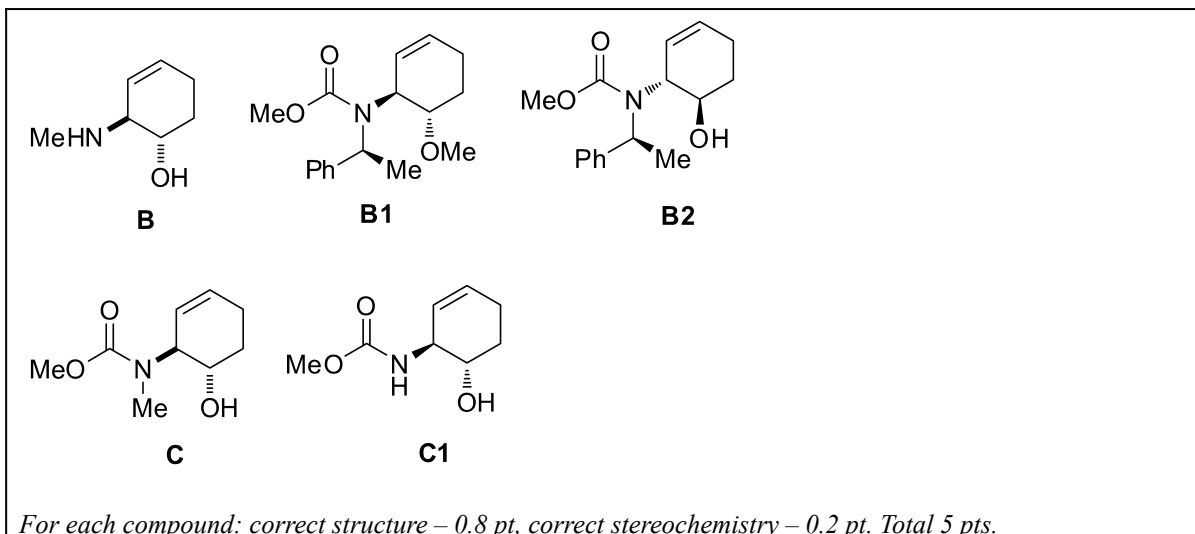
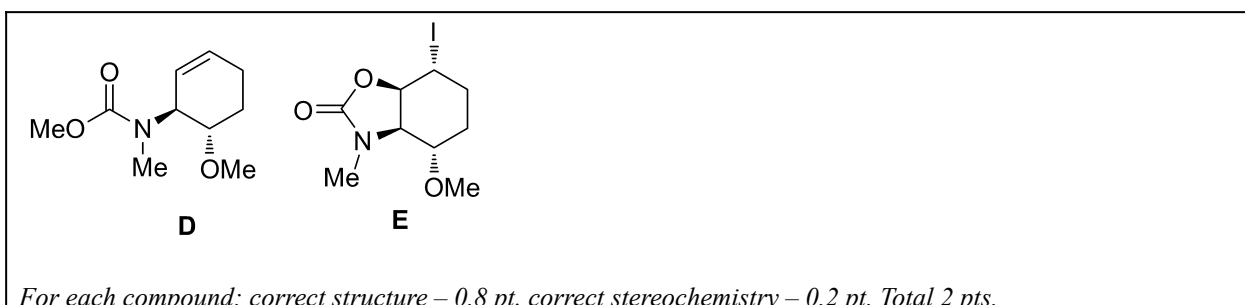


**Solutions**  
**Problem 2. Fortamine**

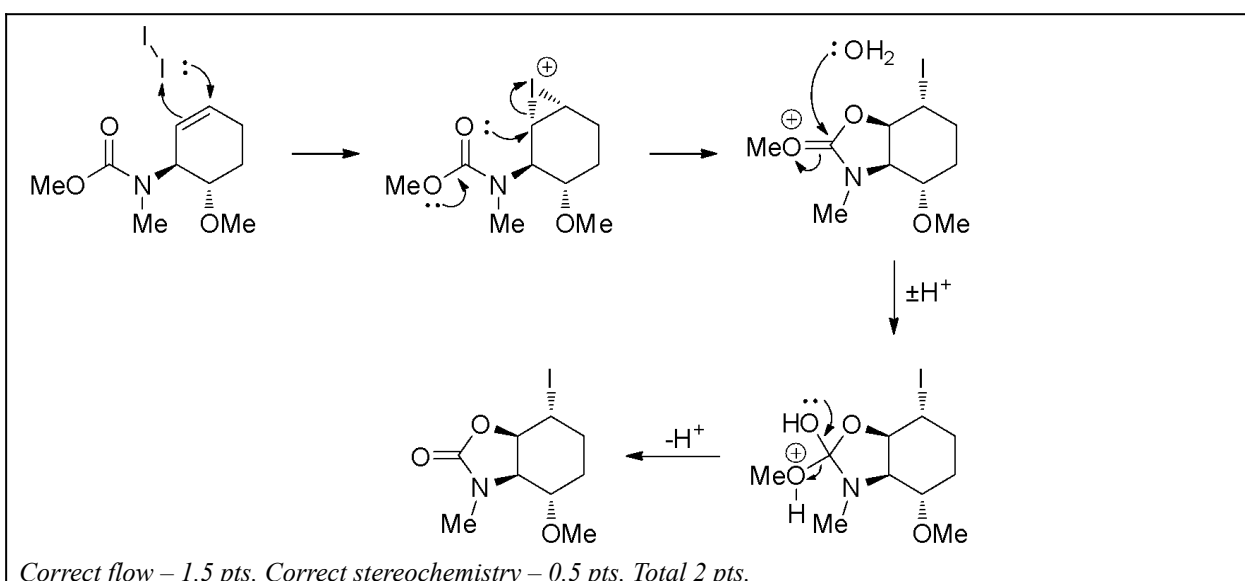
1. Draw the structures of compounds **B**, **B1**, **B2**, **C** and **C1**.



