



# Baltic Chemistry Competition

**BIO SAN**

Medical - Biological Research and Technologies

[www.biosan.lv](http://www.biosan.lv)

**2011**

**FINAL ROUND, PROBLEMS**

Solve all problems provides. Fill answer sheets and till 13:00, March 20, 2011 send them to e-mail: [kimijas\\_olimpiades@inbox.lv](mailto:kimijas_olimpiades@inbox.lv) You will receive answer that your solutions are received and will be graded in few days.

This round consists from two parts. Part A – 60 multiple choice questions with one correct answer each. Maximum points for this round is 30 points. Part B – 6 short answer problems. Each problem is graded with maximum 5 points. Points for final round are added to points gained in first three rounds.

## Part A – Multiple choice test

Choose one correct answer for each question and write corresponding letter in answer sheet provided.

### Question 1

Which statement about solutions is correct?

- A. When vitamin D dissolves in fat, vitamin D is the solvent and fat is the solute.
- B. In a solution of NaCl in water, NaCl is the solute and water is the solvent.
- C. An aqueous solution consists of water dissolved in a solute.
- D. The concentration of a solution is the amount of solvent dissolved in 1 dm<sup>3</sup> of solution.

### Question 2

Which is the best definition of *electronegativity*?

- A. Electronegativity is the energy required for a gaseous atom to gain an electron.
- B. Electronegativity is the attraction of an atom for a bonding pair of electrons.
- C. Electronegativity is the attraction between the nucleus and the valence electrons of an atom.
- D. Electronegativity is the ability of an atom to attract electrons from another atom.

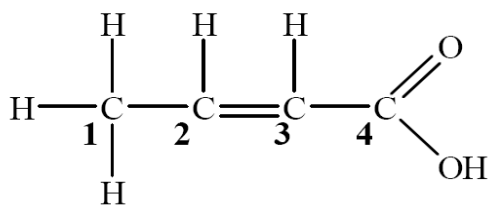
Question 3

Which statements best describe the structure of sodium chloride, NaCl?

- I. Each sodium ion is surrounded by six chloride ions.
  - II. The chloride ions are arranged octahedrally around each sodium ion.
  - III. The lattice forms a cubic structure.
- A. I and II only
- B. I and III only
- C. II and III only

Question 4

Identify the hybridization of carbon atoms in this molecule



	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
A.	sp <sup>3</sup>	sp <sup>2</sup>	sp <sup>2</sup>	sp <sup>2</sup>
B.	sp <sup>2</sup>	sp <sup>2</sup>	sp <sup>2</sup>	sp
C.	sp <sup>3</sup>	sp	sp <sup>2</sup>	sp
D.	sp	sp <sup>2</sup>	sp	sp <sup>2</sup>

Question 5

Which structure has delocalized  $\pi$  electrons?

- A. O<sub>3</sub>
- B. CO
- C. HCN
- D. CO<sub>2</sub>

Question 6

Which process represents the C–Cl bond enthalpy in tetrachloromethane?

- A.  $\text{CCl}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{Cl}(\text{g})$
- B.  $\text{CCl}_4(\text{g}) \rightarrow \text{CCl}_3(\text{g}) + \text{Cl}(\text{g})$
- C.  $\text{CCl}_4(\text{l}) \rightarrow \text{C}(\text{g}) + 4\text{Cl}(\text{g})$
- D.  $\text{CCl}_4(\text{l}) \rightarrow \text{C}(\text{s}) + 2\text{Cl}_2(\text{g})$

Question 7

Which reaction has the greatest increase in entropy?

- A.  $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$
- B.  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
- C.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
- D.  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$

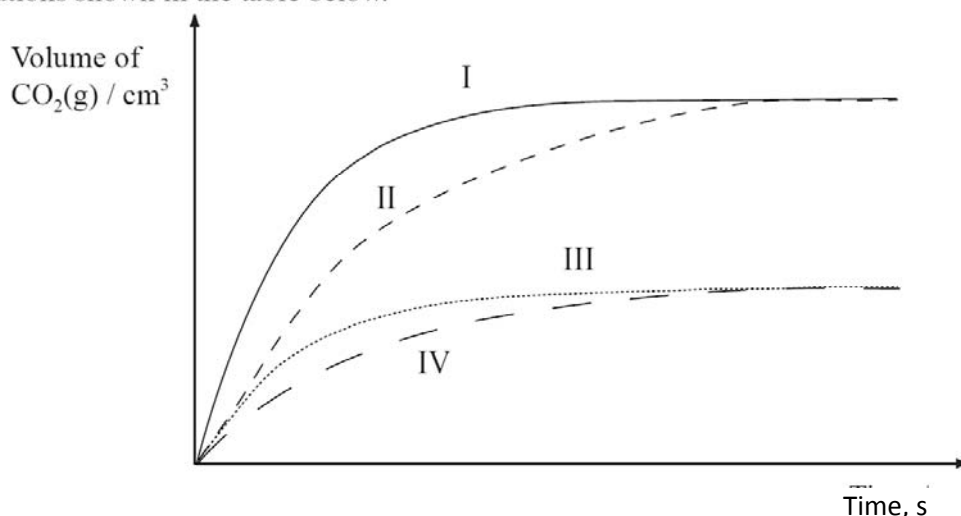
Question 8

What is the best definition of *rate of reaction*?

- A. The time it takes to use up all the reactants
- B. The rate at which all the reactants are used up
- C. The time it takes for one of the reactants to be used up
- D. The increase in concentration of a product per unit time

**Question 9**

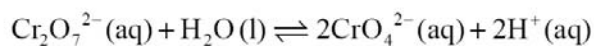
Equal masses of powdered calcium carbonate were added to separate solutions of hydrochloric acid. The calcium carbonate was in excess. The volume of carbon dioxide produced was measured at regular intervals. Which curves best represent the evolution of carbon dioxide against time for the acid solutions shown in the table below.



	25 cm <sup>3</sup> of 2 mol dm <sup>-3</sup> HCl	50 cm <sup>3</sup> of 1 mol dm <sup>-3</sup> HCl	25 cm <sup>3</sup> of 1 mol dm <sup>-3</sup> HCl
A.	I	III	IV
B.	I	IV	III
C.	I	II	III
D.	II	I	III

**Question 10**

Consider the following reversible reaction.

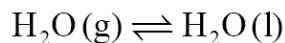


What will happen to the position of equilibrium and the value of  $K_c$  when more  $\text{H}^+$  ions are added at constant temperature?

	Position of equilibrium	Value of $K_c$
A.	shifts to the left	decreases
B.	shifts to the right	increases
C.	shifts to the right	does not change
D.	shifts to the left	does not change

**Question 11**

Consider this equilibrium reaction in a sealed container:



What will be the effect on the equilibrium of increasing the temperature from 20 °C to 30 °C?

- A. More of the water will be in the gaseous state at equilibrium.
- B. More of the water will be in the liquid state at equilibrium.
- C. At equilibrium the rate of condensation will be greater than the rate of evaporation.
- D. At equilibrium the rate of evaporation will be greater than the rate of condensation.

**Question 12**

When equal volumes of four 0.1 mol dm<sup>-3</sup> solutions are arranged in order of increasing pH (lowest pH first), what is the correct order?

- A. CH<sub>3</sub>COOH < HNO<sub>3</sub> < CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> < KOH
- B. HNO<sub>3</sub> < CH<sub>3</sub>COOH < CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> < KOH
- C. CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> < HNO<sub>3</sub> < CH<sub>3</sub>COOH < KOH
- D. KOH < CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> < CH<sub>3</sub>COOH < HNO<sub>3</sub>

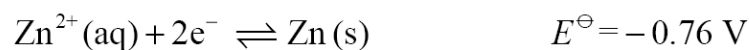
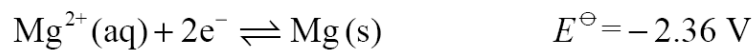
**Question 13**

What happens at the negative electrode in a voltaic cell and in an electrolytic cell?

	<b>Voltaic cell</b>	<b>Electrolytic cell</b>
A.	oxidation	reduction
B.	reduction	oxidation
C.	oxidation	oxidation
D.	reduction	reduction

Question 14

Consider these standard electrode potentials.



What is the cell potential for the voltaic cell produced when the two half-cells are connected?

- A.  $-1.60 \text{ V}$
- B.  $+1.60 \text{ V}$
- C.  $-3.12 \text{ V}$
- D.  $+3.12 \text{ V}$

Question 15

What is the IUPAC name for  $\text{HCOOCH}_2\text{CH}_2\text{CH}_3$ ?

- A. Butanoic acid
- B. Butanal
- C. Methyl propanoate
- D. Propyl methanoate

Question 16

Which conditions are required to obtain a good yield of a carboxylic acid when ethanol is oxidized using potassium dichromate(VI),  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ ?

- I. Add sulfuric acid
  - II. Heat the reaction mixture under reflux
  - III. Distil the product as the oxidizing agent is added
- A. I and II only
  - B. I and III only
  - C. II and III only
  - D. I, II and III

Question 17

Which statements about substitution reactions are correct?

