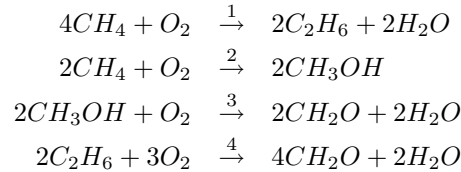


The **bold sans-serif** texts are the problems as given.

1 Stoichiometry

Problem 1

Consider the following set of reactions



(a) **Show, that there are 3 key components within the system!**

The number of key components is the number of species minus rank of the element species matrix.

$$N_{species} - Rg(\underline{B}) = N_{kc}$$

First build the element species matrix:

$$\underline{B} = \left(\begin{array}{c|cccccc} & CH_4 & O_2 & C_2H_6 & H_2O & CH_3OH & CH_2O \\ \hline C & 1 & 0 & 2 & 0 & 1 & 1 \\ O & 0 & 2 & 0 & 1 & 1 & 1 \\ H & 4 & 0 & 6 & 2 & 4 & 2 \end{array} \right)$$

Calculate its rank using the Gauss method:

$$\underline{B} = \left(\begin{array}{cccccc} 1 & 0 & 2 & 0 & 1 & 1 \\ 0 & 2 & 0 & 1 & 1 & 1 \\ 4 & 0 & 6 & 2 & 4 & 2 \end{array} \right) = \left(\begin{array}{cccccc} 1 & 0 & 2 & 0 & 1 & 1 \\ 0 & 2 & 0 & 1 & 1 & 1 \\ 0 & 0 & -2 & 2 & 0 & -2 \end{array} \right)$$

This shows we have 3 linearly independent equations, that is $Rg(\underline{B}) = 3 = N_{nkc}$ (number of non-key components)

$$N_{species} - N_{nkc} = N_{kc} = 6 - 3 = 3$$

The number of key components is 3.

(b) **For the chosen key components CH_4 , O_2 and C_2H_6 the following changes in amount of substance have been measured:**

$$\Delta n_{CH_4} = -8mol, \quad \Delta n_{O_2} = -12mol, \quad \Delta n_{C_2H_6} = 3mol$$

Calculate the changes in amount of substance of the non-key components using the element species matrix!

This can be solved by using the relation:

$$\begin{aligned} \underline{B} \cdot \Delta n &= 0 \\ &= \left(\begin{array}{cccccc} 1 & 0 & 2 & 0 & 1 & 1 \\ 0 & 2 & 0 & 1 & 1 & 1 \\ 4 & 0 & 6 & 2 & 4 & 2 \end{array} \right) \cdot \left(\begin{array}{c} \Delta n_{CH_4} \\ \Delta n_{O_2} \\ \Delta n_{C_2H_6} \\ \Delta n_{H_2O} \\ \Delta n_{CH_3OH} \\ \Delta n_{CH_2O} \end{array} \right) \\ &= \left(\begin{array}{cccccc} 1 & 0 & 2 & 0 & 1 & 1 \\ 0 & 2 & 0 & 1 & 1 & 1 \\ 4 & 0 & 6 & 2 & 4 & 2 \end{array} \right) \cdot \left(\begin{array}{c} -8mol \\ -12mol \\ 3mol \\ \Delta n_{H_2O} \\ \Delta n_{CH_3OH} \\ \Delta n_{CH_2O} \end{array} \right) \end{aligned}$$

Now splitting this into equations of an equation system ...

$$\begin{aligned} -8\text{mol} + 2 \cdot 3\text{mol} + \Delta n_{\text{CH}_3\text{OH}} + \Delta n_{\text{CH}_2\text{O}} &= 0 \\ 2 \cdot -12\text{mol} + \Delta n_{\text{H}_2\text{O}} + \Delta n_{\text{CH}_3\text{OH}} + \Delta n_{\text{CH}_2\text{O}} &= 0 \\ 4 \cdot -8\text{mol} + 6 \cdot 3\text{mol} + 2\Delta n_{\text{H}_2\text{O}} + 4\Delta n_{\text{CH}_3\text{OH}} + 2\Delta n_{\text{CH}_2\text{O}} &= 0 \end{aligned}$$

... one can solve the system. Rearranging gives:

$$\begin{aligned} \Delta n_{\text{CH}_3\text{OH}} + \Delta n_{\text{CH}_2\text{O}} &= 2 \\ \Delta n_{\text{H}_2\text{O}} + \Delta n_{\text{CH}_3\text{OH}} + \Delta n_{\text{CH}_2\text{O}} &= 24 \\ 2\Delta n_{\text{H}_2\text{O}} + 4\Delta n_{\text{CH}_3\text{OH}} + 2\Delta n_{\text{CH}_2\text{O}} &= 14 \end{aligned}$$

This can be written as a matrix again which makes it easier to solve it by using the Gauss method:

$$\begin{pmatrix} 0 & 1 & 1 & 2 \\ 1 & 1 & 1 & 24 \\ 2 & 4 & 2 & 14 \end{pmatrix} \rightsquigarrow \begin{pmatrix} 1 & 1 & 1 & 24 \\ 0 & 1 & 1 & 2 \\ 0 & 2 & 0 & -34 \end{pmatrix}$$

This gives:

$$\begin{aligned} 2\Delta n_{\text{CH}_3\text{OH}} &= -34\text{mol} \rightsquigarrow \Delta n_{\text{CH}_3\text{OH}} = -17\text{mol} \\ -17\text{mol} + \Delta n_{\text{CH}_2\text{O}} &= 2 \rightsquigarrow \Delta n_{\text{CH}_2\text{O}} = 19\text{mol} \\ \Delta n_{\text{H}_2\text{O}} - 17\text{mol} + 19 &= 24 \rightsquigarrow \Delta n_{\text{H}_2\text{O}} = 22\text{mol} \end{aligned}$$

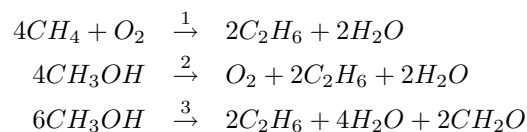
(c) Calculate the number of key reactions and give a set of them!

To do this, we need to write the given reactions in matrix form. Note: The stoichiometric coefficients on the left are to be negated!

