1 (1)	Name: ______________ Student code: ________	1 (1)

1.1 Chemical equations: (2 points)

a) **methane:** $CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$

b) **ethane:** $2\ C_2H_6 + 7\ O_2 \longrightarrow 4\ CO_2 + 6\ H_2O$

Thermodynamic data for the equations: (4 points)

$\Delta H^0 = [2 \cdot (-241.8) - 393.5 - (-74.6)]\ \text{kJ mol}^{-1} = -802.5\ \text{kJ mol}^{-1}$

$\Delta S^0 = [2 \cdot (188.8) + 213.8 - 186.3 - 2 \cdot 205.2]\ \text{J mol}^{-1}\ \text{K}^{-1} = -5.3\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta G^0 = -802.5\ \text{kJ mol}^{-1} - 298.15\ \text{K} \cdot (-5.3\ \text{J mol}^{-1}\ \text{K}^{-1}) = -800.9\ \text{kJ mol}^{-1}$

Methane: $\boldsymbol{\Delta H^0} = -802.5\ \text{kJ mol}^{-1}$ $\boldsymbol{\Delta S^0} = -5.3\ \text{J mol}^{-1}\ \text{K}^{-1}$ $\boldsymbol{\Delta G^0} = -800.9\ \text{kJ mol}^{-1}$

$\Delta H^0 = [6 \cdot (-241.8) - 4 \cdot 393.5 - 2 \cdot (-84.0)]\ \text{kJ mol}^{-1} = -2856.8\ \text{kJ mol}^{-1}$

$\Delta S^0 = [6 \cdot 188.8 + 4 \cdot 213.8 - 2 \cdot 229.2 - 7 \cdot 205.2]\ \text{J mol}^{-1}\ \text{K}^{-1} = +93.2\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta G^0 = -2856.8\ \text{kJ mol}^{-1} - 298.15\ \text{K} \cdot (93.2\ \text{J mol}^{-1}\ \text{K}^{-1}) = -2884.6\ \text{kJ mol}^{-1}$

Ethane: $\boldsymbol{\Delta H^0} = -2856.8\ \text{kJ mol}^{-1}$ $\boldsymbol{\Delta S^0} = +93.2\ \text{J mol}^{-1}\ \text{K}^{-1}$ $\boldsymbol{\Delta G^0} = -2884.6\ \text{kJ mol}^{-1}$

1.2 a) Amount of methane and ethane in 1 m³ natural gas: (7 points)
(idea 2 points)

$m = \rho \cdot V = 0.740\ \text{g L}^{-1} \cdot 1000\ \text{L} = 740\ \text{g}$ (1 point)

$M_{av} = \sum_i x(i)M(i) = 0.0024 \cdot 44.01\ \text{g mol}^{-1} + 0.0134 \cdot 28.02\ \text{g mol}^{-1} + 0.9732 \cdot 16.05\ \text{g mol}^{-1} + 0.011 \cdot 30.08\ \text{g mol}^{-1}$

$= 16.43\ \text{g mol}^{-1}$ (2 points)

$n_{tot} = m\ (M_{av})^{-1} = 740\ \text{g} \cdot (16.43\ \text{g/mol})^{-1} = 45.04\ \text{mol}$ (1 point)

$n(i) = x(i) \cdot n_{tot}$

$\boldsymbol{n(CH_4)} = x(CH_4) \cdot n_{tot} = 0.9732 \cdot 45.04\ \text{mol} = 43.83\ \text{mol}$

$\boldsymbol{n(C_2H_6)} = x(C_2H_6) \cdot n_{tot} = 0.0110 \cdot 45.04\ \text{mol} = 0.495\ \text{mol}$ (1 point)

1.2 b) Energy of combustion, deviation: (2 points)

$E_{comb.}(H_2O(g)) = \sum_i n(i)\Delta_c H°(i) = 43.83\ \text{mol} \cdot (-802.5\ \text{kJ mol}^{-1}) + 0.495\ \text{mol} \cdot 0.5 \cdot (-2856.8\ \text{kJ mol}^{-1})$

$= -35881\ \text{kJ}$

$\boldsymbol{E_{comb.}\ (H_2O(g))} = -35881\ \text{kJ}$ (1 point)

Deviation from PUC

$E_{PUC}(H_2O(g)) = 9.981\ \text{kWh m}^{-3} \cdot 1\ \text{m}^3 \cdot 3600\ \text{kJ (kWh)}^{-1} = 35932\ \text{kJ}$

deviation $\Delta E = (E_{comb.}(H_2O(g)) - E_{PUC}(H_2O(g)) \cdot 100\% \cdot [E_{comb.}(H_2O(g))]^{-1}$

$= (35881\ \text{kJ} - 35932\ \text{kJ}) \cdot 100\% \cdot (35881\ \text{kJ})^{-1} = -0.14\%$

deviation = -0.14 % (1 point)

1.3 Energy for heating the water: (**4** points)

Volume of water: $V_{water} = 22.5\ m^3$ (0.5 points)

$n_{water} = V_{water}\ \rho_{water}\ (M_{water})^{-1} = 22.5\ m^3 \cdot 10^6\ g\ m^{-3} \cdot (18.02\ g\ mol^{-1})^{-1} = 1.249 \cdot 10^6\ mol$ (0.5 points)

$E_{water} = n_{water} \cdot C_p \cdot \Delta T = 1.249 \cdot 10^6\ mol \cdot 75.30\ JK^{-1}\ mol^{-1} \cdot 14\ K = 1316\ MJ$ (0.5 points)

E_{water} = 1316 **MJ** (1.5 points)

Energy for heating the air

Volume of the house is: $V_{air} = 15\ m \cdot 8\ m \cdot 3\ m + 0.5 \cdot 15\ m \cdot 8\ m \cdot 2\ m = 480\ m^3$ (1 point)

$n_{air} = pV \cdot (RT)^{-1} = 1.013 \cdot 10^5\ Pa \cdot 480\ m^3 \cdot (8.314\ J\ (K\ mol)^{-1} \cdot 283.15\ K)^{-1} = 2.065 \cdot 10^4\ mol$ (0.5)

$C_p(air) = 0.21 \cdot 29.4\ J\ (K\ mol)^{-1} + 0.79 \cdot 29.1\ J\ (K\ mol)^{-1} = 29.16\ J\ (K\ mol)^{-1}$ (0.5 points)

