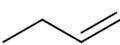
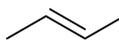


Practice exam questions/answers M&M

P. J. Deuss

1. Oil refineries produce a fraction that consists of a mixture of butenes shown below together with their boiling points (bp), melting points (mp), water solubility (W_{sol}) and density as a liquid (d_{liquid}).

				
	A	B	C	D
bp	266.9 K	274.0 K	286.9 K	266.3 K
mp	87.8 K	167.7 K	134.3 K	132.9 K
W_{sol}	insoluble	insoluble	insoluble	insoluble
d_{liquid}	0.62 g/cm ³	0.63 g/cm ³	0.64 g/cm ³	0.59 g/cm ³

- a. Name all four components **A-D** of this mixture

A: but-1-ene, B: E-but-2-ene, C: Z-but-2-ene, D: 2-methylpropene

- b. Indicate what type of isomers components **A-D** are.

A-(B/C)-D structural (constitutional) isomers

B-C Geometric isomers

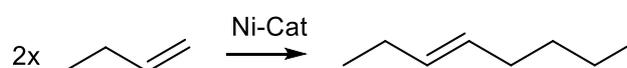
- c. Which of components **A-D** is the most stable (the inverse of reactivity of the double bond)

Most stable B (internal double bond and trans)

- d. Explain the boiling point difference between component **B** and **C** and give a reason why this could be different in the melting point.

B and C: C has electron density located on one side of the molecule making it more polar and thus have stronger polar interaction between molecules causing a higher boiling point. In a solid form the packing also becomes important which could be better for a more linear molecules.

The butenes are commonly dimerized to produce plasticizers. An example reaction is shown below. For this reaction the whole mixture is used to obtain a new mixture that is used for further reactions



During the dimerization reaction, the location of the double bond is also varied by an ongoing secondary isomerization reaction.

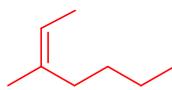
- e. Provide an additional 10 products (draw the structures) and name them (do not worry about selectivity or stability of the products just make sure the product can be formed by dimerization followed by isomerization).



2-methylhept-2-ene



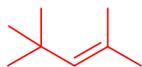
(E)-3-methylhept-2-ene



(Z)-3-methylhept-2-ene



(E)-oct-2-ene



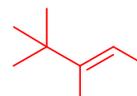
2,4,4-trimethylpent-2-ene



(E)-2,2-dimethylhex-3-ene



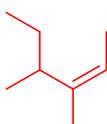
oct-1-ene



(E)-3,4,4-trimethylpent-2-ene



(Z)-3,4,4-trimethylpent-2-ene



(Z)-3,4-dimethylhex-2-ene

Note: These are 10 examples, many more possible structures
Points are also awarded for correct names for wrong structures

- f. Give 2 reasons why this is a favorable reaction for industry even though a complex mixture of products is obtained (look at feedstock and the products).

100% atom economy so no waste (low E-factor), extremely cheap feedstock, conversion of a gas to a liquid, higher carbons are obtained that are more valuable (e.g. polymer additives, special fuel additives)

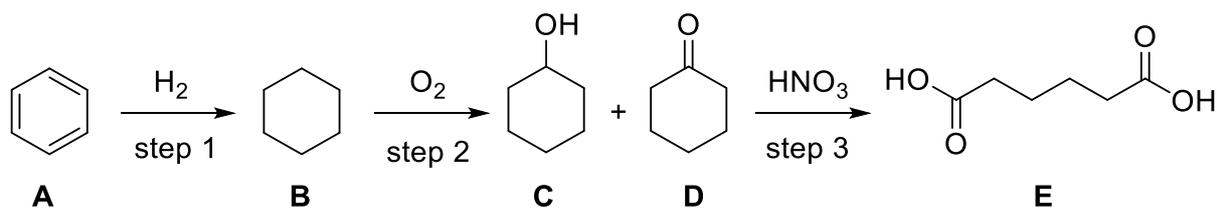
- g. Use the provided physical properties to explain why butenes are used as a mixture and not as separate components.

