Problem 6: Chemical Kinetics of the Peroxodisulfate Ion

The peroxodisulfate ion is one of the strongest oxidants that are known, although the oxidation reaction is relatively slow.
Peroxodisulfate ions are able to oxidize all halides, except fluoride, to halogens.
The initial rate (r_0) of the iodine-formation according to $S_2O_8^{2-} + 2\ I^- \rightarrow 2\ SO_4^{2-} + I_2$
was determined as a function of the initial concentrations (c_0) of the reactants at 25°C:

| $c_0(S_2O_8^{2-})$ [mol·L^{-1}]	$c_0(I^-)$ [mol·L^{-1}]	r_0 [10^{-8} mol·L^{-1}·s^{-1}]
0.0001	0.010	1.1
0.0002	0.010	2.2
0.0002	0.005	1.1

6.1 *Draw the line-bond structure of the peroxodisulfate ion and determine the oxidation states of all atoms.*

6.2 *Write down the rate equation for the reaction shown above.*

6.3 *Write down the total order and the partial orders of the reaction shown above.*

6.4 *Prove that the rate constant of the reaction is 0.011 L·mol^{-1}·s^{-1}.*

The activation energy of the reaction mentioned above is 42 kJ·mol^{-1}.

6.5 *What temperature (in °C) has to be chosen to decuple the rate constant?*

Iodine reacts with thiosulfate ions ($S_2O_3^{2-}$) forming iodide ions rapidly.

6.6 *Write down the reaction scheme of this reaction.*

6.7 *Write down the rate equation for the reaction*

$$S_2O_8^{2-} + 2\ I^- \rightarrow 2\ SO_4^{2-} + I_2$$
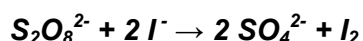
assuming that there is an excess of thiosulfate ions relative to the peroxodisulfate ions and the iodide ions in the solution.

Problem 7: Catalytic Hydrogenation of Ethylene

At the beginning of the last century, ethylene, that is a colourless gas, was considered to be a chemical curiosity without any practical importance.
Today, large amounts of ethylene are produced: in Germany, 60 kg per capita were produced in 2001.
Ethylene can be converted into ethane by various catalysts. By using a zinc oxide catalyst, the reaction is so slow that the reaction mechanism can be analyzed.
The pictures below show the reaction steps of the hydrogenation of ethylene (charges and stoichiometric coefficients are neglected in all the following tasks).

7.1 *Write down the correct order of the steps by numbering them consecutively.*

No.		No.	
	H————H ...——O——...—Zn—...—O—...		H $H_2C{=\!=\!=}CH_2$ H | ↓ | ...——O——...—Zn—...—O—...
	H H | | ...——O——...—Zn—...—O—...		$H_3C{-\!-}CH_3$ ...——O——...—Zn—...—O—...
	$H_2C{=\!=\!=}CH_2$ H H | | ...——O——...—Zn—...—O—...		H H | | ...——O——...—Zn—...—O—...
	CH$_3$ | H CH$_2$ | | ...——O——...—Zn—...—O—...		

$\theta(H)$ describes the fraction of surface sites that are occupied by hydrogen atoms, $\theta(C_2H_4)$ describes the fraction of surface sites that are occupied by ethylene molecules and $\theta(C_2H_5)$ describes the fraction of surface sites that are occupied by the adsorbed intermediate.