$E_{air} = n_{air} \cdot C_p(air) \cdot \Delta T = 2.065 \cdot 10^4\ mol \cdot 29.17\ J\ (K\ mol)^{-1} \cdot 20\ K = 12.05\ MJ$ (0.5 points)

E_{air} = 12.05 **MJ** (2.5)

1.4 Energy for maintaining the temperature: (**2** points)

surface area of the house:

$A_{house} = 3\ m \cdot 46\ m + 8\ m \cdot 2\ m + ((2\ m)^2 + (4\ m)^2)^{1/2} \cdot 2 \cdot 15\ m = 288.16\ m^2$ (1 point)

Heat conductivity: $\lambda_{wall} = 1\ J\ (s\ K\ m)^{-1}$

Energy flux along a temperature gradient (wall thickness d = 0.2 m)

$J = E_{loss}\ (A \cdot \Delta t)^{-1} = \lambda_{wall} \cdot \Delta T \cdot d^{-1}$

$E_{loss} = 288.16\ m^2 \cdot (12 \cdot 60 \cdot 60\ s) \cdot 1\ J\ (s\ K\ m)^{-1} \cdot 25\ K \cdot (0.2\ m)^{-1} = 1556\ MJ$ (1 point)

E_{loss} = 1556 MJ

1.5 Total energy and costs: (3 points)

total energy: $E_{tot} = E_{water} + E_{air} + E_{loss}$ = 1316 MJ + 12 MJ + 1556 MJ = 2884 MJ

total energy E_{tot} = 2884 **MJ** (0.5)

2884 MJ corresponds to $2.884 \cdot 10^6$ kJ · (3600 s h^{-1} · 9.981 kJ s^{-1} m^{-3} · 0.9)$^{-1}$ = 89.18 m^3

volume of gas V = 89.18 m^3 (1)

2884 MJ correspond to a cost of:

0.40 €m^{-3} · 89.18 m^3	= 35.67 €
rent for equipment:	150.00 €
total cost of gas heating	= 185.67 € (0.5)

2884 MJ correspond to a cost of

$2.884 \cdot 10^6$ kJ · 0.137 € · (3600 s h^{-1}·1 kJ s^{-1} h)$^{-1}$	= 109.75 €
rent for equipment:	100.00 €
total cost of electric heating	= 209.75 € (1)

2 [1]	Name: ______________________ Student code: ____________	2 [1]

2.1 Reaction equations: (3 points)

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$
$$2\,NO + 2\,CO \longrightarrow N_2 + 2\,CO_2$$
$$2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O$$

2.2 Questions concerning the λ probe: (3 points)

	true	false	no decision possible
If the λ-value is in the range of the λ-window, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.	x	☐	☐
With $\lambda > 1$, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.	x	☐	☐
With $\lambda < 0.975$, nitrogen oxides can be reduced poorly.	☐	x	☐

2.3 a) Surface coverage: (1 point)

$$\theta = \frac{0.85 kPa^{-1} \cdot 0.65 kPa}{1 + 0.85 \cdot 0.65}$$

$\theta = 0.356$ or 35.6 %

2.3 b) Pressure at which 15% of the surface is covered: (2 points)

$$\theta = \frac{K \cdot p}{1 + K \cdot p} \Leftrightarrow K \cdot p = \theta + \theta \cdot K \cdot p \Leftrightarrow p \cdot (K - \theta \cdot K) = \theta \Leftrightarrow p = \frac{\theta}{K - \theta \cdot K}$$ (1 point)

$\theta = 0.15$

p = 0.21 kPa (1 point)

2.3 c) Orders of decomposition: (3 points)

order of the decomposition reaction at low gas pressures	1	(1.5 points)
order of the decomposition reaction at high gas pressures	0	(1.5 points)

notes:

$$r = k \cdot \theta = k \cdot \frac{K \cdot p}{1 + K \cdot p}, \quad p \text{ low} \Rightarrow p << \frac{1}{K} \Rightarrow r = k \cdot K \cdot p \quad \text{reaction order 1.}$$

$$p \text{ high} \Rightarrow p >> \frac{1}{K} \Rightarrow r = k \quad \text{reaction order 0.}$$

2.3 d) Gas volume $V_{a,max}$ and product $K \cdot V_{a,max}$: (4 points)

$$\frac{1}{\theta} = \frac{1}{K \cdot p} + 1 = \frac{V_{a,max}}{V_a} \quad \Rightarrow \quad \frac{1}{K \cdot V_{a,max}} + \frac{p}{V_{a,max}} = \frac{p}{V_a}$$ (2)

slope: $\frac{1}{V_{a,max}} = 1.9\, cm^{-3}$ $\Rightarrow$ $V_{a,max} = 0.53\ cm^3$ (1)

intercept: $\frac{1}{K \cdot V_{a,max}} = 6 \cdot 10^2\ Pa\ cm^{-3}$ $\Rightarrow$ $K \cdot V_{a,max} = 1.7 \cdot 10^{-3}\ Pa^{-1}\ cm^3$ (1)

2.4 Equation for reaction rate: (7 points)

The information given in the text leads directly to $r = k_2 \cdot \theta_{CO_2}$ (2)

The law of mass action for the first step of the mechanism is given by

$\theta_{CO_2} = \frac{k_1}{k_{-1}} \cdot \theta_{co} \cdot \theta_{O_2}^{\frac{1}{2}}$, (2) $\Rightarrow$ $r = k_2 \cdot \frac{k_1}{k_{-1}} \cdot \theta_{co} \cdot \theta_{O_2}^{\frac{1}{2}}$. (1)

The Langmuir isotherm gives:

$$\theta_{CO} = \frac{K_{CO} \cdot p_{CO}}{1 + K_{CO_2} \cdot p_{CO_2} + K_{CO} \cdot p_{CO} + K_{O_2} \cdot p_{O_2}} \quad \text{and} \quad \theta_{O_2} = \frac{K_{O_2} \cdot p_{O_2}}{1 + K_{CO_2} \cdot p_{CO_2} + K_{CO} \cdot p_{CO} + K_{O_2} \cdot p_{O_2}}$$ (1.5)

$$r = k_2 \frac{k_1}{k_{-1}} \frac{K_{CO} \cdot p_{CO} \cdot \left(K_{O_2} \cdot p_{O_2}\right)^{\frac{1}{2}}}{\left(1 + K_{CO_2} \cdot p_{CO_2} + K_{CO} \cdot p_{CO} + K_{O_2} \cdot p_{O_2}\right)^{\frac{3}{2}}}.$$ (0.5)

