Problem 1. Polar winter in Antarctic

Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions that bring about the Antarctic ozone hole. Worsnop *et al.* has measured thermodynamic parameters for sublimation of nitric acid mono-, di- and trihydrates at 220 K:

	$\Delta_r G°$, kJ·mol^{-1}	$\Delta_r H°$, kJ·mol^{-1}
$HNO_3 \cdot H_2O(s) \rightarrow HNO_3(g) + H_2O(g)$	46.2	127
$HNO_3 \cdot 2H_2O(s) \rightarrow HNO_3(g) + 2H_2O(g)$	69.4	188
$HNO_3 \cdot 3H_2O(s) \rightarrow HNO_3(g) + 3H_2O(g)$	93.2	237

a) Calculate $\Delta_r G°$ at 190 K (the conditions of the polar winter stratosphere). Assume that $\Delta_r H°$ and $\Delta_r S°$ do not depend on temperature.

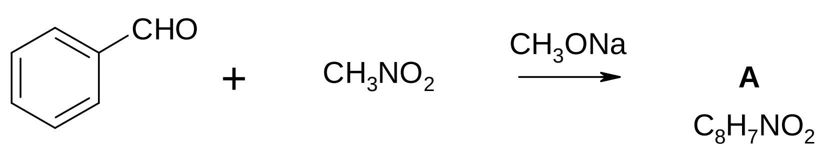
a) Which hydrate is thermodynamically most stable at 190 K if $p(H_2O) = 1.3 \cdot 10^{-7}$ bar and $p(HNO_3) = 4.1 \cdot 10^{-10}$ bar? Standard pressure is 1 bar.

Problem 2. Synthesis of bicyclic compound

The bicyclic skeleton of compound **X** appears in many naturally occurring alkaloids. The simple approach to the synthesis of title compound is outlined in this problem. At the heart of the synthesis is a nitro-aldol reaction between benzaldehyde and nitromethane.

a) Explain, why nitromethane is acidic enough for an aldol reaction to occur?

b) Under basic reaction conditions benzaldehyde and nitromethane in nitro-aldol reaction give compound **A** (molecular formula $C_8H_7NO_2$). Based on the knowledge of the classical aldol reaction suggest structure of **A**.



c) **A** is fully reduced with hydrogen using palladium on charcoal as a catalyst to give **B** (molecular formula $C_8H_{11}N$). **B** is fairly basic and readily forms salts with acids. Draw the structure of compound **B**.

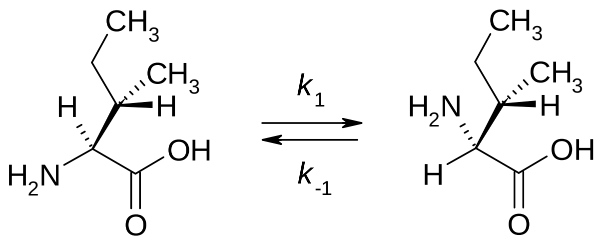
$$\underset{C_8H_7NO_2}{\mathbf{A}} \xrightarrow{H_2,\ Pd(C)} \underset{C_8H_{11}N}{\mathbf{B}}$$

d) **B** under acidic reaction conditions reacts with formaldehyde to give final compound **X**. This transformation proceeds through formation of **C** (molecular formula $C_9H_{11}N$), which under these reaction conditions undergoes cyclization to form bicyclic **X** (molecular formula $C_9H_{11}N$). **X** is fairly basic and is usually isolated in a form of salt. Using your knowledge of reactivity of carbonyl compounds suggest structures of **C** and **X**.

$$\underset{C_8H_{11}N}{\mathbf{B}} \xrightarrow{HCHO,\ HCl} \left[\underset{C_9H_{11}N}{\mathbf{C}}\right] \longrightarrow \underset{C_9H_{11}N}{\mathbf{X}}$$

Problem 3. Isoleucine dating

The rate of isomerization of isoleucine in fossilized bone can be used as an indication of the average temperature of the sample storage.



L-isoleucine D-alloisoleucine

At 20°C this reaction has a half-life of 125000 years and its activation energy is 139.7 kJ/mol. After a very long time, the ratio allo/iso reaches an equilibrium value of 1.38. You may assume that this equilibrium constant does not depend on temperature.

The time dependence of concentration for a reversible reaction is given by equation:

$$\ln\left(\frac{[A]-[A]_{eq}}{[A]_0-[A]_{eq}}\right)=-(k_1+k_{-1})t$$

For a hippopotamus *mandible* which lived near a warm spring in South Africa, the present allo/iso ratio in bones is 0.42. Radiocarbon dating, which is temperature independent, determined the age of hippo tooth, which was 38600 years.

a) Assuming that no allo was present initially, determine constants for forward and reverse reactions and overall isomerization constant (k_1 + k_{-1}).

b) Calculate an average conservation temperature of the hippopotamus remains in soil.

