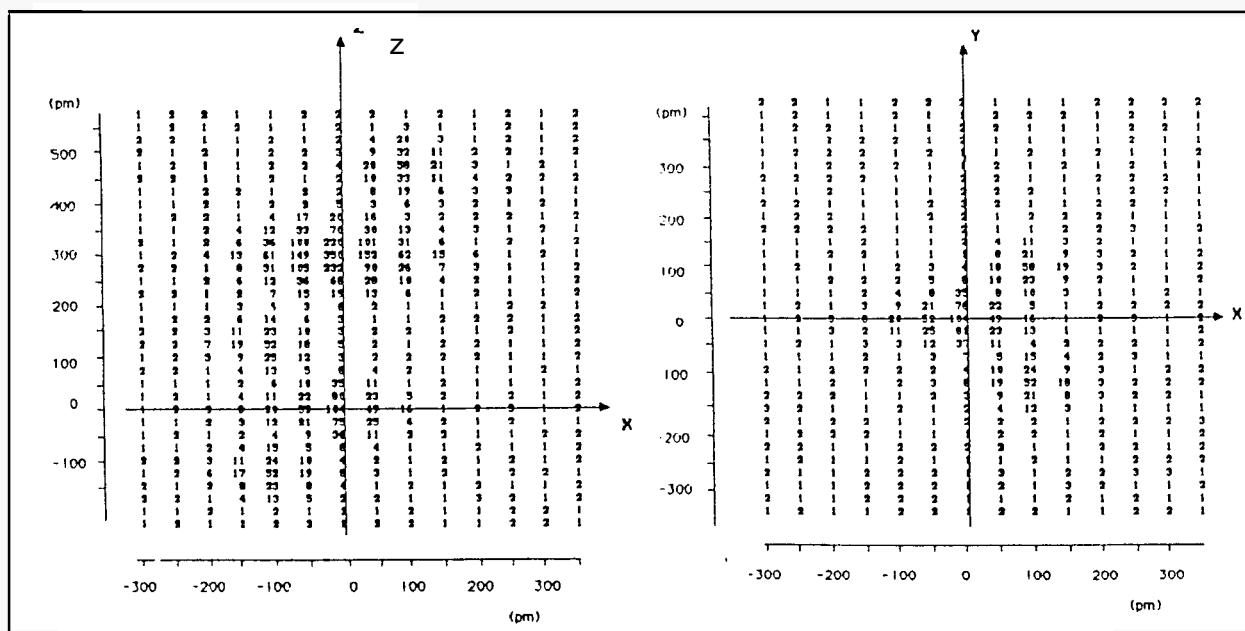
## PROBLEM 2

Upon heating of a mixture of **A** and fluorine (molar ratio 1 : 9, pressure approximately 1 MPa) to 900 °C three compounds (**B**, **C** and **D**) are formed. All three products are crystalline solids at ambient temperature with melting points below 150 °C. The fluorine content of **C** is found to be 36.7 % and that of **D** 46.5 % (by weight). When **B** is treated with anhydrous HOSO<sub>2</sub>F at -75 °C a compound **E** is formed:



**E** is a solid which is stable for weeks at 0 °C, but decomposes in days at room temperature. The electron density distribution of **E** obtained through X-ray diffraction studies is shown on two intersecting, mutually perpendicular planes (see Fig. 1).

Fig. 1



The numbers indicated on the maps relate to the electron density in the neighbourhood of the atoms of **E** as a function of the spatial coordinates. The maxima found in these maps coincide with the locations of the atoms and the values are approximately proportional to the number of electrons in the atom in question.

- a) Show where the maxima lie by drawing the contour curves around the maxima, connecting points of equal electron densities. Label each maximum to show the identities of the atoms in **E**.

- b) When 450.0 mg of **C** was treated with an excess of mercury, 53.25 ml of **A** was liberated at a pressure of 101.0 kPa and a temperature of 25 °C. Calculate the relative atomic mass of **A**.
- c) Identify **A**, **B**, **C**, **D** and **E**.
- d) Use the valence-shell electron-pair repulsion theory (VSEPR) to propose electron-pair geometries for **B** and **C**. Using the two electron density maps, sketch the molecular geometry of **E**.

The original mixture was hydrolysed in water. **B** reacts to **A** while liberating oxygen and producing aqueous hydrogen fluoride. Hydrolysis of **C** leads to **A** and oxygen (in molar ratio of 4 : 3) and yields an aqueous solution of  $\text{AO}_3$  and hydrogen fluoride. **D** hydrolyses to an aqueous solution of  $\text{AO}_3$  and hydrogen fluoride.

- e) Write the equations for the three hydrolysis reactions.
- f) Quantitative hydrolysis of a mixture of **B**, **C** and **D** gives 60.2 ml of gas (measured at 290 K and 100 kPa). The oxygen content of this gas is 40.0% (by volume). The amount of  $\text{AO}_3$  dissolved in water is titrated with an aqueous 0.1 molar  $\text{FeSO}_4$  solution and 36.0 ml used thereby. During the titration  $\text{Fe}^{2+}$  is oxidized to  $\text{Fe}^{3+}$  and  $\text{AO}_3$  is reduced to **A**. Calculate the composition (% by moles) of the original mixture of **B**, **C** and **D**.