The Gauss method is used again to calculate the rank of the matrix.

$$\begin{aligned} \underline{N}^T &= \left(\begin{array}{c|cccccc} & \text{CH}_4 & \text{O}_2 & \text{C}_2\text{H}_6 & \text{H}_2\text{O} & \text{CH}_3\text{OH} & \text{CH}_2\text{O} \\ \hline I & -4 & -1 & 2 & 2 & 0 & 0 \\ II & -2 & -1 & 0 & 0 & 2 & 0 \\ III & 0 & -1 & 0 & 2 & -2 & 2 \\ IV & 0 & -3 & -2 & 2 & 0 & 4 \end{array} \right) \\ &= \begin{pmatrix} -4 & -1 & 2 & 2 & 0 & 0 \\ 0 & 1 & 2 & 2 & -4 & 0 \\ 0 & -1 & 0 & 2 & -2 & 2 \\ 0 & -3 & -2 & 2 & 0 & 4 \end{pmatrix} = \begin{pmatrix} -4 & -1 & 2 & 2 & 0 & 0 \\ 0 & 1 & 2 & 2 & -4 & 0 \\ 0 & 0 & 2 & 4 & -6 & 2 \\ 0 & 0 & 4 & 8 & -12 & 4 \end{pmatrix} \\ &= \begin{pmatrix} -4 & -1 & 2 & 2 & 0 & 0 \\ 0 & 1 & 2 & 2 & -4 & 0 \\ 0 & 0 & 2 & 4 & -6 & 2 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

This shows us, that $Rg(\underline{N}^T) = 3 \rightsquigarrow$ hence we have 3 key reactions. We will build them from the last step of the Gauss elimination (negative ν on the left and positive on the right side).



(d) Calculate the extents of reaction with the changes in amount of substance given in (1b) and use them to determine again the changes in number of moles of the non-key components!

We know the relation $\underline{N} \cdot \underline{\xi}_j = \underline{\Delta n}_i$ and use the transposed matrix from (1c) skipping the 4th reaction which had been found to be linearly dependent with reaction 3. Since $\underline{N}^{TT} = \underline{N}$ we can use it.

$$\underline{N} \cdot \underline{\xi}_j = \begin{pmatrix} -4 & -2 & 0 \\ -1 & -1 & -1 \\ 2 & 0 & 0 \\ 2 & 0 & 2 \\ 0 & 2 & -2 \\ 0 & 0 & 2 \end{pmatrix} \cdot \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix} = \begin{pmatrix} -8mol \\ -12mol \\ 3mol \\ \Delta n_4 \\ \Delta n_5 \\ \Delta n_6 \end{pmatrix}$$

Now writing this as an equation system in matrix form, we get:

$$\begin{pmatrix} -4 & -2 & 0 & -8 \\ -1 & -1 & -1 & -12 \\ 2 & 0 & 0 & 3 \\ 2 & 0 & 2 & \Delta n_4 \\ 0 & 2 & -2 & \Delta n_5 \\ 0 & 0 & 2 & \Delta n_6 \end{pmatrix} = \begin{pmatrix} \underline{N}_1 \\ \underline{N}_2 \end{pmatrix}$$

Let's now split the matrix into the upper three ($N_1 \rightsquigarrow$ key components) and the lower three ($N_2 \rightsquigarrow$ non-key components) matrices. Of which the latter one needs to be calculated. Since it is possibly easier to read, let's write

$$\underline{N}_1 = \begin{pmatrix} -4 & -2 & 0 & -8 \\ -1 & -1 & -1 & -12 \\ 2 & 0 & 0 & 3 \end{pmatrix} \rightsquigarrow \begin{cases} -4\xi_1 - 2\xi_2 = -8 \\ -1\xi_1 - 1\xi_2 - 1\xi_3 = -12 \\ 2\xi_1 = 3 \end{cases}$$

One can easily see the first solution and the other solutions just depend on that first one:

$$\begin{aligned} 2\xi_1 = 3 &\rightsquigarrow \xi_1 = 1,5 \\ -4 \cdot 1,5 - 2\xi_2 = -8 &\rightsquigarrow \xi_2 = 1 \\ -1 \cdot 1,5 - 1 - 1\xi_3 = -12 &\rightsquigarrow \xi_3 = 9,5 \end{aligned}$$

Now it is easy to re-calculate the 3 non-key components again, using \underline{N}_2 .

$$\begin{aligned} 2 \cdot 1,5 + 2 \cdot 9,5 &= \Delta n_4 \rightsquigarrow \Delta n_4 = 22mol \\ 2 \cdot 1 - 2 \cdot 9,5 &= \Delta n_5 \rightsquigarrow \Delta n_5 = -17mol \\ 2 \cdot 9,5 &= \Delta n_6 \rightsquigarrow \Delta n_6 = 19mol \end{aligned}$$

Since this is the same result as above, we are done ;-)

Problem 2

An unknown system with the species CH_3OH , O_2 , CH_2O , H_2O and CO is investigated.

(a) For the so-called formula conversion $\Delta n_{ij} = \nu_{ij}$ the following formula is valid

$$\underline{B} \cdot \underline{N} = 0$$

Assume the number of key reactions and key components being equal and give a set of key reactions!

NOTE: Choose the stoichiometric coefficients of your chosen key components in such a way, that there is only one key component left in each equation!

First let's set up the element species matrix and determine its rank:

$$\begin{aligned} \underline{B} &= \left(\begin{array}{c|ccccc} & CH_3OH & O_2 & CH_2O & H_2O & CO \\ \hline C & 1 & 0 & 1 & 0 & 1 \\ O & 1 & 2 & 1 & 1 & 1 \\ H & 4 & 0 & 2 & 2 & 0 \end{array} \right) \\ &= \begin{pmatrix} 1 & 0 & 1 & 0 & 1 \\ 0 & 2 & 0 & 1 & 0 \\ 0 & 0 & -2 & 2 & -4 \end{pmatrix} \end{aligned}$$

Hence $Rg(\underline{B}) = 3$ and therefore we have 2 key components ($N_c - Rg(\underline{B}) = N_{kc}$). Now we build up \underline{N} , which yields:

$$\begin{aligned} \underline{B} \cdot \underline{N} &= 0 \\ &= \underline{B} \cdot \begin{pmatrix} \nu_{1,1} & \nu_{1,2} \\ \nu_{2,1} & \nu_{2,2} \\ \nu_{3,1} & \nu_{3,2} \\ \nu_{4,1} & \nu_{4,2} \\ \nu_{5,1} & \nu_{5,2} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 & 0 & 1 \\ 0 & 2 & 0 & 1 & 0 \\ 4 & 0 & 2 & 2 & 0 \end{pmatrix} \cdot \begin{pmatrix} \nu_{1,1} & \nu_{1,2} \\ 1 & 0 \\ \nu_{3,1} & \nu_{3,2} \\ \nu_{4,1} & \nu_{4,2} \\ 0 & 1 \end{pmatrix} \end{aligned}$$

The choice for $\nu_{2,1}$, $\nu_{2,2}$, $\nu_{5,1}$ and $\nu_{5,2}$ is done because of the condition that each key component shall only appear once per key reaction.