3_1	**Name:** ______________________ **Student code:** ____________	3_1

3.1 Chemical equations: (3 points)

(a) $CaCl_2 + Ca \longrightarrow 2\ CaCl$

(b) $2\ CaCl_2 + H_2 \longrightarrow 2\ CaCl + 2\ HCl$

(c) $4\ CaCl_2 + C \longrightarrow 4\ CaCl + CCl_4$

3.2 (2 points)

silvery metallic particles: Ca

colorless crystals: $CaCl_2$

Note: CaCl cannot be obtained by a conventional solid state reaction of Ca and $CaCl_2$

3.3 Empirical formula: (4 points)

100 % –(m/m% Ca + m/m% Cl) = m/m% X

100 % –(52.36% + 46.32%) = 1.32% X (1)

mol% of Ca = 52.36 m/m% / M(Ca)
= 52.36 m/m% / 40.08 g mol^{-1}
= 1.31 mol% (0.5)

mol% of Cl = 46.32 m/m% / M (Cl)
= 46.32 m/m% / 35.45 g mol^{-1}
= 1.31 mol% (0.5)

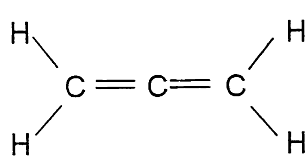
mol% of X = 1.32 % X / M (H)
= 1.32 % X / 1.01 g mol^{-1}
= 1.31 mol% (1)

$n(Ca) : n(Cl) : n(H) = 1 : 1 : 1$

empirical formula CaClH (1)

Notes: The reaction of $CaCl_2$ with hydrogen does not lead to CaCl. The hydride CaClH is formed instead. The structure of this compound was determined by X-ray structure analysis which is not a suitable method to determine the position of light elements like hydrogen. Thus, the presence of hydrogen was missed and CaClH was thought to be CaCl for quite a long time.

3.4 a) Structures only: (2 points)



$H-C\equiv C-CH_3$

3₂	Name: ____________ Student code: ________	3₂

3.4 b) Empirical formula of the compound formed: (2 points)

$Ca_3C_3Cl_2$

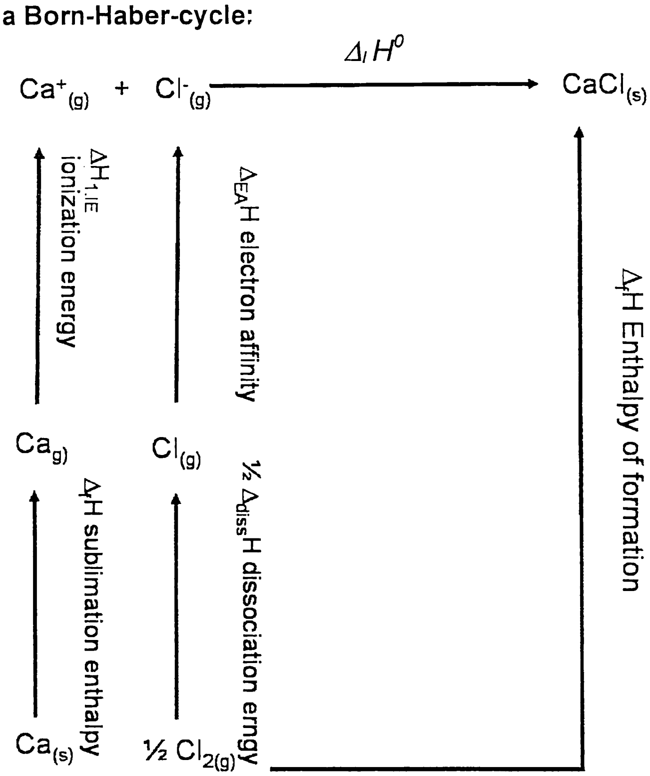
Notes: If the ratio of n(Ca):n(Cl) = 1.5 : 1 [or better = 3 : 2 which can be rewritten as $CaCl_2 \cdot 2Ca^{2+}$ = $Ca_3Cl_2^{4+}$] is given and the reduction product must contain a C_3^{4-} anion which needs two Ca^{2+} cations for electroneutrality, the composition $Ca_3C_3Cl_2$ will follow.

3.5 a) Structure type CaCl likely to have: (1 point)

$r(Ca^+)/r(Cl^-)$ = 120 pm/167 pm = 0.719

NaCl	CsCl	ZnS	BN	no decision possible
x	☐	☐	☐	☐

3.5 b) $\Delta_f H^0$(CaCl) with a Born-Haber-cycle: (5 points)



Summing up of all the single steps of the Born-Haber-cycle:

$\Delta_f H^0$ (CaCl) = $\Delta_{subl}H^0$(Ca) + $\Delta_{1.IE}H$(Ca) + ½ $\Delta_{diss}H(Cl_2)$ + $\Delta_{EA}H$(Cl) + $\Delta_L H$(CaCl)

= (159.3 + 589.7 + 120 - 349.0 - 751.9) kJ mol^{-1}

(1) (0.5) (1) (0.5) (1)

$\Delta_f H^0$**(CaCl)** = -231.9 kJmol^{-1} (1)

3.6 Stability to disproportionation: (2 points)

2 CaCl ⟶ $CaCl_2$ + Ca

$\Delta H = \Delta_f H^0(CaCl_2) - 2\,\Delta_f H^0(CaCl)$ = -796.0 kJ mol^{-1} + 463.8 kJ mol^{-1} = -332.2 kJ mol^{-1} (1)

disproportionation	yes	no	no decision possible, more information needed	
	☐	x	☐	(1)

4₁	**Name:** ____________________ **Student code:** __________	**4**₁

4.1 Atomic mass of X, symbol of X, structures: (7 points)

1) $X + 2\,H_2 \longrightarrow XH_4$ (1)

2) $2\,X + 3\,H_2 \longrightarrow X_2H_6$ (1)

I) $5.0\text{ g} = [n_1(X) + n_2(X)] \cdot M(X)$

II) $5.628\text{ g} = n_1(XH_4) \cdot [M(X) + 4 \cdot 1.01\text{ g mol}^{-1}] + n_2(X_2H_6) \cdot [2M(X) + 6 \cdot 1.01\text{ g mol}^{-1}]$

III) $n_1(XH_4) = 2n_2(X_2H_6)$ (2)

