

36th International Chemistry Olympiad



Preparatory Problems and Worked Solutions

Kiel, Germany

January, 2004

Preface

The problems have been designed to challenge and stimulate the students who take part in the 36th IChO in Kiel, Germany. They cover a wide range of subjects but most of them can be solved by applying a basic knowledge of chemistry. Problems and answers are very detailed to give students the opportunity to learn and to understand the background.

You will find the problems on the internet: www.icho.de ... Chemistry (without solutions). The solutions will be published on the site at the end of May 2004.

On the same page (... Participation) you will find

- the regulations of the IChO
- the syllabus for the practical and the theoretical part
- the safety rules and recommendations set up by the International Jury
- the hazard warning symbols, their designations and their explanations, R-ratings and S-provisions.

A note to the mentors:

The periodic table of elements and roughly the same list of constants and useful formulas as in the preparatory problems will be provided in the theoretical exam. If you want to have additional or different material please mail.

In the exams the students get a booklet with exam questions and separate answer sheets. Everything written in the boxes on the answer sheets will be marked but nothing else.

During the examination an official English version of the problems will be available on request but only for clarification.

Every answer which needs calculation can only be graded if the calculation is shown.

We place great importance on safety. On page 45 preceding the practical problems you will find a list of rules concerning safety precautions and procedures to be followed in Kiel. At the registration in Kiel, we will ask the headmentors to sign a form saying that the students in their teams know these rules and are trained and able to follow them.

Finally, despite proof reading efforts you will uncover some mistakes. Please let us know. We welcome any comments concerning the problems. (Hampe@t-online.de)

Welcome to the 36th IChO, welcome to Germany, welcome to Kiel.

Wolfgang Hampe

36th International Chemistry Olympiad

Kiel, Germany
July 18 - 27, 2004

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Contents

| | Problem | Solution |
|---|---------|----------|
| 1. Combustion Energy | 7 | 61 |
| 2. Haber-Bosch Process | 7 | 63 |
| 3. Thermodynamics in Biochemistry | 9 | 64 |
| 4. Heat Conductivity | 9 | 65 |
| 5. "Green" Chemistry - The Use of Supercritical CO ₂ | 11 | 65 |
| 6. Chemical Kinetics of the Peroxodisulfate Ion | 12 | 66 |
| 7. Catalytic Hydrogenation of Ethylene | 12 | 67 |
| 8. Kinetics of an Enzymatic Reaction | 14 | 68 |
| 9. CaCN ₂ – An Old but still Important Fertilizer | 16 | 69 |
| 10. Closed-Packed Structures | 16 | 70 |
| 11. Titanium carbide – A High-Tech Solid | 18 | 72 |
| 12. Metal Nanoclusters | 19 | 73 |
| 13. Absorption of Light by Molecules | 19 | 75 |
| 14. Observing Single Molecules | 20 | 75 |
| 15. Infrared Spectroscopy of Tetrahedral Molecules | 22 | 76 |
| 16. Spectroscopy in Bioorganic Chemistry | 23 | 77 |
| 17. DNA, RNA, Proteins | 25 | 79 |
| 18. Fatty Acid Degradation | 26 | 80 |
| 19. Lipids | 27 | 82 |
| 20. Kekulé, Benzene and the Problem of Aromaticity | 28 | 83 |
| 21. Benzene and Cyclohexane | 31 | 85 |
| 22. Non-Benzoid Aromatic Systems | 31 | 86 |
| 23. Pain Relievers | 32 | 88 |
| 24. Carbonyl Chemistry | 34 | 90 |
| 25. Cyclohexanes | 36 | 91 |
| 26. Chiral Compounds | 36 | 92 |
| 27. Monosaccharides | 36 | 92 |
| 28. Epibatidine | 37 | 93 |
| 29. Crixivan® | 37 | 94 |
| 30. Stereoselective Reduction | 38 | 94 |
| 31. Surfactant Micelles | 39 | 95 |
| 32. Self-assembly of Amphiphilic Block Copolymers | 40 | 97 |
| 33. Microemulsions | 42 | 99 |
| 34. Silica Nanostructures | 43 | 100 |

| | Problem | Solution |
|--|---------|----------|
| Notes for the Practical Problems | 45 | |
| 35. Preparation and volumetric determination of strontium peroxide octahydrate | 46 | 102 |
| 36. Preparation and iodometric determination of potassium iodate | 47 | 102 |
| 37. Qualitative analysis of anions in an unknown mixture | 49 | 102 |
| 38. Recycling of Polymethylmethacrylate | 55 | 103 |
| 39. Synthesis of <i>para</i> -chlorobenzyl alcohol – an example of the Cannizzaro Reaction | 57 | 103 |
| 40. Ammonolysis of an activated carbonic acid ester: synthesis of cyano acetamide | 59 | 104 |