2. Draw the structures of compounds **D** and **E**.

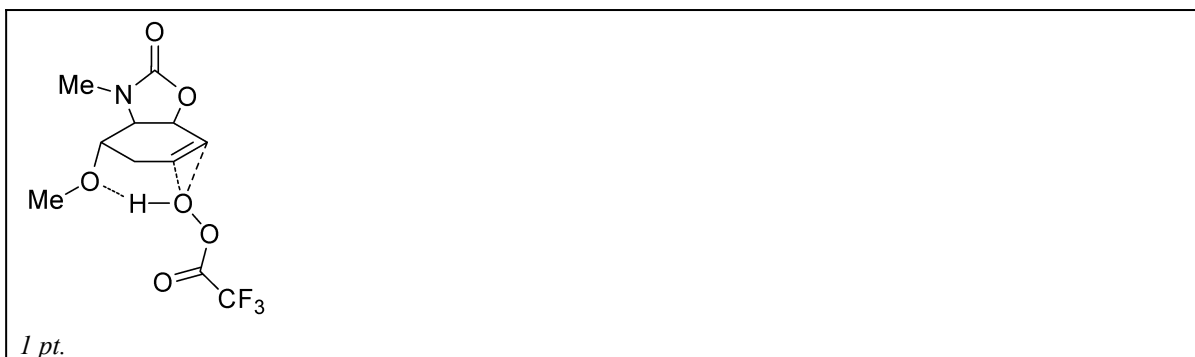


3. Show the mechanism for reaction **D** → **E**.

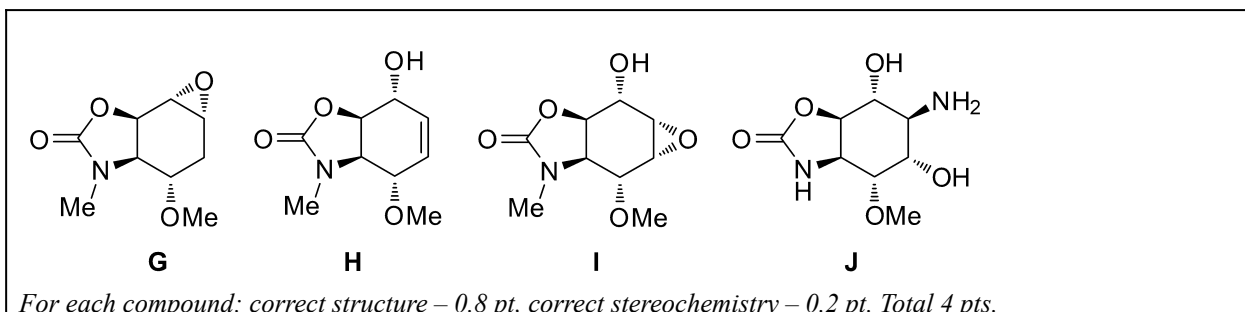




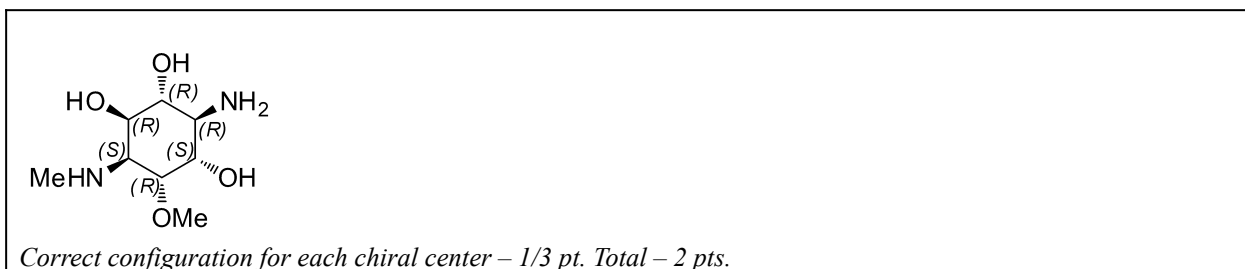
4. Show the structure of the intermediate molecular complex of reaction **F** → **G**.



5. Draw the structural formulas for compounds **G** – **J**.



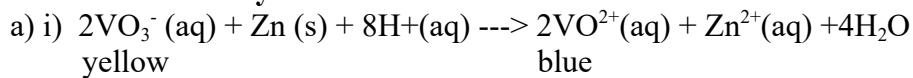
6. Indicate the configuration of all the chiral carbons of Fortamine using R/S nomenclature.



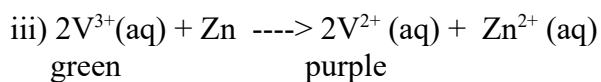
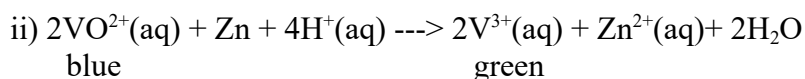
Total for this problem – 16 pts.

