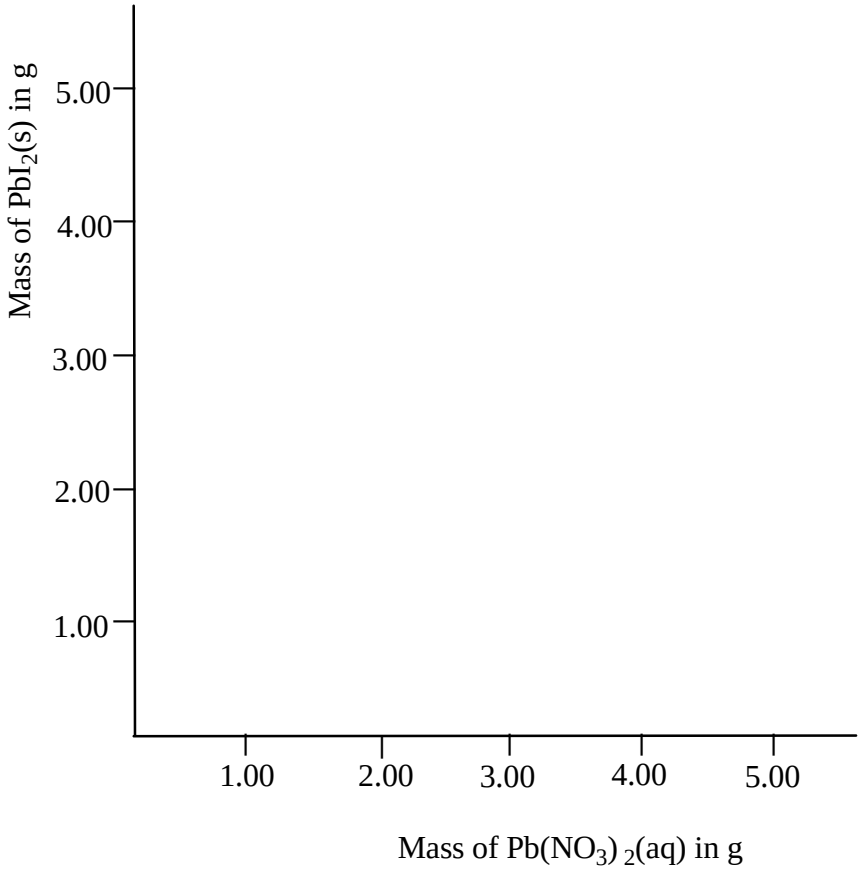
Problem 14: Lead iodide

Lead nitrate ($Pb(NO3)_2$) and potassium iodide (KI) react in aqueous solution to form a yellow precipitate of lead iodide (PbI_2). In one series of experiments the masses of the two reactants were varied, but the *total* mass of the two was held constant at 5.000 g. The lead iodide formed was filtered from solution, washed and dried. Data for a series of reactions are given below, together with a blank graph.

Experiment	Mass of lead nitrate (g)	Mass of lead iodide (g)
1	0.500	0.692
2	1.000	1.388
3	1.500	2.093
4	3.000	2.778
5	4.000	1.391



1. Complete the graph; that is, plot the data and draw the approximate curve(s) connecting the data points. Determine graphically what the maximum mass of precipitate is that can be obtained?

2. Write the balanced equation for the reaction and use it to calculate the maximum mass of PbI_2 and the corresponding amount of $Pb(NO_3)_2$.