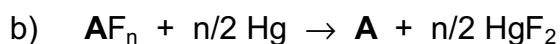
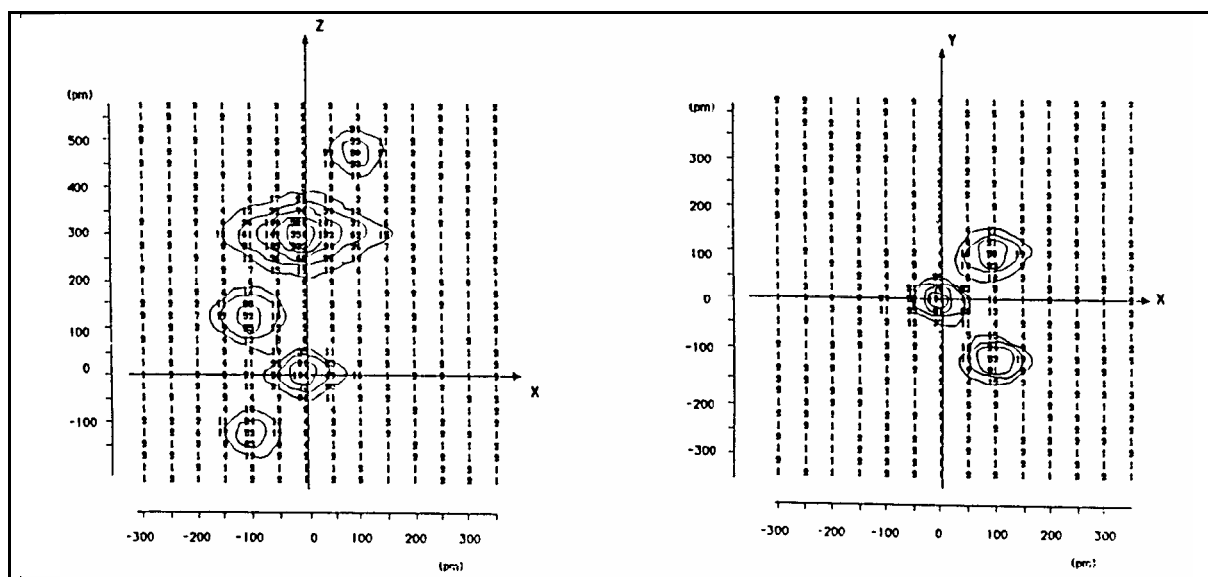
### SOLUTION

Fig. 2 shows the electron densities with maxima 52, 58, 104, and 350. Since compound **E** is supposed to contain the atoms of fluorine, oxygen, sulphur, and **A**, the above maxima can be assign to particular atoms as follows:

Maximum	Element	Atomic number
52	O	8
58	F	9
104	S	16
350	<b>A</b>	?

The atomic number of **A** is 54. Thus, the element **A** is xenon.

Fig. 2



$$n_{\text{gas}} = \frac{pV}{RT} = \frac{101\,000 \text{ Pa} \times 53.25 \times 10^{-6} \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 2.17 \times 10^{-3} \text{ mol} = n(\text{A}) = n(\text{AF}_n)$$

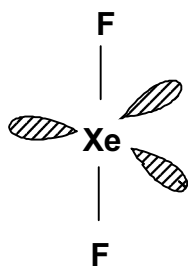
$$\frac{M(\text{AF}_n)}{2.17 \times 10^{-3}} = \frac{0.45}{2.17 \times 10^{-3}} = \underline{207.4 \text{ g mol}^{-1}} = M(\text{A}) + n M(\text{F})$$

$$n M(\text{F}) = 0.367 M(\text{AF}_n) \Rightarrow n = \frac{207 \times 0.367}{19} = 4.0055 \Rightarrow \underline{\text{AF}_4};$$

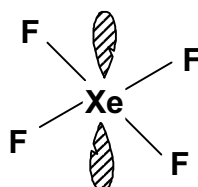
$$M(\text{A}) = M(\text{AF}_n) - n M(\text{F}) = 207.4 - 76.1 = \underline{131.3 \text{ g mol}^{-1}}$$



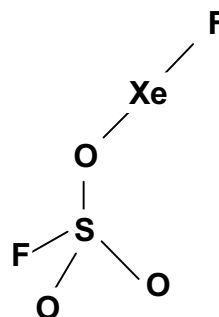
d)