Problem 3. 10 points

**Redox flow battery**



Green colour appears when the  $\text{VO}_3^- / \text{VO}^{2+}$  ratio is close to 1.



b)  $M(\text{vanadium cation}) = 155 \text{ g mol}^{-1}$

The formula is  $[\text{VO}_2(\text{H}_2\text{O})_4]^+$

i) Anode:  $\text{V}^{2+} \xrightarrow{\text{discharge}} \text{V}^{3+} + \text{e}^-$

ii) Cathode:  $\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \xrightarrow{\text{discharge}} \text{VO}^{2+} + \text{H}_2\text{O}$

iii) Summary:  $\text{V}^{2+} + \text{VO}_2^+ + 2\text{H}^+ \xrightarrow{\text{discharge}} \text{V}^{3+} + \text{VO}^{2+} + \text{H}_2\text{O}$

c) i)  $E = E^0(\text{VO}^{2+}/\text{VO}_2^+) - E^0(\text{V}^{2+}/\text{V}^{3+}) - 0.059 \cdot \log\left(\frac{[\text{V}^{3+}][\text{VO}_2^+]}{[\text{V}^{2+}][\text{VO}_2^+][\text{H}^+]^2}\right)$

ii)  $\Delta E = 0.059 \cdot \log(1/[0.1]^2) = 0.118 \text{ V}$

d) i)  $\Delta G^0 = -nFE^0 = -1 \cdot 96485 \cdot 1.4 = -135 \text{ kJ mol}^{-1}$

ii)  $\Delta G^0 = -RT \ln K \rightarrow K = e^{(-\Delta G^0/RT)} = 2 \cdot 10^{-24}$

e) i) The mass of 1 mol battery is  $2 \text{ L} \cdot 1.3 \text{ kg L}^{-1} = 2.6 \text{ kg}$ , and energy density is  $135/2.6 = 51.9 \text{ kJ kg}^{-1} / 3.6 \text{ kJ Wh}^{-1} = 14.4 \text{ Wh kg}^{-1}$ . Thus the energy density of the described VRB is lower than in lead-acid battery.

ii) Increase vanadium salt and sulphuric acid concentration. Newer VRB designs with more concentrated solutions (yet there is a limited solubility) or with a different chemistry are more promising.

1. Stationary state equation:

$$\frac{d[\text{ES}]}{dt} = k_1 \cdot [\text{E}][\text{S}] - k_{-1}[\text{ES}] - k_2[\text{ES}] = 0$$

5 points

(if stationary state equation is wrong max 2 points (if one reaction is missing) but no points for further calculations with wrong equation)

Reaction rate equation as 2<sup>nd</sup> step is rate limiting:

$$v = k_2[\text{ES}]$$

(2 points, also if it is not given as statement but student has used this idea)

Enzyme concentration in solution can be expressed  $C(\text{E, tot}) = [\text{E}] + [\text{ES}]$

$$[E] = C(E) - [ES]$$

$$k_1 \cdot [E][S] - k_{-1}[ES] - k_2[ES] = 0$$

$$k_1 \cdot [E][S] - [ES](k_{-1} + k_2) = 0$$

$$k_1 \cdot [S] \cdot C(E) - [ES](k_{-1} + k_2 + k_1[S]) = 0$$

$$[ES] = \frac{k_1 \cdot [S] \cdot C(E)}{k_{-1} + k_2 + k_1[S]}$$

$$v = \frac{k_2 \cdot k_1 \cdot [S] \cdot C(E)}{k_{-1} + k_2 + k_1[S]}$$

$$\text{abbreviate } k_2 \cdot C(E) = v_{\max}$$

$$\frac{1}{v} = \frac{k_{-1} + k_2 + k_1[S]}{v_{\max} \cdot k_1 \cdot [S]} = \frac{k_{-1} + k_2}{v_{\max} \cdot k_1 \cdot [S]} + \frac{k_1[S]}{v_{\max} \cdot k_1 \cdot [S]}$$

$$\text{abbreviate } \frac{k_{-1} + k_2}{k_1} = K_M$$

$$\frac{1}{v} = \frac{K_M}{v_{\max}} \cdot \frac{1}{[S]} + \frac{1}{v_{\max}} = \frac{K_M + [S]}{v_{\max} \cdot [S]}$$

$$v = \frac{v_{\max} \cdot [S]}{K_M + [S]}$$

(5 points – any mathematical operations leading to final equation)

**Q1 = 12 points**

2. Case a) huge substrate concentration

$$[S] \gg K_M$$

$$K_M + [S] \approx [S]$$

$$v = \frac{v_{\max} \cdot [S]}{[S]} = v_{\max}$$

zero order reaction

(2 points for reaction order, 2 points for explanation)

Case b) small substrate concentration

$$[S] \ll K_M$$

$$K_M + [S] \approx K_M$$

$$v = \frac{v_{\max} \cdot [S]}{K_M}$$

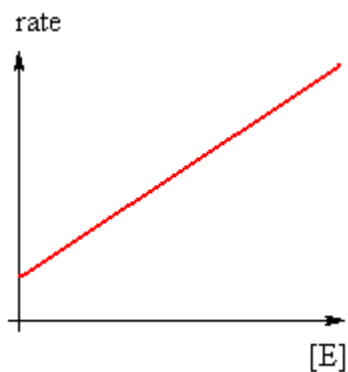
1st order reaction

(2 points for reaction order, 2 points for explanation)

**points**

**Q2 = 8**

3. Graph



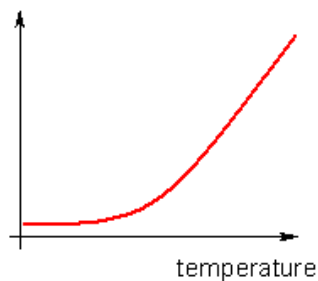
3 points – straight line with positive slope, exponential line or curved line – no points

2 points – line not starting from (0;0) point as reactions proceed also without catalyst

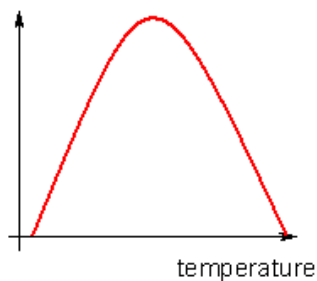
**Q3 = 5 points**

4. Graphs

Case a - classical reaction  
reaction rate



Case b - enzymatic reaction  
reaction rate



Classical reaction: 4 points – exponential line, straight line with positive slope 1 point, other cases – no points. Enzymatic reaction: 4 points – line with maximum, other cases no points.