III,I) → I') $2n_1(X) \cdot M(X) = 5.0\text{ g}$

III,II) → II') $n_1(X) \cdot [2M(X) + 7.07\text{ g mol}^{-1}] = 5.628\text{ g}$

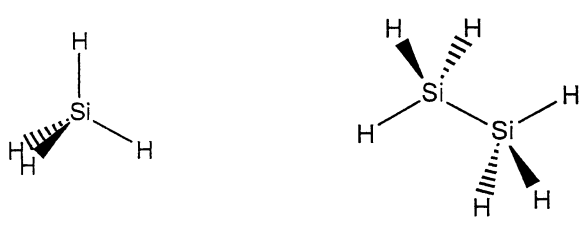
I',II') → VI) $(5.0\text{ g}) \cdot [2M(X)]^{-1} = (5.628\text{ g}) \cdot [2M(X) + 7.07\text{ g mol}^{-1}]^{-1}$ (1)

$M(X) = 3.535\text{ g mol}^{-1} \cdot (5.628\text{ g})^{-1} \cdot [(5.0\text{ g})^{-1} - (5.628\text{ g})^{-1}]^{-1}$

$M(X) = 28.14\text{ g mol}^{-1}$

atomic mass of X $M(X) = 28.14\text{ g mol}^{-1}$ **chemical symbol of X:** Si (1)

3D structures of the two products:



(1)

4$_2$	**Name:** ______________________ **Student code:** ___________	**4**$_2$

4.2 Atomic mass of Y and empirical formula of Argyrodite: (9 points)

$$Ag_aY_bS_{0.5\cdot a+2\cdot b} + b\,H_2 \longrightarrow 0.5a\,Ag_2S + b\,YS + b\,H_2S$$

I) 10 g $= n(Ag_aY_bS_{0.5\cdot a+2\cdot b}) \cdot [a \cdot 107.87\text{ g mol}^{-1} + b\cdot M(Y) + (0.5\cdot a + 2\cdot b)\cdot 32.07\text{ g mol}^{-1}]$ (3)

II) $n(H_2) = \dfrac{p\cdot V(H_2)}{RT}$ $\qquad n(H_2) = \dfrac{100kPa\cdot 0.295\cdot 10^{-3}m^3}{8.314JK^{-1}mol^{-1}\cdot 400K}$

$n(H_2) = 8.871\cdot 10^{-3}$ mol $\qquad n(Ag_aY_bS_{0.5\cdot a+2\cdot b}) = b^{-1}\cdot 8.871\cdot 10^{-3}$ mol (1)

III) $11.88 = \dfrac{a\cdot 107.87gmol^{-1}}{b\cdot M(Y)}$ $\qquad a\cdot 107.87\text{ gmol}^{-1} = 11.88\cdot b\cdot M(Y)$ (1)

II,I) →II') $b\cdot 10\text{ g}\cdot(8.871\cdot 10^{-3}\text{ mol})^{-1} = a\cdot 107.87\text{ g mol}^{-1} + b\cdot M(Y) + (0.5\cdot a + 2b)\cdot 32.07\text{ g mol}^{-1}$

$b\cdot 1127\text{ g mol}^{-1} = a\cdot 107.87\text{ g mol}^{-1} + b\cdot M(Y) + (0.5\cdot a + 2b)\cdot 32.07\text{ g mol}^{-1}$

III,II')→IV) $b\cdot 1127\text{ g mol}^{-1} = 11.88\cdot b\cdot M(Y) + b\cdot M(Y) + (0.5\cdot a + 2b)\cdot 32.07\text{ g mol}^{-1}$

$b\cdot 1127\text{ g mol}^{-1} = 11.88\cdot b\cdot M(Y) + b\cdot M(Y) + (0.5\cdot \dfrac{11.88\cdot b\cdot M(Y)}{107.87gmol^{-1}} + 2b)\cdot 32.07\text{ g mol}^{-1}$

$M(Y) = 72.57\text{ g mol}^{-1}$ (2)

atomic mass **M(Y)** = 72,57 g mol^{-1} (1)

M(Y) = 72.57 g mol^{-1} → III $\qquad$ a:b = 8:1 (1)

chemical symbol of Y: Ge $\qquad$ **empirical formula of Argyrodite:** Ag_8GeS_6

4.3 The force constants of a C-H bond: (1 point)

$$k(\text{C-H}) = [2\pi \cdot c \cdot \tilde{\nu}\,(\text{C-H})]^2 \cdot \frac{1}{N_A} \cdot \frac{3M(C) \cdot M(H)}{3M(C) + 4M(H)}$$

$$= [2\pi \cdot 3 \cdot 10^{10}\ \text{cm} \cdot \text{s}^{-1} \cdot 3030\ \text{cm}^{-1}]^2 \cdot \frac{1}{6.022 \cdot 10^{23}\,mol^{-1}} \cdot \frac{3 \cdot 12.01 \cdot 1.01}{3 \cdot 12.01 + 4 \cdot 1.01} gmol^{-1}$$

$\boldsymbol{k}$**(C-H)** $= 491.94\ \text{N m}^{-1}$

The force constants of a Z-H bond: (1 point)

$$k(\text{Z-H}) = k(\text{C-H}) \cdot \frac{\Delta_b H(Z-H)}{\Delta_b H(C-H)}$$

$$= 491.94\ \text{N m}^{-1} \cdot 450.2\ \text{kJ mol}^{-1} \cdot [438.4\ \text{kJ mol}^{-1}]^{-1}$$

$\boldsymbol{k}$**(Z-H)** $= 505.18\ \text{N m}^{-1}$

The atomic mass and symbol of Z: (2 points)

$$\frac{3M(Z) \cdot M(H)}{3M(Z) + 4M(H)} = \frac{k(Z-H) \cdot N_A}{[2\pi \cdot c \cdot \tilde{\nu}(Z-H)]^2}$$

$$\text{M(Z)} = \frac{4}{3} \cdot \left(\frac{[2\pi \cdot c \cdot \tilde{\nu}(Z-H)]^2}{k(Z-H) \cdot N_A} - \frac{1}{M(H)} \right)^{-1}$$

$$M(\text{Z}) = \frac{4}{3} \cdot \left(\frac{[2\pi \cdot 3 \cdot 10^{10} \cdot 2938.45]^2}{505180 \cdot 6.022 \cdot 10^{23}} - \frac{1}{1.01} \right)^{-1} \text{g mol}^{-1}$$

atomic mass of Z $\boldsymbol{M}$**(Z)** $= 72.68\ \text{g mol}^{-1}$

chemical symbol of Z Ge

Note: Even if the students find different values (± 2) due to different ways of rounding, they will be able to find Ge as Z has to be an analogue of carbon.