A mixture because due to the similar boiling points separation is hard. Product can be more readily separated or application are sought in which the product is used as a whole

- h. Why are the products from the dimerization of component **D** more desirable for application as fuel additive after conversion of the alkene to an alkane (hydrogenation) compared to those originating from component **A** by dimerization and subsequent hydrogenation?

Dimerization and of component **D** yields branched alkanes that have a higher octane number and thus provide less engine knocking.

2. Product **E** is one of the main components of Nylon and is produced from **A** via the steps shown below.



- a. Match the following name with the right compound **A-E**: cyclohexanol, hexanedioic acid, cyclohexane, benzene, cyclohexanone.

A = benzene

B = cyclohexane

C = cyclohexanol

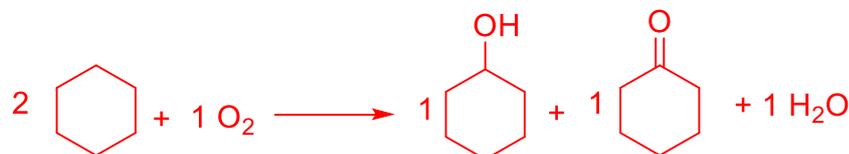
D = cyclohexanone

E = hexanedioic acid

- b. In step 1 is exothermic. However, less energy is released than expected compared to the energy released by the hydrogenation (addition of H_2) of three molecules of ethylene. Why is this?

A is aromatic, this gives additional stabilization which makes the molecule lower in energy

- c. Assuming that step 2 gives a 1 : 1 mixture of **C** and **D** and water is released as a side product, rewrite the reaction equation and balance it. What will change in the equation when the reaction is selective for **C**?

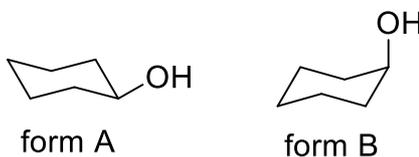


No water is formed when the reaction is selective for **C**

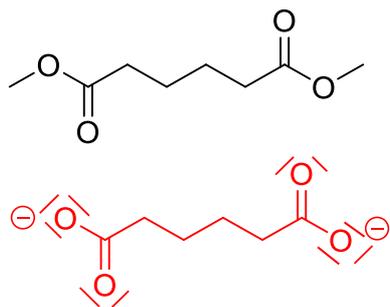
- d. Step 1 and 2 do not happen spontaneously and simply heating the reaction till a reaction takes place will lead to many side reactions. What is required to have these reaction happen selectively to the desired product.

A catalyst to lower the reaction barrier of the desired reaction pathway.

Below, two forms of compound **C** are provided.



- e. What are these two forms of each other and which of the two is more stable? Explain.
Conformers or conformational isomers. Form A is more stable as large groups will sit in an equatorial position to prevent steric interference with axial hydrogens.
- f. Use the Lewis structure of compound **E** and the type of interactions this allows to explain why this compound is water soluble and the compound shown below is not.



Ion-dipole interaction with water, which does not negatively impact intermolecular hydrogen bonding in water. Shown compound can not do this. Also this compound can not form effectively form hydrogen bonds with water as there are no hydrogen in polarized bonds

- g. To form Nylon from acidic compound **E** an acid additive is required that is a stronger acid. Provide the name and chemical formula of such an acid that is largely available and cheap.

Several possible answers:

HCl = hydrochloric acid

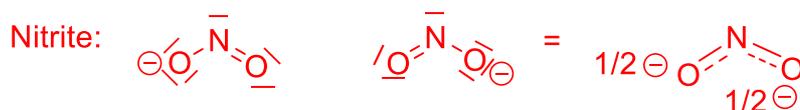
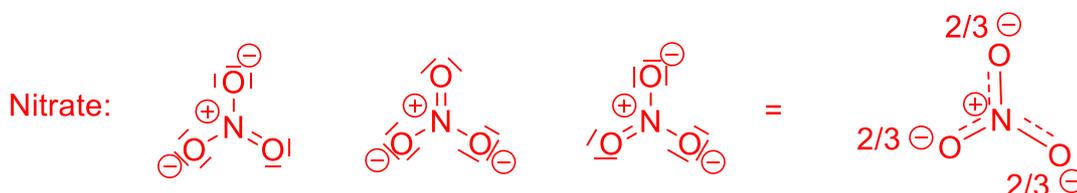
H₂SO₄ = sulfuric acid

