54th Lithuanian National Chemistry Olympiad

Selected problems

Konstantos ir formulės

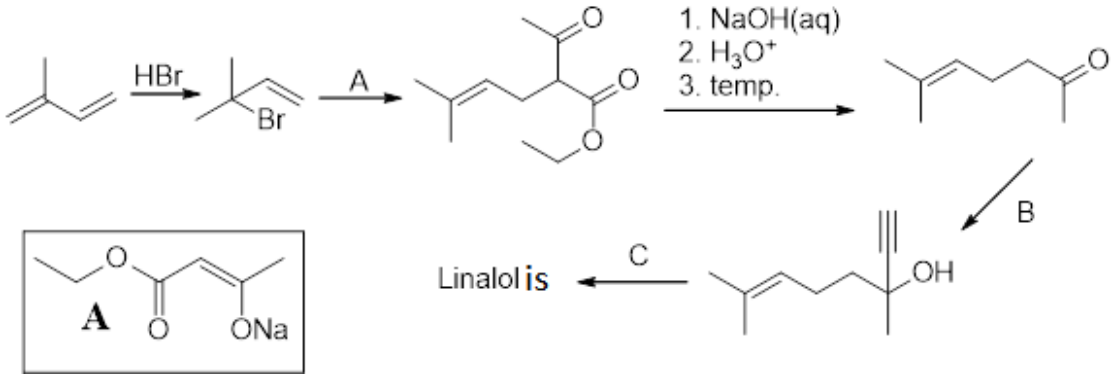
Avogadro konstanta	$N_A = 6{,}02214 \cdot 10^{23}$ mol^{-1}	1 atm slėgis	760 mmHg = 101325 Pa
Universalioji dujų konstanta	$R = 8{,}31447$ J K^{-1} mol^{-1}	Standartinis slėgis	$p° = 1\ bar = 10^5 Pa$
Faraday konstanta	$F = 96485$ C mol^{-1}	Entalpija	$H = U + pV$
Planck'o konstanta	$h = 6{,}62608 \cdot 10^{-34}$ J s	Gibbs'o energija	$G = H - TS$
Šviesos greitis	$c = 2{,}99793 \cdot 10^8$ m s^{-1}	$\Delta_r G° = -RT\ lnK = -nFE°_{cel}$	
Kvanto energija	$E = hv$	$\Delta G = \Delta G° + RT\ ln\frac{c_{prod}}{c_{reag}}$	
Elektromagnetinės bangos ilgio ir dažnio sąryšis	$\lambda \cdot v = c$	Nernst'o lygtis	$E = E° + \frac{RT}{nF}\ ln\frac{c_{ox}}{c_{red}}$
Bangos skaičius	$\tilde{\upsilon} = \frac{1}{\lambda}$	Arrhenius lygtis	$k = A \cdot \exp\left(-\frac{E_A}{RT}\right)$
Boltzmann'o konstanta	$k_B = 1{,}38065 \cdot 10^{-23}$ J K^{-1}	Lambert-Beer dėsnis	$A = lg\frac{I_o}{I} = \varepsilon cl$
Atominės masės vienetas	1 u = $1{,}66054 \cdot 10^{-27}$ kg	Pirmojo laipsnio integruotoji kinetinė lygtis	$ln\frac{[A]_t}{[A]_o} = -kt$
1 eV 1 eV/atomui	$1{,}60218 \cdot 10^{-19}$ J 96,4853 kJ/mol	Antrojo laipsnio integruotoji kinetinė lygtis	$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$
Elektrono masė	$m_e = 9{,}10938 \cdot 10^{-31}$ kg	Dujų plėtimosi darbas esant pastoviam išoriniam slėgiui	$A = -p\Delta V$
Idealiųjų dujų lygtis	$pV = nRT$	Idealiųjų dujų plėtimosi grįžtamosiomis izoterminėmis sąlygomis darbas	$A = nRTln\frac{p_2}{p_1}$

Problem 1. LINALOOL

Linalool – a common fragrance compound, found in cosmetics: soaps, parfume, shampoos, etc. It is estimated that around 60-80% of products contain this organic compound and the commercial synthesis of linalool is important in order to fullfil the demand since natural sources are scarce.

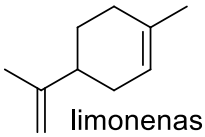
1. Draw a skeletal or structural formula of 3,7-dimethylocta-1,6-dien-3-ol (linalool).
2. Mark an asterisk near any chiral center containing carbon atom. (2p.)

Below you can find the synthetic pathway of linalool.



3. What is the number of all additional mechanistically possible products of HBr addition to isoprene? Draw their structures.
4. Offer reagent/reagents suitable as B and C in the reaction scheme above.
5. Propose a reaction mechanism in the reaction between A and alkene. Draw the mechanism, using curly arrows .

One who takes a good look at linalool's structure can find that this compound can become a 6-membered ring in suitable conditions. Everyone knows that Lithuanian science olympiad asociation volunteers (better known as oranžiniai - „the orange people“) really like oranges. Oranges happen to smell so pleasantly because of limonene – a product of linalool's cyclisation.



6. Suggest a suitable reaction environment (neutral/acidic/basic), reagent and propose the reaction mechanism.

Problem 2. 3D CHEMISTRY: TURN ON THE THIRD DIMENSION

The rearrangement of reacting molecules is very important in organic reactions (especially in enzyme-catalyzed reactions). It usually determines the reactive part of the molecule, the type and the rate of the reaction.

1. Compare benzene and cyclohexane molecules (Fig. 1, Fig. 2): write down the hybridization of each carbon atom and the approximate angle between two adjacent C-C bonds in every molecule. Is every molecule planar or not?

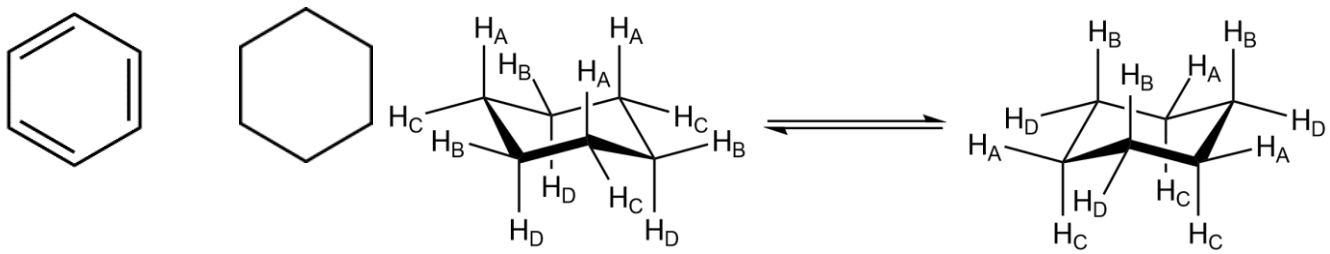
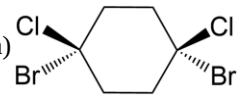
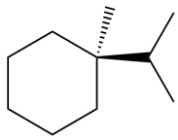


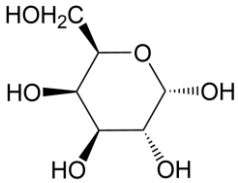
Figure 1. Benzene ***Figure 2. Cyclohexane*** ***Figure 3. Two cyclohexane 'chair' conformations***

The most stable conformation (spatial rearrangement) of cyclohexane is called 'chair' conformation. There are two of them and they always exist in equilibrium one with each other (Fig. 3). In the left conformer H_A and H_D atoms are axial, while H_B and H_C atoms – equatorial. The ring inversion occurs in the right conformer and the positions of hydrogen atoms change. Substituted cyclohexane tries to maintain such a conformation that huge substituents would be equatorial, because this conformation is energetically more stable. In all further questions draw all conformational formulas as shown in Figure 3.