**Q4 = 8 points**

5. Conductometry. 2 points, Other answers or more than one answer – no points.

**Q5 = 2 points**

6. Inverse of Michaelis-Menten equation:

$$\frac{1}{v} = \frac{K_M}{v_{\max}} \cdot \frac{1}{[S]} + \frac{1}{v_{\max}}$$

$$y = ax + b$$

$$y = \frac{1}{v}$$

$$x = \frac{1}{[S]}$$

$$a = \frac{K_M}{v_{\max}}$$

$$b = \frac{1}{v_{\max}}$$

(only first row is required, 5 points, other answers 0 points)

**Q6 = 5 points**

7. As  $b = 1/v_{\max}$ :

$$v_{\max} = \frac{1}{b} = \frac{1}{7968} = 1.26 \cdot 10^{-3} \frac{\text{mol}}{\text{l} \cdot \text{s}}$$

Accept values from  $1.2 \cdot 10^{-3}$  to  $1.3 \cdot 10^{-3}$ . 3 points,  $1 \cdot 10^{-3} = 1$  point  
 Correct units added +2 points (also in case of incorrect numeric value).  
 Total for calculation of  $v(\max)$  = 5 points.

Concentration value at which rate is half of maximum is Michaelis constant.  
 2 points for this (statement is not required, student may calculate  $K_M$  without explanation, then he/she also receive 2 points)

As  $a = K_M/v(\max)$ , we need to calculate slope.

$$\text{slope} = a = \text{tg} \frac{20506 - 7968}{30000} = 0.04179 \text{ s}$$

2 points for correct slope calculation (accept values between 0.04 and 0.045, no units are required)

$$K_M = a \cdot v(\max) = 0.04179 \cdot 1.26 \cdot 10^{-3} = 5.25 \cdot 10^{-5} \text{ M}$$

Accept values from  $5 \cdot 10^{-5}$  to  $5.5 \cdot 10^{-5}$ . 3 points  
 Correct units added +2 points (also in case of incorrect numeric value).  
 Total for calculation of  $K_M$  = 9 points  
 If  $v(\max)$  value is wrong student may receive points for slope, for  $K_M$  idea, for units but not for  $K_M$  value if it is not in interval required.

**Q7 = 14 points**

8.  $v_{\max} = k_2 \cdot C(E)$

$$k_2 = \frac{v_{\max}}{C(E)} = \frac{1.26 \cdot 10^{-3}}{2.00 \cdot 10^{-5}} = 63 \text{ s}^{-1}$$

Accept values from 60 to 65. This gives 3 points. Do not accept any other values (also if they are right from wrong  $v(\max)$ ).  
 Correct units added +2 points (also in case of incorrect numeric value).

**Q8 = 5 points**

9. Correct answers in table:

|          |          |               |
|----------|----------|---------------|
| A2435    | Caffeine | Physostigmine |
| <i>C</i> | <i>A</i> | <i>B</i>      |

Each correct answer 6 points. Each incorrect answer -3 points. Total not less than zero, if it is less than zero points, award 0 points for task.

**Q9 = 18 points**

10. Let's use equation from question 6:

$$\frac{1}{v} = \frac{K_M}{v_{\max}} \cdot \frac{1}{[S]} + \frac{1}{v_{\max}}$$

$$\frac{[S]}{v} = \frac{K_M}{v_{\max}} \cdot \frac{1}{[S]} \times [S] + \frac{1}{v_{\max}} \times [S]$$

$$\frac{[S]}{v} = \frac{1}{v_{\max}} \cdot [S] + \frac{K_M}{v_{\max}}$$

$\frac{[S]}{v}$  is linear function of  $[S]$

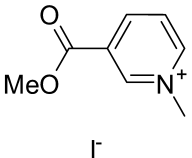
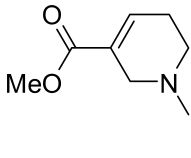
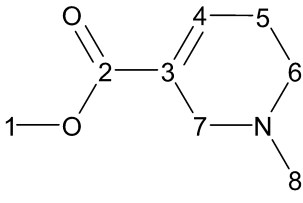
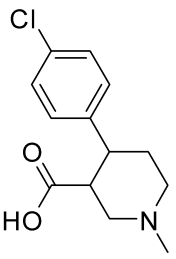
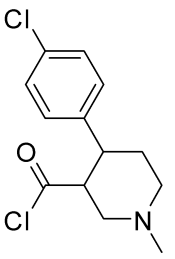
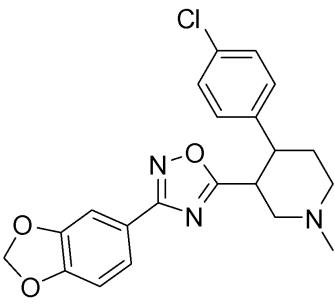
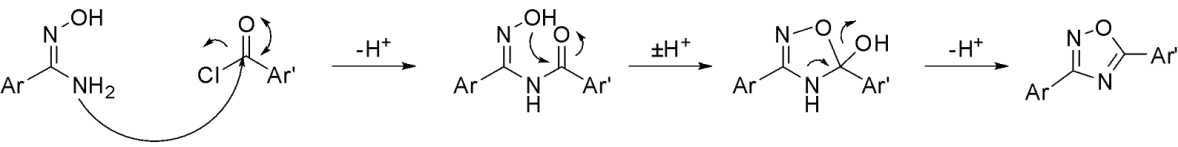
6 points for transformation of equation, 2 points for identification of x, if x is stated as 1/(v(max), then 1 point, other cases – no points