7.2 Which of the following rate equations is correct, if the hydrogenation of the adsorbed intermediate is the slowest step of the reaction?
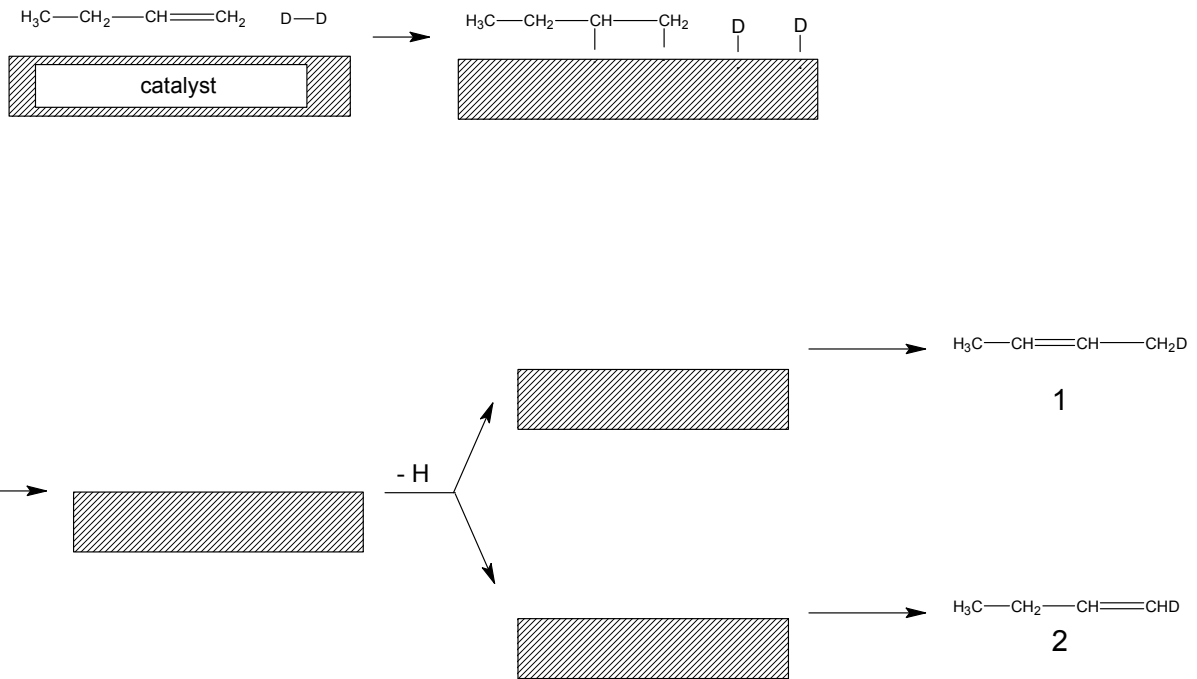
(1) $r = k \cdot \theta(H)$ ☐

(2) $r = k \cdot \theta(C_2H_4)$ ☐

(3) $r = k \cdot \theta(H) \cdot \theta(C_2H_4)$ ☐

(4) $r = k \cdot \theta(H) \cdot \theta(C_2H_5)$ ☐

When zinc oxide is used as a catalyst, the hydrogenation of ethylene is blocked by water.

7.3 Explain this blocking by drawing the interaction between water and the catalyst analogous to that of task 1 of this problem.

If a metal catalyzes the hydrogenation of alkenes, isomer alkenes are formed in a side reaction. When D_2 reacts with 1-butene the side products **1** and **2** will form.

**7.4 Complete the reaction scheme on the next page and write down the structures of the intermediates.**

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H_3C—CH_2—CH=CH_2 D—D $\longrightarrow$ H_3C—CH_2—CH—CH_2 D D

catalyst

$\longrightarrow$ H_3C—CH=CH—CH_2D

1

- H

$\longrightarrow$ H_3C—CH_2—CH=CHD

2

The fraction of surface sites that are occupied by adsorbed gas molecules (θ) may be described in a simple way by using the Langmuir isotherm:

$$\theta = \frac{K \cdot p}{1 + K \cdot p}$$ p: gas pressure, K: adsorption-desorption equilibrium constant

7.5 ***Write down a corresponding formula for the fraction θ(i) of surface sites that are occupied by the gas i, if two or more gases are adsorbed on the catalyst.***

Problem 8: Kinetics of an Enzymatic Reaction

The mechanism of an enzymatic reaction may be described as:

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \overset{k_2}{\longrightarrow} P + E$$
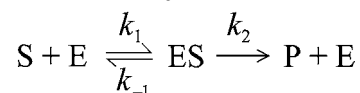
S is the substrate, E is the enzyme, ES is the complex formed by S and E, and P is the product. k_1, k_{-1} and k_2 are the rate constants of the elementary reactions.
The rate of the enzymatic reaction, r, can be expressed as a function of the substrate concentration, c(S):

$$r = \frac{dc(P)}{dt} = k_2 c_T(E) \frac{c(S)}{K_M + c(S)}$$

t is the time,
c(P) is the product concentration,
$c_T(E)$ is the total enzyme concentration
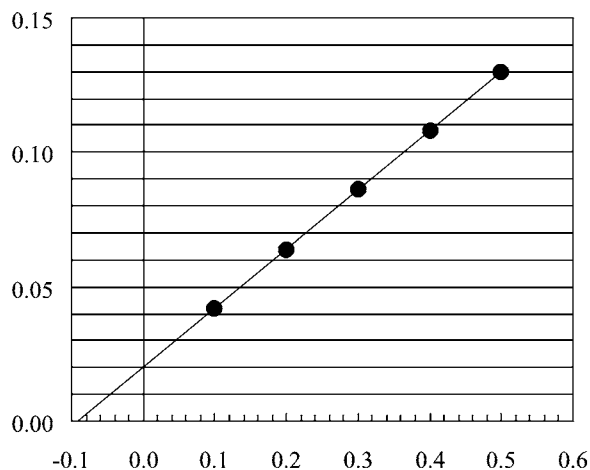and $K_M = (k_{-1} + k_2)/k_1$.
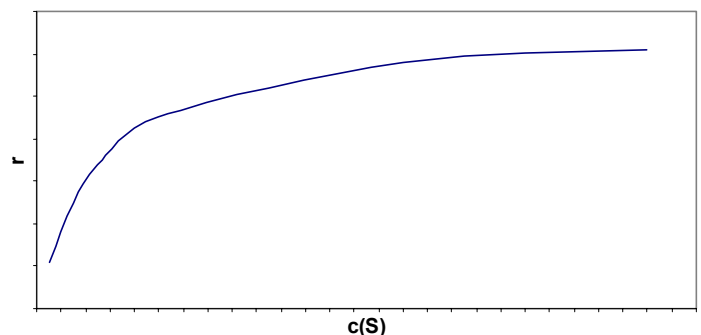
8.1 *Determine the variables x, y and z in the following rate equations:*

$$\frac{dc(S)}{dt} = -k_x c(S)c(E) + k_y c(ES) \qquad \frac{dc(ES)}{dt} = +k_x c(S)c(E) - (k_{-1} + k_2)c^z(ES)$$

8.2 *Complete the following rate equation:*

$$\frac{dc(E)}{dt} =$$

Penicillin (substrate) is hydrolyzed by β-lactamase (enzyme). The following data have been recorded when the total enzyme concentration was 10^{-9} mol·L^{-1}.
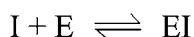

x-axis: $c^{-1}(S) / (10^6 \text{ L·mol}^{-1})$
y-axis: $r^{-1} / (10^6 \text{ L·min·mol}^{-1})$

8.3. *Determine the constants k_2 and K_M.*
   If $c(S) = 0.01 \cdot K_M$, what is the concentration of the complex ES?

A competitive inhibitor I competes with the substrate and may block the active site of the enzyme:

$$I + E \rightleftharpoons EI$$

8.4 *If the dissociation constant of EI is $9.5 \cdot 10^{-4}$ mol·L^{-1} and the total enzyme concentration is $8 \cdot 10^{-4}$ mol L^{-1}, what total concentration of inhibitor will be needed to block 50 % of the enzyme molecules in the absence of substrate?*

8.5 *Decide whether the following statements are true or false.*

	true	false
The rate of the enzymatic reaction, r, is reduced by the competitive inhibitor.	☐	☐
The maximum value of the rate *r* is reduced by the competitive inhibitor.	☐	☐
The concentration of the substrate S is unaffected by the competitive inhibitor.	☐	☐
The activation energy of the <u>enzymatic</u> reaction is increased by the inhibitor.	☐	☐

A more detailed description of an enzymatic reaction includes the reverse reaction of the product back to the substrate. At the end of the enzymatic reaction, a chemical equilibrium is reached between the substrate and the product.