5₁	Name: ____________ Student code: __________	5₁

5.1 Actual $\Delta G'$ of reaction (1): (2 points)

$$\Delta G' = \Delta G^{\circ\prime} + RT \ln \frac{c(ADP^{3-})/(1\ mol L^{-1}) \cdot c(HPO_4^{2-})/(1\ mol L^{-1})}{c(ATP^{4-})/(1\ mol L^{-1})} \quad (0.5)$$

$= -30500\ J\ mol^{-1} + 8.314\ J\ mol^{-1}\ K^{-1} \cdot 298.15\ K \cdot \ln(0.00025 \cdot 0.00165 / 0.00225)$ (1)

$= -30.5\ kJ\ mol^{-1} - 21.3\ kJ\ mol^{-1}$

$= -51.8\ kJ\ mol^{-1}$ (0.5)

$\Delta G'$= $-51.8\ kJ\ mol^{-1}$

5.2 Equilibrium constant *K'* of reaction (2), ratio *c*(glucose 6-phosphate) / *c*(glucose): (3 points)

$\Delta G^{\circ\prime} = -RT \cdot \ln K'$ (0.5)

$K' = e^{-\Delta G^{\circ\prime}/RT}$ (0.5)

$= e^{-13800\ J/mol\ /\ (8.314\ J/(mol\ K) \cdot 298.15\ K)}$

$= 0.0038$ (0.5)

$$K' = \frac{c(\text{glucose 6-phosphate})/(1\ mol\ L^{-1})}{c(\text{glucose})/(1\ mol\ L^{-1}) \cdot c(HPO_4^{2-})/(1\ mol\ L^{-1})} \quad (0.5)$$

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = K' \cdot c(HPO_4^{2-}) \cdot (1\ mol\ L^{-1})^{-1} \quad (0.5)$$

$= 0.0038 \cdot 0.00165$

$= 6.3 \cdot 10^{-6}$ (0.5)

K' = 0.0038 (Σ 1.5)

$$\frac{\textbf{c(glucose 6-phosphate)}}{\textbf{c(glucose)}} = 6.3 \cdot 10^{-6}$$ (Σ 1.5)

5.3 $\Delta G°'$ and K' of reaction (3), ratio c(glucose 6-phosphate) / c(glucose): (4 points)

$$\Delta G°'(3) = \Delta G°'(1) + \Delta G°'(2)$$ (0.5)
$$= -30.5\ \text{kJ mol}^{-1} + 13.8\ \text{kJ mol}^{-1}$$
$$= -16.7\ \text{kJ mol}^{-1}$$ (0.5)

$$\Delta G°' = -RT \cdot \ln K'$$ (0.5)
$$K' = e^{-\Delta G°'/RT}$$
$$= e^{16700\ \text{J/mol} / (8.314\ \text{J/(mol K)} \cdot 298.15\ \text{K})}$$ (0.5)
$$= 843$$ (0.5)

$$K' = \frac{c(\text{glucose 6-phosphate}) \cdot c(ADP^{3-})}{c(\text{glucose}) \cdot c(ATP^{4-})}$$ (0.5)

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = K' \cdot \frac{c(ATP^{4-})}{c(ADP^{3-})}$$ (0.5)
$$= 843 \cdot 2.25\ \text{mmol L}^{-1} / 0.25\ \text{mmol L}^{-1}$$
$$= 7587$$ (0.5)

$\Delta G°' = -16.7$ kJ mol^{-1} (Σ 1) **K'** = 843 (Σ 1.5) $\frac{\text{c(glucose 6-phosphate)}}{\text{c(glucose)}} = 7587$ (Σ 1.5)

5.4 a) Mass of ATP produced per day: (2 points)

Energy available for ATP synthesis: 8000 kJ day^{-1} · 0.5 = 4000 kJ day^{-1} (0.5)
Energy required for synthesis of ATP: 52 kJ mol^{-1}
Amount of ATP produced: 4000 kJ day^{-1} / 52 kJ mol^{-1} = 76.9 mol day^{-1} (0.5)
Mass of ATP produced: 76.9 mol day^{-1}· 503 g mol^{-1} = 38700 g day^{-1} = 38.7 kg day^{-1} (1)

$m_{day^{-1}}$ = 38.7 kg day^{-1}

5.4 b) Mass of ATP in the human body: (1 points)

Average lifetime: 1 day = 1440 min 1 min = 1440^{-1} day (0.5)
Mass of ATP in the body: 38.7 kg day^{-1}/(1440 min day^{-1}) · 1 min = 26.9 g (0.5)

m_{body} = 26.9 g

5.4 c) What happens to the rest of the free energy? Mark one correct answer: (2 points)

It is used to reduce the entropy of the body. ☐

It is released from the body in the O-H bonds of the water molecule and the C=O bonds of the carbon dioxide molecule. ☐

It is used to regenerate the state of the enzymes which act as catalysts in the production of ATP. ☐

It heats the body of the person. x

5.5 a) How many protons are in a spherical mitochondrium with a diameter of 1 μm at pH=7? (2 points)

$V = 4/3\ \pi r^3$

$= 4/3\ \pi\ (0.5 \cdot 10^{-6}\ m)^3$

$= 5.2 \cdot 10^{-19}\ m^3 \quad = 5.2 \cdot 10^{-16}\ L$ (0.5)

$c = 10^{-7}\ mol\ L^{-1}$ (0.5)

$n = V \cdot c \cdot N_A$ (0.5)

$= 5.2 \cdot 10^{-16}\ L \cdot 10^{-7}\ mol\ L^{-1} \cdot 6.022 \cdot 10^{23}\ mol^{-1} = 31$ (0.5)

n = 31

5.5 b) How many protons have to enter a mitochondrium? (2 points)

Number of ATP molecules:

$$n(ATP) = \frac{m(ATP) \cdot N_A}{M(ATP)} = \frac{0.2 \cdot 10^{-15} g \cdot 6.022 \cdot 10^{23} mol^{-1}}{503\ g\ mol^{-1}} = 239400$$ (1)

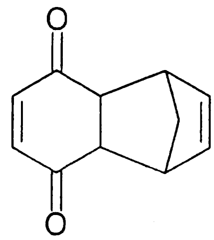
Number of H^+ per cell $\quad n(H^+_{per\ cell}) = n(ATP) \cdot 3 = 718300$ (0.5)

Number of H^+ per mitochondrium: $n(H^+_{mit}) = n(H^+_{per\ cell}) / 1000 = 718$ (0.5)