- I. The reaction between sodium hydroxide and 1-chloropentane predominantly follows an  $S_N2$  mechanism.
  - II. The reaction between sodium hydroxide and 2-chloro-2-methylbutane predominantly follows an  $S_N2$  mechanism.
  - III. The reaction of sodium hydroxide with 1-chloropentane occurs at a slower rate than with 1-bromopentane.
- A. I and II only
  - B. I and III only
  - C. II and III only
  - D. I, II and III

Question 18

Which compound can exist as stereoisomers?

- A.  $\text{CH}_3\text{CH}_2\text{CHO}$
- B.  $\text{CH}_3\text{CH}_2\text{COCH}_3$
- C.  $\text{CH}_3\text{CH}(\text{CH}_3)_2$
- D.  $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$

Question 19

What is the order of increasing energy of the orbitals within a single energy level?

- A.  $d < s < f < p$
- B.  $s < p < d < f$
- C.  $p < s < f < d$
- D.  $f < d < p < s$

Question 20

Which equation best represents the first ionization energy of magnesium?

- A.  $\text{Mg(s)} \rightarrow \text{Mg}^+(\text{s}) + \text{e}^-$
- B.  $\text{Mg(g)} \rightarrow \text{Mg}^{2+}(\text{g}) + 2\text{e}^-$
- C.  $\text{Mg(g)} \rightarrow \text{Mg}^+(\text{g}) + \text{e}^-$
- D.  $\text{Mg(s)} \rightarrow \text{Mg}^+(\text{g}) + \text{e}^-$

Question 21

What are the products of the reaction between chlorine and water?

- A.  $\text{O}_2$ ,  $\text{H}_2$  and  $\text{HCl}$
- B.  $\text{H}_2$  and  $\text{OCl}_2$
- C.  $\text{HCl}$  and  $\text{HOCl}$
- D.  $\text{HOCl}$ ,  $\text{H}_2$  and  $\text{Cl}_2$

Question 22

Which statement best describes the **intramolecular** bonding in  $\text{HCN(l)}$ ?

- A. Electrostatic attractions between  $\text{H}^+$  and  $\text{CN}^-$  ions
- B. Only van der Waals' forces
- C. Van der Waals' forces and hydrogen bonding
- D. Electrostatic attractions between pairs of electrons and positively charged nuclei

Question 23

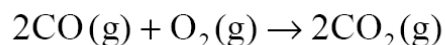
Which of the following best describes the formation of  $\pi$  bonds?

- A. They are formed by the sideways overlap of parallel orbitals.
- B. They are formed by the axial overlap of orbitals.
- C. They are formed by the sideways overlap of an s and p orbital.
- D. They are formed by the axial overlap of either s or p orbitals.



Question 24

What is the standard entropy change,  $\Delta S^\ominus$ , for the following reaction?



	<b>CO(g)</b>	<b>O<sub>2</sub>(g)</b>	<b>CO<sub>2</sub>(g)</b>
$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$	198	205	214

- A. -189
- B. -173
- C. +173
- D. +189

Question 25

Which step(s) is/are endothermic in the Born-Haber cycle for the formation of LiCl?

- A.  $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$  **and**  $\text{Li}(\text{s}) \rightarrow \text{Li}(\text{g})$
- B.  $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$  **and**  $\text{Li}(\text{g}) \rightarrow \text{Li}^+(\text{g}) + \text{e}^-$
- C.  $\text{Li}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{LiCl}(\text{s})$
- D.  $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$  **and**  $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$

Question 26

What is the function of iron in the Haber process?

- A. It shifts the position of equilibrium towards the products.
- B. It decreases the rate of the reaction.
- C. It provides an alternative reaction pathway with a lower activation energy.
- D. It reduces the enthalpy change of the reaction.

Question 27

Consider the following reaction.



The rate expression for the reaction is found to be:

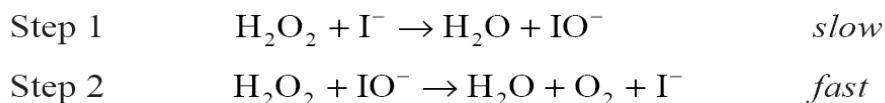
$$\text{rate} = k [\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$$

Which statement is correct?

- A. The overall order is 12.
- B. Doubling the concentration of all of the reactants at the same time would increase the rate of the reaction by a factor of 16.
- C. The units of the rate constant,  $k$ , are  $\text{mol dm}^{-3} \text{s}^{-1}$ .
- D. A change in concentration of  $\text{Br}^-$  or  $\text{BrO}_3^-$  does not affect the rate of the reaction.

Question 28

Consider the following reaction mechanism.



Which statement correctly identifies the rate-determining step and the explanation?

- A. Step 2 because it is the faster step
- B. Step 1 because it is the slower step
- C. Step 1 because it is the first step
- D. Step 2 because it is the last step

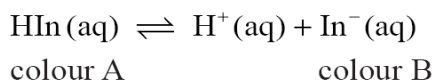
Question 29

$100 \text{ cm}^3$  of a NaOH solution of pH 12 is mixed with  $900 \text{ cm}^3$  of water. What is the pH of the resulting solution?

- A. 1
- B. 3
- C. 11
- D. 13

Question 30

The indicator, HIn is used in a titration between an acid and base. Which statement about the dissociation of the indicator, HIn is correct?



- A. In a strongly alkaline solution, colour B would be observed.
- B. In a strongly acidic solution, colour B would be observed.
- C.  $[\text{In}^-]$  is greater than  $[\text{HIn}]$  at the equivalence point.
- D. In a weakly acidic solution colour B would be observed.

Question 31

Which list represents the halogens in **increasing** order of oxidizing strength (weakest oxidizing agent first)?

- A.  $\text{Cl}_2$   $\text{I}_2$   $\text{Br}_2$
- B.  $\text{I}_2$   $\text{Br}_2$   $\text{Cl}_2$
- C.  $\text{I}_2$   $\text{Cl}_2$   $\text{Br}_2$
- D.  $\text{Cl}_2$   $\text{Br}_2$   $\text{I}_2$

Question 32

What structural feature must a molecule have in order to undergo addition polymerization?

- A. Two functional groups
- B. A carbon-carbon double bond
- C. Carbon atoms singly bonded together
- D. A polar covalent bond

Question 33

Which statement is correct about the enantiomers of a chiral compound?

- A. Their physical properties are different.
- B. All their chemical reactions are identical.
- C. A racemic mixture will rotate the plane of polarized light.
- D. They will rotate the plane of polarized light in opposite directions.

Question 34

Which would be the best method to decrease the **random** uncertainty of a measurement in an acid-base titration?

- A. Repeat the titration
- B. Ensure your eye is at the same height as the meniscus when reading from the burette
- C. Use a different burette
- D. Use a different indicator for the titration

Question 35

What is the correct sequence for the processes occurring in a mass spectrometer?

- A. vaporization, ionization, acceleration, deflection
- B. vaporization, acceleration, ionization, deflection
- C. ionization, vaporization, acceleration, deflection
- D. ionization, vaporization, deflection, acceleration

Question 36

What type of solid materials are typically hard, have high melting points and poor electrical conductivities?

- I. Ionic
  - II. Metallic
  - III. Covalent-network
- A. I and II only
  - B. I and III only
  - C. II and III only
  - D. I, II and III

Question 37

Which reaction has the most negative  $\Delta H^\ominus$  value?

- A.  $\text{LiF(s)} \rightarrow \text{Li}^+(\text{g}) + \text{F}^-(\text{g})$
- B.  $\text{Li}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{LiF(s)}$
- C.  $\text{NaCl(s)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$
- D.  $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl(s)}$

**Question 38**

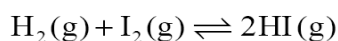
What is the order of reaction with respect to  $\text{NO}_2(\text{g})$  and  $\text{F}_2(\text{g})$  given the following rate data at a certain temperature?

$[\text{NO}_2(\text{g})]/\text{mol dm}^{-3}$	$[\text{F}_2(\text{g})]/\text{mol dm}^{-3}$	Rate / $\text{mol dm}^{-3} \text{ min}^{-1}$
0.1	0.2	0.1
0.2	0.2	0.4
0.1	0.4	0.2

	Order with respect to $\text{NO}_2(\text{g})$	Order with respect to $\text{F}_2(\text{g})$
A.	first	first
B.	first	second
C.	second	first
D.	second	second

**Question 39**

For the reaction below:



at a certain temperature, the equilibrium concentrations, in  $\text{mol dm}^{-3}$ , are

$$[\text{H}_2(\text{g})] = 0.30, [\text{I}_2(\text{g})] = 0.30, [\text{HI}(\text{g})] = 3.0$$

What is the value of  $K_c$ ?

- A.  $1.0 \times 10^{-2}$
- B. 10
- C. 33
- D.  $1.0 \times 10^2$

**Question 40**

Which methods will distinguish between equimolar solutions of a strong base and a strong acid?

- I. Add magnesium to each solution and look for the formation of gas bubbles.
  - II. Add aqueous sodium hydroxide to each solution and measure the temperature change.
  - III. Use each solution in a circuit with a battery and lamp and see how bright the lamp glows.
- A. I and II only
  - B. I and III only
  - C. II and III only
  - D. I, II and III

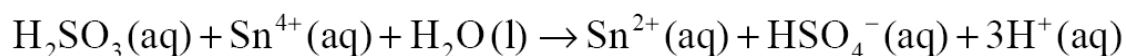
Question 41

Which statement about indicators is **always** correct?