**B**

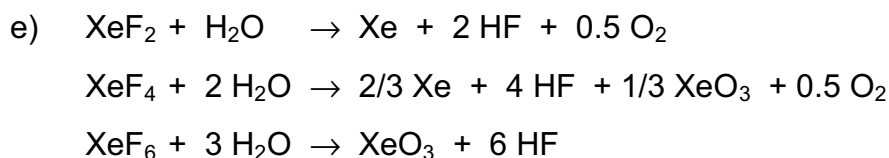


**C**



**E**





f) 
$$n_{\text{gas}} = \frac{pV}{RT} = \frac{100\,000 \text{ Pa} \times 60.2 \times 10^{-6} \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 290 \text{ K}} = 2.50 \times 10^{-3} \text{ mol}$$

$$n(\text{O}_2) = 0.4 \times n_{\text{gas}} = 1.00 \times 10^{-3} \text{ mol}$$

$$n(\text{Xe}) = 1.50 \times 10^{-3} \text{ mol}$$

Assume  $n(\text{XeF}_2) = a$ ;  $n(\text{XeF}_4) = b$ ;  $n(\text{XeF}_6) = c$

$$n(\text{Xe}) = a + 2/3 b;$$

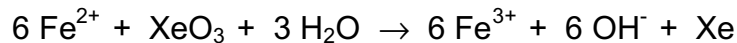
$$n(\text{O}_2) = 1/2 a + 1/2 b;$$

$$n_{\text{gas}} = n(\text{Xe}) + n(\text{O}_2) = 3/2 a + 7/6 b = 2.50 \times 10^{-3} \text{ mol}$$

$$n(\text{O}_2) = 1/2 a + 1/2 b = 1.00 \times 10^{-3} \text{ mol}$$

Solution of the equations:

$$a = 0.5 \times 10^{-3} \text{ mol}; \quad b = 1.5 \times 10^{-3} \text{ mol}$$



$$\begin{aligned} n(\text{XeO}_3) &= 1/6 n(\text{Fe}^{2+}) = 1/6 [c(\text{Fe}^{2+}) V(\text{Fe}^{2+})] = 1/6 \times 0.100 \times 36.0 \times 10^{-3} \text{ mol} = \\ &= 6.00 \times 10^{-4} \text{ mol} = 1/3 b + c \end{aligned}$$

$$c = 0.6 \times 10^{-3} - 0.5 \times 10^{-3} = 1 \times 10^{-4}$$

<u>molar composition:</u>	$\text{XeF}_2$ :	$0.5 \times 10^{-3} \text{ mol}$	(23.8 %)
	$\text{XeF}_4$ :	$1.5 \times 10^{-3} \text{ mol}$	(71.4 %)
	$\text{XeF}_6$ :	$1 \times 10^{-4} \text{ mol}$	(4.8 %)

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### PROBLEM 3

A typical family car has four cylinders with a total cylinder volume of 1600 cm<sup>3</sup> and a fuel consumption of 7.0 l per 100 km when driving at a speed of 90 km/h. During one second each cylinder goes through 25 burn cycles and consumes 0.4 g of fuel. Assume that fuel consists of 2,2,4-trimethylpentane, C<sub>8</sub>H<sub>18</sub>. The compression ratio of the cylinder is 1:8.

- a) Calculate the air intake of the engine (m<sup>3</sup>/s). The gasified fuel and air are introduced into the cylinder when its volume is largest until the pressure is 101.0 kPa. Temperature of both incoming air and fuel are 100 °C. Air contains 21.0 % (by volume) of O<sub>2</sub> and 79.0 % of N<sub>2</sub>. It is assumed that 10.0 % of the carbon forms CO upon combustion and that nitrogen remains inert.
- b) The gasified fuel and the air are compressed until the volume in the cylinder is at its smallest and then ignited. Calculate the composition (% by volume) and the temperature of the exhaust gases immediately after the combustion (exhaust gases have not yet started to expand). The following data is given:

Compound	$\Delta H_f$ (kJ/mol)	$C_p$ (J/mol K)
O <sub>2</sub> (g)	0.0	29.36
N <sub>2</sub> (g)	0.0	29.13
CO(g)	-110.53	29.14
CO <sub>2</sub> (g)	-395.51	37.11
H <sub>2</sub> O(g)	-241.82	33.58
2,2,4-trimethylpentane	-187.82	

- c) Calculate the final temperature of the leaving gases assuming that the piston has moved to expand the gases to the maximum volume of the cylinder and that the final gas pressure in the cylinder is 200 kPa.
- d) To convert CO(g) into CO<sub>2</sub>(g) the exhaust gases are led through a bed of catalysts with the following work function:

$$\frac{n(\text{CO})}{n(\text{CO}_2)} = \frac{1}{4} k \left[ \frac{n(\text{CO})}{n(\text{CO}_2)} \right]_1 v e^{-\frac{T}{T_0}}$$

where  $[n(\text{CO}) / n(\text{CO}_2)]_1$  is the molar ratio before the catalyst,  $v$  is the flow rate in

mol/s and  $T$  the temperature of the gases entering the catalyst (the same as the temperature of the leaving exhaust gases).  $T_0$  is a reference temperature (373 K) and  $k$  is equal to 3.141 s/mol. Calculate the composition (% by volume) of the exhaust gases leaving the catalyst.