H₃PO₄ = phosphoric acid

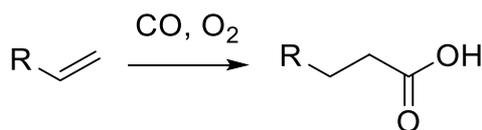
HNO₃ = nitric acid

Step 3 is not very selective and generates a lot of side products in the form of nitrate (NO₃⁻) and nitrite salts (NO₂⁻).

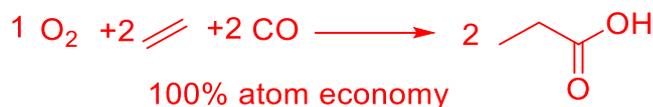
- h. Draw the resonance contributors for both the nitrate and nitrite anion as well as the final resonance hybrid.



A more direct route to compound **C** would be via oxidative carbonylation of an alkene (reaction scheme shown below).



- i. Balance the reaction equation for R = H (ethylene) and provide atom economy.



- j. Provide the E-factor for R = H (ethylene) given that for every 1000 Kg of product 50 Kg of side products are generated. Is that suitable for industrial implementation of the process for this bulk chemical?

$50/1000 = 0.05$, yes Bulk chemicals operate typically in the Efactor range of 1-5

- k. What oil-derived starting compound that is obtained as a major product steam cracker would be the ideal starting material for a direct route to compound C? Draw and name.



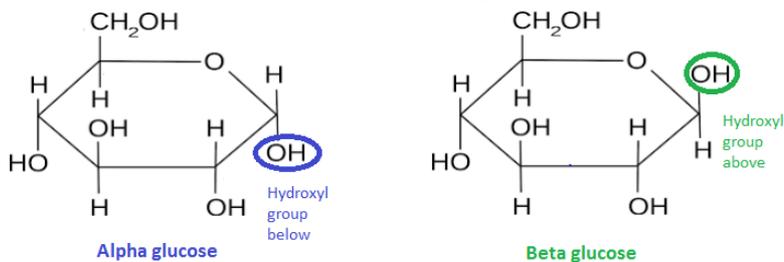
E. Jurak

- 1) Starch and cellulose are two of the main polysaccharides used in various industrial application

- a) Which are the single unit building blocks of starch and cellulose

Cellulose – beta glucose, starch – alpha glucose

- b) Draw the fisher projection of the building blocks of starch and cellulose



- c)

- d) What chemical bond is binding the building blocks (please name all the bonds in the corresponding biomasses with full chemical names)

Starch, alpha, 1-4- glycosidic bond and alpha 1,6 glycosidic bond. Cellulose beta 1-4 glycosidic bonds

- e) Describe in detail the 3 step industrial process of converting semicrystalline starch to glucose syrup (think of the original structure, bonds in the structure, enzymes, temperature...)

Gelatinisation – breaking down amylose part of starch with water (hydrogen bonds break) by using alpha amylase (or enzyme to cleave alpha 1-4 bond) and high temperature, Liquefaction – solubilisation of gelatinized starch by high temperature, Saccharification- cleaving the remaining alpha 1-6 bond to release glucose

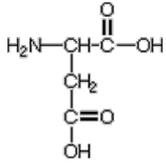
- f) By degrading starch and cellulose, fermentable sugars are obtained. Give a definition of fermentable sugars (3)

Fermentable sugars are sugars that are converted (1) by yeast (1) to carbon dioxide, biomass and ethanol (1). Or fermentable sugars are sugars that a microorganism can ferment to carbon dioxide, biomass and alcohol or organic acid.