- A. The mid-point of the pH range of an indicator is 7.
- B. The pH range is greater for indicators with higher  $pK_a$  values.
- C. The colour red indicates an acidic solution.
- D. The  $pK_a$  value of the indicator is within its pH range.

Question 42

Consider the following reaction:



Which statement is correct?

- A.  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes reduction.
- B.  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes oxidation.
- C.  $\text{Sn}^{4+}$  is the oxidizing agent because it undergoes oxidation.
- D.  $\text{Sn}^{4+}$  is the reducing agent because it undergoes oxidation.

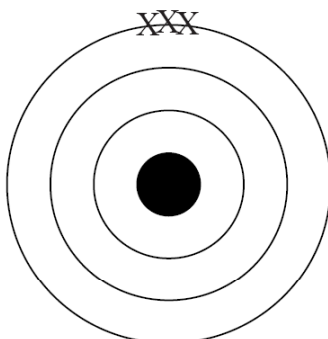
Question 43

Which combination is correct for the complex ion in  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Br}$ ?

	<b>Oxidation state of cobalt</b>	<b>Shape of the complex ion</b>	<b>Overall charge of the complex ion</b>
A.	+2	Octahedral	+2
B.	+3	Octahedral	-1
C.	+2	Octahedral	+1
D.	+2	Tetrahedral	+1

Question 44

The following diagram shows a set of experimental data points, X, determined when one experimental measurement was repeated three times. The centre of the diagram represents the ideal value calculated from theory. What statement is correct about these measurements?



- A. The measurements involve low accuracy and low precision.
- B. The measurements involve low accuracy and high precision.
- C. The measurements involve high accuracy and low precision.
- D. The measurements involve high accuracy and high precision.

Question 45

The geometry and bond angle of the sulfite ion ( $\text{SO}_3^{2-}$ ) are best described as

- A. pyramidal,  $107^\circ$ .
- B. tetrahedral,  $109^\circ$ .
- C. bent,  $104^\circ$ .
- D. trigonal planar,  $120^\circ$ .

Question 46

As the size of the halogen molecules,  $\text{X}_2$ , increases down the group, their boiling points

- A. decrease due to decreasing electronegativity.
- B. decrease due to decreasing bond energies.
- C. increase due to increasing permanent dipole–dipole attraction.
- D. increase due to increasing van der Waals' forces.

Question 47

Which quantity will **not** change for a sample of gas in a sealed rigid container when it is cooled from 100 °C to 75 °C at constant volume?

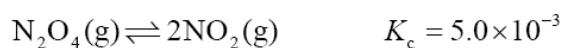
- A. The average energy of the molecules
- B. The average speed of the molecules
- C. The pressure of the gas
- D. The density of the gas

Question 48

Which statement(s) is(are) correct about the effect of adding a catalyst to a system at equilibrium?

- I. The rate of the forward reaction increases.
  - II. The rate of the reverse reaction increases.
  - III. The yield of the products increases.
- A. I only
  - B. III only
  - C. I and II only
  - D. I, II and III

Question 49



In an equilibrium mixture of these two gases,  $[\text{N}_2\text{O}_4] = 5.0 \times 10^{-1} \text{ mol dm}^{-3}$ . What is the equilibrium concentration of  $\text{NO}_2$  in  $\text{mol dm}^{-3}$ ?

- A.  $5.0 \times 10^{-1}$
- B.  $5.0 \times 10^{-2}$
- C.  $5.0 \times 10^{-3}$
- D.  $2.5 \times 10^{-4}$

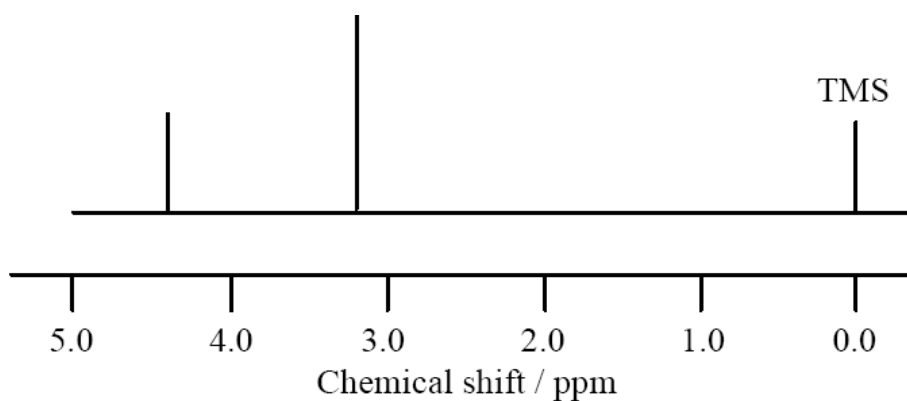


Question 50

Two moles of electrons are passed through an electrolytic cell containing molten sodium chloride. The same charge is passed through a second cell containing aqueous sodium chloride. In both cells the electrodes are made of platinum. Which statement is correct?

- A. One mole of sodium metal will be formed in the first cell.
- B. Chlorine gas will be formed at the cathodes of both cells.
- C. One mole of hydrogen gas will be formed in the second cell.
- D. One mole of oxygen gas will be formed at the anode of the second cell.

Question 51



The low resolution  $^1\text{H-NMR}$  spectrum shown above could be given by

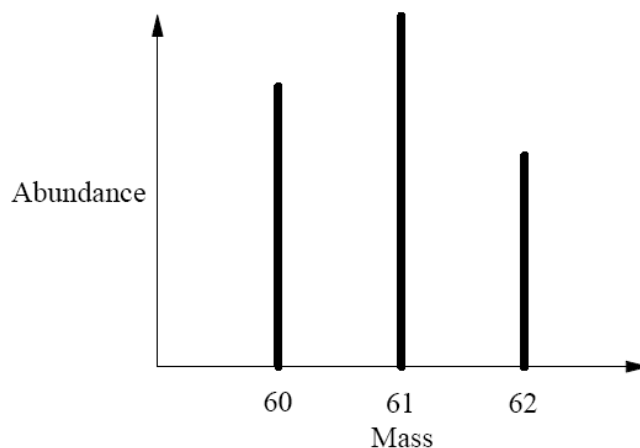
- A.  $\text{CH}_3\text{OH}$ .
- B.  $\text{CH}_3\text{CH}_2\text{OH}$ .
- C.  $\text{HCHO}$ .
- D.  $\text{HCOOH}$ .

Question 52

The electron transition between which two levels **releases** the most energy?

- A. First to third
- B. Fourth to ninth
- C. Sixth to third
- D. Second to first

Question 53



The mass spectrum of an element is shown above. Which statement about this element is correct?

- A. The three isotopes are separated after being converted to negative ions
- B. The isotope with mass 62 will be deflected more than the isotopes with masses 60 or 61
- C. The most abundant isotope contains 61 neutrons
- D. Its atomic mass will be between 60 and 61

Question 54

Which pair of species is listed in **increasing** order of the property given?

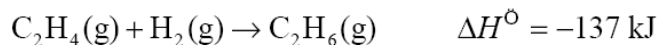
- A. Ionisation energy: O, F
- B. Radius: Mg, Mg<sup>2+</sup>
- C. Melting point: I<sub>2</sub>, Br<sub>2</sub>
- D. Covalent character: HI, HBr

Question 55

Which species does **not** contain at least one 90° bond angle?

- A. CF<sub>4</sub>
- B. PF<sub>5</sub>
- C. SF<sub>6</sub>
- D. SiF<sub>6</sub><sup>2-</sup>

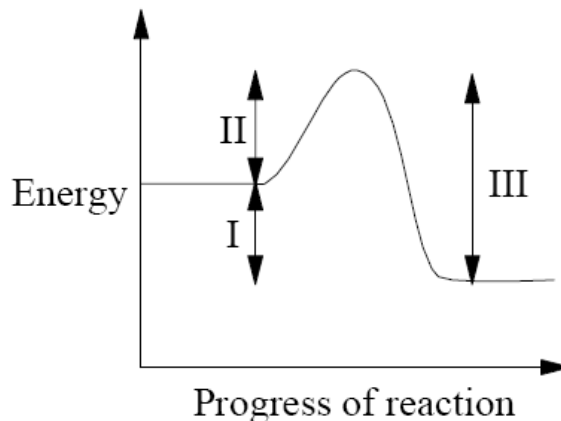
Question 56



Which statement about the information above is correct?

- A. The total energy of the bonds broken in the reactants is **greater** than the total energy of the bonds formed in the product
- B. The bonds broken and the bonds made are of the same strength
- C. The total energy of the bonds broken in the reactants is **less** than the total energy of the bonds formed in the product
- D. No conclusion can be made about the sums of the bond enthalpies in the product compared with the reactants.

Question 57



Which energy value(s) will change when a catalyst is added?

