

Problem 1 – THERMO – Polar winter in Antarctic

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

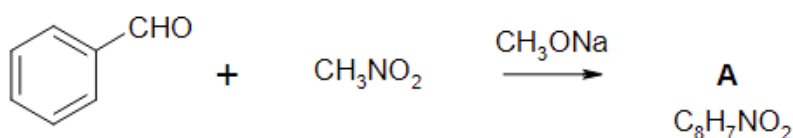
	ΔG_r° [kJ mol ⁻¹]	ΔH_r° [kJ mol ⁻¹]
$\text{HNO}_3 \cdot \text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + \text{H}_2\text{O}(\text{g})$	46.2	127
$\text{HNO}_3 \cdot 2\text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	69.4	188
$\text{HNO}_3 \cdot 3\text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + 3\text{H}_2\text{O}(\text{g})$	93.2	237

- Calculate ΔG_r° at 190 K (the conditions of the polar winter stratosphere). Assume that ΔH_r° and ΔS_r° do not depend on temperature.
- Explain which hydrate is thermodynamically most stable at 190 K if $p(\text{H}_2\text{O}) = 1.3 \cdot 10^{-2}$ Pa and $p(\text{HNO}_3) = 4.1 \cdot 10^{-5}$ Pa?

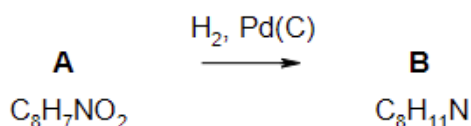
Problem 2 – SYNTH – Synthesis of bicyclic compound

The bicyclic skeleton of compound **X** appears in many naturally occurring alkaloids. At the heart of the synthesis of **X** is the nitro-aldol reaction between benzaldehyde and nitromethane.

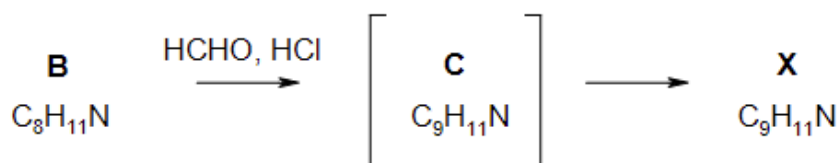
- Explain why nitromethane is acidic enough for an aldol reaction to occur.
- Under basic reaction conditions, benzaldehyde and nitromethane in nitro-aldol reaction give compound **A** ($\text{C}_8\text{H}_7\text{NO}_2$). Based on the knowledge of the classical aldol reaction, suggest the structure of **A**.



- A** is fully reduced with hydrogen using palladium on charcoal as a catalyst to give **B** ($\text{C}_8\text{H}_{11}\text{N}$). **B** is fairly basic and readily forms salts with acids. Draw the structure of compound **B**.

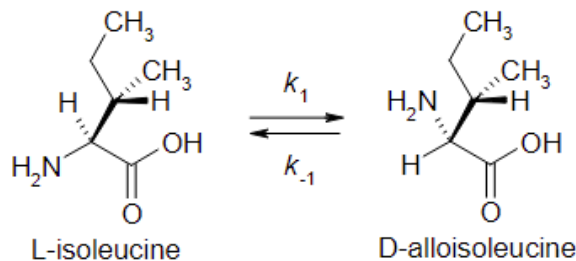


- B**, under acidic reaction conditions, reacts with formaldehyde to give final compound **X**. This transformation proceeds through the formation of **C** ($\text{C}_9\text{H}_{11}\text{N}$), which under these reaction conditions undergoes cyclization to form bicyclic **X** ($\text{C}_9\text{H}_{11}\text{N}$). **X** is fairly basic and is usually isolated in the form of a salt. Using your knowledge of the reactivity of carbonyl compounds, suggest structures of **C** and **X**.



Problem 3 – KINETICS – Isoleucine dating

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



At 20 °C, this reaction has a half-life of 125000 years, and its activation energy is 139.7 kJ mol⁻¹. 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 the equation:

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

For a hippopotamus *mandible* that 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 the hippo tooth, which was 38600 years.

- Assuming that no *allo* was present initially, determine constants for forward and reverse reactions and overall isomerization constant ($k_1 + k_{-1}$).
- Calculate the average conservation temperature of the hippopotamus remains in the soil.

Problem 4 – CRYSTAL – Goblin's element

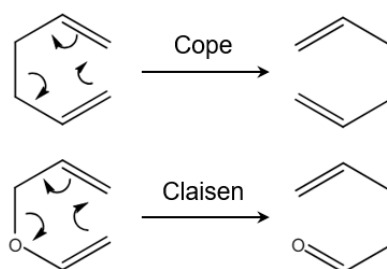
Metal **X** was discovered in 1735. Its name is derived from a German word meaning “goblin” or “evil spirit”. A sample of metal **X** immersed in H₂O weighs 13.031 g. Meanwhile, the weight of the same sample in CCl₄ is 12.046 g. The density of CCl₄ is 1.5940 g cm⁻³. Neutron diffraction is used to identify the metal **X**. The diffraction pattern is specific to the FCC structure, and the angle of reflection (2θ) from the (222) plane is 76.956°. The velocity of neutrons in the diffractometer is 3115.0 m s⁻¹. The same sample is heated in the O₂ atmosphere until metal **X** has reacted completely. The product of the reaction is compound **A** containing 26.577% oxygen (by mass). All of compound **A** reacts with dilute HCl releasing 1.0298 dm³ of O₂ at 25.00 °C 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 [XCl₂Br₂I₂]ⁿ⁻ and it is paramagnetic. Complex carbonyl compound **D** is prepared by heating metal **X** under high pressure of carbon monoxide. The formula of compound **D** is [X₂(CO)₈] and it is diamagnetic. 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**.