8.6 *Decide whether the following statements are true or false.*

	true	false
The concentration of the product in the equilibrium is increasing with increasing concentration of the substrate.	☐	☐
The concentration of the product in the equilibrium is increasing with increasing concentration of the enzyme.	☐	☐
The concentration of the product in the equilibrium is higher, when the rate constant k_2 is larger.	☐	☐

Problem 9: $CaCN_2$ – An Old but still Important Fertilizer

Calcium cyanamide ($CaCN_2$) is a very versatile and powerful fertilizer. It can be produced easily from cheap and common chemicals such as $CaCO_3$. The thermal decomposition of $CaCO_3$ leads to a white solid X_A and a colourless gas X_B which does not sustain combustion. A greyish solid X_C and a gas X_D form by the reduction of X_A with carbon. X_C and X_D can be further oxidized. The reaction of X_C with nitrogen finally leads to $CaCN_2$.

9.1 *How can calcium cyanamide be synthesized? Complete the reaction scheme below.*

(1) $CaCO_3$ $\xrightarrow{\Delta T}$ X_A + X_B

(2) X_A + 3 C $\longrightarrow$ X_C + X_D

(3) X_C + N_2 $\longrightarrow$ $CaCN_2$ + C
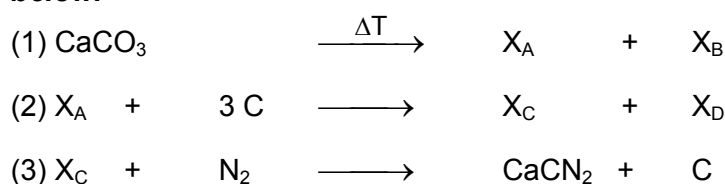
9.2 *What gas forms by the hydrolysis of $CaCN_2$? Write down the equation of the reaction of $CaCN_2$ with water.*

9.3 *In solid state chemistry the CN_2^{2-} ion shows constitutional isomerism. The free acids of both anions (at least in the gas phase) are known. Draw the structural formulas of both isomeric free acids. Indicate on which side the equilibrium is located.*

Problem 10: Closed-Packed Structures

About two-thirds of the metallic elements have closed-packed structures. Each atom is surrounded by as many neighbouring atoms as possible. All the atoms in the structure are identical.

10.1 *Draw a two-dimensional model of a closed-packed assembly of spheres.*

10.2 *Change this model into a three-dimensional one. How many different possibilities are there of stacking a) three or b) an infinite number of layers? What is the coordination number of each atom?*

Atoms packed together are closed-packed when they occupy the minimum volume possible (assuming they are incompressible spheres). They have the maximum possible packing

efficiency, defined as the ratio of volume of atoms to volume of space used.

The following arrangement is called 'cubic-F':
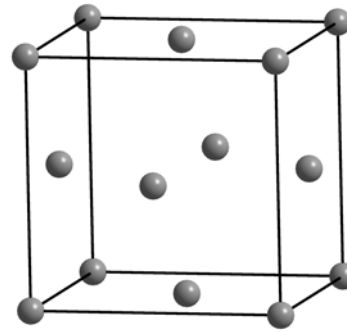
10.3 Insert the closed-packed layers into this illustration.

10.4 Calculate the packing efficiency and compare it with that of a cubic-primitive packing of spheres.

10.5 Insert the tetrahedral and octahedral cavities into a cubic closed-packed structure.

The arrangements of ions in a crystal depend to a great extent on the relative sizes of the ions as shown in the table below.
The radius of the particles X that form the holes is r.
The radii of the largest particles M that fit into the holes without distorting them
are $0.225 \cdot r$ for a tetrahedral hole
and $0.414 \cdot r$ for an octahedral hole.

Radius ratios for the arrangements of rigid spheres.

| coordination number of M	arrangement of X	radius ratio $r(M^{m+})/r(X^{x-})$	crystal structure corresponding to coordin. number
2	linear	<0.150	
3	triangular	0.150-0.225	
4	tetrahedral	0.225-0.414	ZnS
6	octahedral	0.414-0.732	NaCl
8	cubic	0.732-1.00	CsCl
12	cuboctahedron	1.0	closed packed

10.6 Show that the ideal r_M/r_X value for the cation-anion and anion-anion contacts of a tetrahedral arrangement of anions around a cation is 0.225.
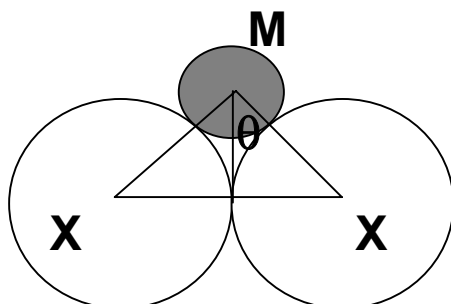
One edge of a tetrahedron with two anions touching and the cation in the center of the tetrahedron.