- A. I only
- B. II only
- C. II and III only
- D. I, II and III

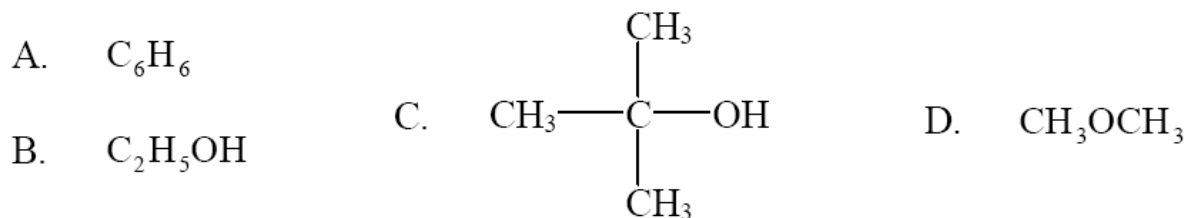
Question 58

Which is the correct combination?

	Intermolecular forces	Boiling point	$\Delta H_{vap}$
A.	weak	low	low
B.	weak	low	high
C.	strong	high	low
D.	strong	low	low

Question 59

Which compound gives **two** distinct peaks in its NMR spectrum?



Question 60

When the compounds below are listed in order of **decreasing** boiling point (highest to lowest) what is the correct order?

1. ethane      2. fluoroethane      3. ethanol      4. ethanoic acid
- A. 4, 3, 1, 2
- B. 4, 3, 2, 1
- C. 3, 4, 1, 2
- D. 2, 1, 3, 4



# Baltic Chemistry Competition

BIO SAN

Medical - Biological Research and Technologies

[www.biosan.lv](http://www.biosan.lv)

2011

FINAL ROUND, PROBLEMS

## Part B – Short answer questions

### Problem 1

#### Chemical crossword – inorganic chemistry (8 points)

Letters A, B, D ect. stands for unknown inorganic compounds, which react as shown in table. Formulas for all organic compounds are known.

- Compound A contains transition metal and transition metal content is approximately 72% (by mass)
- Solutions of compounds U, N, Ģ are strongly basic. There are no information about solutions of other compounds.
- Solutions of compounds O and N colors gas flame yellow, while compounds U un Ō colors flame purple red.
- Water solutions of compounds V, P and L are blue.
- Substances E, G, H, M, R, S, Ā contain only one chemical element.
- Three transition metals are mentioned in this crossword.
- Equations in crossword are not balanced.

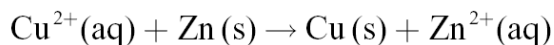
Write chemical formulas for all compounds abbreviated with letters.

A	+	B	→	G	+	D			<chem>C2H5NO2</chem>	+	F	←	<chem>C2H6</chem>	+	Y	
+		↑		+		+							+			
E		I		J		H			U	+	<chem>C2H5Cl</chem>	→	Ō	+	<chem>C2H5OH</chem>	
↓		+		↓		↓			+				↑			
F	+	H	←	E	+	B		D	+	F	→	Č		S	<chem>C2H6</chem>	
+				+				+		+		+		+	+	
G	+	L	→	K	+	M		R		Ā		Ģ		<chem>CH3Cl</chem>	I	
		+				+		↑		↓		↓			↓	
		N				Q		B		Ē		Ķ	→	N	+	D
		↓				↓		+		+		+		+	+	+
E		O		R	+	F	→	Ž	+	E		F		I		F
+		+		+		+								↓		
U		P	+	Q	→	V	+	F		Š	+	F	→	G	+	E
↑				↓		+		↓								+
F				Ā		W		I	+	Z	+	F	→	Y		<chem>C2H4</chem>
+				+				+		+						↓
T	←	S	+	E		I	+	E	→	F						<chem>C2H6</chem>

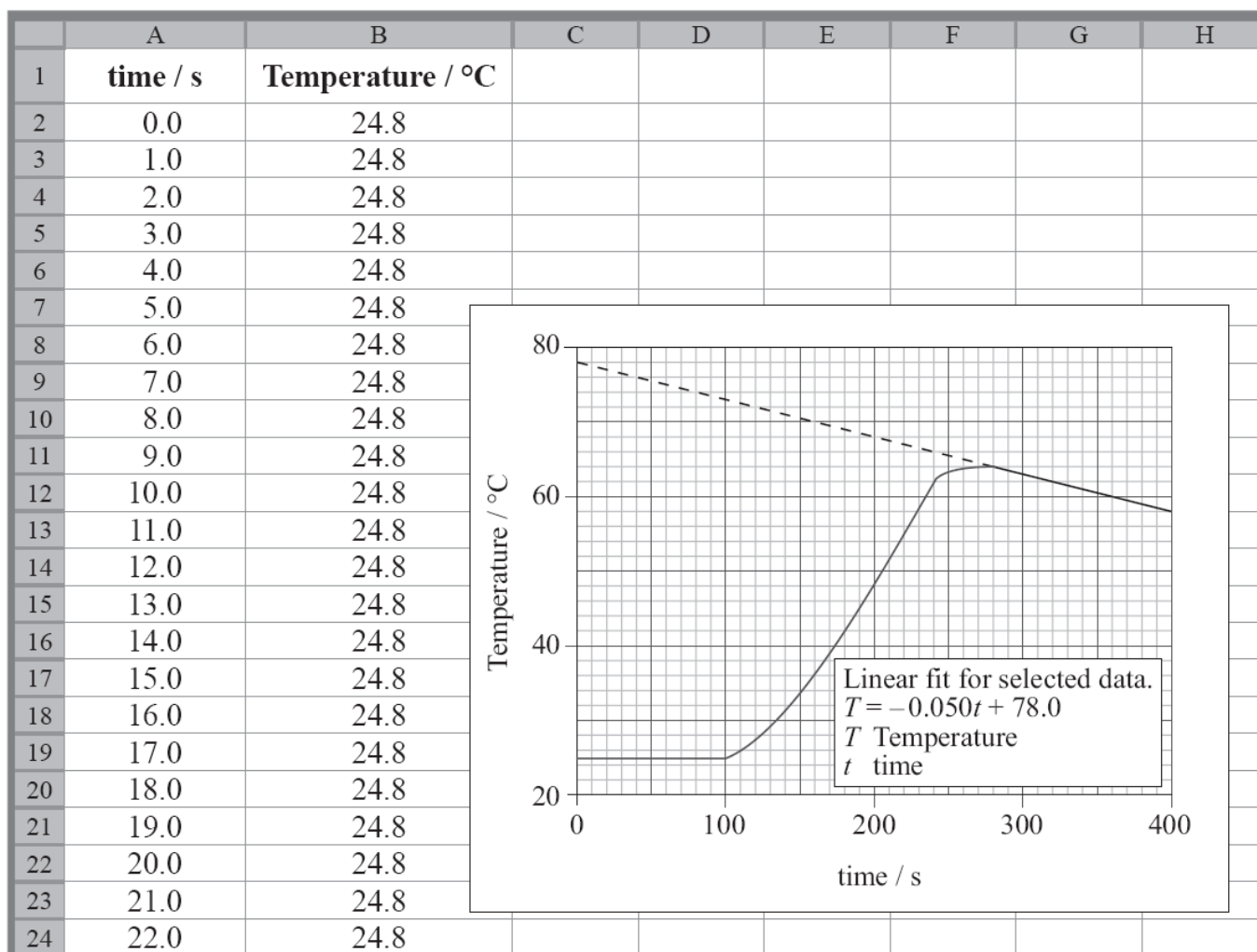
## Problem 2

### Use of math to describe chemical processes – physical chemistry (10 points)

The data below are from an experiment to measure the enthalpy change for the reaction of aqueous copper(II) sulfate,  $\text{CuSO}_4(\text{aq})$  and zinc,  $\text{Zn}(\text{s})$ .



$50.0 \text{ cm}^3$  of  $1.00 \text{ mol dm}^{-3}$  copper(II) sulfate solution was placed in a polystyrene cup and zinc powder was added after 100 seconds. The temperature-time data was taken from a data-logging software program. The table shows the initial 23 readings.



A straight line has been drawn through some of the data points. The equation for this line is given by the data logging software as

$$T = -0.050t + 78.0$$

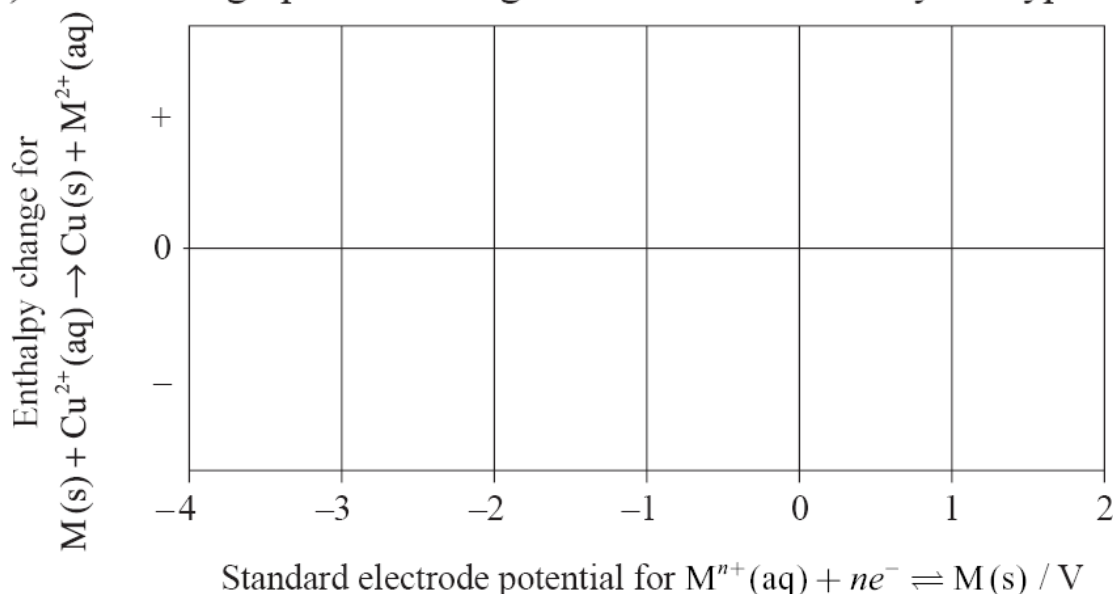
where  $T$  is the Temperature at time  $t$ .