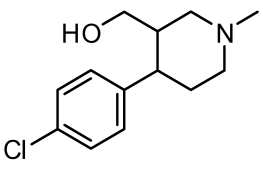
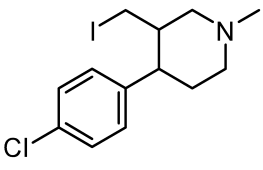
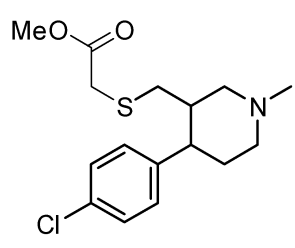
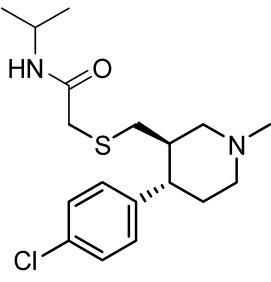
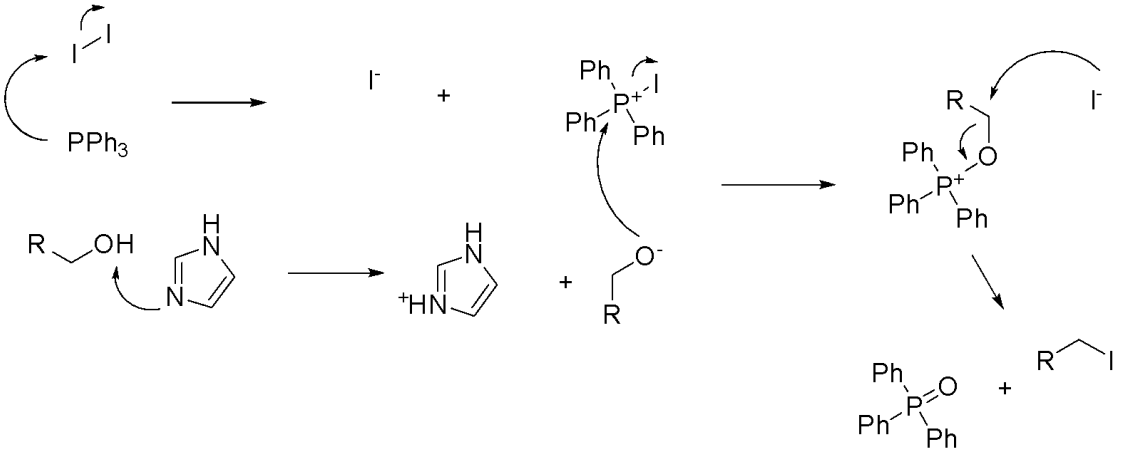
**Q9 = 8 points**

**TOTAL 85 trial points**



## Problem 5 Nocaine

|   |   |   |
|---|---|---|
| <p><b>1. A</b></p>  <p>I<sup>-</sup></p> | <p><b>B</b></p>   |   |
| <p><b>2.</b></p>                         | <p><sup>1</sup>H:</p> <p>1 – 3.74<br/>           4 – 7.00<br/>           5 – 2.37<br/>           6 – 2.50<br/>           7 – 3.15<br/>           8 – 2.41</p> | <p><sup>13</sup>C:</p> <p>1 – 53.2<br/>           2 – 166.9<br/>           3 – 128.9<br/>           4 – 137.5<br/>           5 – 26.5<br/>           6 – 50.7<br/>           7 – 51.4<br/>           8 – 45.6</p> |
| <p><b>3. C</b></p>                      | <p><b>D</b></p>   | <p><b>X</b></p>   |
| <p><b>4. D → X</b></p>                |   |   |

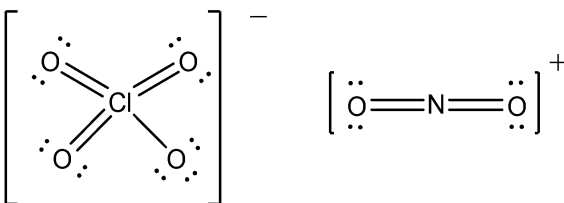
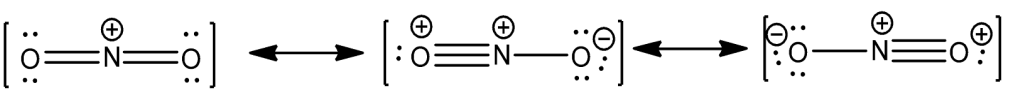
|  |   |   |
|--|---|---|
| <p><b>5. E</b></p>    | <p><b>F</b></p>  | <p><b>G</b></p>  |
| <p><b>6.</b></p>    |   |   |
| <p><b>7. E → F</b></p>    |   |   |
| <p><b>8.</b> A Kolonēlinē chromatografija<br/> <b>B</b> Nokaino L-laktato perkristalinimas<br/> C Nokaino acetato perkristalinimas<br/> D Distiliacija</p> |   |   |