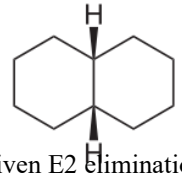
2. Draw both 'chair' conformers for each given compound. Indicate which of them is more stable.

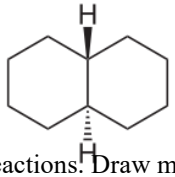
a) 

b) 

c) 

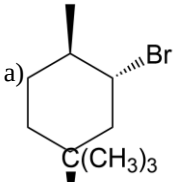
3. Draw the most stable 'chair' conformers of *cis*-decalin and *trans*-decalin (including marked H atoms) and indicate which compound, *cis*-decalin or *trans*-decalin, is more stable. Comment your opinion.

cis-decalin 

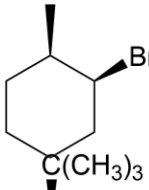


trans-decalin

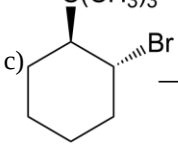
4. Write down the products of given E2 elimination reactions. Draw mechanisms of these reactions (using 'chair' conformational formulas). One of these reactions does not occur. Indicate which and explain why.

a) 

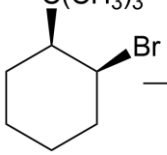
$$\xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-}$$

b) 

$$\xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-}$$

c) 

$$\xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-}$$

d) 

$$\xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-}$$

Problem 3. Vitamin C

Vitamin C (ascorbic acid – $C_6H_8O_6$) is a water-soluble vitamin. It participates in the synthesis of collagen or neurotransmitter noradrenaline. Also, ascorbic acid neutralizes free radicals and acts like a reducing agent in redox reactions.

Vitamin C is a diprotic acid with $pKa_1 = 4.10$ and $pKa_2 = 11.60$.

1. 600 mg tablet of vitamin C with 11% of inert impurities is dissolved in 150 mL water. Calculate the pH of a solution.
2. Vitamin C can be also found in human urine (pH = 6.00). Calculate which species of ascorbic acid are dominant in urine.

4% of human body vitamin C reserve usually is **excreted** in the urine on a **daily** basis. However, it is not possible to measure the concentration of ascorbic acid in the urine by using acid-base titration because there are other hydrogen proton sources in the solution too (uric acid, proteins) which would enlarge the value of answer. Therefore, Tillman's reagent is used ($C_{12}H_7Cl_2NO_2$).

10.00 mL sample of urine is taken for the analysis of vitamin C (urine is collect all day – 1.500 L / per day - because the concentration of vitamin C varies during the day). The sample is diluted with little water and acidified with 1 mL of concentrated acetic acid. The endpoint of titration was reached after 14.40 mL of Tillman's reagent had been added (colour changes to reddish).

3. Calculate the mass of vitamin C in human body if the substances react with each other in molar ratio 1:1.

Problem 4. Thermodynamics

Refrigerators are heat pumps that are designed to move thermal energy by absorbing it from a cold space and releasing it to a warmer one. This is usually achieved by in separate compartments evaporating and condensing gases, e.g. SO_2. This gas is nowadays replaced with less harmful compounds, but it used to be widely used because of its large enthalpy of vaporisation. SO_2 gas is obtained by combustion of hydrogen sulphide.

1. Write reaction equation for combustion of H_2S
2. Using bond dissociation enthalpies ($\Delta H°$) find the enthalpy change for this reaction.

Bond	$\Delta H°, kJ/mol$
$H-S$	339
$O=O$	497
$H-O$	426
$S=O$	536

3. The entropy change for combustion of $H_2S, \Delta S° = 153\ Jmol^{-1}K^{-1}$. Find the change in Gibbs free energy ($\Delta G°$) at 25°C. What does the sign of ΔG tells us about how the reaction proceeds?

If SO_2 occupies large volume at relatively low pressure, the perfect gas model can be used. It is known that specific heat for SO_2, $C_{p,m} = 40.0\ JK^{-1}mol^{-1}$ if $p = const$.

A certain number of moles of SO_2 are confined in a container by a piston which is free to move; the external pressure is 1 bar. The system is allowed to come to equilibrium at 298 K and it is found that the gas occupies a volume of 100 cm^3. 1 J of heat is then supplied to the gas; the gas is heated and expands against the constant external pressure.

4. Calculate the temperature rise of the gas and hence the new volume it occupies. Further find the work done in the expansion and the change in internal energy of the gas.

N. Carnot, a French scientist of 19th century, attempted in designing a perfect heat engine, capable of converting all supplied heat into work. In the end, he proved that such a machine is impossible, but his work had a large impact on perfecting steam engines and laid grounds for further development of the science of thermodynamics.

The Carnot cycle is comprised of four steps during which the internal energy (U) of the system (gas) changes.

- Reversible adiabatic compression (A – B) (No heat leaves or enters system during an adiabatic process, only work is done by or on the gas.)
- Reversible isothermal expansion (B – C)
- Reversible adiabatic expansion (C – D)
- Reversible isothermal compression (D – A)

5. State the first law of thermodynamics for a closed system.

6. Draw a schematic diagram of Carnot cycle as volume – pressure and volume – temperature dependence.

7. At which steps system either loses or gains a) work and b) heat?

8. What is the physical meaning of the area bounded by the curve in the p-V diagram?

9. How does the internal energy of a gas changes going from B to C and from D to A? (Increases, decreases or stays the same?) Why? How does internal energy change if the gas undergoes the whole cycle?