- (a) The heat produced by the reaction can be calculated from the temperature change,  $\Delta T$ , using the expression below.

$$\text{Heat change} = \text{Volume of CuSO}_4(\text{aq}) \times \text{Specific heat capacity of H}_2\text{O} \times \Delta T$$

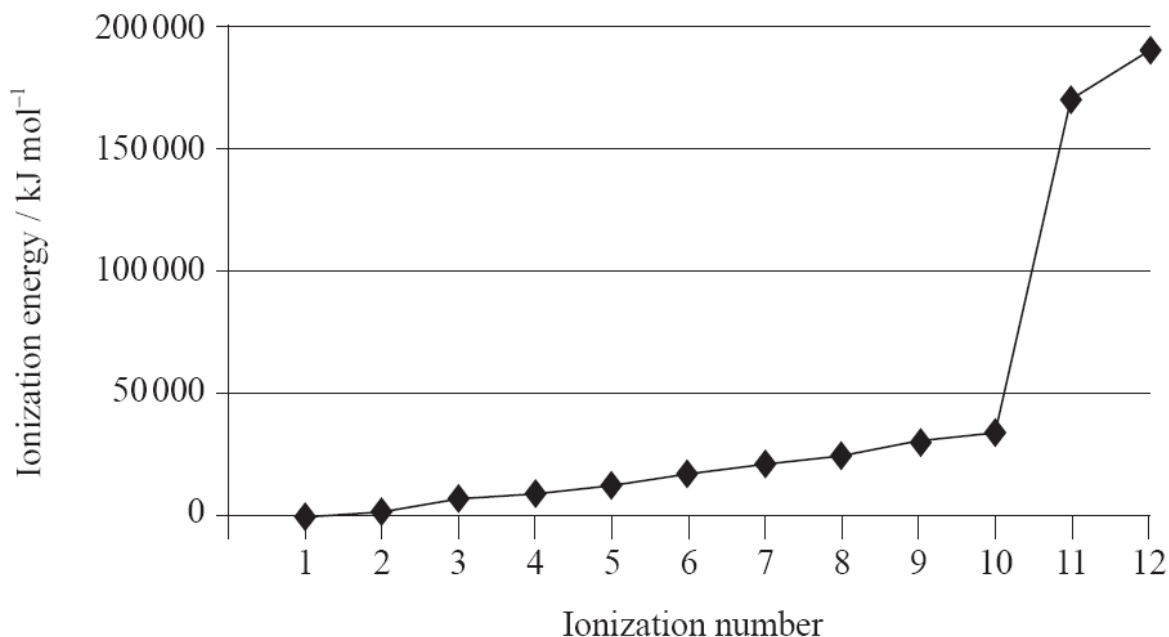
Describe **two** assumptions made in using this expression to calculate heat changes.

- (b) (i) Use the data presented by the data logging software to deduce the temperature change,  $\Delta T$ , which would have occurred if the reaction had taken place instantaneously with no heat loss.
- (ii) Calculate the heat, in kJ, produced during the reaction using the expression given in part (a).
- (c) The colour of the solution changed from blue to colourless. Deduce the amount, in moles, of zinc which reacted in the polystyrene cup.
- (d) Calculate the enthalpy change, in  $\text{kJ mol}^{-1}$ , for this reaction.
- (e) An experiment was designed to investigate how the enthalpy change for a displacement reaction relates to standard electrode potentials. The standard electrode potentials of some half reactions,  $\text{M}^{n+}(\text{aq}) + n\text{e}^- \rightleftharpoons \text{M}(\text{s})$ , are listed in **wikipedia**. The following metals were available: copper, iron, magnesium, silver and zinc. Excess amounts of each metal were added to  $1.00 \text{ mol dm}^{-3}$  copper(II) sulfate solution. The temperature change was measured and the enthalpy change calculated.
- (i) Suggest a possible hypothesis for the relationship between the enthalpy change that occurs when the metal, M, is added to copper(II) sulfate(aq) and the standard electrode potential for the half reaction  $\text{M}^{n+}(\text{aq}) + n\text{e}^- \rightleftharpoons \text{M}(\text{s})$ .
- (ii) Sketch a graph on the diagram below to illustrate your hypothesis.



- (f) Explain the origin of colour in transition metal complexes and use your explanation to suggest why copper(II) sulfate,  $\text{CuSO}_4(\text{aq})$ , is blue, but zinc sulfate,  $\text{ZnSO}_4(\text{aq})$ , is colourless.
- (g)  $\text{Cu}^{2+}(\text{aq})$  reacts with ammonia to form the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ . Explain this reaction in terms of an acid-base theory, and outline how the bond is formed between  $\text{Cu}^{2+}$  and  $\text{NH}_3$ .

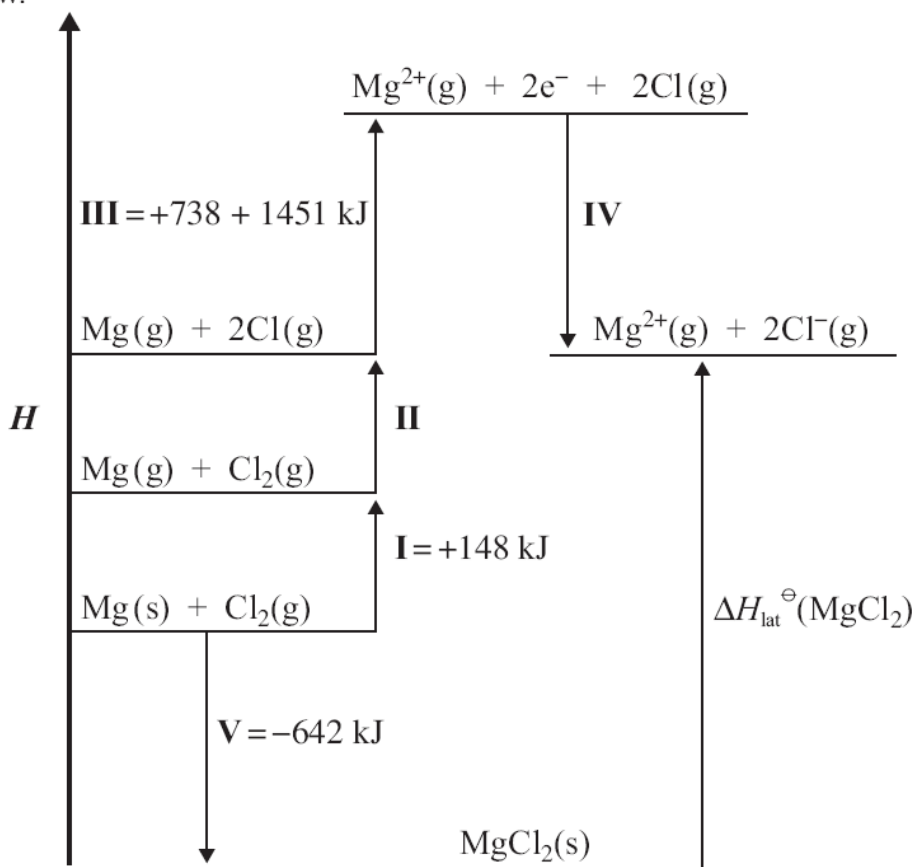
Magnesium is the eighth most abundant element in the earth's crust. The successive ionization energies of the element are shown below.



- (h) (i) Define the term *first ionization energy* and state the equation for the first ionization of magnesium.
- (ii) Explain the general increase in successive ionization energies of the element.
- (iii) Explain the large increase between the tenth and eleventh ionization energies.
- (i) Magnesium can be produced from the electrolysis of molten magnesium chloride,  $\text{MgCl}_2$ .
- (i) Explain how molten magnesium chloride conducts an electric current.
- (ii) Identify the electrode where oxidation occurs during electrolysis of molten magnesium chloride and state an equation for the half-reaction.
- (iii) Explain why magnesium is not formed during the electrolysis of aqueous magnesium chloride solution.



- (j) The lattice enthalpy of magnesium chloride can be calculated from the Born-Haber cycle shown below.



- (i) Identify the enthalpy changes labelled by **I** and **V** in the cycle.
- (ii) Use the ionization energies given in the cycle above and further data from wikipedia or other source to calculate a value for the lattice enthalpy of magnesium chloride.

### Problem 3

#### Some organic chemistry (6 points)

Consider the following sequence of reactions.



$\text{RCH}_3$  is an unknown alkane in which R represents an alkyl group.