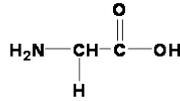
- g) Provide two examples of fermentable sugars (2)

1. Glucose; 2. Mannose but also xylose or arabinose (2)

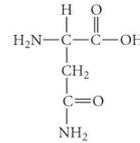
2) Please connect the following amino acids by peptide bond in correct order: polar-hydrophobic-charged. (10p)



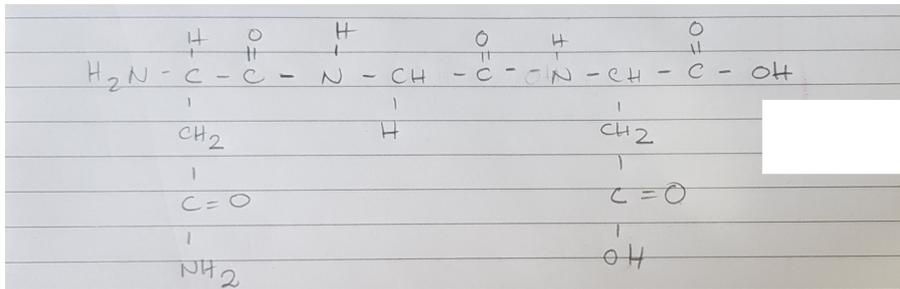
Aspartic acid



Glycine



Serine



3) Please give a definition of an enzyme and describe how an enzyme works (6 points)

Enzyme is a protein that catalyzes a chemical reaction/metabolic pathway (3p).

Enzymes bind substrate(s) in the active site, stabilize transition state to lower energy required for reaction (and releases products when reaction complete) (3p).

4) Which of the following words/terms go instead of the numbers in bold? (6p)

V_{max} , substrate, cofactor, amount, protein, enzyme, Michaelis-Menten kinetics, K_m , inhibitor, V_o

The rate of **1(enzyme)** catalysed reaction depends on the **2(amount)** of enzyme and the amount of the **3 (substrate)** available. **4 (K_m)** a measure of the affinity of an enzyme for its substrate, and is a parameter unique to each enzyme. With the substrate concentration **5(V_o)** increases, until enzyme becomes saturated with substrate and reaches **6(V_{max})**.

Bart Kooi

Exercise 1: Mechanical properties of materials (8 pt)

- a. A brass (Cu-Zn alloy) bar, with a diameter of 20 mm, is loaded parallel along its long axis. The diameter of the bar changes 5 μm as a consequence of the loading. Compute the

value of the load (in kilograms) that has been put on the bar. Assume that the bar is loaded completely elastic. However, check after the calculation whether this assumption was justified. The yield strength of the brass is 75 MPa, its Young's modulus 97 GPa, its Poisson's ratio 0.34. (4 pt)

- b. Describe 2 methods by which a metal (material) can be strengthened. Explain concisely why strengthening occurs. A certain type of defects plays a crucial role. What is the name of these defects; describe their role. (4 pt)

Exercise 2: Electrical properties of materials (10 pt)

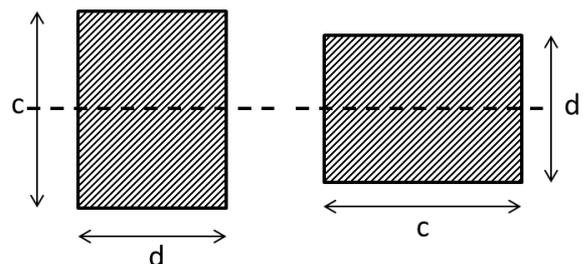
Pure copper has at 20 °C a conductivity of $6.0 \cdot 10^7 (\Omega\text{m})^{-1}$. Pure silver has $6.8 \cdot 10^7 (\Omega\text{m})^{-1}$.