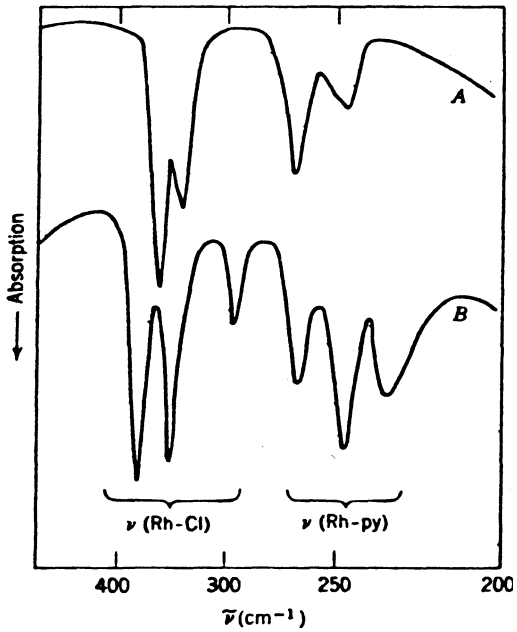
Problem 15: Octahedral complexes

The doubly charged metal ions of the first row transition elements with the configuration d^1, d^2, … d^9 form mainly octahedral complexes of the general formula ML_6^{2+} (L = neutral monodentate ligand). From the magnetic behavior point of view these complexes are of two types. Those with the same number of unpaired electrons with the $M_{(g)}^{2+}$, the so called "high spin" complexes, and those in which this number is smaller or even zero, the "low spin" ones. If the separation between the energy levels t_{2g} and e_g is Δ and the pairing energy (the energy necessary for two electrons to be coupled into a singlet) is P, predict the ground state electron configuration for these

complexes. Hint: The Aufbau principle and the Pauli exclusion principle must be obeyed.

Problem 16: Isomerism in Inorganic Chemistry

Isomerism is traditionally introduced in Organic chemistry courses. However, Inorganic Chemistry also offers many different types of isomerism, especially structural. The modern study of coordination compounds began with Alfred Werner[1] and Sophus Mads Jorgensen, more than one hundred years ago. It was their experiments that established the octahedron as the premier structural entity for coordination number six (6) rather than the planar hexagon or the trigonal prism, for example in the complex ion $Co(NH_3)_6^{3+}$. Thus, there are two isomers corresponding to the chemical formula $CoCl_3{\cdot}4NH_3$, the *praseo* and *violeo* complexes. There are also two structural isomers for the complex $Rh(py)_3Cl_3$ (py: pyridine – only its N-atom need be considered). The far infrared spectra in the 450–200 cm^{-1} region of these two complexes are shown in the figure below.



Rotation of plane polarized light is not limited to organic molecules with a chiral carbon atom. The general condition for optical activity is that the molecule or ion should not possess an improper axis of rotation, and because $S_2 \equiv i$ and $S_1 \equiv \sigma$ the molecule may not possess a center or plane of symmetry. Thus, although there is only one *cis*–$[Co(NH_3)_4Cl_2]Cl$ complex, there are two *cis*–$[Co(en)_2Cl_2]Cl$ complexes (en: ethylene diamine or 1,2 diamino ethane, a symmetric bidentate ligand) which are enantiomers.

[1] Nobel prize in Chemistry 1913

Questions:

1. What is the electronic configuration of Co in $Co(NH_3)_6^{3+}$?
2. What is the type of bonding of NH_3 in $Co(NH_3)_6^{3+}$, which is a low spin complex, and of fluoride ion in CoF_6^{3-}, which is a high spin complex? Place electrons from the ligands in appropriate metal orbitals according to Valence Bond Theory.
3. Write the stereochemical formulae and structures for the *praseo* and *violeo* complexes.
4. Write the stereochemical formulae and structures for the two $Rh(py)_3Cl_3$ complexes. Assign the spectra to each of the two complexes.
5. How many isomers does the complex with the formula $[Co(en)_3]I_3$ exibit ?