- (a) The alkane contains 82.6 % by mass of carbon. Determine its empirical formula, showing your working.
- (b) A 1.00 g gaseous sample of the alkane has a volume of 385 cm<sup>3</sup> at standard temperature and pressure. Deduce its molecular formula.
- (c) State the reagent and conditions needed for *reaction 1*.
- (d) *Reaction 1* involves a free-radical mechanism. Describe the stepwise mechanism, by giving equations to represent the initiation, propagation and termination steps.
- (e) The mechanism in *reaction 2* is described as S<sub>N</sub>2. Explain the mechanism of this reaction using curly arrows to show the movement of electron pairs, and draw the structure of the transition state.
- (f) There are four structural isomers with the molecular formula C<sub>4</sub>H<sub>9</sub>Br. One of these structural isomers exists as two optical isomers. Draw diagrams to represent the three-dimensional structures of the two optical isomers.
- (g) All the isomers can be hydrolysed with aqueous sodium hydroxide solution. When the reaction of one of these isomers, **X**, was investigated the following kinetic data were obtained.

Experiment	Initial [X] / mol dm <sup>-3</sup>	Initial [OH <sup>-</sup> ] / mol dm <sup>-3</sup>	Initial rate of reaction / mol dm <sup>-3</sup> min <sup>-1</sup>
1	2.0 × 10 <sup>-2</sup>	2.0 × 10 <sup>-2</sup>	4.0 × 10 <sup>-3</sup>
2	2.0 × 10 <sup>-2</sup>	4.0 × 10 <sup>-2</sup>	4.0 × 10 <sup>-3</sup>
3	4.0 × 10 <sup>-2</sup>	4.0 × 10 <sup>-2</sup>	8.0 × 10 <sup>-3</sup>

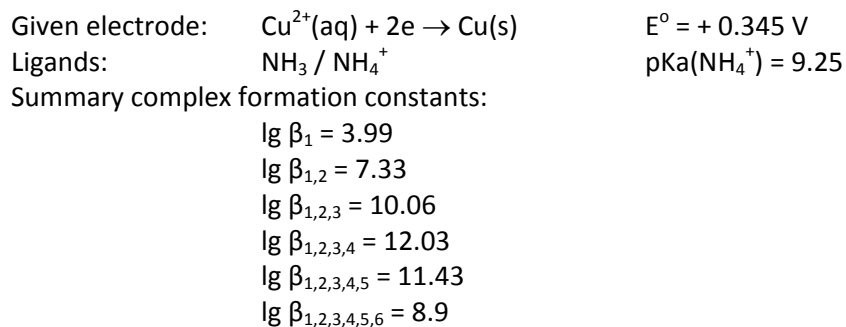
- (i) Deduce the rate expression for the reaction.
- (ii) Determine the value of the rate constant for the reaction and state its units.
- (iii) State the name of isomer **X** and explain your choice.
- (iv) State equations for the steps that take place in the mechanism of this reaction and state which of the steps is slow and which is fast.

## Problem 4

### Complex formation and red-ox properties (6 points)

You have to investigate 1<sup>st</sup> type electrode using software MS Excel (or analogue). The first type electrode consists from metal (M(s)) and it's ions in solution (M<sup>x+</sup>(aq)). This time solution also contain protolytic pair from which conjugated base acts as ligands and form complex ions with M<sup>x+</sup>.

Draw graph to show how reduction standard potential is dependent on pH if free ligand concentration in solution is a) 0.1 M, b) 1.0 M and 5.0 M.



#### Hints:

1. Assume that concentration sum for conjugate acid and base and acid are constant (if base are used for complex formation it is added to solution to maintain constant concentration or concentration of base is huge enough and stays almost constant).
2. Write mathematical equations for calculation real reduction standard potentials depending from molar fraction of metal ions in solution.

Example:

$$E(\text{o,r}) = E(\text{o}) + 0.059 \cdot \lg x(\text{Me})/z$$

$$x(\text{Me}) = 1 / (1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \dots + \beta_6[\text{L}]^6) = 1 / (1 + 10^{(\lg\beta_1 - \text{pL})} + 10^{(\lg\beta_2 - 2\text{pL})} + \dots + 10^{(\lg\beta_6 - 6\text{pL})})$$

$$[\text{L}] = c_{\text{L}} \cdot x_{\text{B}} = c_{\text{L}} \cdot (1 / (1 + 10^{(\text{pKa} - \text{pH})}))$$

3. Using MS Excel program calculate real standard potential values, if pH changes from 0 to 14 (step 0.5). Made calculation in three cases: a) conjugate acid and base concentration sum is  $c_{\text{L}} = 0.1 \text{ M}$ , b)  $c_{\text{L}} = 1 \text{ M}$  and c)  $c_{\text{L}} = 5 \text{ M}$ . All calculation results collect in table.



# Baltic Chemistry Competition

**BIO SAN**

Medical - Biological Research and Technologies

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2011

FINAL ROUND, SOLUTIONS

## Part A – Multiple choice test

Q. number	Answer
1.	B
2.	B
3.	D
4.	A
5.	A
6.	B
7.	A
8.	D
9.	C
10.	D
11.	A
12.	B
13.	A
14.	B
15.	D
16.	A
17.	B
18.	B
19.	B
20.	C
21.	C
22.	D
23.	A
24.	B
25.	A
26.	C
27.	B
28.	B
29.	C
30.	A
31.	B
33.	D

No correct answer, D, all statements are true

32.	B
33.	D
34.	A
35.	A
36.	B
37.	B
38.	C
39.	D
40.	A
41.	D
42.	B
43.	C
44.	B
45.	A
46.	D
47.	A
48.	A
49.	B
50.	B
51.	B
52.	D
53.	D
54.	A
55.	A
56.	C
57.	C
58.	A
59.	C
60.	B

# Part B – Short answer questions

## Problem 1

Chemical crossword – corrections (made with red color)

A	+	B	→	G	+	D			C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	+	F	←	C <sub>2</sub> H <sub>6</sub>	+	Y	
+		↑		+		+							+			
E		I		J		H			U	+	C <sub>2</sub> H <sub>5</sub> Cl	→	Ö	+	C <sub>2</sub> H <sub>5</sub> OH	
↓		+		↓		↓			+				↑			
F	+	H	←	E	+	B		D	+	F	→	Č		S	C <sub>2</sub> H <sub>6</sub>	
+				+				+		+		+		+	+	
G	+	L	→	K	+	M		R		Ā		Ğ		CH <sub>3</sub> Cl	I	
		+				+		↑		↓		↓			↓	
		N				Q		B		Ē		Ƙ	→	N	+	D
		↓				↓		+		+		+		+		+
E		O		R	+	F	→	Ž	+	E		F		F (not I)		F
+		+		+		+								↓		
U		P	+	Q	→	V	+	F		Š	+	F	→	Ğ (not G)	+	E
↑				↓		+		↓								+
F				Å		W		I	+	Z	+	F	→	Y		C <sub>2</sub> H <sub>4</sub>
+				+				+		+						↓
T	←	S	+	E		I	+	E	→	F						C <sub>2</sub> H <sub>6</sub>

Answers:

A – Fe<sub>3</sub>O<sub>4</sub> or other oxide which contains 72% metal, Mn<sub>3</sub>O<sub>4</sub>, Rh<sub>2</sub>O<sub>5</sub>, CaO – is not accepted wrong chemistry

B – CO

D – CO<sub>2</sub>

E – H<sub>2</sub>

F – H<sub>2</sub>O

G – Fe

H – C

I – O<sub>2</sub>

J – HCl

K – FeCl<sub>2</sub>

L – CuCl<sub>2</sub>

M – Cu

N – NaOH

O – NaCl

P – Cu(OH)<sub>2</sub>

Q – H<sub>2</sub>SO<sub>4</sub>

R – Zn or other metal

S – Li or other alkali metal

T – LiH or other alkali metal

U – LiOH or other alkali metal

V – CuSO<sub>4</sub>  
 W – SO<sub>2</sub>  
 Z – NO<sub>2</sub>  
 Y – HNO<sub>3</sub>  
 Š – CaH<sub>2</sub>, Ca accepted  
 Ž – ZnO  
 Ā – Al  
 Č – H<sub>2</sub>CO<sub>3</sub>  
 Ě – Li[Al(OH)<sub>4</sub>]  
 Ğ – Ca(OH)<sub>2</sub>  
 Ķ – CaCO<sub>3</sub>  
 Ń – CaO  
 Ō – LiCl or other metal  
 Å – ZnSO<sub>4</sub>

### **Problem 2**

- (a) all heat is transferred to water/copper sulfate solution / no heat loss;  
 specific heat capacity of zinc is zero/negligible / no heat is absorbed by the zinc;  
 density of water/solution = 1.0 / density of solution = density of water;  
 heat capacity of cup is zero / no heat is absorbed by the cup;  
 specific heat capacity of solution = specific heat capacity of water;  
 temperature uniform throughout solution; **[2 max]**  
*Award [1] each for any two.*  
*Accept energy instead of heat.*

- (b) (i)  $T_{\text{final}} = 73.0$  (°C);  
*Allow in the range 72 to 74 (°C).*  
 $\Delta T = 48.2$  (°C); **[2]**  
*Allow in the range 47 to 49 (°C).*  
*Award [2] for correct final answer*  
*Allow ECF if  $T_{\text{final}}$  or  $T_{\text{initial}}$  correct.*