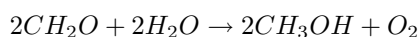
We now split the problem into two parts (one per reaction) - and we also use the matrix (\underline{B}) we got by using the Gauss method (this allowed because the matrix is the same anyway, it just looks differently - sure, one could also take the original matrix, but this would require more work):

$$\begin{aligned} \underline{B} \cdot \underline{N}_1 &= \begin{pmatrix} 1 & 0 & 1 & 0 & 1 \\ 0 & 2 & 0 & 1 & 0 \\ 0 & 0 & -2 & 2 & -4 \end{pmatrix} \cdot \begin{pmatrix} \nu_{1,1} \\ 1 \\ \nu_{3,1} \\ \nu_{4,1} \\ 0 \end{pmatrix} = 0 \\ \underline{B} \cdot \underline{N}_2 &= \begin{pmatrix} 1 & 0 & 1 & 0 & 1 \\ 0 & 2 & 0 & 1 & 0 \\ 0 & 0 & -2 & 2 & -4 \end{pmatrix} \cdot \begin{pmatrix} \nu_{1,2} \\ 0 \\ \nu_{3,2} \\ \nu_{4,2} \\ 1 \end{pmatrix} = 0 \end{aligned}$$

Now writing the first one as an equation system:

$$\rightsquigarrow \left\{ \begin{array}{l} \nu_{1,1} + \nu_{3,1} = 0 \\ \nu_{4,1} = -2 \\ -2\nu_{3,1} + 2\nu_{4,1} = 0 \rightsquigarrow \nu_{4,1} = \nu_{3,1} \end{array} \right\} \rightsquigarrow \nu_{1,1} = 2$$

This yields the first reaction equation now (check again if it's balanced \rightarrow it is!):



Now do the same for the second reaction:

$$\rightsquigarrow \left\{ \begin{array}{l} \nu_{1,2} + \nu_{3,2} = -1 \\ \nu_{4,2} = 0 \\ -2\nu_{3,2} + 2\nu_{4,2} = 4 \rightsquigarrow \nu_{3,2} = -2 \end{array} \right\} \rightsquigarrow \nu_{1,2} = 1$$

The resulting reaction equation looks like this:



(b) Calculate the changes in amount of substance of CH_3OH , CH_2O and H_2O with given $\Delta n_{O_2} = 10mol$ and $\Delta n_{CO} = 2mol$!

Because the relation $\Delta n_{ij} = \nu_{ij}$ allows us to interchange the values for the stoichiometric coefficients ν and the change in amount of substance Δn , we can employ the already known relation:

$$\underline{B} \cdot \Delta n = 0$$

$$\begin{pmatrix} 1 & 0 & 1 & 0 & 1 \\ 1 & 2 & 1 & 1 & 1 \\ 4 & 0 & 2 & 2 & 0 \end{pmatrix} \cdot \begin{pmatrix} \Delta n_1 \\ \Delta n_2 \\ \Delta n_3 \\ \Delta n_4 \\ \Delta n_5 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 & 0 & 1 \\ 1 & 2 & 1 & 1 & 1 \\ 4 & 0 & 2 & 2 & 0 \end{pmatrix} \cdot \begin{pmatrix} \Delta n_1 \\ 10mol \\ \Delta n_3 \\ \Delta n_4 \\ 2mol \end{pmatrix} = 0$$

Let's now develop the equation system from the matrix:

$$\begin{pmatrix} 1 & 0 & 1 & 0 & 1 \\ 1 & 2 & 1 & 1 & 1 \\ 4 & 0 & 2 & 2 & 0 \end{pmatrix} \rightsquigarrow \left\{ \begin{array}{l} \Delta n_1 + \Delta n_3 = -2mol \\ \Delta n_1 + \Delta n_3 + \Delta n_4 = -22mol \\ 4\Delta n_1 + 2\Delta n_3 + 2\Delta n_4 = 0mol \end{array} \right.$$

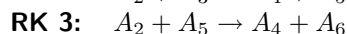
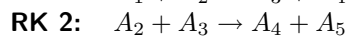
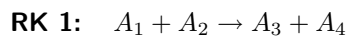
Now writing this in matrix form while skipping column 2 and 5 (i.e. the given components Δn_2 and Δn_5) again will make things easier:

$$\underline{M} = \left(\begin{array}{c|ccc|c} \text{Column} & \Delta n_1 & \Delta n_3 & \Delta n_4 & \text{Result} \\ \hline & 1 & 1 & 0 & -2 \\ & 1 & 1 & 1 & -22 \\ & 4 & 2 & 2 & 0 \end{array} \right) = \begin{pmatrix} 1 & 1 & 0 & -2 \\ 0 & 0 & 1 & -20 \\ 0 & -2 & 2 & 8 \end{pmatrix}$$

$$\rightsquigarrow \left\{ \begin{array}{l} \Delta n_4 = -20mol \\ \Delta n_3 = -24mol \\ \Delta n_1 = 22mol \end{array} \right.$$

Problem 3

Consider the following set of reactions:



There are three key reactions within the system. Calculate the changes in number of moles Δn_2 , Δn_4 and Δn_5 , when the following changes have been measured:

$$\Delta n_1 = -1 \text{ mol}$$

$$\Delta n_3 = -2 \text{ mol}$$

$$\Delta n_6 = 2 \text{ mol}$$

HINT: Set up the matrix of stoichiometric coefficients and make use of the extents of reaction. We already know the relation:

$$\underline{N} \cdot \underline{\xi}_j = \underline{\Delta n}_i$$

$$\underline{N} = \left(\begin{array}{c|ccc} & I & II & III \\ \hline A_1 & -1 & 0 & 0 \\ A_2 & -1 & -1 & -1 \\ A_3 & 1 & -1 & 0 \\ A_4 & 1 & 1 & 1 \\ A_5 & 0 & 1 & -1 \\ A_6 & 0 & 0 & 1 \end{array} \right); \quad \underline{\xi}_j = \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix}; \quad \underline{\Delta n}_i = \begin{pmatrix} \Delta n_1 \\ \Delta n_2 \\ \Delta n_3 \\ \Delta n_4 \\ \Delta n_5 \\ \Delta n_6 \end{pmatrix}$$

$$\begin{pmatrix} -1 & 0 & 0 \\ -1 & -1 & -1 \\ 1 & -1 & 0 \\ 1 & 1 & 1 \\ 0 & 1 & -1 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix} = \begin{pmatrix} \Delta n_1 \\ \Delta n_2 \\ \Delta n_3 \\ \Delta n_4 \\ \Delta n_5 \\ \Delta n_6 \end{pmatrix} = \begin{pmatrix} -1 \text{ mol} \\ \Delta n_2 \\ -2 \text{ mol} \\ \Delta n_4 \\ \Delta n_5 \\ 2 \text{ mol} \end{pmatrix}$$

Writing this equation system as a matrix makes things easy again:

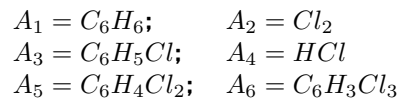
$$\left(\begin{array}{c|cccc} A_1 & -1 & 0 & 0 & -1 \\ A_3 & 1 & -1 & 0 & -2 \\ A_6 & 0 & 0 & 1 & 2 \end{array} \right) \rightsquigarrow \begin{cases} \xi_1 = 1 \\ \xi_3 = 2 \\ \xi_2 = 3 \end{cases}$$