**Problem 6**

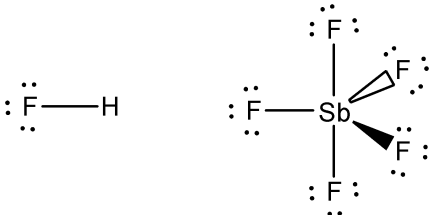
**11 points Superacids**

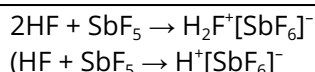
1. Provide the chemical formula for **A** and **B** and Lewis structure formulas for both ions in **B**! What geometrical shape do these ions owe? Write down all resonance structures of the cation in **B**!

|  |                            |
|--|----------------------------|
| <p><b>A</b> = HClO<sub>4</sub></p> <p><b>B</b> = NO<sub>2</sub><sup>+</sup>ClO<sub>4</sub><sup>-</sup></p> | <p>0.5 pt.</p> <p>1 pt</p> |
|                           |                            |
| <p>1 pt.</p> <p>NO<sub>2</sub><sup>+</sup> = linear; ClO<sub>4</sub><sup>-</sup> = tetrahedral</p>         | <p>0.5 pt</p>              |
|                          | <p>1 pt.</p>               |

A binary superacid **C** is considered to be the strongest between superacids known so far, and is prepared in a simple reaction between a Lewis superacid **D** and Brønsted superacid **E**, both being binary compounds containing a common chemical element. The ratio of the weight fraction of this element in **D** and **E** is 2.1667. It is known that **C** is ionic and consists of two ions **C**<sub>+</sub> and **C**<sub>-</sub>.

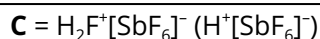
2. Give the chemical formulas and Lewis structures of **D** and **E**. What is the geometrical shape of **D**? Write down the equation of the chemical reaction described!

|   |                                 |
|---|---------------------------------|
| <p><b>D</b> = SbF<sub>5</sub>, <b>E</b> = HF</p>  | <p>1.5+0.5 pt.</p>              |
| <p>The only binary superacid is HF. The common element therefore is fluorine F. Weight fraction of F in HF is 0.94962, therefore in <b>D</b> it is 0.94962/2.1667 = 0.43828. We have to find the element which forms binary fluoride YF<sub>n</sub> (<b>D</b>), where weight percent of F is:</p> |                                 |
| $w_F = \frac{n \cdot A_F}{n \cdot A_F + A_Y} = 0.43828$ $A_Y = \frac{n \cdot A_F (1 - w_F)}{w_F} = \frac{10.6727n}{0.43828} = 24.351n$  |                                 |
| <p>By varying n and calculating the atomic masses of the unknown element we find that the only suitable solution is n = 5 and A<sub>Y</sub> = 121.76 → <b>Sb</b>.</p>   |                                 |
|    |                                 |
| <p>SbF<sub>5</sub> = trigonal bipyramidal.</p>  | <p>0.75 pt.</p> <p>0.25 pt.</p> |



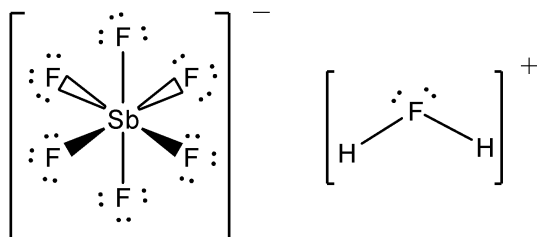
1 pt.  
0.5 pt.)

3. Give the chemical formula of **C**. Give the Lewis structures of **C<sub>+</sub>** and **C<sub>-</sub>**.  
What is the geometrical shape of these ions?



0.5 pt (only

if no equation of the chemical reaction is given in point 2)

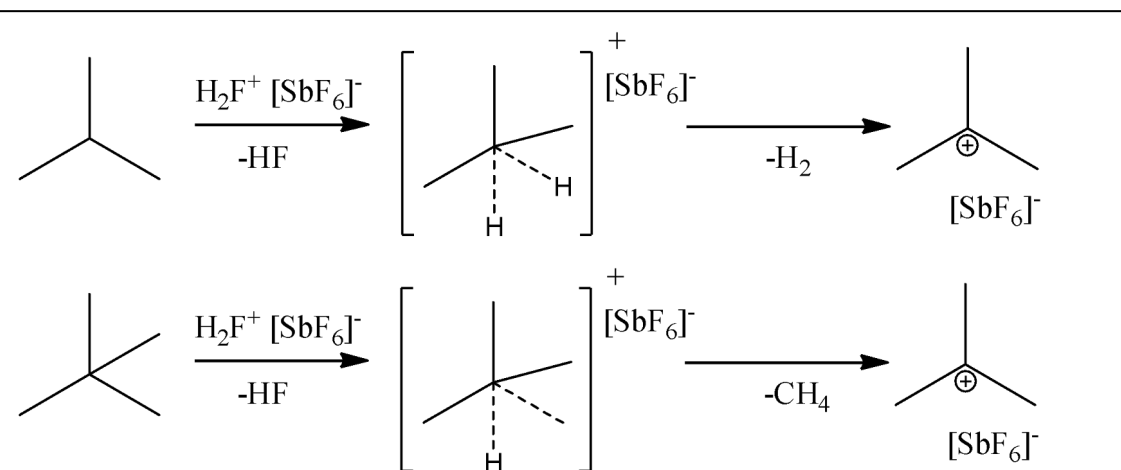


$\text{H}_2\text{F}^+$  = bent,  $[\text{SbF}_6]^-$ , = octahedral.

1 pt.  
0.5 pt.