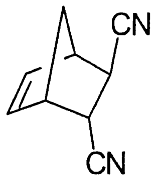
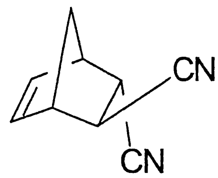
$n(H^+_{mit}) = 718$

6₁	Name: ______________________ Student code: ___________	6₁

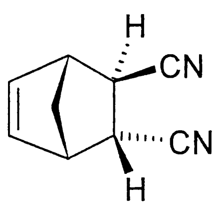
6.1 Structure of A only: (2 points)

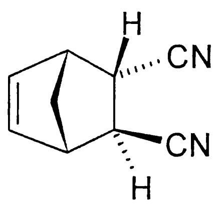
[A]: 

6.2 Structures of D1, D2 only: (2 points)

D1:  (1) **D2:**  (1)

alternatively, the following structures are also correct:





Note: The two compounds are enantiomers

6.3 Correct structure of B (circle only one): (4 points)

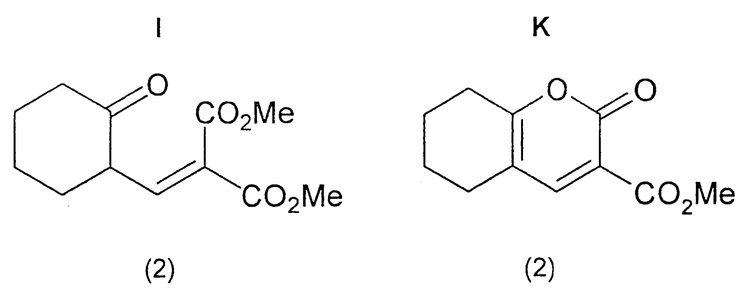
1 **[2]** **3** **4** **5** **6**

Notes: The Diels-Alder reaction gives products with an endo-stereochemistry. The preference of this configuration was outlined in problem 6.2, structure **C**. *As shown in structure* **C** *this endo-configuration is characterized by the two H atoms and the* CH_2*-bridge of the bicyclic system being on the same side of the ring. Only structures* **1** *and* **2** *of the six stereoisomers have an endo,endo stereochemistry. All other isomers have at least one exo configuration. In structure* **1** *the three rings form a U-shaped molecule which is sterically more hindered than structure* **2** *which has a zig-zag structure.*
2 points are given for answer 1.

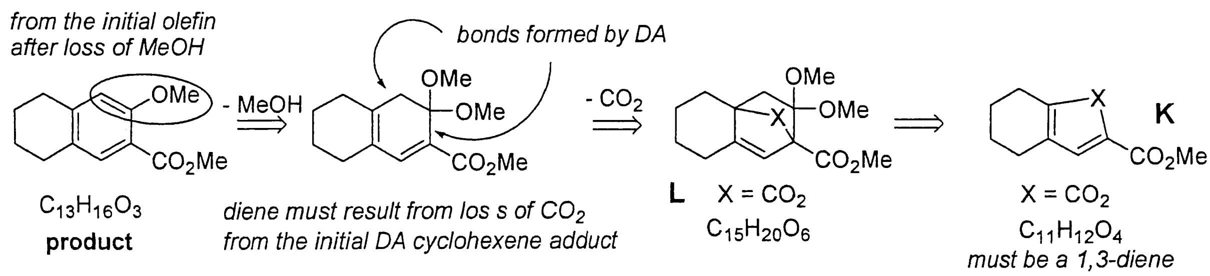
6.4 Decide the questions concerning the Diels-Alder reaction. (6 points)

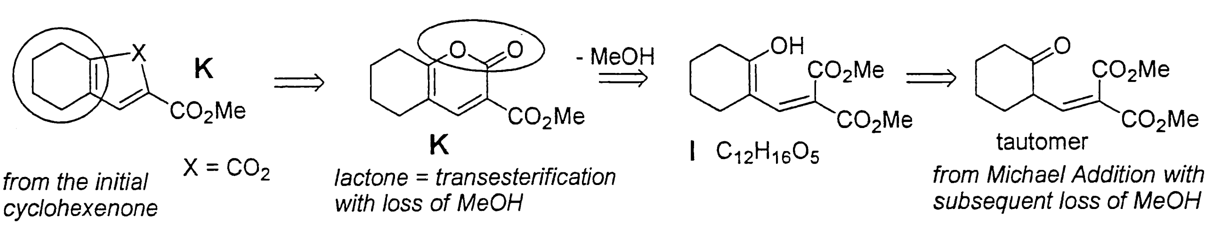
	true	false	no decision possible
The Diels-Alder reaction is reversible	x	☐	☐
The formation of B in the original reaction is thermodynamically controlled	☐	x	☐
B is thermodynamically more stable than E	☐	x	☐
E is thermodynamically less stable than F	x	☐	☐
G is an enantiomer of B	☐	x	☐
G is thermodynamically more stable than F	☐	☐	x

6.5 Structures of I, K, L only: (6 points)



Notes:





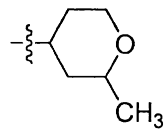
Name: ____________________

Student code: ____________

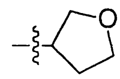
7 1

7.1 Fill in < or > (A < B means A has a priority lower than B) : (3 points)

-§-SCH_3 [>] -§-$P(CH_3)_2$



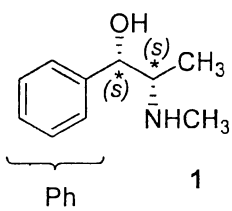
[<]



-§-CCl_3 [<] -§-CH_2Br

1 point each

7.2 (4 points)



1

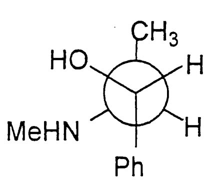
* : 0.25 points each
S: 0.75 points each
Σ: 2 points

highest priority → **lowest priority**

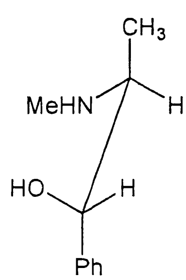
OH	$CH(NHCH_3)CH_3$	Ph	H	(1)
$NHCH_3$	$CH(OH)Ph$	CH_3	H	(1)

(Penalty: each wrongly indicated stereocenter, minus 0.5 point)

7.3 Newman projection or sawhorse projection of 1:



or

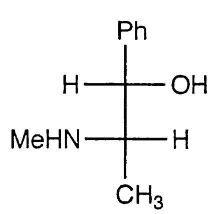


(Me = CH_3)

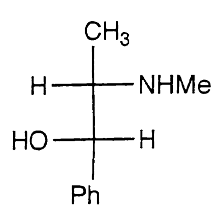
0.5 points for each correct stereocenter.