10. Find the work done on 1.00 mol of gas and the heat absorbed by the system going from B to C and from D to A, given that

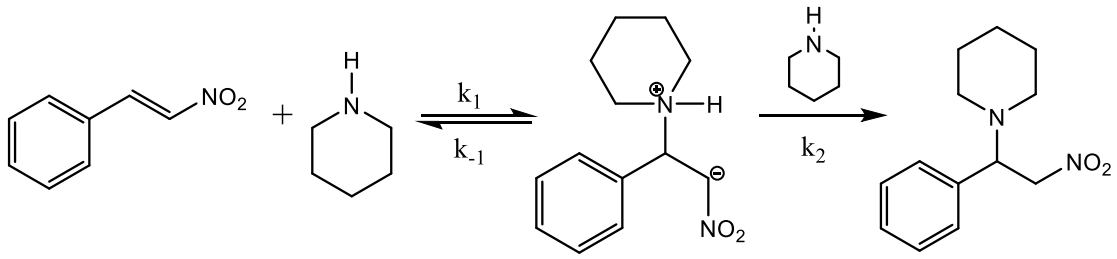
$$T_B = T_C = 400K,\ \ T_A = T_D = 300K,\ \ p_A = 1.00\ bar,\ \ p_B = 1.42\ bar,\ \ p_C = 1.20\ bar,$$

$$p_D = 0.845\ bar$$

11. Find the efficiency coefficient if it is defined as follows: $\eta = \left|\frac{work\ suplied\ to\ the\ system}{heat\ obtained\ from\ the\ cooler\ sink}\right|$

Problem 5. Kinetics and transition state theory

In this problem we are going to investigate β-nitrostyrene and piperidine Michael reaction kinetics and its transition state. Reaction scheme:



Reaction rate equation:

$$v = \frac{k_1}{k_{-1}} k_2 [\beta - nitrostyrene][piperidine]^2 \qquad \text{(1st equation)}$$

1. Which is the overall order of the reaction and with respect to β-nitrostyrene and piperidine? Suggest a method how the reaction kinetic parameters could be investigated using pseudo first order kinetics.

2. It is known that the first step of the reaction has established equilibrium, the second step is catalysed by piperidine molecule and it is rate limiting. Both steps are elementary reactions. Derive product rate equation (1st equation). What is the observed rate constant?

Below are given the kinetic data of the reaction under investigation at different temperatures. MeCN was used as the solvent together with a large excess of piperidine ([piperidine] > 0.01 M).

T / K	288	293	298	303	308
k_{obs} / $M^{-2}\ s^{-1}$	550	490	428	389	334

Arrhenius equation: $$\boldsymbol{k_{obs} = Ae^{\frac{-E_a}{RT}}} \qquad \text{(3rd equation)}$$

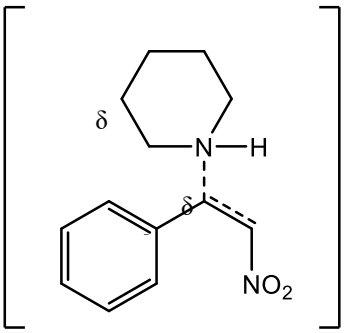
3. Using Arrhenius equation approximately calculate Arrhenius parameter A and activation energy E_a. It is not required to draw a graph or use all the data.

You probably have noticed that the reaction is slowing down with increasing temperature. Therefore, *from Arrhenius equation* one obtains a negative activation energy. How could we explain this phenomena? For majority of chemical reactions bond breaking is the phase what mainly limits the reaction rate. For this reason when the temperature is increased the molecules have more energy and can more easily break their bonds and

the rate of the reaction increases. However, this particular reaction is limited by another factor which is favoured by lower temperatures.

4. What is this factor and explain how it determines that the reaction has negative activation energy?

Now let‘s use transition state theory to investigate this reaction even further. Transition state is highest energy molecules configuration, during which bonds are being redistributed, i.e. it is though that old bonds are not fully broken and new bonds are not fully formed. An example of a transition state for the first step of the reaction is given below:



Theory assumes that an equilibrium establishes between the reactants and the transition state with equilibrium constant of activation $K^{\ddagger}$. Symbol ‡ means that the parameter is connected to the transition state. Using Eyring equation it is possible to connect reaction rate and equilibrium constant of activation: (k_B – Boltzmann, h – Planck constant):

Eyring equation: $\boldsymbol{k_{obs} = \frac{k_B T}{h} K^{\ddagger}}$ $\quad \boldsymbol{\Delta G^{\circ,\ddagger} = -RT \ln(K^{\ddagger})}$ $\quad \boldsymbol{\Delta G^{\circ,\ddagger} = \Delta H^{\circ,\ddagger} - T\Delta S^{\circ,\ddagger}}$

5. Using Eyring equation and other given equations above derive:

$$\boldsymbol{k_{obs} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\circ,\ddagger}}{R}\right) \exp\left(\frac{-\Delta H^{\circ,\ddagger}}{RT}\right)}$$

6. Using the result from part 5 derive straight line graph equation:

$$\boldsymbol{ln\left(\frac{k_{obs}}{T}\right) = ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\circ,\ddagger}}{R} - \frac{\Delta H^{\circ,\ddagger}}{R}\frac{1}{T}}$$

y = c + k x

7. Using kinetic data from the table and by drawing a graph determine $\Delta S^{\circ,\ddagger}$ and $\Delta H^{\circ,\ddagger}$.

Negative enthalpy of activation ($\Delta H^{\circ,\ddagger}$) proves that the reaction proceeds by formation of a stable intermediate. High negative entropy of activation ($\Delta S^{\circ,\ddagger}$) suggests that the transition state of the second step of the reaction is particularly structured – bonds are being redistributed by forming a six-membered ring while piperidine reacts with the intermediate (refer to reaction scheme).

At low piperidine concentrations the obtained entropy of activation is much less negative and the reaction proceeds by a slightly different mechanism. The transition state of the second step still contains bond redistribution in a six-membered ring but this time piperidine molecule does not participate. A tautomer of the product is being formed.

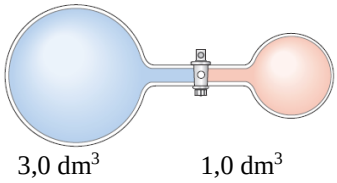
8. Draw both transition state structures mentioned above.

Problem 6. Ideal gas

1. Suggest one chemical method how oxygen gas could be produced in the laboratory. Write balanced chemical equation.

2. Suggest one chemical method how NO gas could be produced in the laboratory. Write balanced chemical equation.

For the experiments with gases special vessel consisting from two glass bulbs connected by valve was used (see fig. in the right). One bulb is 3 dm^3 and other 1 dm^3 of volume. At the beginning valve was closed. Experiment starts when valve is opened. Assume that temperature all the time remains constant.



3. The left bulb was filled with helium gas (pressure 0.40 atm)., the right bulb was filled with neon gas (pressure 0.80 atm). Calculate the total gas pressure when the valve is opened.

In an another experiment the left bulb was filled with NO, ant the right bulb with O_2 gas. Pressure in the both bulbs was 100.0 torr. When the valve was opened, NO irreversibly reacted with O_2 and NO_2 gas was produced. Product of this reaction reversibly dimerizes producing N_2O_4 gas. After establishing of equilibrium total gas pressure in the vessel was 70.0 tor.

4. Calculate molar fraction of each gas presented in the vessel after establishing of equilibrium.

5. Calculate NO_2 dimerization reaction equilibrium constant K_p (subscript p indicates, that partial pressures of gases should be used in the calculation).