### SOLUTION

- a)  $M_r(\text{C}_8\text{H}_{18}) = 114.0$ ,  
 Cylinder volume ( $V_0$ ) =  $4.00 \times 10^{-4} \text{ m}^3$ ,  $p_0 = 101\,000 \text{ Nm}^{-2}$ ,  $T_0 = 373 \text{ K}$   
 Considering one cylinder during one burn cycle one obtains (f = fuel):  
 $m_f = 0.400 / 25 \text{ g} = 0.0160 \text{ g}$ ,  $n_f = 1.4004 \times 10^{-4} \text{ mol}$   
 ( $m_f$  = mass of fuel,  $n_f$  = amount of substance of fuel)  
 $n_G = n_f + n_A = p_0 V_0 / (RT_0) = 0.0130 \text{ mol}$   
 ( $n_G$  = number of moles of gases,  $n_A$  = moles of air)  
 $\Rightarrow n_A = 0.0129 \text{ mol}$   
 $\Rightarrow$  Air intake of one cylinder during 25 burn cycles:  
 $V_A = 25 n_A R T_0 / p_0 = 9.902 \times 10^{-3} \text{ m}^3/\text{s}$   
 $\Rightarrow$  The air intake of the whole engine is therefore:  $V_{\text{total}} = 4 V_A = 0.0396 \text{ m}^3/\text{s}$
- b) The composition of the exhaust gases of one cylinder during one burn cycle is considered:  
 before:  $n_{\text{O}_2} = 0.21 n_A = 2.709 \text{ mmol}$   
 $n_{\text{N}_2} = 0.79 n_A = 10.191 \text{ mmol}$
- $0.1 \times \text{C}_8\text{H}_{18} + 8.5 \text{ O}_2 \rightarrow 8 \text{ CO} + 9 \text{ H}_2\text{O} \quad (10\% \text{ C})$   
 $0.9 \times \text{C}_8\text{H}_{18} + 12.5 \text{ O}_2 \rightarrow 8 \text{ CO}_2 + 9 \text{ H}_2\text{O} \quad (90\% \text{ C})$   
 $\text{C}_8\text{H}_{18} + 12.1 \text{ O}_2 \rightarrow 0.8 \text{ CO} + 7.2 \text{ CO}_2 + 9 \text{ H}_2\text{O}$

Amounts of substances (in mol) before and after combustion:

	C <sub>8</sub> H <sub>18</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O
before	$1.404 \times 10^{-4}$	$2.709 \times 10^{-3}$	0	0	0
after	0	$10.10 \times 10^{-4}$	$1.123 \times 10^{-4}$	$10.11 \times 10^{-4}$	$12.63 \times 10^{-4}$

The composition of the gas after combustion is therefore:

Component	N <sub>2</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	Total
mol × 10 <sup>4</sup>	101.91	10.10	1.12	10.11	12.63	135.87
%	75.0	7.4	0.8	7.5	9.3	100

From thermodynamics the relation between the enthalpy and temperature change is given by

$$\Delta H = \int_{T_1}^{T_2} \sum_{i=1}^{j=k} c_{pi} n_i dT = \sum_{i=1}^{i=k} c_{pi} n_i (T_2 - T_1)$$

$$\Delta H = n_f [0.8 \Delta H_f(\text{CO}) + 7.2 \Delta H_f(\text{CO}_2) + 9 \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_8\text{H}_{18})] = -0.6914 \text{ kJ}$$

This yields to:  $691.4 = 0.4097 (T_2 - 373)$  and  $T_2 = \underline{2060 \text{ }^\circ\text{C}}$

- c) The final temperature of the leaving gases from one cylinder:

$$p_2 = 200\,000 \text{ Pa}, V_0 = 4.00 \times 10^{-4} \text{ m}^3,$$

$$n_G = \text{moles of exhaust gases in one cylinder} = 0.01359 \text{ mol}$$

$$T_2 = \frac{p_2 V_0}{n_G R} = \underline{708 \text{ K}}$$

- d) The flow from all four cylinders is given:  $v = 4 \times 25 \times n_G = 1.359 \text{ mol/s}$ , so that

$$\frac{n(\text{CO})}{n(\text{CO}_2)} = 0.25 \times 3.141 \times \frac{1.12 \times 10^4}{10.11 \times 10^4} \times 1.359 \times e^{\frac{708}{373}} = 0.01772$$

During catalysis:	CO	+	0.5 O <sub>2</sub>	→	CO <sub>2</sub>
moles × 10 <sup>4</sup> (4 cylinders):					
initial	4.48		40.40		40.44
final	4.48 - x		40.40 - 0.5 x		40.44 + x

$$0.01772 (40.44 + x) = 4.48 + x \Rightarrow x = 3.70$$

Thus, the composition of the gas after the catalyst is:

Component	N <sub>2</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	Total
mol × 10 <sup>4</sup>	407.64	40.40 - 0.5x	4.48 - x	40.44 + x	50.52	541.63
		38.55	0.78	44.14		
%	75.26	7.12	0.15	8.14	9.33	100

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#### PROBLEM 4

Chloride ions are analytically determined by precipitating them with silver nitrate. The precipitate is undergoing decomposition in presence of light and forms elemental silver and chlorine. In aqueous solution the latter disproportionates to chlorate(V) and chloride. With excess of silver ions, the chloride ions formed are precipitated whereas chlorate(V) ions are not.