(1 point)

Fischer projection of 1:



or

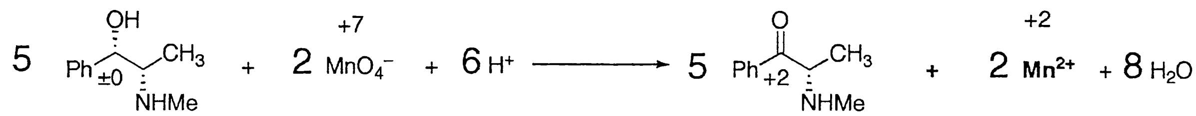


(Me = CH_3)

1 point for each correct stereocenter. Any projection which shows the correct stereo-center is accepted. (2 points)

7 [2]	Name: ____________________ Student code: ____________	7 [2]

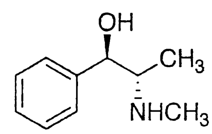
7.4 Equation with oxidation numbers and stereochemically correct structure of 2: (**4** points)



1 **2**

1 point for structure **2**, 1 point for stoichiometry, 2 points for oxidation numbers (0.5 points for each)

7.5a) Structure of 3 (correct stereochemistry): (**2** points)



1 point for correct formula, 1 point for correct stereochemistry

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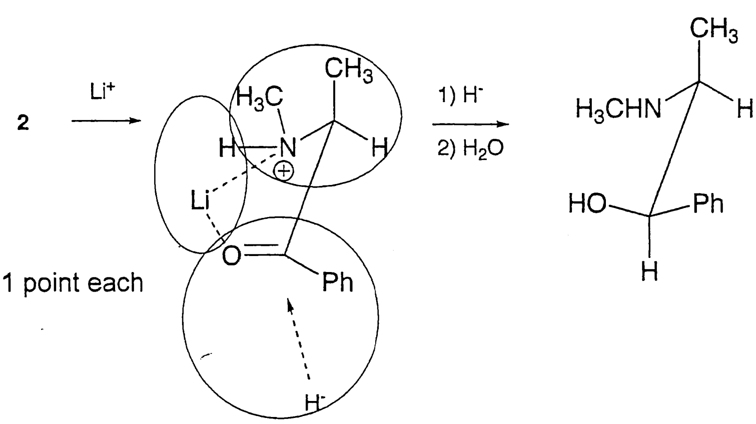
7.5b) Statements concerning isomers: (**2** points)

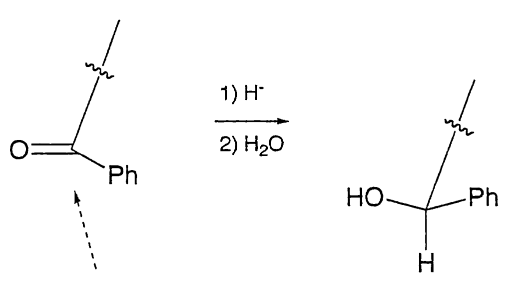
	true	false	
1 and **3** are stereo-isomers	x	☐	
1 and **3** are enantiomers	☐	x	
1 and **3** are diastereomers	x	☐	
1 and **3** are conformational isomers	☐	x	0.5 points each

7.5c) Draw a structural model to rationalize the exclusive formation of 3 from 2 (**3** points)



1 point each

Notes: Attack of hydride occurs from the sterically least hindered side.
Full points will also be given for an explanation using the formation of a hydrogen bond.
1 point will be given for any representation indicating the attack of hydride on the correct face of the carbonyl group, i.e.



8.1 pH of solution B: (3 points)

$K_{b2} = \frac{c(HCO_3^-)/(1\ mol\ L^{-1}) \cdot c(OH^-)/(1\ mol\ L^{-1})}{c(CO_3^{2-})/(1\ mol\ L^{-1})}$ (1) $K_{b2} = \frac{10^{-14}}{10^{-10.33}}$

$K_{b2} = 2.14 \cdot 10^{-4}$ $K_{b1} = 2.34 \cdot 10^{-8}$

Since $K_{b2} >> K_{b1}$, only one protonation step of the CO_3^{2-} has to be considered.

$c(HCO_3^-) = c(OH^-) = x$ and $c(CO_3^{2-}) = c_0(CO_3^{2-}) - x$

$c_0(Na_2CO_3) = \frac{1.700\ g\ L^{-1}}{105.99\ g\ mol^{-1}}$ $c_0(Na_2CO_3) = c_0(CO_3^{2-}) = 0.016\ mol\ L^{-1}$ (0.5)

$K_{b2} = \frac{x^2/(1\ mol\ L^{-1})}{(c_0(CO_3^{2-}) - x)}$ (1) $x = c(OH^-) = 1.75 \cdot 10^{-3}\ mol\ L^{-1}$

Solving equation: 0.5 points

pH = 11.2

8.2 $Ca(OH)_2$, $CaCO_3$ in the precipitate? (6 points)

$M(CaCl_2) = 110.98\ g\ mol^{-1}$ pH = 10 , $c(OH^-) = 10^{-4}\ mol\ L^{-1}$ (0.5)

$c_0(Na_2CO_3) = \frac{1.700\ g\ L^{-1}}{105.99\ g\ mol^{-1} \cdot 2}$ $c(CaCl_2) = \frac{1.780\ g\ L^{-1}}{110.98\ g\ mol^{-1} \cdot 2}$

$c_0(Na_2CO_3) = 8.0 \cdot 10^{-3}\ mol\ L^{-1}$ (0.5) $c(CaCl_2) = c_0(Ca^{2+}) = 8.0 \cdot 10^{-3}\ mol\ L^{-1}$ (0.5)

Calculations for $Ca(OH)_2$:

$c(OH^-)^2 \cdot c_0(Ca^{2+}) = 8 \cdot 10^{-11}\ mol^3\ L^{-3} < 6.46 \cdot 10^{-6}\ mol^3\ L^{-3} = K_{sp}(Ca(OH)_2)$ no precipitate

(1) (0.5)

Calculations for $CaCO_3$:

(regarding proteolysis: 1 point)

$K_{b2} = \frac{c(HCO_3^-) \cdot c(OH^-)}{c(CO_3^{2-})}$, $c(HCO_3^-) = \frac{K_{b2}}{c(OH^-)} \cdot c(CO_3^{2-})$