6. Draw Lewis formula of N_2O_4.

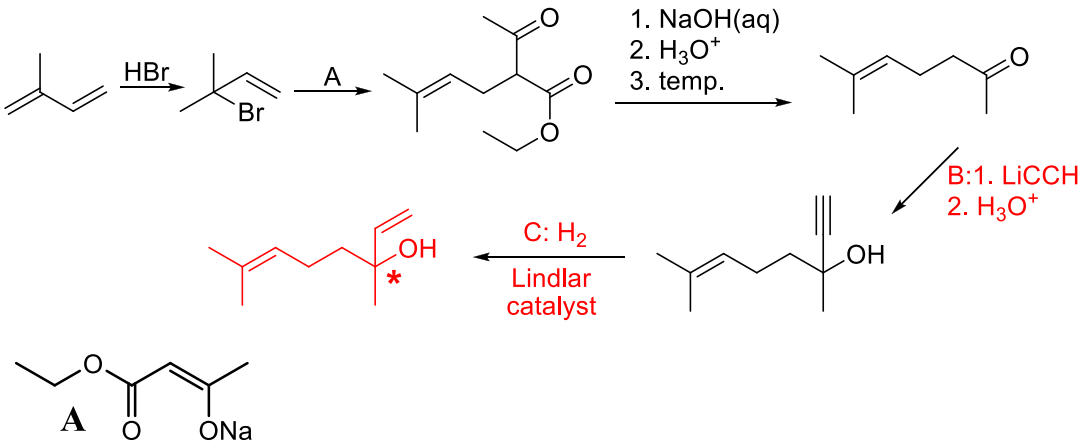
Answers

Problem 1.

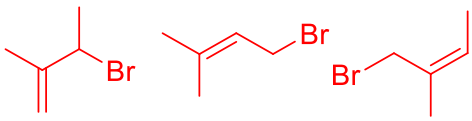
Linalool – a common fragrance compound, found in cosmetics: soaps, parfume, shampoos, etc. It is estimated that around 60-80% of products contain this organic compound and the commercial synthesis of linalool is important in order to fullfil the demand since natural sources are scarce.

1. Draw a skeletal or structural formula of 3,7-dimethylocta-1,6-dien-3-ol (linalool).. (3p.) [answer is drawn in the scheme]
2. Mark an asterisk near any chiral center containing carbon atom. (2p.) [asterisk is marked in the scheme]

Below you can find the synthetic pathway of linalool.

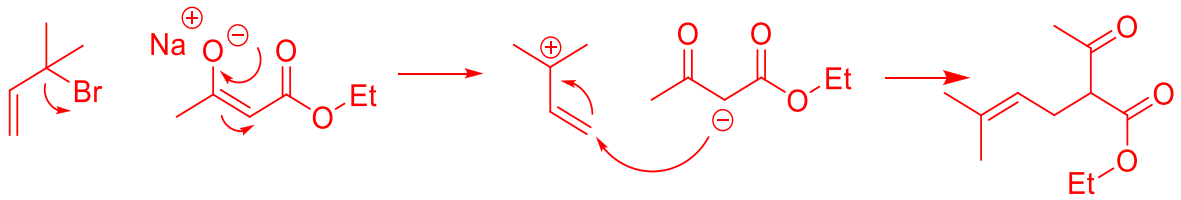


3. What is the number of all additional mechanistically possible products of HBr addition to isoprene? Draw their structures.

3 more products (1p.): 

(2p. For each product – overall 6p.)

4. Offer reagent/reagents suitable as B and C in the reaction scheme above.(4p. for B and 4p. for C)[answer in the scheme]
5. Propose a reaction mechanism in the reaction between A and alkene. Draw the mechanism, using curly arrows. (6p.)



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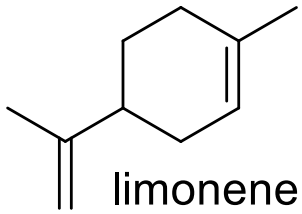
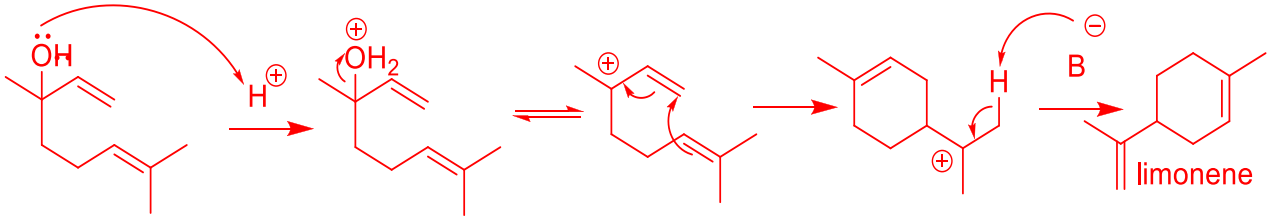


6. Suggest a suitable reaction environment (neutral/acidic/basic), reagent and propose the reaction mechanism.

It should be an acidic environment, H_2SO_4 could work both as an acid and a weak base (anion) capable of deprotonation in the final mechanistic step. (3p.)

Possible reaction mechanism (6p.):



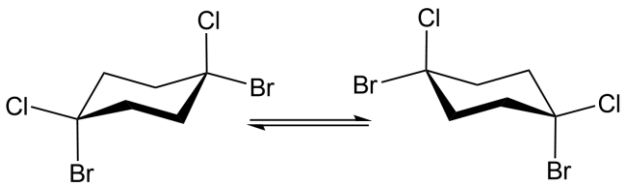
Overall: 35 points.

Problem 2

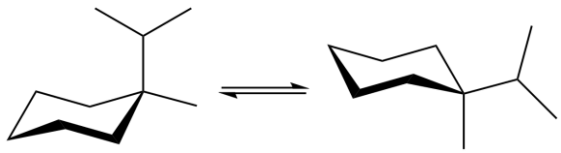
3D CHEMISTRY: TURN ON THE THIRD DIMENSION

1. Benzene: hybridization of all carbon atoms sp^2,
angle between C-C bonds 120° (allowed answers 118° -122°),
molecule is planar.
Cyclohexane: hybridization of all carbon atoms sp^3,
angle between C-C bonds 109,5° (allowed answers 107° -112°),
molecule is not planar.

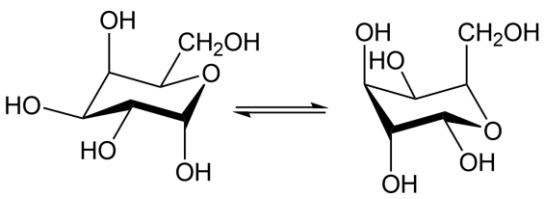
2. a) it is the same conformer, so there is no point discussing about the stability;



b) the second is more stable;

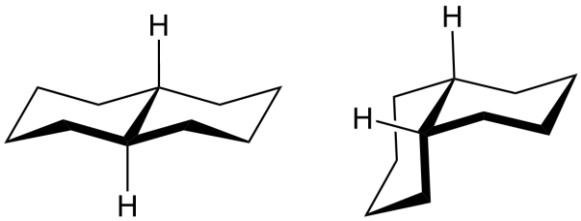


c) the first is more stable.