Periodic table of elements

with atom masses / u

| | | | | | | | | | | | | | | | | | |
|----------------------------------|---------------------------------|---------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| 1 H 1.01 | | | | | | | | | | | | | | | | | 2 He 4.00 |
| 3 Li 6.94 | 4 Be 9.01 | | | | | | | | | | | 5 B 10.81 | 6 C 12.01 | 7 N 14.01 | 8 O 16.00 | 9 F 19.00 | 10 Ne 20.18 |
| 11 Na 22.99 | 12 Mg 24.31 | | | | | | | | | | | 13 Al 26.98 | 14 Si 28.09 | 15 P 30.97 | 16 S 32.07 | 17 Cl 35.45 | 18 Ar 39.95 |
| 19 K 39.10 | 20 Ca 40.08 | 21 Sc 44.96 | 22 Ti 47.88 | 23 V 50.94 | 24 Cr 52.00 | 25 Mn 54.94 | 26 Fe 55.85 | 27 Co 58.93 | 28 Ni 58.69 | 29 Cu 63.55 | 30 Zn 65.39 | 31 Ga 69.72 | 32 Ge 72.61 | 33 As 74.92 | 34 Se 78.96 | 35 Br 79.90 | 36 Kr 83.80 |
| 37 Rb 85.47 | 38 Sr 87.62 | 39 Y 88.91 | 40 Zr 91.22 | 41 Nb 92.91 | 42 Mo 95.94 | 43 Tc 98.91 | 44 Ru 101.07 | 45 Rh 102.91 | 46 Pd 106.42 | 47 Ag 107.87 | 48 Cd 112.41 | 49 In 114.82 | 50 Sn 118.71 | 51 Sb 121.76 | 52 Te 127.60 | 53 I 126.90 | 54 Xe 131.29 |
| 55 Cs 132.91 | 56 Ba 137.3 | 57-71 | 72 Hf 178.49 | 73 Ta 180.95 | 74 W 183.84 | 75 Re 186.21 | 76 Os 190.23 | 77 Ir 192.22 | 78 Pt 195.08 | 79 Au 196.97 | 80 Hg 200.59 | 81 Tl 204.38 | 82 Pb 207.19 | 83 Bi 208.98 | 84 Po 208.98 | 85 At 209.99 | 86 Rn 222.02 |
| 87 Fr 223 | 88 Rd 226 | 89-103 | 104 Rf 261 | 105 Db 262 | 106 Sg 263 | 107 Bh 264 | 108 Hs 265 | 109 Mt 268 | | | | | | | | | |
| | | | 57 La 138.91 | 58 Ce 140.12 | 59 Pr 140.91 | 60 Nd 144.24 | 61 Pm 144.92 | 62 Sm 150.36 | 63 Eu 151.96 | 64 Gd 157.25 | 65 Tb 158.93 | 66 Dy 162.50 | 67 Ho 164.93 | 68 Er 167.26 | 69 Tm 168.93 | 70 Yb 173.04 | 71 Lu 174.97 |
| | | | 89 Ac 227 | 90 Th 232 | 91 Pa 231 | 92 U 238 | 93 Np 237 | 94 Pu 244 | 95 Am 243 | 96 Cm 247 | 97 Bk 247 | 98 Cf 251 | 99 Es 252 | 100 Fm 257 | 101 Md 258 | 102 No 259 | 103 Lr 262 |

Constants and useful formulars

| | | | | | | | | |
|----------------------------|---------------------------|--------------------------|---------------------------|---------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| f | p | n | μ | m | k | M | G | T |
| femto 10 ⁻¹⁵ | pico 10 ⁻¹² | nano 10 ⁻⁹ | micro 10 ⁻⁶ | milli 10 ⁻³ | kilo 10 ³ | mega 10 ⁶ | giga 10 ⁹ | tera 10 ¹² |