$c(HCO_3^-) = 2.14 \cdot c(CO_3^{2-})$ and $c(HCO_3^-) + c(CO_3^{2-}) = c_0(Na_2CO_3)$

$2.14 \cdot c(CO_3^{2-}) + c(CO_3^{2-}) = 8.0 \cdot 10^{-3}\ mol\ L^{-1}$ (1)

Initial concentration of CO_3^{2-} in solution C: $c(CO_3^{2-}) = 2.55 \cdot 10^{-3}\ mol\ L^{-1}$ (0.5)

Initial concentration of Ca^{2+} in solution C: $c(Ca^{2+}) = 8.0 \cdot 10^{-3}\ mol\ L^{-1}$

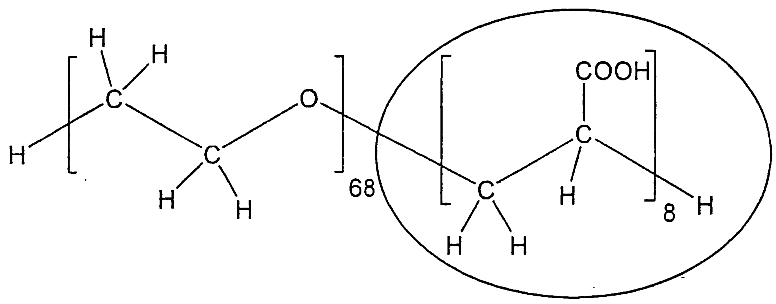
hence $c(CO_3^{2-}) \cdot c(Ca^{2+}) = 2.04 \cdot 10^{-5}\ mol^2\ L^{-2} > 3.31 \cdot 10^{-9}\ mol^2\ L^{-2} = K_{sp}(CaCO_3)$ precipitate

(0.5)

$Ca(OH)_2$ will be found in the precipitate **yes** ☐ **no** x

$CaCO_3$ will be found in the precipitate **yes** x **no** ☐

8.3 Circle the block that attaches to the $CaCO_3$ crystal: (1 point)



Notes: Both polymer blocks are hydrophilic. The acrylic acid block will preferably bind to the crystal since it is more polarized and additionally charged. The polymer binds to the surface at positions where there is an excess of calcium ions on the surface of the ionic crystal.

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles? (7 points)

$$RCOOH + OH^- \rightleftharpoons RCOO^- + H_2O \qquad pK_b = 9.12$$

pH and pK_a lead to the total concentration of COOH groups in the solution: (1)

$c(COO^-) = x$ $\quad c(COOH) = c_0(COOH) - x$ $\quad x = c_0(OH^-) - c(OH^-)$ (1)

$c_0(OH^-) = \frac{50\ mL}{250\ mL} 0.19\ mol\ L^{-1}$ $\quad c_0(OH^-) = 0.038\ mol\ L^{-1}$

$c(OH^-) = 10^{-1.7}\ mol\ L^{-1} = 0.02\ mol\ L^{-1}$ (0.5) $\quad x = 0.018\ mol\ L^{-1}$ (0.5)

$$K_b = \frac{(c_0(COOH) - x)/(1\ mol\ L^{-1}) \cdot c(OH^-)/(1\ mol\ L^{-1})}{x/(1\ mol\ L^{-1})}$$

$c_0(COOH) = \frac{K_b x \cdot (1\ mol\ L^{-1})}{c(OH^-)} + x$ (1) $\quad c_0(COOH) = \left(\frac{0.018 \cdot 10^{-9.12}}{0.02} + 0.018\right) mol \cdot L^{-1}$

$c_0(COOH) = 0.018\ mol \cdot L^{-1}$

(Or as pH >> pK_a: $c_0(COOH) = c(COOH) + x \approx x$)

(calculate polymer mass from $c_0(COOH)$: 0.5 point)

Total concentration of polymer chains $\quad c(polymer) = \frac{c_0(COOH)}{8}$ (0.5)

$M(polymer) = M(C_{160}O_{84}H_{306}) = 3574.66\ g\ mol^{-1}$

(0.5) (0.5)

$m(polymer) = c(polymer) \cdot V \cdot M(polymer)$ (0.5)

$m(polymer) = \frac{c_0(COOH) \cdot V \cdot M(polymer)}{8} = \frac{0.018 \cdot 0.250 \cdot 3574.66}{8} g = 2.0\ g$ (0.5)

8$_3$	Name: ______________ Student code: __________	8$_3$

8.5 Modification of $CaCO_3$: (**5** points)

The charge of the particles is caused by the number of protolized COOH groups per particle.
$c(COO^-) \approx c_0(COOH)$, $\alpha \approx 1$

Number of COOH groups per particle: $N_{COOH} = \frac{|Z|}{\alpha}$ $N_{COOH} = 800$ (1)

Number of polymer chains per particle: : $N_{polymer} = \frac{N_{COOH}}{8} = 100$ (1)

The number of polymers per particle indicates the mass of polymer per particle. Thus, the mass of the calcium carbonate particle can be calculated:

$M(CaCO_3\text{ particle}) = M(\text{total particle}) - N_{polymer} \cdot M(\text{polymer})$ (1)

$M(CaCO_3\text{ particle}) = 8.01 \cdot 10^8 \text{ g mol}^{-1} - 100 \cdot 3574.66 \text{ g mol}^{-1}$

$M(CaCO_3\text{ particle}) = 8.01 \cdot 10^8 \text{ g mol}^{-1}$

Mass of one $CaCO_3$ particle: $m(CaCO_3\text{particle}) = M(CaCO_3\text{ particle}) \cdot N_A^{-1}$ (0.5)

and with the volume of the spherical particle ($V = \frac{4}{3} \cdot \pi \cdot r^3$) the density can be calculated:

$$\rho(CaCO_3) = \frac{m(CaCO_3\ particle)}{V(CaCO_3\ particle)} = \frac{3 \cdot m(CaCO_3\ particle)}{4\pi \cdot r^3} \quad (1)$$

$$= \frac{3(M\ (total\ particle) - N_{polymer} \cdot M(polymer))}{N_a \cdot 4\pi \cdot r^3}$$

$$= \frac{3 \cdot 8.01 \cdot 10^8\ g\ mol^{-1}}{N_A \cdot 4\pi\ (5 \cdot 10^{-6} cm)^3} = 2.54 \text{ g cm}^{-3} \quad (0.5)$$

The modification of calcium carbonate is **Calcite** ☐ **Vaterite** x **Aragonite** ☐