3.

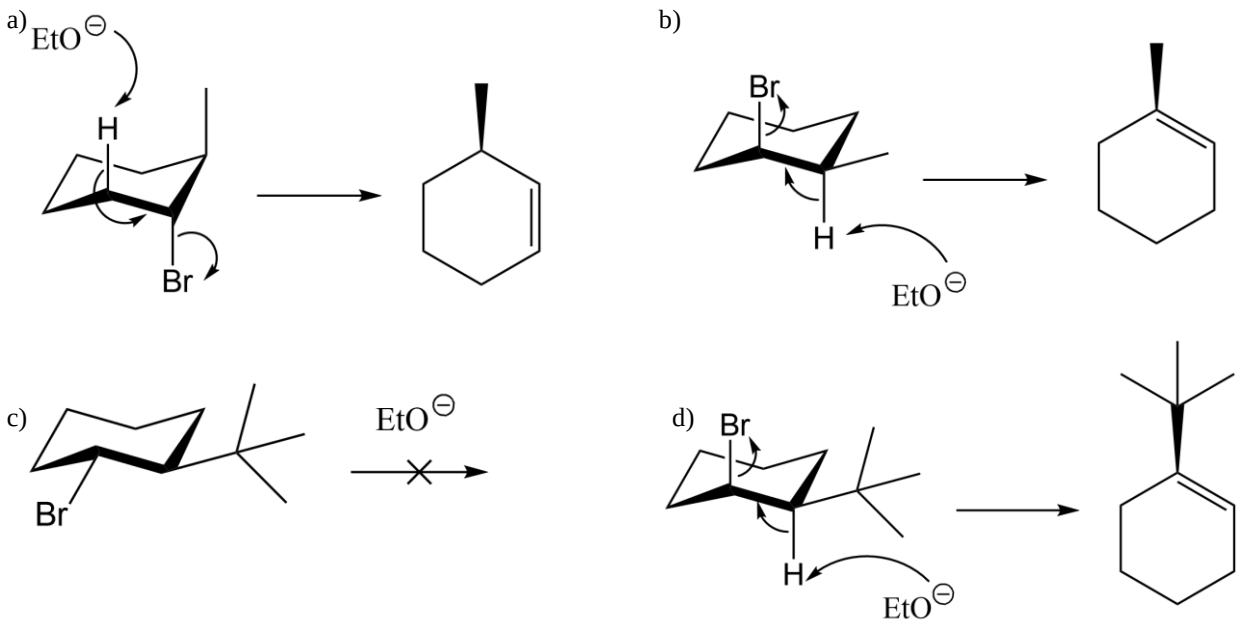
trans-decalin



cis-decalin

Trans-decalin is more stable because all alkyl substituents are equatorial, while cis-decalin has one axial and one equatorial alkyl substituent from the viewpoint of each ring.

4. For E2 elimination to occur, both hydrogen atom attacked by the base and the leaving group must be on adjacent carbon atoms and must be axial. Thus, the reaction c does not occur because for the reaction to occur bromine atom and also very big tret-butyl substituent must be axial, which is not energetically beneficial.



Problem 3.

Vitamin C (ascorbic acid – $C_6H_8O_6$) is a water-soluble vitamin. It participates in the synthesis of collagen or neurotransmitter noradrenaline. Also, ascorbic acid neutralizes free radicals and acts like a reducing agent in redox reactions.

Vitamin C is a diprotic acid with $pKa_1 = 4.10$ and $pKa_2 = 11.60$.

1. 600 mg tablet of vitamin C with 11% of inert impurities is dissolved in 150 mL water. Calculate the pH of a solution.

   It is allowed to neglect the second dissociation constant because $Ka_1 >> Ka_2$. (1 point)

   $m\ (vit.C) = 600 * \frac{100-11}{100} = 534\ (mg)$ (1 point)

$M\ (vit.C) = 176\ g/mol$ (1 point)

$c\ (vit.C) = \frac{m}{M*V} = \frac{534}{176*150} = 0.0202\ (M)$ (1 point)

Let's mark ascorbic acid as H_2A.

$$K_{a_1} = \frac{c(H^+) * c(A^-)}{c(H_2A)}$$

$c(H^+) = \sqrt{K_{a_1} * c(H_2A)} = \sqrt{10^{-4.1} * 0.0202} = 1.3 * 10^{-3}(M)$ (1 point)

$pH = -lg\ c(H^+) = -lg\ 1.3 * 10^{-3} = 2.9$ (1 point)

Answer: pH = 2.9

2. Vitamin C can be also found in human urine (pH = 6.00). Calculate which species of ascorbic acid are dominant in urine.

$$K_{a_1} = \frac{(H^+) * (HA^-)}{(H_2A)}$$

$$K_{a_2} = \frac{(H^+) * (A^{2-})}{(HA^-)}$$

f(X) – the fraction of species X, where X can be $C_6H_8O_6$, $C_6H_7O_6^-$, $C_6H_6O_6^{2-}$.

$$f(X) = \frac{(X)/(HA^-)}{\frac{(H_2A)}{(HA^-)} + 1 + \frac{(A^{2-})}{(HA^-)}} = \frac{(X)/(HA^-)}{(H^+)^2 + (H^+) * K_{a_1} + K_{a_1}K_{a_2}}$$ (1 point)

$$\frac{(H_2A)}{(HA^-)} = \frac{(H^+)}{K_{a_1}}$$

$$\frac{(A^{2-})}{(HA^-)} = \frac{K_{a_2}}{(H^+)}$$

$$f(H_2A) = \frac{(H^+)^2}{(H^+)^2 + (H^+) * K_{a_1} + K_{a_1}K_{a_2}} = \frac{(10^{-6})^2}{(10^{-6})^2 + (10^{-6}) * 10^{-4.1} + 10^{-4.1} * 10^{-11.6}} = 1.24 * 10^{-2}$$ (1 point)

$$f(HA^-) = \frac{(H^+) * K_{a_1}}{(H^+)^2 + (H^+) * K_{a_1} + K_{a_1}K_{a_2}} = \frac{(10^{-6}) * 10^{-4.1}}{(10^{-6})^2 + (10^{-6}) * 10^{-4.1} + 10^{-4.1} * 10^{-11.6}} = 0.986$$ (1 point)

$$f(A^{2-}) = \frac{K_{a_1}K_{a_2}}{(H^+)^2 + (H^+) * K_{a_1} + K_{a_1}K_{a_2}} \frac{10^{-4.1} * 10^{-11.6}}{(10^{-6})^2 + (10^{-6}) * 10^{-4.1} + 10^{-4.1} * 10^{-11.6}} = 2.48 * 10^{-6}$$ (1 point)

Answer: $C_6H_7O_6^-$ species are the most abundant (1 point)

4% of human body vitamin C reserve usually is **excreted** in the urine on a **daily** basis. However, it is not possible to measure the concentration of ascorbic acid in the urine by using acid-base titration because there are other hydrogen proton sources in the solution too (uric acid, proteins) which would enlarge the value of answer. Therefore, Tillman's reagent is used ($C_{12}H_7Cl_2NO_2$).