- Write the balanced equations of the reactions mentioned above.
- The gravimetric determination yielded a precipitate of which 12 % by mass was decomposed by light. Determine the size and direction of the error caused by this decomposition.
- Consider a solution containing two weak acids HA and HL, 0.020 molar and 0.010 molar solutions, respectively. The acid constants are  $1 \times 10^{-4}$  for HA and  $1 \times 10^{-7}$  for HL. Calculate the pH of the solution.
- M forms a complex ML with the acid  $H_2L$  with the formation constant  $K_1$ . The solution contains another metal ion N that forms a complex NHL with the acid  $H_2L$ . Determine the conditional equilibrium constant,  $K'_1$  for the complex ML in terms of  $[H^+]$  and  $K$  values.

$$K_1 = \frac{[ML]}{[M][L]}$$

$$K'_1 = \frac{[ML]}{[M'][L']}$$

$[M']$  = total concentration of M not bound in ML

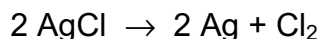
$[L']$  = the sum of the concentrations of all species containing L except ML

In addition to  $K_1$ , the acid constants  $K_{a1}$  and  $K_{a2}$  of  $H_2L$  as well as the formation constant  $K_{NHL}$  of NHL are known.

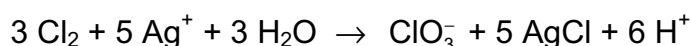
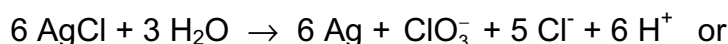
$$K_{NHL} = \frac{[NHL]}{[N][L][H^+]}$$

You may assume that the equilibrium concentration  $[H^+]$  and  $[N]$  are known, too.

**SOLUTION**



Total:



- b) From 100 g AgCl 12 g decompose and 88 g remain. 12 g equals 0.0837 mol and therefore, 0.04185 mol Cl<sub>2</sub> are liberated. Out of that  $(12 \times 107.9) / 143.3 = 9.03$  g Ag remain in the precipitate.  $5/6 \times 0.837$  mol AgCl are newly formed (= 10.0 g), so that the total mass of precipitate (A) yields:

$$A = 88 \text{ g} + 9.03 \text{ g} + 10.0 \text{ g} = \underline{107.03 \text{ g}}; \text{ relative error} = \underline{7.03 \%}$$



$$[\text{HA}] + [\text{A}^-] = 0.02 \text{ mol dm}^{-3} \quad \text{p}K(\text{HA}) = \text{pH} + \text{p}[\text{A}^-] - \text{p}[\text{HA}] = 4$$

$$[\text{HL}] + [\text{L}^-] = 0.01 \text{ mol dm}^{-3} \quad \text{p}K(\text{HL}) = \text{pH} + \text{p}[\text{L}^-] - \text{p}[\text{HL}] = 7$$

For problems like these, where no formal algebraic solution is found, only simplifications lead to a good approximation of the desired result, e.g.

1.  $[\text{H}^+] = [\text{A}^-]$  (since HA is a much stronger acid than HL then  $[\text{A}^-] \gg [\text{L}^-] + [\text{OH}^-]$ )

$$[\text{H}^+]^2 + K_{(\text{HA})}[\text{H}^+] - K_{(\text{HA})}0.02 = 0$$

$$[\text{H}^+] = 1.365 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = \underline{2.865}$$

2. Linear combination of the equations

$$[\text{H}^+] = K_{(\text{HA})} \frac{[\text{HA}]}{[\text{A}^-]} = K_{(\text{HL})} \frac{[\text{HL}]}{[\text{L}^-]};$$

$$[\text{HA}] = 0.02 - [\text{A}^-];$$

$$[\text{HL}] = 0.01 - [\text{L}^-];$$

$$[\text{H}^+] = [\text{A}^-] + [\text{L}^-] + [\text{OH}^-]$$

yields:

$$[A] = \frac{0.02 \times K_{(HA)}}{[H^+] + K_{(HA)}}$$

$$[L] = \frac{0.01 \times K_{(HL)}}{[H^+] + K_{(HL)}}$$

$$[H^+] = \frac{0.02 \times K_{(HA)}}{[H^+] + K_{(HA)}} + \frac{0.01 \times K_{(HL)}}{[H^+] + K_{(HL)}} + \frac{K_w}{[H^+]}$$

The equation above can only be solved by numerical approximation methods. The result is pH = 2.865. We see that it is not necessary to consider all equations. Simplifications can be made here without loss of accuracy. Obviously it is quite difficult to see the effects of a simplification - but being aware of the fact that already the so-called exact solution is not really an exact one (e.g. activities are not being considered), simple assumption often lead to a very accurate result.