Now let's calculate the missing (non-key) changes in amount of substance:

$$\left(\begin{array}{c|cccc} A_2 & -1 & -1 & -1 & \Delta n_2 \\ A_4 & 1 & 1 & 1 & \Delta n_4 \\ A_5 & 0 & 1 & -1 & \Delta n_5 \end{array} \right) \rightsquigarrow \begin{cases} -\xi_1 - \xi_2 - \xi_3 = \Delta n_2 = -6 \text{ mol} \\ \xi_1 + \xi_2 + \xi_3 = \Delta n_4 = 6 \text{ mol} \\ \xi_2 - \xi_3 = \Delta n_5 = 1 \text{ mol} \end{cases}$$

Problem 4

The following species are involved in a set of reactions:



Calculate the changes in number of moles Δn_1 , Δn_2 and Δn_4 , when the following changes have been measured:

$$\begin{aligned}\Delta n_3 &= -2mol \\ \Delta n_5 &= 1mol \\ \Delta n_6 &= 2mol\end{aligned}$$

HINT: Use the element-species matrix. The number of key components has not to be calculated.

Just set up the element-species matrix (\underline{B}):

$$\underline{B} = \left(\begin{array}{c|cccccc} & A_1 & A_2 & A_3 & A_4 & A_5 & A_6 \\ \hline C & 6 & 0 & 6 & 0 & 6 & 6 \\ H & 6 & 0 & 5 & 1 & 4 & 3 \\ Cl & 0 & 2 & 1 & 1 & 2 & 3 \end{array} \right); \quad \underline{\Delta n_i} = \begin{pmatrix} \Delta n_1 \\ \Delta n_2 \\ \Delta n_3 \\ \Delta n_4 \\ \Delta n_5 \\ \Delta n_6 \end{pmatrix} = \begin{pmatrix} \Delta n_1 \\ \Delta n_2 \\ -2mol \\ \Delta n_4 \\ 1mol \\ 2mol \end{pmatrix}$$

The following formula is to be used:

$$\underline{B} \cdot \Delta n = 0$$

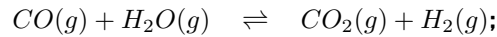
Writing this as an equation system and rearranging gives:

$$\leadsto \begin{cases} 6\Delta n_1 = -6 & \leadsto \Delta n_1 = -1mol \\ 6 \cdot -1 + \Delta n_4 = 0 & \leadsto \Delta n_4 = 6mol \\ 2\Delta n_2 = -12 & \leadsto \Delta n_2 = -6mol \end{cases}$$

2 Thermodynamics

Problem 1

During the production of synthesis gas, the conversion to water gas is a side reaction:



the equilibrium is adjustable by the reaction conditions.

The reaction is carried out at constant temperature in a closed vessel until equilibrium is reached. Following thermodynamic data is given:

1. Standard molar heats of formation:

$$\begin{aligned} CO(g): \quad \Delta H_f^0 &= -111 \frac{kJ}{mol} \\ CO_2(g): \quad \Delta H_f^0 &= -393 \frac{kJ}{mol} \\ H_2O(fl): \quad \Delta H_f^0 &= -283 \frac{kJ}{mol} \end{aligned}$$

2. Vaporization of water:

$$H_2O(fl) \rightarrow H_2O(g): \quad \Delta H_{vap}^0 = - + 41 \frac{kJ}{mol}$$

3. Constant pressure heat capacities:

$$\begin{aligned} \Delta c_p &= A + BT + CT^2 + DT^3 \quad \text{with } [T] = K \text{ and } [\Delta c_p] = \frac{cal}{mol \cdot K} \\ 1cal &= 4,184J \end{aligned}$$

Species	Coefficients			
	A	B	C	D
CO_2	4,728	$1,754 \cdot 10^{-2}$	$-1,338 \cdot 10^{-5}$	$4,097 \cdot 10^{-9}$
CO	7,373	$-0,307 \cdot 10^{-2}$	$6,662 \cdot 10^{-6}$	$-3,037 \cdot 10^{-9}$
H_2O	7,701	$4,595 \cdot 10^{-4}$	$2,521 \cdot 10^{-6}$	$-0,859 \cdot 10^{-9}$
H_2	6,483	$2,215 \cdot 10^{-3}$	$-3,298 \cdot 10^{-6}$	$1,826 \cdot 10^{-9}$

(a) Calculate the standard enthalpy change on reaction ΔH_R^0 using the given thermodynamical data! (Consider the molecules' state of aggregation!)

Using the following relation, we can easily calculate the reaction enthalpy:

$$\begin{aligned} \Delta H_R^0 &= \sum_{i=1}^N \nu_i \Delta H_{f,i} \\ &= \underbrace{-(-111)}_{CO(g)} - \underbrace{(-283 + 41)}_{H_2O(g)} - \underbrace{393}_{CO_2(g)} + \underbrace{0}_{H_2(g)} \left[\frac{kJ}{mol} \right] \\ &= -40 \frac{kJ}{mol} \end{aligned}$$

Hence the reaction is exothermic (i.e. it produces heat).

(b) In which direction is the equilibrium shifted in response to the following changes within the system?

1. Feed of further CO
2. Removal of a fixed amount of CO_2 out of the vessel
3. Feed of further H_2
4. Addition of a catalyst
5. Increase in temperature
6. Increase in pressure

The solution can be easily determined by using the different K_x and some basic chemical knowledge:

1. \rightarrow In favor for products, use K_c
2. \rightarrow In favor for products, use K_c
3. \leftarrow In favor for educts, use K_c
4. \rightleftharpoons No change. Catalysts only speed up or slow down reactions. The equilibrium is never affected!
5. \leftarrow In favor for educts, use K_a . The reaction is exothermic and therefore produces heat itself. Adding heat shifts the equilibrium!
6. \rightleftharpoons No change, use K_p . There is no change in volume during the reaction. Hence the partial pressures of all species should be the same and the quotient remains constant.

(c) Calculate the enthalpy change on reaction $\Delta H_{R,1000}$ for a temperature of 1000 K using the given thermodynamical data!