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

| | | | |
|-------------------|---|----------------------|--------------------------------|
| Gas constant | R = 8.314 JK ⁻¹ mol ⁻¹ | Faraday constant | F = 96485 C mol ⁻¹ |
| Standard pressure | p = 1.013·10 ⁵ Pa | Standard temperature | 25°C = 298.15K |
| Avogadro number | N _A = 6.022·10 ²³ mol ⁻¹ | Planck constant | h = 6.626·10 ⁻³⁴ Js |
| Speed of light | c = 3.00·10 ⁸ ms ⁻¹ | | |

$$\Delta G = \Delta H - T \cdot \Delta S$$

$$\Delta G = - nEF$$

$$\Delta G^0 = - RT \cdot \ln K$$

$$\Delta G = \Delta G^0 + RT \cdot \ln Q \quad \text{with } Q = \frac{\text{product of } c(\text{products})}{\text{product of } c(\text{react.})}$$

$$\Delta H(T_1) = \Delta H^0 + \int_{298.15}^{T_1} C_p dT$$

if C_p = constant:

$$\Delta H(T_1) = \Delta H^0 + (T_1 - 298.15 \text{ K}) \cdot C_p$$

Arrhenius equation

$$k = A \cdot e^{-\frac{E_a}{RT}}$$

Perfect gas law

$$p \cdot V = n \cdot RT$$

for osmotic pressure Π : $\Pi \cdot V = n \cdot RT$

Nernst equation

$$E = E^0 + \frac{RT}{nF} \cdot \ln \frac{c_{ox}}{c_{red}}$$

Bragg's law

$$n \cdot \lambda = 2d \cdot \sin \theta$$

Law of Lambert Beer

$$A = \log \frac{P_0}{P} = \epsilon \cdot c \cdot d$$

Energy of a photon

$$E = h \cdot c \cdot \lambda^{-1}$$

kinetic energy = $\frac{1}{2} mv^2$

$$\rho = \frac{F}{A}$$

$$F = m \cdot a$$

$$V(\text{cylinder}) = \pi \cdot r^2 \cdot h$$

$$A(\text{sphere}) = 4\pi \cdot r^2$$

$$V(\text{sphere}) = \frac{4}{3} \pi \cdot r^3$$

$$1 \text{ J} = 1 \text{ Nm}$$

$$1 \text{ N} = 1 \text{ kg ms}^{-2}$$

$$1 \text{ Pa} = 1 \text{ N m}^{-2}$$

$$1 \text{ W} = 1 \text{ J s}^{-1}$$

Problem 1: Combustion Energy

- 1.1 Write down the chemical equations for the total burning of propane and butane gas in air. Indicate whether the substances are liquid (l), gaseous (g), or solid (s) under standard conditions.
- 1.2 Calculate the combustion energies for the burning of 1 mol of propane and butane. It can be assumed that all reactants and products are obtained under standard conditions.
- 1.3 How much air (volume composition: 21% of oxygen and 79% of nitrogen) is used up in this process?
Assume that oxygen and nitrogen behave like ideal gases.

The products are usually not obtained under standard conditions but at increased temperatures. Assume for the following that the products are produced at a temperature of 100° C and at standard pressure, while the reactants react at standard conditions.

- 1.4 Calculate the combustion energies for the burning of 1 mol of propane and butane gas in air under these conditions.
- 1.5 What is the efficiency in % of the process in 1.4. compared to 1.2. and how is the energy difference stored?
- 1.6 Calculate the efficiency of the combustion process as a function of the temperature of the products between 25°C and 300 °C. Assume that the water does not condense. Plot the efficiency as a function of the temperature (reactants still react at standard conditions).
- 1.7 Compare the combustion energy stored in a 1 liter bottle of propane and butane. Assume that the product temperature is 100 °C.
The density of liquid propane is 0.493 g cm⁻³, while the density of liquid butane is 0.573 gcm⁻³.