d)

$$K_1 = \frac{[ML]}{[M]([L] + [HL] + [NHL] + [H_2L])} = \frac{K_1 [L]}{([L] + [HL] + [NHL] + [H_2L])}$$

$$[HL] = \frac{K_{a1} [H_2L]}{[H]}$$

$$[HL] = \frac{[L] [H]}{K_{a2}}$$

$$[L] = \frac{K_{a2} [HL]}{[H]} = \frac{K_{a1} K_{a2} [H_2L]}{[H]^2}$$

$$[NHL] = K_{NHL} [N] [L] [H]$$

$$K_1 = \frac{K_1}{\left[ 1 + \frac{[H]}{K_{a1}} + \frac{[H]^2}{K_{a1} K_{a2}} + K_{NHL} [N] [H] \right]}$$



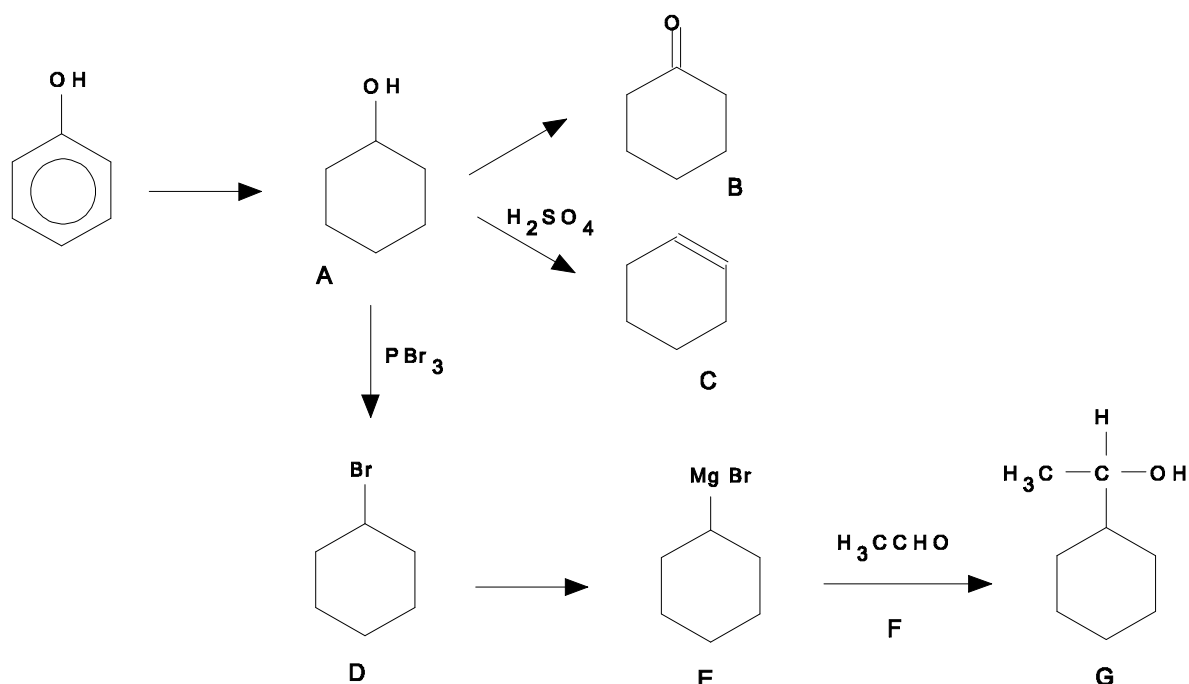
### PROBLEM 5

A common compound **A** is prepared from phenol and oxidized to compound **B**. Dehydration of **A** with  $\text{H}_2\text{SO}_4$  leads to compound **C** and treatment of **A** with  $\text{PBr}_3$  gives **D**. In the mass spectrum of **D** there is a very strong peak at  $m/e = 83$  (base peak) and two molecular ion peaks at  $m/e = 162$  and  $164$ . The ratio of intensities of the peaks 162 and 164 is 1.02. Compound **D** can be converted to an organomagnesium compound **E** that reacts with a carbonyl compound **F** in dry ether to give **G** after hydrolysis. **G** is a secondary alcohol with the molecular formula  $\text{C}_8\text{H}_{16}\text{O}$ .

- Outline all steps in the synthesis of **G** and draw the structural formulae of the compounds **A – G**.
- Which of the products **A – G** consist of configurational stereoisomeric pairs?
- Identify the three ions in the mass spectrum considering isotopic abundances given in the text.