We will have to calculate the reaction enthalpy at a given temperature upon the basis of the already calculated standard reaction enthalpy:

$$\Delta H_R(T) = \Delta H_R^0 + \int_{T_0}^T \Delta c_p(T) dT$$

Given the function for Δc_p we have:

$$\begin{aligned} \Delta H_{R,1000} &= -40 \frac{kJ}{mol} + \int_{298}^{1000} (A_R + B_R \cdot T + C_R \cdot T^2 + D_R \cdot T^3) dT \\ &= -40 \frac{kJ}{mol} + \left(A_R + B_R \cdot T \Big|_{298}^{1000} + C_R \cdot T^2 \Big|_{298}^{1000} + D_R \cdot T^3 \Big|_{298}^{1000} \right) \end{aligned}$$

For the constants A , B , C and D , given for each species, we apply the following formula to get the overall constants A_R , B_R , C_R and D_R :

$$Z_R = \sum_{i=1}^N \nu_i Z_i \quad \text{where } Z = [A, B, C, D]$$

Let's calculate:

$$\begin{aligned} A_R &= -7,373 - 7,701 + 4,728 + 6,483 \\ &= -3,863 \\ B_R &= -(-0,307 \cdot 10^{-2}) - 4,595 \cdot 10^{-4} + 1,754 \cdot 10^{-2} + 2,215 \cdot 10^{-3} \\ &= 0,0223655 \\ C_R &= -6,662 \cdot 10^{-6} - 2,521 \cdot 10^{-6} - 3,298 \cdot 10^{-6} + 1,338 \cdot 10^{-5} \\ &= -2,586110^{-5} \\ D_R &= 3,037 \cdot 10^{-9} + 0,859 \cdot 10^{-9} + 1,826 \cdot 10^{-9} + 4,097 \cdot 10^{-9} \\ &= 9,819 \cdot 10^{-9} \end{aligned}$$

Now it is possible to calculate the final result (partially without units):

$$\begin{aligned} &\int_{298}^{1000} (A_R + B_R \cdot T + C_R \cdot T^2 + D_R \cdot T^3) dT \\ &= -3,863 \cdot T \Big|_{298}^{1000} + 0,0223655 \cdot \frac{1}{2} T^2 \Big|_{298}^{1000} + -2,5861 \cdot 10^{-5} \cdot \frac{1}{3} T^3 \Big|_{298}^{1000} \\ &\quad + 9,819 \cdot 10^{-9} \cdot \frac{1}{4} T^4 \Big|_{298}^{1000} \\ &= -3,863 \cdot (1000 - 298) + \frac{1}{2} (0,0223655 \cdot (1000^2 - 298^2)) + \frac{1}{3} (-2,5861 \cdot 10^{-5} \cdot (1000^3 - 298^3)) \end{aligned}$$

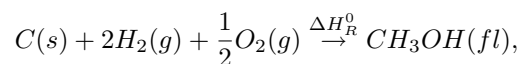
$$\begin{aligned}
& +\frac{1}{4} (9,819 \cdot 10^{-9} \cdot (1000^4 - 298^4)) \\
= & -2711,826 + 10189,67707 - 8392,208349 + 2435,391472 = 1521,034193 \frac{\text{cal}}{\text{mol}} \\
= & 1,521034193 \frac{\text{kcal}}{\text{mol}} = 6,364007065 \frac{\text{kJ}}{\text{mol}}
\end{aligned}$$

Now plugging this into the above equation:

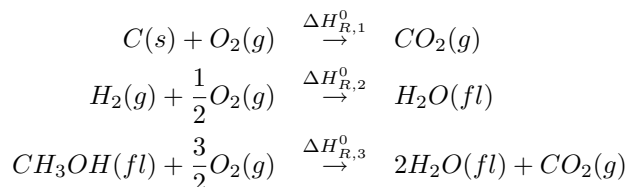
$$\begin{aligned}
\Delta H_{R,1000} & = \Delta H_R^0 + \int_{298}^{1000} \Delta c_p(T) dT \\
& = -40 \frac{\text{kJ}}{\text{mol}} + 6,364007065 \frac{\text{kJ}}{\text{mol}} \\
& = -33,635992935 \frac{\text{kJ}}{\text{mol}}
\end{aligned}$$

Problem 2

The heat tonality of the experimentally not realizable formation of methanol from the elements (see the equation) cannot be measured directly:



but the heats of combustion of carbon, hydrogen and methanol can be measured calorimetrically:



(a) Calculate the enthalpy change on reaction ΔH_R^0 of the formation of methanol from the elements! NOTE: Represent the methanol's formation reaction by a linear combination of the three combustion processes.

We have know formula to calculate the enthalpy change on reaction from the formation enthalpies:

$$\Delta H_R^0 = \sum_{i=1}^N \nu_i \Delta H_{f,i}^0$$

Furthermore we know, that $\Delta H_{f,i}^0$ for any element is zero. Let's use this, since it will cancel out several unknowns (following the sums in form $\nu_i \Delta H_{f,i}^0$):

$$\begin{aligned} \text{Form. from elem.: } \Delta H_R^0 &= -1 \cdot 0 - 2 \cdot 0 - \frac{1}{2} \cdot 0 + 1 \cdot \Delta H_{f,CH_3OH}^0 \\ \text{RK1: } \Delta H_{R,1}^0 &= -1 \cdot 0 - 1 \cdot 0 + 1 \cdot \Delta H_{f,CO_2}^0 \rightsquigarrow \Delta H_{f,CO_2}^0 = -393 \frac{kJ}{mol} \\ \text{RK2: } \Delta H_{R,2}^0 &= -1 \cdot 0 - \frac{1}{2} \cdot 0 + 1 \cdot \Delta H_{f,H_2O}^0 \rightsquigarrow \Delta H_{f,H_2O}^0 = -285 \frac{kJ}{mol} \\ \text{RK3: } \Delta H_{R,3}^0 &= -1 \cdot \Delta H_{f,CH_3OH}^0 - \frac{3}{2} \cdot 0 + 2 \cdot \Delta H_{f,H_2O}^0 + 1 \cdot \Delta H_{f,CO_2}^0 \end{aligned}$$

For the third equation we now know the two remaining unknowns $\Delta H_{f,H_2O}^0$ and $\Delta H_{f,CO_2}^0$, hence the equation look now like this:

$$\begin{aligned} \text{RK3: } \Delta H_{R,3}^0 &= -1 \cdot \Delta H_{f,CH_3OH}^0 + 2 \cdot -285 \frac{kJ}{mol} + 1 \cdot -393 \frac{kJ}{mol} \\ &= -\Delta H_{f,CH_3OH}^0 - 570 \frac{kJ}{mol} - 393 \frac{kJ}{mol} = -\Delta H_{f,CH_3OH}^0 - 963 \frac{kJ}{mol} \\ \rightsquigarrow \Delta H_{R,3}^0 + 963 \frac{kJ}{mol} &= -\Delta H_{f,CH_3OH}^0 = -724 \frac{kJ}{mol} + 963 \frac{kJ}{mol} \\ \rightsquigarrow \Delta H_{f,CH_3OH}^0 &= -239 \frac{kJ}{mol} \end{aligned}$$

Now we'll have to use the equation ("Form. from elem.") from above to get the result for ΔH_R^0 of the formation of methanol from the elements:

$$\begin{aligned} \Delta H_R^0 &= -1 \cdot 0 - 2 \cdot 0 - \frac{1}{2} \cdot 0 + 1 \cdot \Delta H_{f,CH_3OH}^0 \\ \Delta H_R^0 &= \Delta H_{f,CH_3OH}^0 = -239 \frac{kJ}{mol} \end{aligned}$$

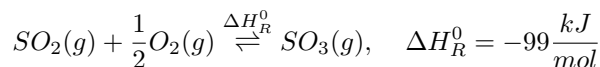
(b) Is the reaction in problem 2a exothermic or endothermic? methanol from the elements!