Thermochemical data:

| | | |
|-----------------------|---|--|
| Propane (g): | $\Delta_f H^0 = -103.8 \text{ kJ mol}^{-1}$ | $C_p = 73.6 \text{ J mol}^{-1} \text{K}^{-1}$ |
| Butane (g): | $\Delta_f H^0 = -125.7 \text{ kJ mol}^{-1}$ | $C_p = 140.6 \text{ J mol}^{-1} \text{K}^{-1}$ |
| CO ₂ (g): | $\Delta_f H^0 = -393.5 \text{ kJ mol}^{-1}$ | $C_p = 37.1 \text{ J mol}^{-1} \text{K}^{-1}$ |
| H ₂ O (l): | $\Delta_f H^0 = -285.8 \text{ kJ mol}^{-1}$ | $C_p = 75.3 \text{ J mol}^{-1} \text{K}^{-1}$ |
| H ₂ O (g): | $\Delta_f H^0 = -241.8 \text{ kJ mol}^{-1}$ | $C_p = 33.6 \text{ J mol}^{-1} \text{K}^{-1}$ |
| O ₂ (g): | $\Delta_f H^0 = 0 \text{ kJ mol}^{-1}$ | $C_p = 29.4 \text{ J mol}^{-1} \text{K}^{-1}$ |
| N ₂ (g): | $\Delta_f H^0 = 0 \text{ kJ mol}^{-1}$ | $C_p = 29.1 \text{ J mol}^{-1} \text{K}^{-1}$ |

Problem 2: Haber-Bosch Process

Ammonia is one of the most important intermediates. It is used, for example, for the production of fertilizers. Usually, ammonia is produced from hydrogen and nitrogen in the Haber-Bosch process.

- 2.1 Write down the chemical equation for this reaction.

2.2 Calculate the thermodynamic properties (reaction enthalpy, entropy, and Gibbs energy) for this reaction under standard conditions. Use the values in Table 1. Is the reaction exothermic or endothermic? Is it exergonic or endergonic?

2.3 What will happen if you mix nitrogen and hydrogen gas at room temperature? Explain your reasoning.

2.4 Calculate the thermodynamic properties (reaction enthalpy, entropy, and Gibbs energy) for this chemical reaction at 800 K and 1300 K at standard pressure. Is the reaction exothermic or endothermic? Is it exergonic or endergonic?

The temperature dependence of the heat capacity and the entropy are described by $C_p(T) = a + b \cdot T + c \cdot T^2$ and $S(T) = d + e \cdot T + f \cdot T^2$. The values of the constants a-f can be found in Table 2.

2.5 Calculate the mole fraction of NH_3 that would form theoretically at 298.15 K, 800 K and 1300 K and standard pressure.

Assume that all the gases behave like ideal gases and that the reactants are added in the stoichiometric ratio.

In an industrial process, the reaction has to be fast and result in high yields. Task 2.3 shows that the activation energy of the reaction is high and task 2.5 shows that the yield decreases with increasing temperatures. There are two ways of solving this contradiction.

2.6 The reaction can proceed at lower temperatures by using a catalyst (for example iron oxide). How does the catalyst influence the thermodynamic and kinetic properties of the reaction?

2.7 It is also possible to increase pressure. How does the pressure change influence the thermodynamic and kinetic properties of the reaction?

2.8 What are the best conditions for this reaction?

Table 1:

| Chemical Substance | $\Delta_f H^0 \cdot (kJ mol^{-1})^{-1}$ | $S^0 \cdot (J mol^{-1} K^{-1})^{-1}$ | $C_p^0 \cdot (J mol^{-1} K^{-1})^{-1}$ |
|--------------------|---|--------------------------------------|--|
| $N_2 (g)$ | 0.0 | 191.6 | 29.1 |
| $NH_3 (g)$ | - 45.9 | 192.8 | 35.1 |
| $H_2 (g)$ | 0.0 | 130.7 | 28.8 |

Table 2:

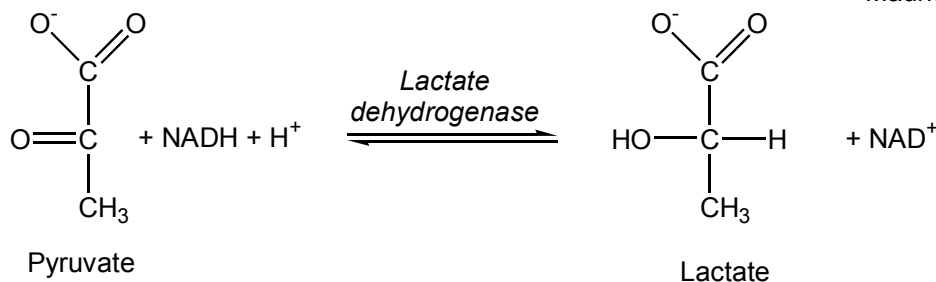
| Chemical Substance | $a \cdot (J mol^{-1} K^{-1})^{-1}$ | $b \cdot (J mol^{-1} K^{-2})^{-1}$ | $c \cdot (J mol^{-1} K^{-3})^{-1}$ | $d \cdot (J mol^{-1} K^{-1})^{-1}$ | $e \cdot (J mol^{-1} K^{-2})^{-1}$ | $f \cdot (J mol^{-1} K^{-3})^{-1}$ |
|--------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| $N_2 (g)$ | 27.3 | $5.2 \cdot 10^{-3}$ | $-1.7 \cdot 10^{-9}$ | 170.5 | $8.1 \cdot 10^{-2}$ | $-2.3 \cdot 10^{-5}$ |
| $NH_3 (g)$ | 24.2 | $4.0 \cdot 10^{-2}$ | $-8.2 \cdot 10^{-6}$ | 163.8 | $1.1 \cdot 10^{-1}$ | $-2.4 \cdot 10^{-5}$ |
| $H_2 (g)$ | 28.9 | $-5.8 \cdot 10^{-4}$ | $1.9 \cdot 10^{-6}$ | 109.8 | $8.1 \cdot 10^{-2}$ | $-2.4 \cdot 10^{-5}$ |

Problem 3: Thermodynamics in Biochemistry

Muscle cells need an input of free energy to be able to contract. One biochemical pathway for energy transfer is the breakdown of glucose to pyruvate in a process called glycolysis. In the presence of sufficient oxygen in the cell, pyruvate is oxidized to CO_2 and H_2O to make further energy available. Under extreme conditions, such as an Olympic 100m sprint, the blood can not provide enough oxygen, so that the muscle cell produces lactate according to the following reaction:



Maurice Greene, AFP



$$\Delta G^{\circ'} = -25.1 \text{ kJ mol}^{-1}$$

In living cells the pH value usually is about pH = 7. The proton concentration is therefore constant and can be included into ΔG° which is then called $\Delta G^{\circ'}$, a quantity commonly used in biochemistry.

3.1 Calculate ΔG° for the reaction given above.

3.2 Calculate the reaction constant K' (the proton concentration is included again in the constant, $K' = K \cdot c(\text{H}^+)$) for the reaction above at 25°C and pH = 7.

$\Delta G^{\circ'}$ indicates the free enthalpy of the reaction under standard conditions if the concentration of all reactants (except for H^+) is 1 mol L^{-1} . Assume the following cellular concentrations at pH = 7: pyruvate 380 $\mu\text{mol L}^{-1}$, NADH 50 $\mu\text{mol L}^{-1}$, lactate 3700 $\mu\text{mol L}^{-1}$, NAD^+ 540 $\mu\text{mol L}^{-1}$!

3.3 Calculate $\Delta G'$ at the concentrations of the muscle cell at 25°C!

Problem 4: Heat Conductivity

When considering the design of houses, the heat conductivity through walls, roofs, and the floor plays an important role. The heat conductivities (λ) of some building materials are described in Table 1.

4.1 Calculate the heat flow through a wall of 150 m^2 (typical of a single-family house in Central Europe) that consists of a brick layer with a thickness of $d = 24 \text{ cm}$ and through the wall that consists, however, of a brick layer with a thickness of $d = 36 \text{ cm}$. There is a temperature of 25°C inside and 10°C outside.

- 4.2 The heat loss can be minimized by using a layer of polystyrene foam. Calculate the heat loss through a 10 cm polystyrene insulation foam. The wall area again is 150 m².**

It is advantageous to use the heat resistance Λ^{-1} for the calculation of the heat conductivity through a wall consisting of different layers:

$$\frac{1}{\Lambda} = \frac{d_1}{\lambda_1} + \frac{d_2}{\lambda_2} + \frac{d_3}{\lambda_3} + \dots$$

For the different parts of the house (window, wall) the diathermal coefficient can be calculated as:

$$k = \frac{\Lambda_1 A_1}{A_{\text{tot}}} + \frac{\Lambda_2 A_2}{A_{\text{tot}}} + \frac{\Lambda_3 A_3}{A_{\text{tot}}} + \dots$$

Energy-saving actions are of vital importance to decrease the energy requirements of the world. Good insulation is not only positive for the environment (reduction of CO₂ emissions) but also good for the economy. Presently, an energy-saving house has a maximum diathermal coefficient of 0.50 W·m⁻²·K⁻¹