- Calculate the density of metal **X** in g cm⁻³.
- Calculate the unit cell parameter (*a*) of metal **X** in pm.
- Calculate the molar mass of metal **X** in g mol⁻¹. What element is metal **X**?
- Write a chemical formula of compound **A**.

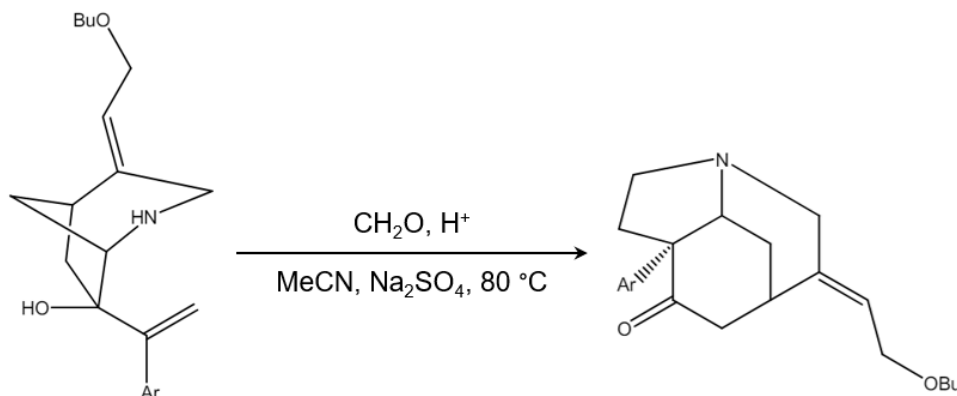
- e) Write the equation of the reaction of compound **A** with diluted HCl.
- f) Sketch the spatial structures of all possible isomers (including structural, geometrical and optical) of ion **C**.
- g) Count the number of unpaired electrons in ion **C**. Consider halogenides as weak field ligands.
- h) Sketch the spatial structure of compound **D**.

Problem 5 – MECH – Sigmatropic rearrangement

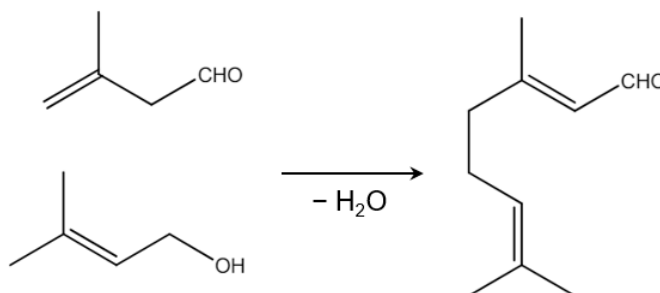
Pericyclic reactions are concerted processes that occur through a cyclic transition state in which more than one bond is formed or broken within the cycle. The so-called sigmatropic rearrangements constitute a large group of pericyclic reactions. Of all the sigmatropic rearrangements, the [3,3]-sigmatropic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



The sigmatropic rearrangement has been used in many syntheses of complex molecules and has industrial applications as well. The key step in the synthesis of the alkaloid strychnine was made by use of this chemistry:



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



Write the reaction mechanism (except for the loss of water in example 2) and possible intermediates for both reactions. *Hint: by treating acetaldehyde with ethanol under the same reaction conditions as in example 2, vinyl ethyl ether could be obtained.*

Problem 6 – ABC, CRYSTAL, THERMO – Dolomite

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

- Determine metallic elements **A** and **B**.
- Calculate the atomic radii for atoms of **A** and **B**.
- Calculate by how many percent the initial atomic radius of both metals decreases when they are ionized into their corresponding ions. It is known that the oxides of both elements have sodium chloride crystal structure and the radius of anion is $1.28 \text{ \AA}$. The unit cell parameters for both oxides are $4.213 \text{ \AA}$ and $4.811 \text{ \AA}$, respectively.

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

- Write equations of all the chemical reactions described above and calculate the time for electrolysis which has to be performed to isolate 1.0 tons of metal **A**. The current intensity is 9.0 kA. Faraday constant $F = 96485 \text{ C mol}^{-1}$.

One of the students' favorite reactions is burning metal **A** in the air. The reaction produces a huge amount of UV light and two binary compounds, one of which is an oxide of metal **A**.

- Write equations of the described reactions.

Metal **A** is also used in the army to prepare food in field conditions. To heat food wrapped in aluminum foil, a special heater, which contains 30 cm^3 water, is used. The heating material is a composite, where powder of metal **A** and iron are associated in a matrix of high-density polyethylene. In the presence of chloride ions, metal **A** reacts with water, forming hydroxide and hydrogen, which is available for burning to obtain extra heat.

- Using thermodynamic constants shown below, calculate the minimum mass of element **A**, which is needed to heat 1.0 dm^3 of water from 20°C to 100°C . Assume that all chemical reactions proceed under standard conditions.

Compounds	$\Delta H_{f,298} [\text{kJ mol}^{-1}]$	$\Delta S^\circ [\text{J mol}^{-1} \text{K}^{-1}]$	$C_p [\text{J mol}^{-1} \text{K}^{-1}]$
$\text{H}_2 (\text{g})$	0	130.52	28.83
$\text{H}_2\text{O} (\text{g})$	-241.81	188.72	33.61
$\text{H}_2\text{O} (\text{l})$	-285.83	69.85	75.30
Metal A (s)	0	32.68	24.89
Hydroxide of metal A (s)	-924.66	63.18	76.99

- Metal **A** hydroxide, which forms in the reaction, is slightly soluble. Calculate the solubility (mg dm^{-3}) of the mentioned hydroxide in distilled water. $pK_{sp} = 11.25$.