10.00 mL sample of urine is taken for the analysis of vitamin C (urine is collect all day – 1.500 L / per day - because the concentration of vitamin C varies during the day). The sample is diluted with little water and acidified with 1 mL of concentrated acetic acid. The endpoint of titration was reached after 14.40 mL of Tillman's reagent had been added (colour changes to reddish).

3. Calculate the mass of vitamin C in human body if the substances react with each other in molar ratio 1:1.

$m\ (reagent) = 14.4/1000 * 4.06 * 10^{-2} = 5.85 * 10^{-4}\ (g)$ (1 taškas)

$M\ (reagent) = 268\ g/mol$ (1 taškas)

$n\ (reagent) = n\ (vit.C) = \frac{m}{M} = \frac{5.85 * 10^{-4}}{268} = 2.18 * 10^{-6}\ (mol)$ (1 taškas)

$M\ (vit.C) = 176\ g/mol$

$m\ (vit.C) = \frac{2.18 * 10^{-6} * 176 * 1500 * 100}{10 * 4} = 1.44\ (g)$ (1 taškas)

Answer: 1.44 g (usually the value varies from 300 mg to 2 g)

Problem 4.

1. $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$

2. $\Delta H_r = -2 \cdot 2 \cdot \Delta H°(S = O) - 2 \cdot 2 \cdot \Delta H°(H - O) + 2 \cdot 2 \cdot \Delta H°(H - S) + 3 \cdot \Delta H°(O = O) = -4 \cdot 536 - 4 \cdot 426 + 4 \cdot 339 + 3 \cdot 497 = -1001\ kJ/mol$

   For 1 mol of H_2S: $\Delta H°_r = \frac{1}{2}\Delta H_r = -500.5\ kJ/mol$

3. $\Delta G° = \Delta H° - T\Delta S° = -500.5 \cdot 10^3 - (273 + 25) \cdot 153\ = -546.1 kJ/mol$

4. $p_1 = 1.00 \cdot 10^6 Pa$ $\quad T_1 = 298\ K$ $\quad V_1 = 1.00 \cdot 10^{-4} m^3$

$\Delta H = 1.00 J$ $\quad C_p = 40.0\ J/K$

$$n_1 = \frac{pV}{RT} = \frac{1.00 \cdot 10^5 \cdot 100 \cdot 10^{-6}}{8.314 \cdot 298} = 4.04 \cdot 10^{-3} mol$$

$$\Delta H = C_p \cdot \Delta T$$

$$\Delta T = \frac{\Delta H}{C_{p,m} \cdot n_1} = \frac{1.00}{40.0 \cdot 4.04 \cdot 10^{-3}} = 6.19\ K$$

After the gas has expanded:

$p_1 = p_2 = 1.00 \cdot 10^6 Pa$ $\quad T_2 = T_1 + \Delta T = 298 + 6.19 = 304 K$

$n_1 = n_2 = 4.04 \cdot 10^{-3}\ mol$

$$V_2 = \frac{n_2 R T_2}{p_2} = \frac{4.04 \cdot 10^{-3} \cdot 8.314 \cdot 304}{1.00 \cdot 10^6} = 1.02 \cdot 10^{-4}\ m^3$$

$$w = -p\Delta V = -1.0 \cdot 10^5 \cdot (1.02 \cdot 10^{-4} - 100 \cdot 10^6) = -0.200 J$$

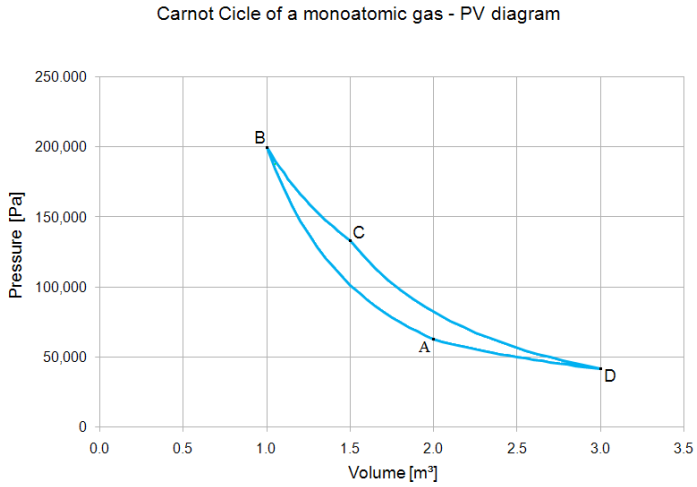
$$\Delta H = \Delta U + p_{ext}\Delta V$$

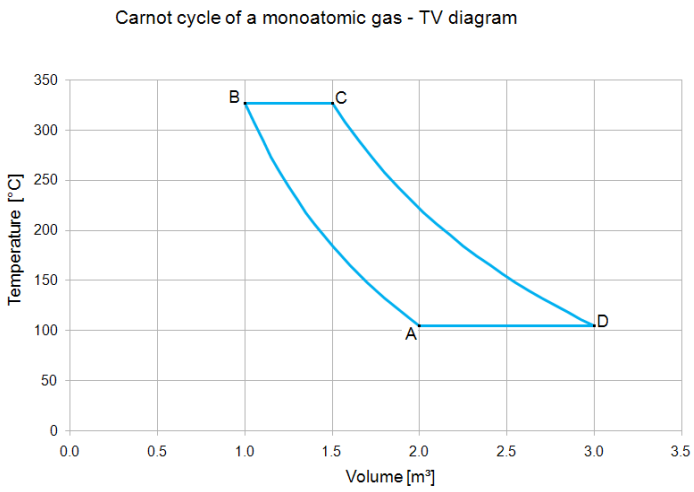
$$\Delta U = \Delta H - p\Delta V = 1.00 - 0.200 = 0.80\ J$$

5. The change in internal energy of a closed system is equal to the energy that passes through its boundary as heat or work.

$$\Delta U = q + w$$

6.





7. a) Work is done either by or on the gas in all steps.

The total work, $w' = w_{AB} + w_{BC} + w_{CD} + w_{DA}$

b) Heat is transferred only in B – C and D – A steps.