This extraordinarily strong acid is able to protonate nearly all organic compounds. It has been shown it removes  $\text{H}_2$  from isobutane (2-methylpropane) and methane from 2,2-dimethylpropane. *Note that in this way cation **K<sub>+</sub>** is obtained!*

4. Write down the equations of these chemical reactions by showing the carbon atom which will be protonated. What considerations will determine which carbon atom gets protonated?



2 pt.

Considering all possible sites of protonation, the most stable intermediate and resulting carbocation is that being more substituted

0.5 pt.

Recently a group of scientists from Freiburg, Germany had reported the superacidity of **F**, which is prepared in a simple reaction between a Brønsted acid **G** and a Lewis acid **H**, both containing a common chemical element. It is known that the weight fraction of element **X** (not present in **G**) in **H** is 0.10112, and also

that **F** is ionic and its anion can exist in two chemically distinct forms for which molecular weight ratio  $F_{-B} : F_{-A}$  is 1.7695.

5. Give the chemical formula of **F**,  $F_{-A}$ ,  $F_{-B}$ , **G** and **H**. Give the Lewis structures and predict the geometry of  $F_{-A}$  and **H**. Illustrate the geometry of  $F_{-B}$ .

**G** = HBr, **H** = AlBr<sub>3</sub>, **F** = H[AlBr<sub>4</sub>] 1+1+1 pt.

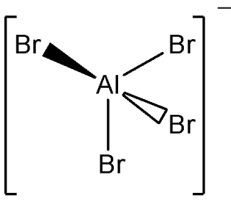
As possible Brønsted acids we will check HCl and HBr. Therefore the common element is either Cl or Br. Weight fraction of **X** in Lewis acid is therefore given as:

$$w_X = \frac{A_X}{n \cdot A_{Cl/Br} + A_X} = 0.10112$$

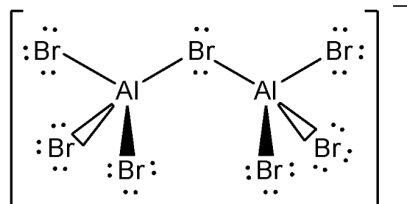
$$A_X = \frac{w_X \cdot n \cdot A_{Cl/Br}}{1 - w_X} = \frac{0.10112 \cdot n \cdot A_{Cl/Br}}{0.89888} = 0.11250 \cdot n \cdot A_{Cl/Br}$$

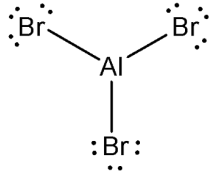
By varying n and halogen, and calculating the atomic masses of the unknown element we find that the only suitable solution is for Br with n = 3 and  $A_X = 26.97 \rightarrow$  **Al**.

$F_{-A} = [AlBr_4]^-$  and  $F_{-B} = [Al_2Br_7]^-$  1 pt for  $[Al_2Br_7]^-$  (and 0.5 pt. for  $[AlBr_4]^-$  but only if **F** is not given)



$[AlBr_4]^-$  = tetrahedral and AlBr<sub>3</sub> = trigonal planar.

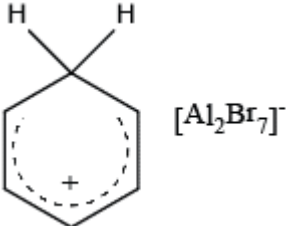




0.5 pt. + 1 pt. for  $[Al_2Br_7]^-$   
0.5 pt.

**F** can protonate benzene by producing an ionic compound **J** containing anion  $F_{-B}$ .

6. Write down the chemical structure of **J**! How many signals there will be in the <sup>1</sup>H, <sup>13</sup>C and **X** NMR spectra of **J**?



1.5 pt.

2 in <sup>1</sup>H, 2 in <sup>13</sup>C and 1 in <sup>27</sup>Al (as all the 5 hydrogens and 5 carbons in the disturbed benzene are identical).  
and 4 in <sup>13</sup>C 1 pt. (0.5 points for 4 in <sup>1</sup>H)

Interestingly, the reaction between the Lewis acid **H** and 2-bromo-2-methylpropane produced an ionic compound **K** with the same anion  $F_{-B}$  and a cation  $K_+$ .

7. Write down the chemical structure of **K**! How many signals there will be in the <sup>1</sup>H, <sup>13</sup>C and **X** NMR spectra of **K**?



It has been shown that for ionic compounds similar to **K** thermodynamic characteristics can be calculated by the use of empiric equations. As an input data experimentally determined compound properties or those obtained from quantum chemical calculations can be used. Equations for calculation of vaporization, solvation (enthalpy for transition from ions in gas phase to ions in the liquid state) and lattice enthalpies are given below:

$$\Delta_{vap} H = aV_m^{\frac{2}{3}} + bH_g^* + c$$

$$\Delta_{solv} H = -(\Delta_{vap} H + \Delta_{diss} H)$$

$$\Delta_{latt} H = d\Delta_{solv} H + e,$$

where  $a = -224 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{nm}^{-2}$ ,  $b = 0.0929$ ,  $c = 194 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $d = -0.685$ , and  $e = 172 \text{ kJ}\cdot\text{mol}^{-1}$ .

8. Use the provided equations (consistent with Born-Haber cycle) to calculate the lattice enthalpy of **K**, if  $V_m$  of **K** is  $0.4175 \text{ nm}^3$  (determined by single-crystal X-Ray diffraction),  $H_g^* = 394.9 \text{ kJ}\cdot\text{mol}^{-1}$ , and  $\Delta_{diss} H = 395.9 \text{ kJ}\cdot\text{mol}^{-1}$  (both found by quantum chemical calculations).

$$\Delta_{vap} H = aV_m^{\frac{2}{3}} + bH_g^* + c = -224 \cdot (0.4175)^{\frac{2}{3}} + 0.0929 \cdot 394.9 + 194 = 105.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{solv} H = -(\Delta_{vap} H + \Delta_{diss} H) = -(105.6 + 395.9) = -501.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{latt} H = d\Delta_{solv} H + e = 515.5 \text{ kJ}\cdot\text{mol}^{-1}$$

2 pt.