Problem 4. Goblin's element

Metal **X** was discovered in 1735. Its name has derived from a German word meaning "goblin" or "evil spirit".

A sample of metal **X** immersed in H_2O weights 13.031 g. Meanwhile the weight of the same sample in CCl_4 is 12.046 g. The density of CCl_4 is 1.5940 g/cm^3.

In order to identify the metal **X**, neutron diffraction is used. The diffraction pattern is specific to the FCC structure and the angle of the reflection (2θ) from the (222) plane is 76.956°. The velocity of neutrons in the diffractometer is 3115.0 m/s.

The same sample is heated in O_2 atmosphere until metal X has reacted completely. The product of the reaction is compound **A** containing 26.577% of oxygen (by mass). All the amount of compound **A** reacts with diluted HCl releasing 1.0298 L of O_2 at 25.00ºC temperature and 100.0 kPa pressure, giving salt **B** and water only.

Compound **B** is dissolved in an aqueous solution containing Cl^-, Br^- and I^- ions. Complex ion **C** forms as one of the products. The formula of ion **C** is $[XCl_2Br_2I_2]^{n-}$ and it is a paramagnetic.

Complex carbonyl compound **D** is prepared by heating metal **X** under a high pressure of carbon monoxide. The formula of compound **D** is [$\mathbf{X}_2(CO)_8$] and it is a diamagnetic. The both atoms of metal **X** are equivalent in the structure of compound **D**. A CO molecule donates a pair of electrons to form a single bond only but not all the CO molecules are equivalent in the structure of compound **D**.

a) Calculate the density of metal **X** in g/cm^3.

b) Calculate the unit cell parameter (*a*) of metal **X** in pm.

c) Calculate the molar mass of metal **X** in g/mol. What element is metal **X**?

d) Write a chemical formula of compound **A**.

e) Write a balanced chemical equation of the reaction of compound **A** with diluted HCl.

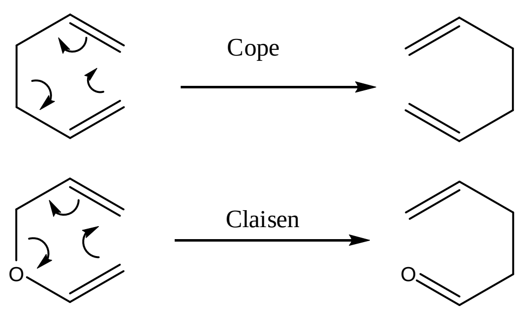
f) Sketch the spatial structures of all possible isomers (including structural, geometrical and optical) of ion **C**.

g) Count the number of unpaired electrons in ion **C**. Consider halogenides as weak field ligands

h) Sketch the spatial structure of compound **D**.

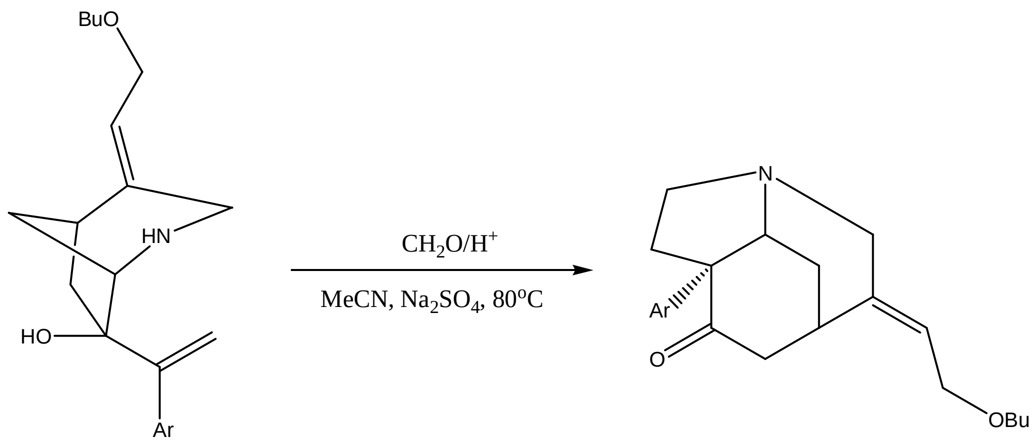
Problem 5. Sigmatropic rearrangement

Pericyclic reactions are concerted processes that occur by way of a cyclic transition state in which more than one bond is formed or broken within the cycle. The so called sigmatropic rearrangements constitute a large group of pericyclic reactions. Of all the sigmatropic rearrangements, the [3,3]-sigmatropic rearrangement has been used most in organic synthesis. The reaction involves the transformation of 1,5-dienes and all-carbon system is known as the Cope rearrangement, whereas with an allyl vinyl ether the reaction is termed a Claisen rearrangement. The examples of these reactions are given bellow:

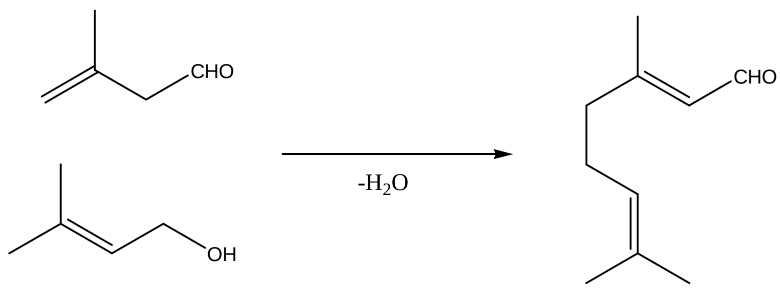


The sigmatropic rearrangement has been use in many syntheses of the complex molecules and has industrial applications as well.

1. The key step in the synthesis of the alkaloid strychnine was made by use of this chemistry:



2. The chemical company BASF manufactures citral (intermediate in the synthesis of vitamin A) by the remarkable synthesis shown bellow:



Write the reaction mechanism (except for the loss of water in the example 2) and possible intermediates for both reactions.

HINT: by treating acetaldehyde with ethanol under the same reaction conditions as in example 2, vinylethyl ether could be obtained.

Problem 6. Dolomite

One of the most widespread minerals is dolomite, which in huge amounts is also in bowels of the earth of Baltic States. Dolomite contains two metallic elements **A** and **B**. Metal **A** crystallizes in hexagonal close packed atomic structure (unit cell parameters: a = 3.2094 Å, b = 3.2094 Å, c = 5.2108 Å and $\gamma = 120^o$), while metal **B** crystallizes in cubic close packed atomic structure (unit cell parameter: a = 5.5884 Å).

a) What are metals **A** and **B**? Calculate atomic radii for these elements!

b) Calculate by how many percent (of initial atomic radii) reduce radii for both metallic elements, when ions are produced from atoms. It is known that oxides of both elements have sodium chloride structure and radii of oxide anion is 1.28 Å. Unit cell parameters for both oxides are 4.213 Å un 4.811 Å, respectively.

Industrially metal **A** can be produced from sea water. To purify chloride of metal **A** from other salts hydroxide of metal **B** is added to sea water. The obtained white precipitate is dissolved in hydrochloric acid and evaporated, till metal **A** salt hydrate forms. Then the hydrate is heated and salt melted and electrolyzed.

c) Write down equations of all chemical reactions described above and calculate time for electrolysis which has to be performed to isolate 1.0 ton of metal **A**. Current intensity 9.0 kA.

One of the most favorite reactions for students is burning of metal **A** in the air. Reaction produces huge amount of UV light and two binary compounds, one of them is oxide of metal **A**.

d) What is the second compound that is produced in this reaction? Write equations of both reactions and propose chemical reactions which could be useful for experimental identification of this compound.

Metal **A** also is used in army of USA, for preparing food in field conditions. To heat food wrapped in aluminum foil a special heater (in English Flameless Ration Heater), which contains 30 mL water, is used. Heating material is a composite, where powder of metal **A** and iron are associated in matrix of high density polyethylene. In presence of chloride ions metal **A** reacts with water, forming hydroxide and hydrogen, which is available for burning to obtain extra heat.

e) Using thermodynamical constants shown below calculate minimal mass of element **A**, which is needed for heating 1.0 L of water from temperature 20°C to 100°C. Assume that all chemical reactions proceed under standard conditions.

Compound	$\Delta H_{f,298}$ (kJ/mol)	C_p (J/(mol·K))
H_2, *g*	0	28,83
H_2O, *g*	−241,81	33,61
H_2O, *l*	−285,83	75,30
Metal **A**, *s*	0	24,89
Hydroxide of metal **A**, *s*	−924,66	76,99

f) Metal **A** hydroxide, which forms in reaction, is slightly soluble. Calculate solubility (mg/L; milligrams per liter) of mentioned hydroxide in distilled water. pK_s = 11,25.