- (ii) 10.1 (kJ); **[1]**  
*Allow in the range 9.9 to 10.2 (kJ).*

(c)  $\left( n_{\text{Zn}} = n_{\text{CuSO}_4} = \frac{1.00 \times 50.0}{1000} \right) = 0.0500 \text{ (mol)};$  [1]

(d)  $-201 \text{ (kJ mol}^{-1}\text{)};$  [1]

*Allow in the range  $-197$  to  $-206 \text{ (kJ mol}^{-1}\text{)}$ .*

*Value must be negative to award mark.*

(e) (i) the more negative the electrode potential the more negative the enthalpy change / the more exothermic the reaction / *OWTTE*;  
*Accept electrode potential proportional to the enthalpy change.*  
*Do not accept greater enthalpy change.* [1]

(ii) any line (straight or curve) with positive gradient;  
*Accept if curve becomes flat for electrode potentials above 0.25.*

which passes through  $\Delta H = 0$  at standard electrode potentials between 0.25 and 0.50;

*Accept either positive or zero enthalpy change for electrode potentials greater than value of copper (in range 0.25 to 0.50).* [2]

(f) d orbitals are split (into two sets of different energies);  
frequencies of (visible) light absorbed by electrons moving from lower to higher d levels;

colour due to remaining frequencies/complementary colour transmitted;

$\text{Cu}^{2+}$  has unpaired electrons/partially filled d sub-level;

$\text{Zn}^{2+}$  has filled d sub-shell;

electronic transitions/d-d transitions possible for  $\text{Cu}^{2+}$  / no electronic/d-d transitions possible for  $\text{Zn}^{2+}$ ;

*Allow wavelength as well as frequency.* [4 max]

(g)  $\text{NH}_3$ : Lewis base /  $\text{Cu}^{2+}$ : Lewis acid;

each  $\text{NH}_3$ /ligand donates an electron pair (to  $\text{Cu}^{2+}$ );

$\text{NH}_3$  replace  $\text{H}_2\text{O}$  ligands around  $\text{Cu}^{2+}$  ion/around central ion;

forming coordinate (covalent)/dative covalent bond;

[3 max]

- (h) (i) energy (per mole) needed to remove one/first/most loosely bound electron from a (neutral) atom;  
in the gaseous state;  
 $\text{Mg (g)} \rightarrow \text{Mg}^+ \text{(g)} + \text{e}^-$ ; [3]  
*Gaseous state symbols needed.*  
*Accept e instead of e<sup>-</sup>.*  
*Only penalize omission of gas phase once in either the second marking point or the third marking point.*
- (ii) successive electrons (are more difficult to remove because each is) taken from more positively charged ion/ *OWTTE*;  
increased electrostatic attraction; [2]
- (iii) 10<sup>th</sup> electron comes from 2<sup>nd</sup> energy level/ $n=2$  **and** 11<sup>th</sup> electron comes from 1<sup>st</sup> first energy level/ $n=1$  / *OWTTE*;  
electron in 1<sup>st</sup> energy level closer to nucleus;  
electron in 1<sup>st</sup> energy level not shielded by inner electrons / exposed to greater effective nuclear charge; [3]
- (i) (i) contains ions which are free to move (only) in molten state;  
 $\text{Mg}^{2+}$  move to cathode/negative electrode and  $\text{Cl}^-$  move to anode/positive electrode / *OWTTE*; [2]
- (ii) anode/positive electrode;  
 $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$  /  $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$ ; [2]  
*Accept e instead of e<sup>-</sup>.*  
*Do not accept  $\text{Cl}^- \rightarrow \text{Cl} + \text{e}^-$ .*  
*Ignore state symbols.*
- (iii) magnesium has large negative electrode potential /  $E^\ominus$ ;  
reduction of  $\text{H}_2\text{O}/\text{H}^+$  to  $\text{H}_2$  has less negative electrode potential;  
 $\text{Mg}^{2+}$  not readily reduced (in comparison to  $\text{H}_2\text{O}$ );  
if formed, magnesium would (immediately) react with water to form  $\text{Mg}^{2+}$ ;  
magnesium more reactive than hydrogen; [1 max]  
*Do not accept Mg too reactive.*



(i) (i) *I*:  
atomization/sublimation (of Mg) /  $\Delta H_{\text{atomization}}^{\ominus}(\text{Mg})$  /  $\Delta H_{\text{sublimation}}^{\ominus}(\text{Mg})$ ;

*V*:

enthalpy change of formation of  $(\text{MgCl}_2)$  /  $\Delta H_{\text{formation}}^{\ominus}(\text{MgCl}_2)$ ; [2]

(ii) *Energy value for II*:  
+243;

*Energy value for III*:

$$738 + 1451 = 2189;$$

*Energy value for IV*:

$$2(-349);$$

$$\Delta H_{\text{lat}}^{\ominus}(\text{MgCl}_2) = 642 + 148 + 243 + 2189 = (+)2252(\text{KJ});$$
 [4]

### Problem 3

(a)  $n_C = \frac{82.6}{12.01} = 6.88$  and  $n_H = \frac{17.4}{1.01} = 17.2$ ;

ratio is 1:2.5;

$C_2H_5$ ;

No penalty for using 12 and 1.

[3]

(b)  $\left(M = \frac{22400}{385}\right) = 58.2$  /  $\left(M = \frac{mRT}{PV}\right) = 58.3$ ;

$C_4H_{10}$ ;

[2]

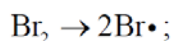
(c)  $Br_2$ /bromine;

UV/ultraviolet light;

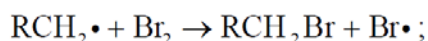
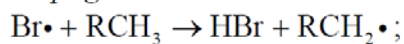
Accept  $hf/h\nu$ /sunlight.

[2]

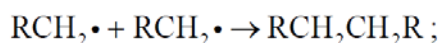
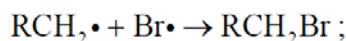
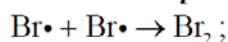
(d) Initiation:



Propagation:



Termination: [1 max]

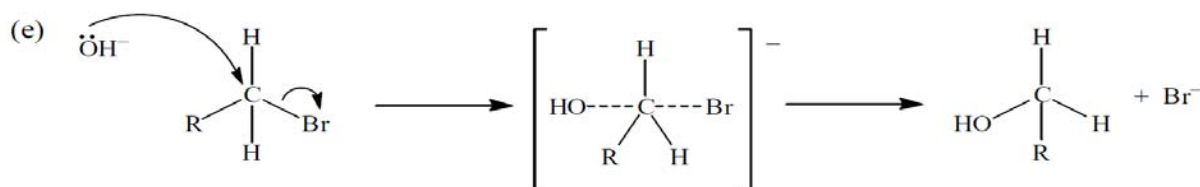


[4 max]

Award [1] for any termination step.

Accept radical with or without  $\cdot$  throughout.

Do not penalise the use of an incorrect alkane in the mechanism.



curly arrow going from lone pair/negative charge on O in  $OH^-$  to C;

Do not allow curly arrow originating on H in  $OH^-$ .

curly arrow showing Br leaving;

Accept curly arrow either going from bond between C and Br to Br in bromoethane or in the transition state.

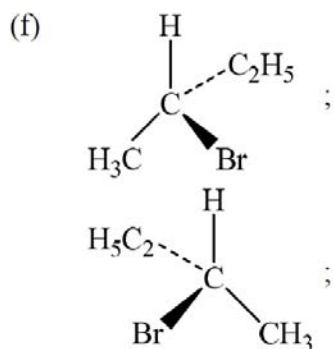
representation of transition state showing negative charge, square brackets and partial bonds;

Do not penalize if HO and Br are not at  $180^\circ$  to each other.

Do not award M3 if  $OH \cdots C$  bond is represented unless already penalised in M1.

Do not penalise the use of an incorrect alkyl chain in the mechanism

[3]



[2]

First and second structures should be mirror images. Tetrahedral arrangement around carbon must be shown.

- (g) (i) order with respect to  $\text{OH}^- = 0$  ;  
 order with respect to  $\text{X} = 1$  ;  
 rate =  $k[\text{X}]$  ;  
 Award [3] for final correct answer.

[3]

- (ii) 0.2(0);  
 $\text{min}^{-1}$ ;

[2]

- (iii) 2-bromo-2-methyl-propane;  
 Do not penalize missing hyphens or added spaces.  
 Accept 2-bromomethylpropane.

tertiary (structure);

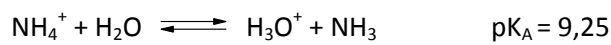
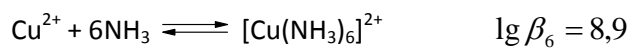
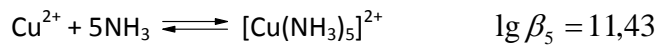
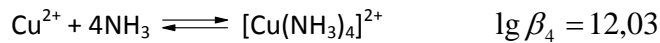
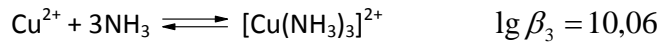
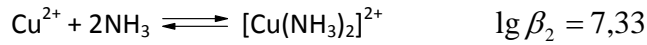
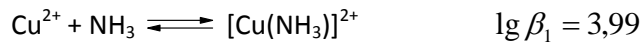
[2]

- (iv)  $\text{C}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{H}_9^+ + \text{Br}^-$  / in equation with curly arrows **and** slow;  
 $\text{C}_4\text{H}_9^+ + \text{OH}^- \rightarrow \text{C}_4\text{H}_9\text{OH}$  / in equation with curly arrows **and** fast;  
 No penalty if primary structure is shown.  
 No credit for  $\text{S}_{\text{N}}2$  mechanism, except by ECF.