Total heat, $q' = q_{BC} + q_{DA}$

8. The area corresponds to the work done by gas in one cycle.

9. B – C and D – A steps correspond to isothermal expansion or compression, therefore, the internal energy of gas does not change. After a full cycle, the pressure, volume and temperature become the same as before the cycle. Thus, $\Delta U = 0$.

$$\Delta U_{cycle} = 0 = w' + q'$$

$$q' = -w'$$

$$-(w_{AB} + w_{BC} + w_{CD} + w_{DA}) = q_{BC} + q_{DA}$$

10. Reversible isothermal process: $w = nRTln\frac{p_2}{p_1}$

$$w_{BC} = 1.00 \cdot 8.314 \cdot 400 \cdot \ln\left(\frac{1.20}{1.42}\right) = -560\,J$$

$\Delta U = 0$: $\quad q_{BC} = -w_{BC} = 560\,J$

$$w_{DA} = 1.00 \cdot 8.314 \cdot 300 \cdot \ln\left(\frac{1.00}{0.845}\right) = 420\,J$$

$$q_{DA} = -w_{DA} = -420\,J$$

11. From part 9: $-(w_{AB} + w_{BC} + w_{CD} + w_{DA}) = q_{BC} + q_{DA}$

$$\eta = \left|\frac{w_{AB} + w_{BC} + w_{CD} + w_{DA}}{q_{BC}}\right| = \left|\frac{q_{BC} + q_{DA}}{q_{BC}}\right| = \frac{560 - 420}{560} = 25\%$$

Or

$$\eta = \frac{T_B - T_A}{T_B} = \frac{400 - 300}{400} = 25\%$$

Problem 5.

The problem is based on a scientific paper:

Ik-Hwan Um, Ji-Sun Kang, and Jong-Yoon Park, 'Kinetic Study on Michael-Type Reactions of β-Nitrostyrenes with Cyclic Secondary Amines in Acetonitrile: Transition-State Structures and Reaction Mechanism Deduced from Negative Enthalpy of Activation and Analyses of LFERs', **J. Org. Chem. 2013**, 78, 5604−5610.

1. β-nitrostyrene – 1st order (1 p.)
   Piperidine – 2nd order (1 p.)
   Reaction is overall 3rd order (1 p.)
   To use a large excess of piperidine with respect to β-nitrostyrene. (2 p.)

   5 points

2. Substitute:
   β-nitrostyrene – [β] Intermediate – [I] Piperidine – [pip]
   $v = k_2[pip][I]$ (1) (2 p.)
   Use equiliubrium equation: $\frac{k_1}{k_{-1}} = \frac{[I]}{[\beta][pip]} \Longrightarrow [I] = \frac{k_1}{k_{-1}}[\beta][pip]$ (2 p.)
   Substitute to (1):
   $v = \frac{k_1}{k_{-1}} k_2 [\beta][pip]^2$ (1 p.)
   $k_{exp} = \frac{k_1}{k_{-1}} k_2$ (2 p.)

   7 points

3. Arrhenius equation: $k_{exp} = Ae^{\frac{-E_a}{RT}}$;
   Using properties of logarithms rearrange to: $\ln(k_{exp}) = \ln(A) - \frac{E_a}{RT}$;
   Make up simultaneous equations:

$$\begin{cases} \ln(k_{exp}(T_1)) = \ln(A) - \frac{E_a}{RT_1}; \\ \ln(k_{exp}(T_2)) = \ln(A) - \frac{E_a}{RT_2}; \end{cases}$$ (7 p.)

After solving the simultaneous equations (the answer given was obtained after drawing a graph, therefore the exact estimates obtained by students may vary):
A = 0.288 $M^{-2}\,s^{-1}$ (3 p.)

E_a = -18 100 J mol^{-1} (3 p.)

13 points

4. The reaction is limited by ordering of the molecules in space into a very structured transition state which is required for the reaction to proceed. This process is unfavourable entropically, therefore increasing temperate lowers the probability for molecules to organise themselves into the transition state geometry what leads to slowing down of the reaction with increasing temperature. From Arrhenius equation this gives a negative activation energy.

4 points each if students mention the ordering of molecules, entropy and lowering of probability. 3 points are given for fluidness of the answer and whether or not the arguments coherently explain the negative activation energy. Other logical explanations will also provide points for students depending on the showcased level of understanding.

15 points

Additional information:

When reaction rate is related to temperature via Arrhenius equation, it automatically leads to negative activation energy if the rate decreases with increasing temperature due to exponential relationship. However, this does not mean that the reaction requires negative energy or removal of energy in order for it to proceed, negative activation energy is like a proportionality constant between the rate and the temperature implied from a very simple Arrhenius model. The actual energy required to activate the reaction is given by Gibbs energy of activation which is always positive. $\boldsymbol{\Delta G^{\circ,\ddagger} = \Delta H^{\circ,\ddagger} - T\Delta S^{\circ,\ddagger}}$, in the equation note that $\Delta G^{\circ,\ddagger}$ increases with increasing temperature if the entropy of activation is negative.

5. $\Delta G^{\circ,\ddagger} = -RT\ln(K^{\ddagger})$ rearrange:

$K^{\ddagger} = e^{\frac{-\Delta G^{\circ,\ddagger}}{RT}}$, then substitute to Eyring equation $k_{exp} = \frac{k_B T}{h} K^{\ddagger}$: (1 p.)

$\boldsymbol{k_{exp} = \frac{k_B T}{h} e^{\frac{-\Delta G^{\circ,\ddagger}}{RT}}}$, then substitute $\boldsymbol{\Delta G^{\circ,\ddagger} = \Delta H^{\circ,\ddagger} - T\Delta S^{\circ,\ddagger}}$: (2 p.)

$k_{exp} = \frac{k_B T}{h} \exp(\frac{-\Delta H^{\circ,\ddagger}}{RT} + \frac{\Delta S^{\circ,\ddagger}}{R})$ rearrange: (2 p.)

$\boldsymbol{k_{exp} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\circ,\ddagger}}{R}\right) \exp\left(\frac{-\Delta H^{\circ,\ddagger}}{RT}\right)}$. (1 p.)

6 points

6. First of all rearrange:

$\boldsymbol{\frac{k_{exp}}{T} = \frac{k_B}{h} \exp\left(\frac{\Delta S^{\circ,\ddagger}}{R}\right) \exp\left(\frac{-\Delta H^{\circ,\ddagger}}{RT}\right)}$. (1 p.)

Then use the properties of logaritms:

$\boldsymbol{\ln\left(\frac{k_{exp}}{T}\right) = \ln(\frac{k_B}{h} \exp\left(\frac{\Delta S^{\circ,\ddagger}}{R}\right) \exp\left(\frac{-\Delta H^{\circ,\ddagger}}{RT}\right))}$. (1 p.)