NOTE: Represent the methanol's formation reaction by a linear combination of the three combustion processes.

The result ($\Delta H_R^0 = -239 \frac{kJ}{mol}$) clearly shows, that this reaction is exothermic.

Problem 3

The temperature dependence of the balanced reaction:



is of decisive importance for the production of sulphuric acid.

The standard molar Gibbs free energies of formation are known:

$$\begin{aligned} SO_2 : \Delta G_f^0 &= -300 \frac{kJ}{mol} \\ SO_3 : \Delta G_f^0 &= -371 \frac{kJ}{mol} \end{aligned}$$

(a) Calculate the standard Gibbs free energy change on reaction ΔG_R^0 !

We use the following relation:

$$\begin{aligned} \Delta G_R^0 &= \sum_{i=1}^N \nu_i \Delta G_{f,i} \\ &= -1 \cdot \Delta G_{f,SO_2} + \left(-\frac{1}{2}\right) \cdot \Delta G_{f,O_2} + 1 \cdot \Delta G_{f,SO_3} \\ &= -\left(-300 \frac{kJ}{mol}\right) - \left(\frac{1}{2} \cdot \underbrace{0 \frac{kJ}{mol}}_{\text{zero for elements!}}\right) + \left(-371 \frac{kJ}{mol}\right) \\ &= -71 \frac{kJ}{mol} \end{aligned}$$

(b) Calculate the standard activity equilibrium ratio K_a^0 !

$$\begin{aligned} G_R^0 &= -RT \cdot \ln K_a \\ \leadsto -\frac{G_R^0}{RT} &= \ln K_a \\ \leadsto K_a &= \exp\left(-\frac{G_R^0}{RT}\right) \\ \leadsto K_a^0 &= \exp\left(-\frac{G_R^0}{R \cdot 298K}\right) = \exp\left(-\frac{-71 \frac{kJ}{mol}}{8,314 \frac{J}{mol \cdot K} \cdot 298K}\right) = e^{28,6570884721009} = 2790071872271,74 \end{aligned}$$

This means, that the standard activity equilibrium shifts the balance to the product's side:

$$K_a^0 = \frac{[SO_3]}{[SO_2][O_2]} = 2,79007187227174 \cdot 10^{12}$$

(c) Calculate the activity equilibrium ratio K_a for the following temperatures:

T = 713K; 733K; 753K; 773K; 873K; 973K; 1073K; 1173K

Using the relation from (b), we could easily determine K_a for changing T if we knew $G_R(T)$:

$$K_a = \exp\left(-\frac{G_R^0}{RT}\right) = \exp\left(-\frac{G_R(T)}{RT}\right)$$

This is not the case, hence we have to use another relation:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H_R^0}{RT^2} = \leadsto \int_{K_a^0}^{K_a} d \ln K_a = \int_{T_0}^T \frac{\Delta H_R^0}{RT^2} dT = \ln K_a - \ln K_a^0$$

Rearranging it gives:

$$\ln K_a = \ln K_a^0 + \int_{T_0}^T \frac{\Delta H_R^0}{RT^2} dT$$

Moving the constants out of the integral:

$$\ln K_a(T) = \ln K_a^0 + \frac{\Delta H_R^0}{R} \cdot \int_{T_0}^T \frac{dT}{T^2} = \ln K_a^0 + \frac{\Delta H_R^0}{R} \cdot \left. -\frac{1}{T} \right|_{T_0}^T$$

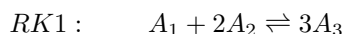
Now plugging all known variables in and calculating for each given temperature yields:

$$\begin{aligned} \ln K_a(T) &= 28,6570884721009 + \frac{-99000 \frac{J}{mol}}{8,314 \frac{J}{mol \cdot K}} \cdot \left. -\frac{1}{T} \right|_{298}^T \\ \ln K_a(713K) &= 28,6570884721009 + \frac{99000 \frac{J}{mol}}{8,314 \frac{J}{mol \cdot K}} \cdot \frac{1}{713K} - \frac{1}{298K} = 5,39935029229595 \\ \ln K_a(733K) &= 28,6570884721009 + \frac{99000 \frac{J}{mol}}{8,314 \frac{J}{mol \cdot K}} \cdot \frac{1}{733K} - \frac{1}{298K} = 4,9436685107031 \\ \ln K_a(753K) &= 28,6570884721009 + \frac{99000 \frac{J}{mol}}{8,314 \frac{J}{mol \cdot K}} \cdot \frac{1}{753K} - \frac{1}{298K} = 4,51219293264772 \\ \ln K_a(773K) &= 28,6570884721009 + \frac{99000 \frac{J}{mol}}{8,314 \frac{J}{mol \cdot K}} \cdot \frac{1}{773K} - \frac{1}{298K} = 4,10304468075303 \\ \ln K_a(873K) &= 28,6570884721009 + \frac{99000 \frac{J}{mol}}{8,314 \frac{J}{mol \cdot K}} \cdot \frac{1}{873K} - \frac{1}{298K} = 2,33850496897352 \\ \ln K_a(973K) &= 28,6570884721009 + \frac{99000 \frac{J}{mol}}{8,314 \frac{J}{mol \cdot K}} \cdot \frac{1}{973K} - \frac{1}{298K} = 0,936666122924645 \\ \ln K_a(1073K) &= 28,6570884721009 + \frac{99000 \frac{J}{mol}}{8,314 \frac{J}{mol \cdot K}} \cdot \frac{1}{1073K} - \frac{1}{298K} = -0,203879368781479 \\ \ln K_a(1173K) &= 28,6570884721009 + \frac{99000 \frac{J}{mol}}{8,314 \frac{J}{mol \cdot K}} \cdot \frac{1}{1173K} - \frac{1}{298K} = -1,14995845098955 \\ K_a(713K) &= \exp(5,39935029229595) = 221,262613469784 \\ K_a(733K) &= \exp(4,9436685107031) = 140,283939879604 \\ K_a(753K) &= \exp(4,51219293264772) = 91,1214227140278 \\ K_a(773K) &= \exp(4,10304468075303) = 60,5242844733766 \\ K_a(873K) &= \exp(2,33850496897352) = 10,365727887841 \\ K_a(973K) &= \exp(0,936666122924645) = 2,55146096592772 \\ K_a(1073K) &= \exp(-0,203879368781479) = 0,815560747340286 \\ K_a(1173K) &= \exp(-1,14995845098955) = 0,316649925596806 \end{aligned}$$

This shows us, that the equilibrium shifts to the left (educts) when adding heat to the exothermic reaction.