$2 \cdot \theta = 109.5°$.

10.7 *Calculate the ideal r_M/r_X ratio for cation-anion and anion-anion contacts of an octahedral arrangement of anions around a cation as illustrated in one plane in the figure below.*
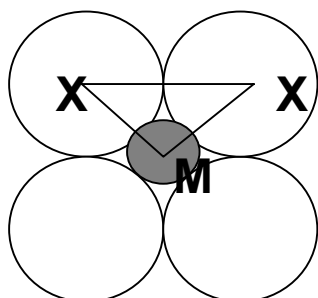
Cation-anion and anion-anion contacts in one plane of an octahedron.
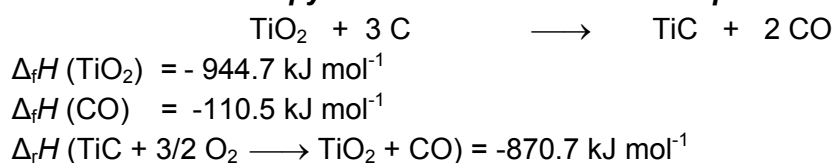
Problem 11: Titanium carbide – A High-Tech Solid

Transition metal carbides, such as TiC, are widely used for the production of cutting and grinding tools, because they are very hard, very corrosion-resistant and have high melting points. Apart from these properties, titanium carbide has a high electric conductivity that is almost independent of temperature, so that it is important in the electronics industry.

11.1 *What kind of structure is TiC likely to adopt, if the radii are $r(Ti^{4+})$ = 74.5 and $r(C^{4-})$ = 141.5 pm?*

TiC is technically obtained from TiO_2 by the reduction with carbon. The enthalpy change of this reaction can directly be measured only with difficulty. However, the heats of combustion of the elements and of TiC can be measured directly. As energy is always conserved and the enthalpy change for a given process does not depend on the reaction pathway (this special application of the First Law of Thermodynamics is often referred to as Hess´s Law), the missing thermodynamic data can be calculated.

11.2 *Calculate the enthalpy of reaction of the technical production process of TiC:*

$$TiO_2 + 3\,C \longrightarrow TiC + 2\,CO$$

$\Delta_f H\ (TiO_2)\ = -944.7$ kJ mol^{-1}

$\Delta_f H\ (CO)\ = -110.5$ kJ mol^{-1}

$\Delta_r H\ (TiC + 3/2\ O_2 \longrightarrow TiO_2 + CO) = -870.7$ kJ mol^{-1}

In 1919, Born and Haber independently applied the First Law of Thermodynamics to the formation of solids from their elements. In this way, getting exact information about lattice energies for solids was possible for the first time.
Potassium chloride is isotypic to TiC and crystallizes in the NaCl structure.

11.3 *Use the given data to construct a thermodynamical Born-Haber-cycle of the formation of potassium chloride from its elements and calculate the lattice energy of potassium chloride.*

sublimation enthalpy for potassium	$K_{(s)} \rightarrow K_{(g)}$	$\Delta_{sub}H$ = 89 kJ mol^{-1}
dissociation energy of chlorine	$Cl_{2(g)} \rightarrow 2\ Cl$	$\Delta_{diss}H$ = 244 kJ mol^{-1}
electron affinity of chlorine	$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$	$\Delta_{EA}H$ = -355 kJ mol^{-1}
ionization energy of potassium	$K_{(g)} \rightarrow K^+_{(g)} + e^-$	$\Delta_{IE}H$ = 425 kJ mol^{-1}
enthalpy of formation for KCl	$K_{(s)} + ½\ Cl_{2(g)} \rightarrow KCl_{(s)}$	$\Delta_f H$ = -438 kJ mol^{-1}