- a. Approximately determine the value for the conductivity of Cu at 170 °C. Explain why the change in conductivity occurs with temperature change. (3 pt)
- b. The Cu is alloyed with 2 at.% Ag. Does the conductivity of the alloy becomes worse or better than the one of pure Cu? Explain your answer. (2 pt)
- c. Intrinsic GaAs has at room temperature a conductivity of $10^{-6} (\Omega\text{m})^{-1}$. The mobility of the electrons and the holes is 0.88 and 0.04 $\text{m}^2/(\text{Vs})$, respectively. The unit charge $e = 1.6 \cdot 10^{-19} \text{ C}$, Avogadro's number $N_{\text{Av}} = 6 \cdot 10^{23} (\text{mole})^{-1}$ and Boltzmann's constant $k = 8.617 \cdot 10^{-5} \text{ eV/K}$. What is the number of conduction electrons and what is the number of holes at room temperature? (3 pt)
- d. Does the conductivity of an intrinsic semiconductor increase or decrease when the temperature is increased? Motivate your answer. (2 pt)

Exercise 3: Materials selection and design (8 pt)

In the figure below a so-called 'Ashby map' is shown, in which the stiffness (Young's modulus E) is plotted versus the density (ρ) for a large number of materials (classes). We want to design an axis of a turbine with a minimum weight. When the axis is loaded in torsion and the design has to be sufficiently stiff, materials with the highest possible value for $E^{0.5}/\rho$ are most suitable. When the axis is loaded in tension, materials with the highest possible value for E/ρ are most suitable. We can choose between aluminum alloys, titanium alloys and steel.

- a. How do the performances of the 3 materials compare for torsional loading? Motivate your answer. (2 pt)
- b. How do the performances of the 3 materials compare for tensile loading? Motivate your answer. (2 pt)
- c. The shape factor for bending is defined as $\phi_B^e = 4\pi I_{xx}/A^2$ with $I_{xx} = \int y^2 dA$ with y the distance to the bending axis and A the cross-sectional area. We have two rectangular cross-sections with the same area as shown on the right, where in both cases the bending axis is oriented horizontal as indicated by the dashed line. Calculate (in terms of dimensions c and d) for both shapes first the second moment of area I_{xx} (in principle you can do this with one calculation) and then the shape factors. Which one of the two has a larger shape factor and is thus more efficient? (4 pt)



Solutions

Exercise 1

a.

$$\begin{aligned} \sigma_{//} &= E \varepsilon_{//} , \quad \varepsilon_{\perp} = -\nu \varepsilon_{//} \\ \text{THUS: } \left. \begin{aligned} \sigma_{//} &= -\frac{E}{\nu} \varepsilon_{\perp} \\ \varepsilon_{\perp} &= \frac{\Delta d}{d_0} \end{aligned} \right\} \Rightarrow \sigma_{//} = -\frac{E}{\nu} \frac{\Delta d}{d_0} \end{aligned}$$

$$\sigma_{//} = -\frac{97 \cdot 10^9}{0.34} \cdot \frac{-5 \cdot 10^{-6}}{20 \cdot 10^{-3}} = 71.32 \cdot 10^6 \text{ Pa} \\ 71.32 \text{ MPa}$$

$\sigma_{//} < 75 \text{ MPa}$ and load is thus ELASTIC

$$\begin{aligned} F &= \sigma_{//} A = \sigma_{//} \frac{\pi}{4} d_0^2 = 71.32 \cdot 10^6 \frac{\pi}{4} (0.020)^2 \\ &= 22406 \text{ N} \\ &(\approx 2240 \text{ kg}) \end{aligned}$$

b. Describe two of the following four methods:

The four different methods are:

1. Strain hardening / Cold work
2. Grain-size reduction (*Korrelverfijning*)
3. Solid-solution hardening
4. Precipitation hardening

With all 4 methods it becomes harder for dislocations to move/glide through the material (particularly metals), i.e. plastic deformation (dislocation mobility) is hindered and thereby the material becomes harder and stronger. With cold work the dislocation density is increased by a deformation process (such as rolling or wire drawing) and therefore dislocations, by mutual repulsion or attraction, will increasingly hamper each other's movements. With grain-size reduction the relative amount of grain boundary area per unit volume is increased and at these boundaries the structure is more disordered, which makes it more difficult for dislocations to continue moving. Grain boundaries act as obstacles for dislocation movement and therefore grain size reduction increases hardness and strength. With solid solution hardening atoms B are added to (dissolved in) the crystals/grains (predominantly) composed out of atoms A. These B atoms do not fit well in the crystal lattice of A and distort it such that dislocation movement on crystal planes becomes less easy. Moreover the B atoms want to couple to the cores of static dislocations such that these dislocations do not want to move. Both effects increase hardness and strength due to solid-solution hardening. Instead of individual atoms it is also possible to exploit a high density of