### SOLUTION

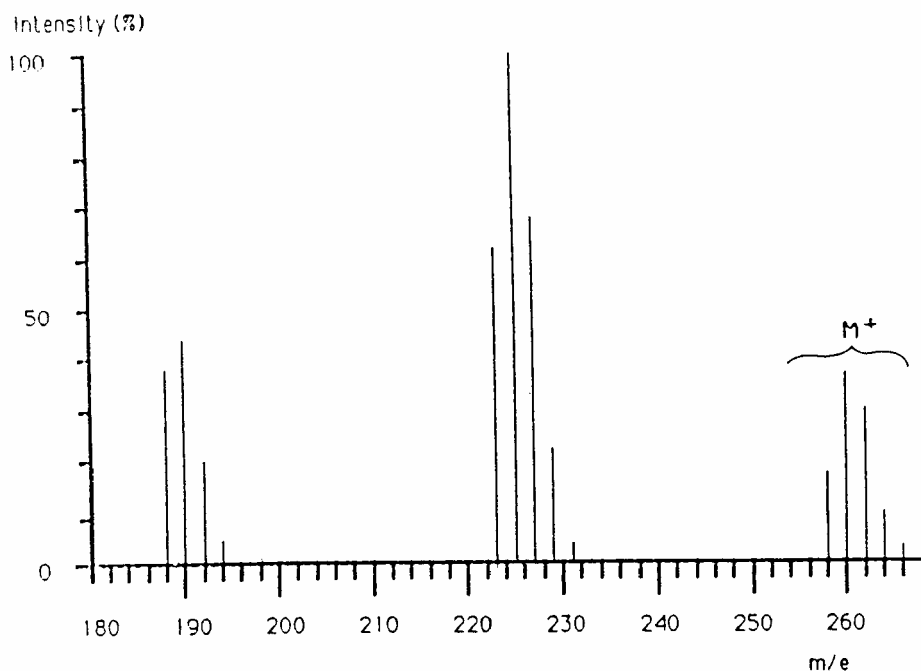
a)



- b) **G** has two stereoisomeric pairs since it has a chiral carbon.
- c) The base peak at  $m/e = 83$  is due to the cyclohexyl-cation,  $C_6H_{11}^+$ , the peaks at  $m/e = 162$  and  $164$  show the same ratio as the abundance of the two bromine isotopes. Therefore, they are the molecular peaks of bromocyclohexane.
-

## PROBLEM 6

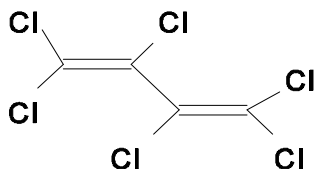
Upon analyzing sea mussels a new bio-accumulated pollutant **X** was found as determined by mass spectroscopy coupled to a gas chromatograph. The mass spectrum is illustrated in figure. Determine the structural formula of **X** assuming that it is produced out of synthetic rubber used as insulation in electrolysis cells that are used for the production of chlorine. Give the name of the compound **X**. The isotopic abundances of the pertinent elements are shown in the figure and table below. Intensities of the ions  $m/e = 196, 233, 268$  and  $270$  are very low and thus omitted. Peaks of the  $^{13}\text{C}$  containing ions are omitted for simplicity.



Element	Mass	Norm.abundanc	Mass	Norm.abundanc	Mass	Norm.abundanc
H	1	100.0	2	0.015		
C	12	100.0	13	1.1		
N	14	100.0	15	0.37		
O	16	100.0	17	0.04	18	0.20
P	31	100.0				
S	32	100.0	33	0.80	34	4.4
Cl	35	100.0			37	32.5
Br	79	100.0			81	98.0

**SOLUTION**

The molecule **X** is hexachlorobutadiene. Butadiene is the monomer of synthetic rubber and freed by decomposition:



## PRACTICAL PROBLEMS

### PROBLEM 1

#### Synthesis of a derivative (NaHX) of the sodium salt of an organic acid

##### *Apparatus:*

1 beaker (250 cm<sup>3</sup>), 2 beakers (50 cm<sup>3</sup>), 1 pipette (10 cm<sup>3</sup>; graduated at intervals of 0.1 cm<sup>3</sup>), 1 measuring cylinder (50 cm<sup>3</sup>), 1 capillary pipette (Pasteur pipette), 1 thermometer, 1 filter crucible (G4), apparatus for suction filtering, 1 glass rod.

##### *Reagents:*

Sodium salt of 1-naphtol-4-sulfonic acid (S), (sodium 1-naphtol-4-sulfonate), ( $M = 246.22 \text{ g mol}^{-1}$ ), sodium nitrite ( $M = 69.00 \text{ g mol}^{-1}$ ), aqueous solution of HCl (2 mol dm<sup>-3</sup>), deionised water, absolute ethanol.

##### *Procedure:*

Mix the given lot of technical grade starting material, labelled I, (contains 1.50 g of sodium 1-naphtol-4-sulfonate, S) and 0.6 g of NaNO<sub>2</sub> with about 10 cm<sup>3</sup> of water in 50 cm<sup>3</sup> beaker. Cool in ice bath (a 250 cm<sup>3</sup> beaker) to the temperature 0 – 5 °C. Keeping the temperature in the 0 – 5 °C range, add dropwise 5 cm<sup>3</sup> of 2 M HCl (aq) to the reaction mixture. Stir for ten more minutes in an ice bath to effect the complete precipitation of the yellow-orange salt NaHX · n H<sub>2</sub>O. Weigh the filter crucible accurately (± 0.5 mg). Filter the product with suction in the crucible and wash with a small amount (ca. 5 cm<sup>3</sup>) of cold water and then twice (about 10 cm<sup>3</sup>) with ethanol. Dry the product in the filter crucible at 110 °C for 30 minutes. Weigh the air-cooled anhydrous material together with the crucible and present it to the supervisor.