The reaction between  $0.100 \text{ mol}$  of **H** and  $0.100 \text{ mol}$  of 2-bromo-2-methylpropane were performed in calorimeter filled with  $2.00 \cdot 10^2 \text{ g}$  of ethanol (specific heat capacity =  $2.44 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ ). By performing the reaction at  $0^\circ\text{C}$  it was found that the temperature of ethanol increased by  $5.94^\circ\text{C}$ , while by performing the same reaction at  $20^\circ\text{C}$ , temperature of ethanol increased by  $2.46^\circ\text{C}$  (assume the calorimeter constant to be 0 and enthalpy being temperature independent). It was determined that the melting point of **K** is  $2^\circ\text{C}$ .

9. Calculate the reaction enthalpy at  $0^\circ\text{C}$  and at  $20^\circ\text{C}$ . Calculate the enthalpy of fusion of **K**.

$$Q_{0^\circ} = m \cdot c_{spec} \cdot \Delta T = 200 \cdot 2.44 \cdot 5.94 = 2899 \text{ J}$$

$$Q_{20^\circ} = m \cdot c_{spec} \cdot \Delta T = 200 \cdot 2.44 \cdot 2.46 = 1200 \text{ J}$$

$$\Delta_{reac} H_{0^\circ} = \frac{-Q}{n} = \frac{-2899}{0.100} = -29.0 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{reac} H_{20^\circ} = \frac{-Q}{n} = \frac{-1200}{0.100} = -12.0 \text{ kJ}\cdot\text{mol}^{-1}$$

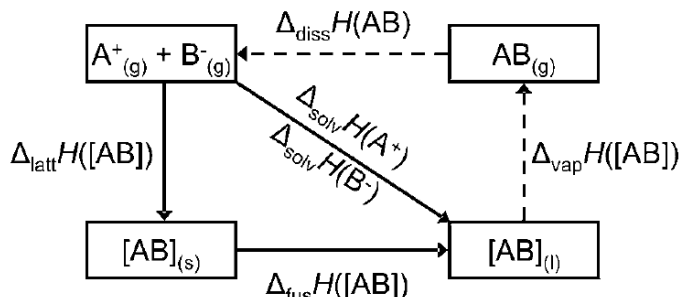
1.5 pt.

$$\Delta_{fus} H = \Delta_{react} H_{20^\circ} - \Delta_{react} H_{0^\circ} = -12.0 - (-29.0) = 17.0 \text{ kJ}\cdot\text{mol}^{-1}$$

1 pt.

10. Use the Born-Haber cycle to calculate the enthalpy of fusion of **K** from the results in point 8! Identify the main cause of errors for each of the approaches used to determine the enthalpy of fusion!

The Born-Haber cycle can be written as:



Therefore enthalpy of fusion can be calculated as:

$$\Delta_{fus} H = -\Delta_{latt} H + \Delta_{solv} H = -(-515.5) + (-501.5) = 14.0 \text{ kJ}\cdot\text{mol}^{-1}$$

or

$$\Delta_{fus} H = -\Delta_{latt} H - \Delta_{diss} H - \Delta_{vap} H = -(-515.5) - 395.9 - 105.6 = 14.0 \text{ kJ}\cdot\text{mol}^{-1}$$

2 pt (for cycle or correct equation with signs) + 1 pt. (for correct result)

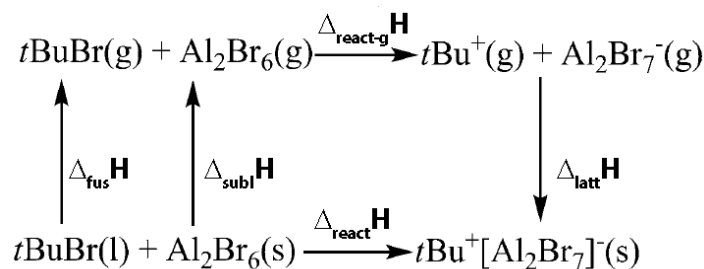
The main causes of errors for calorimetric method are: reaction yield is not 100%, possible heat losses. The main causes of errors for computational method are: calculations are not completely accurate, the constants in equations can be inappropriate for the compound studied.

1 pt.

Experimental enthalpy of vaporization of 2-bromo-2-methylpropane (+32 kJ·mol<sup>-1</sup>) and the sublimation enthalpy of **H** (+85 kJ·mol<sup>-1</sup>) are tabulated in handbooks of physical chemistry.

11. Use the Born-Haber cycle to calculate the reaction enthalpy for reaction between **H** and 2-bromo-2-methylpropane in gas phase (where separated ions **F<sub>-B</sub>** and **K<sub>+</sub>** in gaseous state are obtained).

The Born-Haber cycle can be written as:



Therefore reaction enthalpy in gas phase can be calculated as:

$$\Delta_{react-g} H = \Delta_{latt} H - \Delta_{react} H + \Delta_{subl} H + \Delta_{fus} H = -515.5 - (-29.0) + 32 + 85 = 370 \text{ kJ}\cdot\text{mol}^{-1}$$

2 pt (for cycle or correct equation with signs) + 1 pt. (for correct result)