very small crystals dispersed in other bigger crystals of the material (e.g. small Al₂Cu particles in Al crystals). These small particles are called precipitates. Movement of dislocations is generally not possible through the precipitates and therefore dislocations have to find ways to move around (bypass) the precipitates. This leads to a strong reduction in dislocation mobility and this increases hardness and strength.

Exercise 2

- For pure metals we can assume that the resistivity shows a dependence on (absolute) temperature which is about linear proportional. Room temperature (20 °C) corresponds to about 300 K. When the temperature is increased to 170 °C the increased is thus 150 K and the absolute temperature thus increases with a factor 3/2. The conductivity is 1 over (i.e. reciprocal of) the resistivity. The conductivity thus changes a factor 2/3 and becomes ca. $4 \cdot 10^7 (\Omega\text{m})^{-1}$. It is possible to perform the calculation more accurately, but this does not make much sense, because the directly proportional relation is anyhow an approximation.
- If impurities are added to a pure metal then the conductivity always decreases initially, also when the impurity metal itself in pure form has a much higher conductivity. The reason for the initial decrease is that the impurity atoms distort the crystal lattice of the pure metal. This distortion in return make it harder for the conduction electrons (under influence of the applied electric field) to move smoothly through the crystals. They experience more scattering, resulting in a reduced electron mobility and the conductivity thus reduces.

- In case of conduction in an intrinsic semiconductor: $\sigma = n|e|\mu_e + p|e|\mu_h$ with $n=p$. Therefore it holds:

$$n = p = \frac{\sigma}{|e|(\mu_e + \mu_h)}$$

Filling in the numbers provided yields $n=p=6.79 \cdot 10^{12} \text{m}^{-3}$ (i.e. a number per cubic meter).

- The conductivity increases exponentially. At higher temperature the probability that an electron can jump from the valence band over the bandgap into the conduction band increases exponentially. The numbers of n and p (where it holds $n=p$) in the equation $\sigma = n|e|\mu_e + p|e|\mu_h$ thus increase exponentially with temperature. The mobilities reduce with increasing temperature, but this is a small effect compare to the increase in values for n and p.

Exercise 3

- For torsion it holds that all materials, which are positioned in an 'Ashby map' on a single line with slope ' $E^{0.5}/\rho = \text{constant}$ ', perform equally (well or poor). The more this line is shifted to the upper-left corner in the map, the better the performance of the materials that are positioned on the line. Using this principle, it holds that aluminium (Al ALLOYS not ALUMINAS, because the latter is Al-oxide, which is a ceramic, very brittle and not a construction material) is the best, titanium (Ti ALLOYS) is average and steel (STEELS) performs worst upon torsion loading.

b. For tension it holds that all materials, which are positioned in an 'Ashby map' on a single line with slope $E/\rho = \text{constant}$, perform equally (well or poor). The more this line is shifted to the upper-left corner in the map, the better the performance of the materials that are positioned on the line. Al ALLOYS, Ti ALLOYS en STEELS appear to be positioned more or less on a single line and thus perform more or less equally well.

c. Left section: $I_{xx} = d \int_{-0.5c}^{0.5c} y^2 dy = 2d \int_0^{0.5c} y^2 dy = \frac{1}{12} c^3 d$. Right section is thus: $I_{xx} = \frac{1}{12} cd^3$

Left section $\varnothing_B^e = \frac{4\pi I_{xx}}{A^2} = \frac{4\pi \frac{1}{12} c^3 d}{(cd)^2} = \frac{\pi c}{3 d}$. Right section is thus: $\varnothing_B^e = \frac{\pi d}{3 c}$. Since $c > d$, shape factor of the left section is larger than shape factor of the right section. Left one is thus more efficient. This can be seen directly without any calculation, because left section has more area at larger distance to the bending axis.