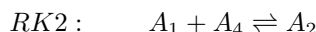
Problem 4

Consider the following gas-phase reaction in equilibrium



with standard heat of reaction $\Delta H_{R,1}^0$, A_1 being H_2 , and all species behaving like ideal gases.

(a) Calculate the standard heat of reaction $\Delta H_{R,1}^0$ when there is given a second reaction



with the standard heat of reaction $\Delta H_{R,2}^0 = 100 \frac{kJ}{mol}$ and the following standard molar heats of formation for A_3 and A_4 :

$$\Delta H_{f,3}^0 = 20 \frac{kJ}{mol}; \quad \Delta H_{f,4}^0 = 50 \frac{kJ}{mol}$$

We need to employ the already known relation:

$$\Delta H_R^0 = \sum_{i=1}^N \nu_i \cdot \Delta H_{f,i}^0$$

This is a simple linear equation system. We know several of the variables, so let's start:

$$(RK2): \quad \Delta H_{R,2}^0 = 100 \frac{kJ}{mol} = \underbrace{-1 \cdot 0}_{A_1} + \underbrace{(-1) \cdot 50 \frac{kJ}{mol}}_{A_4} + 1 \cdot \Delta H_{f,2}^0 \quad \leadsto \quad \Delta H_{f,2}^0 = 150 \frac{kJ}{mol}$$

So, why is $\Delta H_{f,1}^0 = 0$? Because H_2 is an element and this is one condition for elements!

Now we can calculate $\Delta H_{R,1}^0$:

$$\Delta H_{R,1}^0 = \underbrace{-1 \cdot 0}_{A_1} + \underbrace{(-2) \cdot 150 \frac{kJ}{mol}}_{A_2} + \underbrace{3 \cdot 20 \frac{kJ}{mol}}_{A_3} = (-300 + 60) \frac{kJ}{mol} = -240 \frac{kJ}{mol}$$

(b) Does it favor the formation of educts or products in the reaction (RK1), when the partial pressures p_1 and p_2 of the species A_1 and A_2 are both 25% of the total pressure p ?

For the following relation

$$K_p = \prod_{i=1}^N p_i^{\nu_i},$$

and under the condition, that the overall pressure must be 100% ($p = p_1 + p_2 + p_3 = 1 = 0,25 + 0,25 + p_3 \leadsto p_3 = 0,5 = 50\%$) we get

$$K_p = p_3^{\nu_3} \cdot p_1^{\nu_1} \cdot p_2^{\nu_2} = p_3^3 \cdot p_1^{-1} \cdot p_2^{-2} = \frac{p_3^3}{p_1 \cdot p_2^2} = \frac{0,5^3}{0,25^1 \cdot 0,25^2} = \frac{0,5^3}{0,25^3} = 8.$$

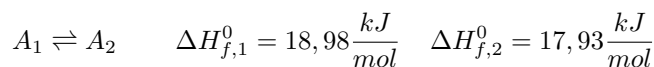
Hence the equilibrium shifts in favor for the products (i.e. \rightarrow).

(c) In which direction is the equilibrium shifted in the case the reaction is endothermic and a catalyst is added?

First of all, the reaction is exothermic. So this question needs not to be answered. And anyway, the addition of a catalyst does not influence the equilibrium. It just speeds up or slows down the reaction.

Problem 5

The isomerisation reaction



is in equilibrium at standard conditions, the equilibrium conversion X_1^* is **0,45**.

(a) Calculate K_c^0 and K_a^0 using the stoichiometric table.

The stoichiometric table can be found in the **Summary** or can be built.

First of all we assume a batch system.

$$\nu_1 A_1 + \nu_2 A_2 = 0$$

Species	n_{i0}	$\Delta n_i = -\frac{\nu_i}{\nu_k} n_{k0} X_k$	$n_i = n_{i0} + \Delta n_i$
A_1	n_{10}	$-n_{10} X_1$	$n_1 = n_{10} - n_{10} X_1$
A_2	n_{20}	$-\frac{\nu_2}{\nu_1} n_{10} X_1$	$n_2 = n_{20} - \frac{\nu_2}{\nu_1} n_{10} X_1$
Sum	$n_{\text{sum}0}$	–	$n_{\text{sum}} = n_{\text{sum}0} - (1 + \frac{\nu_2}{\nu_1}) n_{10} X_1$

We know, that $n_{20} = 0$ before the reaction starts. From the power law we know $K_a^0 = \prod_{i=1}^N c_i^{\nu_i}$ and $c_i = \frac{n_i}{V}$, hence:

$$K_a^0 = c_1^{-1} \cdot c_2^1 = \frac{c_2}{c_1} = \frac{n_2}{V} \cdot \frac{V}{n_1} = \frac{n_2}{n_1}$$

Now from the stoichiometric table and the condition $c_{20} = n_{20} = 0$ we know:

$$K_a^0 = \frac{n_2}{n_1} = \frac{n_{20} - \frac{\nu_2}{\nu_1} \cdot n_{10} \cdot X_1}{n_{10} - n_{10} \cdot X_1} = \frac{-\frac{\nu_2}{\nu_1} \cdot n_{10} \cdot X_1}{(1 - X_1) \cdot n_{10}} = \frac{-\frac{\nu_2}{\nu_1} \cdot X_1}{1 - X_1} = \frac{1 \cdot X_1}{1 - X_1} = \frac{0,45}{1 - 0,45} = \frac{0,45}{0,55} = 0,8181\bar{1}$$

(b) Calculate the standard heat of reaction.

We already know how to do that:

$$\Delta H_R^0 = \sum_{i=1}^N \nu_i \Delta H_{f,i} = -1 \cdot 18,98 \frac{\text{kJ}}{\text{mol}} + 1 \cdot 17,93 \frac{\text{kJ}}{\text{mol}} = -1,05 \frac{\text{kJ}}{\text{mol}}$$

(c) Calculate K_a at a temperature of 400 K.

$$\begin{aligned} \ln K_a(T) &= \ln K_a^0 + \int_{T_0}^T \frac{\Delta H_R^0}{RT^2} dT \\ \ln K_a(400K) &= \ln 0,8181\bar{1} + \int_{298K}^{400K} \frac{-1,05 \frac{\text{kJ}}{\text{mol}}}{8,3145 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot T^2} dT \end{aligned}$$

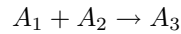
Moving the constants out of the integral we get:

$$\begin{aligned} \ln K_a(400K) &= \ln 0,8181\bar{1} + \frac{-1050 \frac{\text{J}}{\text{mol}}}{8,3145 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \int_{298K}^{400K} \frac{1}{T^2} dT = \ln 0,8181\bar{1} + \frac{-1050 \frac{\text{J}}{\text{mol}}}{8,3145 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left[-\frac{1}{T} \right]_{298K}^{400K} \\ &= \ln 0,8181\bar{1} + \frac{-1050 \frac{\text{J}}{\text{mol}}}{8,3145 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(-\frac{1}{400K} - \left(-\frac{1}{298K} \right) \right) \\ &= \ln 0,8181\bar{1} - 126,285405 \frac{1}{K} \left(\frac{1}{298K} - \frac{1}{400K} \right) = -0,3087337099 \\ K_a(400K) &= 0,7343763011 \end{aligned}$$

3 Microkinetics

Problem 1

In a laboratory experiment, 500ml of a solution of $2\text{kmol}/\text{m}^3$ ethylene oxide (A_1) in water was mixed with 500ml of water (A_2) containing 0,9% (w/w) sulfuric acid:



The concentration of ethylene glycol (A_3) was recorded as a function of time. From this data determine the reaction rate constant.