[2]

Problems for part A and part B exercises 2 and 3 taken from International baccalaureate organization chemistry exam papers.

#### Problem 4



$$\varepsilon = \varepsilon_{red}^0 - \frac{RT}{2 \cdot F} \ln \frac{1}{[\text{Cu}^{2+}]} = \varepsilon_{red}^0 + \frac{RT}{2 \cdot F} \ln [\text{Cu}^{2+}]$$

$$\left\{ \begin{aligned} K_A &= \frac{[\text{H}_3\text{O}^{+}] \cdot [\text{NH}_3]}{[\text{NH}_4^{+}]} \\ C_L &= [\text{NH}_4^{+}] + [\text{NH}_3] + [\{\text{Cu}(\text{NH}_3)_1\}^{2+}] + 2 \cdot [\{\text{Cu}(\text{NH}_3)_2\}^{2+}] + 3 \cdot [\{\text{Cu}(\text{NH}_3)_3\}^{2+}] + \\ &+ 4 \cdot [\{\text{Cu}(\text{NH}_3)_4\}^{2+}] + 5 \cdot [\{\text{Cu}(\text{NH}_3)_5\}^{2+}] + 6 \cdot [\{\text{Cu}(\text{NH}_3)_6\}^{2+}] \\ K_1 &= \frac{[\{\text{Cu}(\text{NH}_3)_1\}^{2+}]}{[\text{Cu}^{2+}] \cdot [\text{NH}_3]} \\ K_2 &= \frac{[\{\text{Cu}(\text{NH}_3)_2\}^{2+}]}{[\text{Cu}^{2+}] \cdot [\text{NH}_3]^2} \\ K_3 &= \frac{[\{\text{Cu}(\text{NH}_3)_3\}^{2+}]}{[\text{Cu}^{2+}] \cdot [\text{NH}_3]^3} \\ K_4 &= \frac{[\{\text{Cu}(\text{NH}_3)_4\}^{2+}]}{[\text{Cu}^{2+}] \cdot [\text{NH}_3]^4} \\ K_5 &= \frac{[\{\text{Cu}(\text{NH}_3)_5\}^{2+}]}{[\text{Cu}^{2+}] \cdot [\text{NH}_3]^5} \\ K_6 &= \frac{[\{\text{Cu}(\text{NH}_3)_6\}^{2+}]}{[\text{Cu}^{2+}] \cdot [\text{NH}_3]^6} \\ C_{Cu} &= [\text{Cu}^{2+}] + [\{\text{Cu}(\text{NH}_3)_1\}^{2+}] + [\{\text{Cu}(\text{NH}_3)_2\}^{2+}] + [\{\text{Cu}(\text{NH}_3)_3\}^{2+}] + [\{\text{Cu}(\text{NH}_3)_4\}^{2+}] + \\ &+ [\{\text{Cu}(\text{NH}_3)_5\}^{2+}] + [\{\text{Cu}(\text{NH}_3)_6\}^{2+}] \end{aligned} \right.$$

$$C_L = [\text{NH}_4^{+}] + [\text{NH}_3] + [\{\text{Cu}(\text{NH}_3)_1\}^{2+}] + 2 \cdot [\{\text{Cu}(\text{NH}_3)_2\}^{2+}] + 3 \cdot [\{\text{Cu}(\text{NH}_3)_3\}^{2+}] + \\ + 4 \cdot [\{\text{Cu}(\text{NH}_3)_4\}^{2+}] + 5 \cdot [\{\text{Cu}(\text{NH}_3)_5\}^{2+}] + 6 \cdot [\{\text{Cu}(\text{NH}_3)_6\}^{2+}]$$

$$C_L = [\text{NH}_4^{+}] + [\text{NH}_3]$$

$$\begin{aligned}
& K_A = \frac{[H_3O^+] \cdot [NH_3]}{[NH_4^+]} \\
& C_L = [NH_4^+] + [NH_3] \Rightarrow [NH_4^+] = C_L - [NH_3] \Rightarrow K_A = \frac{10^{-pH} \cdot [NH_3]}{C_L - [NH_3]} \Rightarrow \\
& \Rightarrow 10^{-pH} \cdot [NH_3] = K_A \cdot C_L - [NH_3] \cdot K_A \Rightarrow (10^{-pH} + K_A) \cdot [NH_3] = K_A \cdot C_L \Rightarrow \\
& \Rightarrow [NH_3] = \frac{K_A \cdot C_L}{10^{-pH} + K_A} \\
& \beta_1 = \frac{[Cu(NH_3)]^{2+}}{[Cu^{2+}] \cdot [NH_3]} \Rightarrow \beta_1 = \frac{[Cu(NH_3)]^{2+}}{[Cu^{2+}] \cdot \left( \frac{K_A \cdot C_L}{10^{-pH} + K_A} \right)} \Rightarrow [Cu(NH_3)]^{2+} = \beta_1 \cdot [Cu^{2+}] \cdot \left( \frac{K_A \cdot C_L}{10^{-pH} + K_A} \right) \\
& \beta_2 = \frac{[Cu(NH_3)_2]^{2+}}{[Cu^{2+}] \cdot [NH_3]^2} \Rightarrow \beta_2 = \frac{[Cu(NH_3)_2]^{2+}}{[Cu^{2+}] \cdot \left( \frac{K_A \cdot C_L}{10^{-pH} + K_A} \right)^2} \Rightarrow [Cu(NH_3)_2]^{2+} = \beta_2 \cdot [Cu^{2+}] \cdot \left( \frac{K_A \cdot C_L}{10^{-pH} + K_A} \right)^2 \\
& \beta_3 = \frac{[Cu(NH_3)_3]^{2+}}{[Cu^{2+}] \cdot [NH_3]^3} \Rightarrow \dots \Rightarrow [Cu(NH_3)_3]^{2+} = \beta_3 \cdot [Cu^{2+}] \cdot \left( \frac{K_A \cdot C_L}{10^{-pH} + K_A} \right)^3 \\
& \beta_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}] \cdot [NH_3]^4} \Rightarrow \dots \Rightarrow [Cu(NH_3)_4]^{2+} = \beta_4 \cdot [Cu^{2+}] \cdot \left( \frac{K_A \cdot C_L}{10^{-pH} + K_A} \right)^4 \\
& \beta_5 = \frac{[Cu(NH_3)_5]^{2+}}{[Cu^{2+}] \cdot [NH_3]^5} \Rightarrow \dots \Rightarrow [Cu(NH_3)_5]^{2+} = \beta_5 \cdot [Cu^{2+}] \cdot \left( \frac{K_A \cdot C_L}{10^{-pH} + K_A} \right)^5 \\
& \beta_6 = \frac{[Cu(NH_3)_6]^{2+}}{[Cu^{2+}] \cdot [NH_3]^6} \Rightarrow \dots \Rightarrow [Cu(NH_3)_6]^{2+} = \beta_6 \cdot [Cu^{2+}] \cdot \left( \frac{K_A \cdot C_L}{10^{-pH} + K_A} \right)^6 \\
& C_{Cu} = [Cu^{2+}] + [Cu(NH_3)]^{2+} + [Cu(NH_3)_2]^{2+} + [Cu(NH_3)_3]^{2+} + [Cu(NH_3)_4]^{2+} + \\
& + [Cu(NH_3)_5]^{2+} + [Cu(NH_3)_6]^{2+} \\
& C_{Cu} = [Cu^{2+}] + [Cu(NH_3)]^{2+} + [Cu(NH_3)_2]^{2+} + [Cu(NH_3)_3]^{2+} + [Cu(NH_3)_4]^{2+} + \\
& + [Cu(NH_3)_5]^{2+} + [Cu(NH_3)_6]^{2+} = \\
& = [Cu^{2+}] \cdot \left( 1 + \beta_1 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right) + \beta_2 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^2 + \beta_3 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^3 + \beta_4 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^4 + \right. \\
& \left. + \beta_5 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^5 + \beta_6 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^6 \right) \\
& [Cu^{2+}] = \frac{1}{1 + \beta_1 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right) + \beta_2 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^2 + \beta_3 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^3 + \beta_4 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^4 + \\
& + \beta_5 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^5 + \beta_6 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^6}
\end{aligned}$$

$$\varepsilon_{red}^i = \varepsilon_{red}^0 + \frac{RT}{2 \cdot F} \ln \left( \frac{1}{1 + \beta_1 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right) + \beta_2 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^2 + \beta_3 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^3 + \beta_4 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^4 + \beta_5 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^5 + \beta_6 \cdot \left( \frac{K_a \cdot C_L}{10^{-pH} + K_a} \right)^6} \right)$$

$$K_a = 10^{-pK_a}$$

$$K_n = 10^{\lg K_n}$$