Calculate the percentage yield of NaHX ( $M = 275.20 \text{ g mol}^{-1}$ ).

The purity of the product NaHX influences your results in Problem 2!

##### *Question:*

Write the reaction equation using structural formulae.

## PROBLEM 2

The spectrophotometric determination of the concentration, acid constant  $K_{a2}$  and  $pK_{a2}$  of  $H_2X$

### *Apparatus:*

7 volumetric flasks (100 cm<sup>3</sup>), 2 beakers (50 cm<sup>3</sup>), 1 capillary pipette (Pasteur), 1 pipette (10 cm<sup>3</sup>; graduated in intervals of 0.1 cm<sup>3</sup>), 1 washing bottle, 1 glass rod, 1 container for waste materials, funnel.

### *Reagents:*

Compound NaHX, aqueous stock solution of Na<sub>2</sub>X (0.00100 mol dm<sup>-3</sup>), aqueous solution of sodium perchlorate (1.00 mol dm<sup>-3</sup>), aqueous solution of HCl (0.1 mol dm<sup>-3</sup>), aqueous solution of NaOH (0.1 mol dm<sup>-3</sup>).

### *Procedure:*

- a) Weigh accurately  $183.5 \pm 0.5$  mg of NaHX and dissolve it in water in a volumetric flask and dilute up to the 100 cm<sup>3</sup> mark. Pipette 15.0 cm<sup>3</sup> of this solution into another 100 cm<sup>3</sup> volumetric flask and fill up to the mark with water to obtain the stock solution of NaHX. If you do not use your own material, you will get the NaHX from the service desk.
- b) Prepare 5 solutions, numbered 1-5, in the remaining five 100 cm<sup>3</sup> volumetric flasks. These solutions have to fulfil the following requirements:
  - The total concentration of ( $[X^{2-}] + [HX^-]$ ) in each solution must be exactly 0.000100 mol dm<sup>-3</sup>.
  - The concentration of sodium perchlorate in each solution must be 0.100 mol dm<sup>-3</sup> to maintain constant ionic strength. The solutions are prepared by pipetting into each volumetric flask 1-5 the accurate volumes of the NaHX and Na<sub>2</sub>X stock solutions, adding a required volume of sodium perchlorate solution and filling up to the mark with water.

- Solution 1 is prepared by pipetting the required amount of the stock solution of NaHX. Add ca. 3 cm<sup>3</sup> of HCl (aq) with the pipette to ensure that the anion is completely in the form HX<sup>-</sup>, before adding the sodium perchlorate solution.
- Solution 5 is prepared by pipetting the required amount of the stock solution of Na<sub>2</sub>X which is provided for you. Add ca. 3 cm<sup>3</sup> of the NaOH(aq) to ensure that the anion is completely in the form X<sup>2-</sup>, before adding the sodium perchlorate solution.
- The three remaining solutions 2-4 are prepared by pipetting the stock solutions of NaHX and Na<sub>2</sub>X in the following ratios before adding the sodium perchlorate solution:

Solution No.	Ratio NaHX(aq) : Na <sub>2</sub> X(aq)
2	7 : 3
3	1 : 1
4	3 : 7

- c) Take the five volumetric flasks to the service centre where their UV-vis spectra will be recorded in the region 300-500 nm for you. In another service centre the accurate pH of each solution will be recorded. You may observe the measurements.
- d) From the plot of absorbance vs. wavelength, select the wavelength most appropriate for the determination of  $pK_{a2}$  of H<sub>2</sub>X, and measure the corresponding absorbance of each solution.
- e) Calculate the  $pK_{a2}$  of H<sub>2</sub>X from the pH-absorbance data when the ionic strength  $I = 0.1$  and the temperature is assumed to be ambient (25 °C). Note that:

$$K_{a2} = \frac{[H^+][X^-]}{[HX^-]} = \frac{c_{H^+} \times c_{X^{2-}}}{c_{HX^-}}$$

$$K_{a2} = \frac{(A - A_{HX^-})[H^+]}{(A_{X^{2-}} - A)} \quad \text{or} \quad A = A_{X^{2-}} - (A - A_{HX^-}) \frac{[H^+]}{K_{a2}}$$

$$pf_{H^+} = \frac{0.509 \times \sqrt{I}}{1 + \sqrt{I}}$$

- f) Which of your prepared solutions shows the largest buffer capacity? Calculate this buffer capacity,  $P$ , by any suitable method. You may use the equations given:

$$P = 2.3 \times \left( [\text{OH}^-] + [\text{H}^+] + \frac{K_a [\text{H}^+] C}{(K_a + [\text{H}^+])^2} \right)$$

$$P = 2.3 \times \left( \frac{K_w}{[\text{H}^+]} + [\text{H}^+] + \frac{[\text{X}^{2-}][\text{HX}^-]}{C} \right)$$

C is the total concentration of the acid.

$K_w = 2.0 \times 10^{-14}$  at  $I = 0.1$  and  $25\text{ }^\circ\text{C}$ .