Time	Concentration of A_3
0,0	0,000
0,5	0,145
1,0	0,270
1,5	0,376
2,0	0,467
3,0	0,610
4,0	0,715
6,0	0,848
10,0	0,957

From the definition of the rate of reaction we get:

$$r = \frac{1}{\nu_i} \cdot \frac{dc_i}{dt} = k \cdot c_1 c_2 = \frac{dc_3}{dt} = \frac{c_3(t_0 + \Delta t) - c_3(t_0)}{\Delta t}$$

We can neglect c_2 because water is in excess.

$$r = k \cdot c_1$$

From the stoichiometric table we know:

$$c_i = c_{i0} - \frac{\nu_i}{\nu_k} c_{k0} X_k \quad \rightsquigarrow \quad c_1 = c_{10} - c_{10} X_1$$

From $c_{30} = 0$ we can derive:

$$c_3 = c_{30} - \frac{\nu_3}{\nu_1} c_{10} X_1 = c_{10} X_1 \quad \rightsquigarrow \quad c_1 = c_{10} - c_3$$

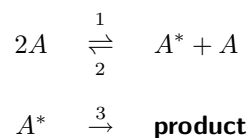
$$r = k \cdot (c_{10} - c_3)^\kappa \quad \rightsquigarrow \quad \underbrace{\log r}_y = \underbrace{\log k}_a + \underbrace{\frac{\kappa}{b}}_b \underbrace{\log(c_{10} - c_3)}_x$$

The value for r can be calculated at different points in time, since we have the data for c_3 and c_{10} from the given table. Plotting $\log r$ against $\log(c_{10} - c_3)$ in an X/Y-diagram allows us to estimate $\log k$ (i.e. a) and κ (i.e. b). Where a is the distance from the X-axis to the curve and b is the (mean-)inclination of the curve.

NOTE: There is also the integral method available, but I believe that in this case it is better to use the differential method.

Problem 2

Consider the following reaction scheme, where A^* is an activated molecule of the species A .



Derive the formula for the rate of the third reaction as a function of the concentration of A and the rate constants by

(a) formulating equations for the reaction rate of each partial reaction assuming elementary reaction,

Reaction rates:

$$\begin{aligned} r_1 &= k_1 c_A^2 \\ r_2 &= k_2 c_A c_{A^*} \\ r_3 &= k_3 c_{A^*} \end{aligned}$$

(b) formulating an equation for the production rate R_{A^*} ,

Production rate for every species:

$$R_{A^*} = r_1 - r_2 - r_3 = k_1 c_A^2 - k_2 c_A c_{A^*} - k_3 c_{A^*}$$

(c) formulating an expression for the concentration of A^* , assuming $R_{A^*} = 0$ and

Concentration of A^* :

$$\begin{aligned} 0 &= k_1 c_A^2 - k_2 c_A c_{A^*} - k_3 c_{A^*} \\ k_1 c_A^2 &= k_2 c_A c_{A^*} + k_3 c_{A^*} \\ k_1 c_A^2 &= c_{A^*} \cdot (k_2 c_A + k_3) \\ c_{A^*} &= \frac{k_1 c_A^2}{k_2 c_A + k_3} \end{aligned}$$

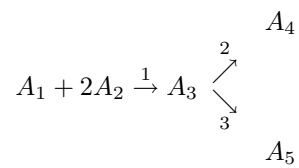
(d) formulating the formula for r_3 .

Reaction rate for reaction 3:

$$r_3 = k_3 \cdot \frac{k_1 c_A^2}{k_2 c_A + k_3}$$

Problem 3

Consider the following set of homogeneous reactions



with the reaction rates

$$r_1 = 120 \frac{\text{kmol}}{\text{m}^3 \cdot \text{s}}; \quad r_2 = 5r_3$$

(a) Formulate the equations for the reaction rate of each partial reaction assuming elementary reaction!

Use the power law:

$$\begin{aligned} r_1 &= k_1 c_1 c_2^2 = 120 \frac{\text{kmol}}{\text{m}^3 \cdot \text{s}} \\ r_2 &= k_2 c_3 = 5r_3 \\ r_3 &= k_3 c_3 = \frac{1}{5} r_2 \end{aligned}$$

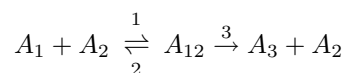
(b) Calculate the net rates R_i for all species assuming the concentration c_3 of species A_3 being constant!

Calculate the net rate using $R_i = \sum_{j=1}^M \nu_{ij} \cdot r_j$

$$\begin{aligned} R_1 &= -r_1 \\ R_2 &= -2r_1 \\ R_3 &= r_1 - r_2 - r_3 \\ R_4 &= r_2 \\ R_5 &= r_3 \end{aligned}$$

Problem 4

The description of a homogeneous catalyzed reaction



follows enzyme kinetics, in which the homogeneous catalyst is represented by A_{12} .

(a) Form the equations for the reaction rate of every partial reaction assuming elementary reaction!

$$r_1 = k_1 c_1 c_2$$

$$r_2 = k_2 c_{12}$$

$$r_3 = k_3 c_{12}$$

(b) Give the net rates of the changes in amount of substance of A_1 , A_2 , A_3 and A_{12} !

$$R_1 = -r_1 = -k_1 c_1 c_2$$

$$R_2 = -r_1 + r_2 + r_3 = k_2 c_{12} - k_1 c_1 c_2 + k_3 c_{12}$$

$$R_3 = k_3 c_{12}$$

$$R_{12} = r_1 - r_2 - r_3 = k_1 c_1 c_2 - k_2 c_{12} - k_3 c_{12}$$

(c) Determine the reaction rate of the formation of product assuming a (not?¹) neglectable amount of A_2 being bound in the complex A_{12} during the reaction and

1. step 3 to be rate determining!

2. the steady state hypothesis to be valid for A_{12} !

¹"not" was in the original script, though it makes no sense. The text without "not" makes sense.