- 4.3 Calculate the thickness of a wall that only consists of brick to achieve this requirement.**
- 4.4 The wall thickness can be minimized by insulation layers. A typical wall consists of a brick layer that has a thickness of $d_1 = 15$ cm at the outside, a concrete layer with a thickness of $d_2 = 10$ cm, an insulation layer (polystyrene foam) of thickness d_3 and a gypsum layer with a thickness of $d_4 = 5$ cm on the inside of the wall. Calculate the thickness of the insulation layer and the total thickness of the wall to fulfil the requirements of an energy-saving house.**
- 4.5 Windows increase the mean value of the energy loss. Assume a wall of 15 m² constructed as in 4.4 including a window of 4 m² with a mean diathermal coefficient of 0.70 W·m⁻²·K⁻¹. By what percentage has the thickness of the foam layer of 4.4 to be increased in order to achieve the same average k-value?**

Table 1: Heat conductivity of different materials

| Material | $\lambda \cdot (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})^{-1}$ |
|-----------------------------|---|
| Concrete | 1.10 |
| Building brick | 0.81 |
| Polystyrene insulation foam | 0.040 |
| Linoleum (floor covering) | 0.17 |
| Gypsum | 0.35 |

Formula:

Heat flow through a wall:
$$P_w = \frac{A}{d} \lambda (T_2 - T_1)$$

Area A, heat conductivity λ , temperature T, thickness d

Problem 5: “Green” Chemistry – The Use of Supercritical CO₂

Recently, reactions in supercritical carbon dioxide (critical temperature $T_c = 304.3$ K; critical pressure $p_c = 72.8 \cdot 10^5$ Pa) have received significant attention. The density of a liquid can be easily tuned near the critical point. Moreover, it can be regarded as a “green” solvent that can replace organic solvents. This solvent has actually been used for caffeine extraction for quite a long time. The fact, however, that carbon dioxide has to be compressed is one of the few disadvantages.

5.1 Calculate the energy needed to compress carbon dioxide from 1 bar to 50 bar (final volume is 50 ml, 298 K, ideal gas).

Real gases can be described by the van-der-Waals equation (although it is still an approximation):

$$\left[p + a \left(\frac{n}{V} \right)^2 \right] (V - nb) = nRT$$

constants for CO₂:
 $a = 3.59 \cdot 10^5 \text{ Pa dm}^6 \text{ mol}^{-2}$
 $b = 0.0427 \text{ dm}^3 \text{ mol}^{-1}$

5.2 Calculate the pressures needed to achieve a density of 220 g dm⁻³, 330 g dm⁻³, and 440 g dm⁻³ at temperatures of 305 K and 350 K.

Properties, such as the solvent power of carbon dioxide and the diffusivity of reactants, are strongly dependent on the density of the fluid. The calculation in the previous task shows that the density can be tuned by pressure variations.

5.3 In which region can these properties of the fluid be tuned more easily – near the critical point or at higher pressure/temperature (consider the critical constants and the results of 5.2)?

The oxidation of alcohols by molecular oxygen in supercritical carbon dioxide, e.g. the oxidation of benzyl alcohol to benzaldehyde, is a supercritical process. The reaction takes place in the presence of a Pd/Al₂O₃ catalyst with a selectivity of 95%.

**5.4 a) Write down the balanced reaction equation of the main reaction path.
b) Which reactions can occur during further oxidation (except total oxidation) ?**

The use of carbon dioxide both as a solvent and as a reactant instead of phosgene or carbon monoxide is another example of supercritical processes. Both the catalytic formation of organic carbonates and formamides have already been described.

**5.5 a) Write a balanced equation of the formation of dimethyl carbonate by the reaction of methanol with carbon dioxide. How can dimethyl carbonate form if phosgene is the reactant?
b) Formyl-morpholine can be synthesized from carbon dioxide and morpholine using an appropriate catalyst. Which additional reactant is needed? Write down the reaction scheme.
How would the scheme change if carbon monoxide was used instead?**

**5.6 From the point of view of “green chemistry” – why should reactions be carried out in CO₂ instead of using carbon monoxide or phosgene (2 reasons)?
Apart from the compression of carbon dioxide, what is the main obstacle in using CO₂ as a reactant in comparison to CO or COCl₂ (1 reason) ?**