Rearrange:

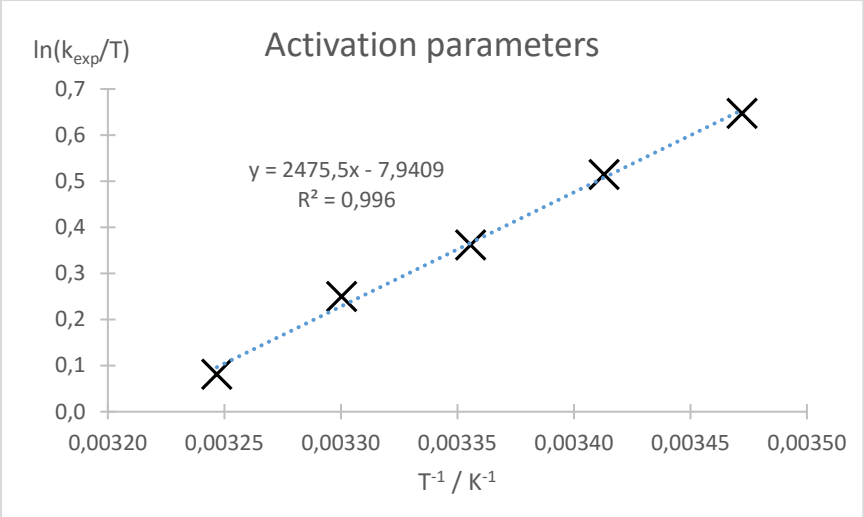
$\boldsymbol{ln\left(\frac{k_{exp}}{T}\right) = ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\circ,\ddagger}}{R} - \frac{\Delta H^{\circ,\ddagger}}{R}\frac{1}{T}}$ (1 p.)

3 points

7.

T / K	288	293	298	303	308
$\boldsymbol{\frac{1}{T} / K^{-1}}$	0,00347	0,00341	0,00336	0,00330	0,00325
$\boldsymbol{ln\left(\frac{k_{exp}}{T}\right)}$	0,647	0,514	0,362	0,250	0,0810

10 points for filling up the table



12 points for drawing the graph

From the graph slope we get:

$$-\frac{\Delta H^{\circ,\ddagger}}{R} = 2\,480$$

$$\Delta H^{\circ,\ddagger} = -\,2\,480 * 8.314 = \ -20\,600 \text{ J mol}^{-1}$$ (6 p.)

Then extrapolate the result for determination of $\Delta S^{\circ,\ddagger}$ it is okay to use any temperature for this matter, the given results were obtained after using 298K.

$$\boldsymbol{ln\left(\frac{k_{exp}}{T}\right) = ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\circ,\ddagger}}{R} - \frac{\Delta H^{\circ,\ddagger}}{R}\frac{1}{T}}$$

Rearrange:

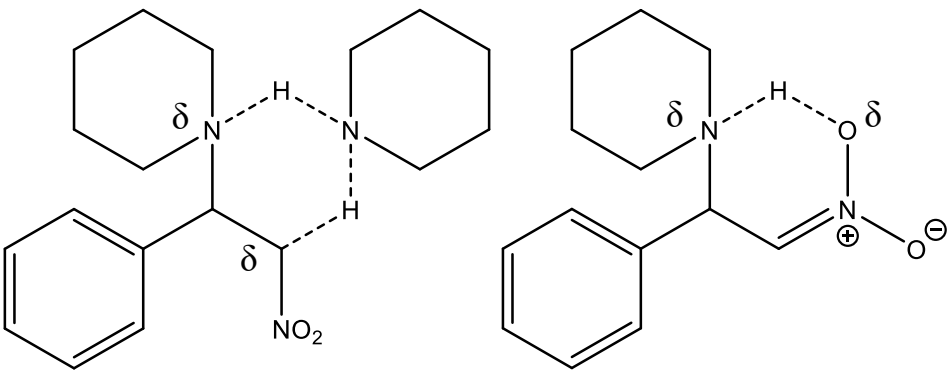
$$\Delta S^{\circ,\ddagger} = R\ ln\left(\frac{k_{exp}}{T}\right) - R\ ln\left(\frac{k_B}{h}\right) + \ \Delta H^{\circ,\ddagger}\ \frac{1}{T}$$

$$\Delta S^{\circ,\ddagger} = 8{,}314 * 0.362 - 8{,}314 * \ln\left(\frac{1.38x10^{-23}}{6.626x10^{-34}}\right) - 20\,600 * 0.00336$$

$$\Delta S^{\circ,\ddagger} = \ -264 \text{ J K}^{-1} \text{ mol}^{-1}$$ (7 p.)

35 points

8. The transition states:



8 points for each structure, 16 points

100 total points

Problem 6.

1. Possible examples: $2\ KClO_3 \rightarrow 2\ KCl + 3O_2$; $2H_2O_2 \rightarrow 2H_2O + O_2$ ir t.t.

2. Possible example: $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

3. $p_1V_1 = p_2V_2$ He partial pressure $0{,}40\times3{,}0 = p\times4{,}0$; $p= 0{,}30$ atm
Ne partial pressure $0{,}80\times1{,}0 = p\times4{,}0$; $p= 0{,}20$ atm

Total pressure 0,30+ 0,20 = 0,50 atm

4.

$2NO$ +	O_2 →	$2NO_2$
3n	n	0
-2n	-n	+2n
n	0	2n

Amount of NO is 3 times bigger than O_2. Let NO is 3n, and O_2 is n. Total amount 4n.

Pressure decree from 100 to 70 torr. This means that in the vessel number of all molecules decreases fro 100% to 70%. So: $4n\times0{,}7= 2{,}8n$.

$2NO_2$	⇄	N_2O_4
2n		0
-2x		+x
2n-2x		x

On the other hand, there are n+ (2n-2x) + x = 3n – x moles of gas in the vessel.

3n – x = 2,8 n Iš čia x= 0,2n

NO mol fraction $\frac{n}{2{,}8n} = 0{,}3571\ or\ 35{,}71\%$

NO_2 mol fraction $\frac{2n-2\cdot0{,}2n}{2{,}8n} = 0{,}5714\ or\ 57{,}14\%$

N_2O_4 mol fraction $\frac{0{,}2n}{2{,}8n} = 0{,}07143\ or\ 7{,}143\%$

Other way of solving (by using partial pressures)
Pvz.

4.

$2NO$ +	O_2 →	$2NO_2$
75	25	0
–50	–25	+50
25	0	50

Before reaction 3p+p = 100. Iš čia p= 25

After first reaction pressure should be 25+50= 75.

It decreases to 70 due to second reaction

$2NO_2$	⇄	N_2O_4
50		0
-2p		+p
50-2p		p

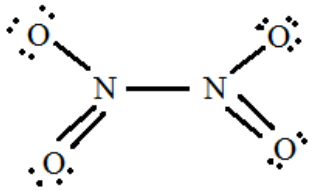
25 + (50-2p) + p = 70 iš čia p= 5

In equilibrium partial pressure of NO_2 is 40 torr, N_2O_4 – 5 torr, NO 25 torr

Pressure fraction is the same as mol fraction:

NO mol fraction $\frac{25}{70} = 0{,}3571\ arba\ 35{,}71\%$

NO_2 mol fraction $\frac{40}{70} = 0{,}5714\ arba\ 57{,}14\%$

N_2O_4 mol fraction $\frac{2}{70} = 0{,}07143\ arba\ 7{,}143\%$

5. NO_2 partial pressure 70 mmHg ×0.5714= 40 torr =0.0526 atm (arba 0.0533 bar) N_2O_4 partial pressure 70 torr ×0.07143= 5 mmHg =0.00658 atm (arba 0.00667 bar) $K_p = \frac{0,00658}{0,0526^2} = 2,4$	6. Number of valence electrons: 2×5 + 4×6 = 34