Problem 17: Tetrahedral and square complexes

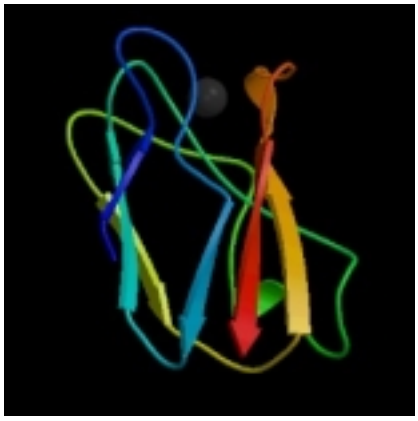
Four coordination is much less common than six coordination in first row d-block elements, mainly due to energy stabilization by the ligands. The most symmetric spatial location of ligands about a central ion is the tetrahedron, but square planar complexes are also well known. In tetrahedral geometry only one MA_2B_2 complex is possible, whereas two isomers are possible in square planar geometry. The hybridization of metal atomic orbitals for tetrahedral geometry is $\mathbf{sp^3}$ or $\mathbf{sd^3}$ and for square planar geometry $\mathbf{dsp^2}$.

Ni^{2+} is $[Ar]3d^8$. With chloride ion a paramagnetic $NiCl_4^{2-}$ complex ion is formed, whereas with cyanide (CN^-) ion a diamagnetic $Ni(CN)_4^{2-}$ complex ion is formed.

Show the distribution of metal ion valence electrons and ligand electrons in the 3d, 4s and 4p subshells for both complexes.

Problem 18: Copper enzyme

Life on our planet is based on the conversion of solar to chemical energy during photosynthesis. Plastocyanin (PC), is a Cu-containing protein that mediates electron transfer in the photosynthetic electron transfer chain. The active site of PC consists of a Cu ion coordinated by the N atoms of the side chains of two histidines and the sulfur atoms of one cysteine and one methionine residue. Electron transfer by PC involves interconversion of the Cu ion between the Cu(I) and Cu(II) oxidation states. The three-dimensional structure of PC can be found at http://www.rcsb.org/, Protein Data Bank file for poplar PC: 1PNC.



1. What is the full electron configuration of Cu, Cu(I), Cu(II) ?
2. Which oxidation state of PC is EPR active ?
3. Based on the amino-acid sequence of PC (the "primary structure" of the protein), the molar mass of PC is 10500. An aqueous solution of oxidized PC has an intense blue color (PC belongs to the family of "Blue Copper Proteins"), since it absorbs strongly at 597 nm (molar absorption coefficient 4500 $mol^{-1}dm^3\ cm^{-1}$). A sample of oxidized PC in a 1cm UV-Vis cell has an absorption of 0,700. Calculate the amount (mg) of PC and the number of Cu(II) ions that are present in 5 cm^3 of this PC solution.
4. The Cu ions of certain Blue Copper proteins can be removed to give the corresponding metal-free proteins, known as apo-proteins. These forms can bind various metal ions such as Co(II), Ni(II), Zn(II) and Cd(II), and the metal sites adopt similar structures with the "native" Cu protein. Which reconstituted Blue Copper Proteins are expected to be redox inactive?

Problem 19: Palladium nanoclusters

Nanoclusters -near monodispersed metal particles that are generally less than 10 nm (100Å) in diameter- have attracted intense interest over the past decade. One reason for this is the belief that nanoclusters will have unique properties, derived in part from the fact that these particles and their properties lie somewhere between those of the bulk and single-particle species. These strange "morsels of matter" have fascinating potential uses; nanoclusters have significant potential especially for catalysis as new types of higher activity and selectivity catalysts.

There are four general synthetic methods for transition metal nanoclusters. These four methods are: (i) transition metal salts reduction (ii) thermal decomposition and photochemical methods (iii) ligand reduction and displacement from organometallics, and (iv) metal vapor synthesis. Furthermore, nanoclusters must be stabilized against aggregation into larger particles. Stabilization can be achieved by electrostatic (charge or "inorganic") stabilization, steric ("organic") stabilization or a combination of both.

Electrostatic stabilization occurs by the adsorption of ions to the often electrophilic metal surface. This adsorption creates an electrical double (real multi-) layer, which results in a Coulombic repulsion force between individual particles (Fig. 1a). Steric stabilization is achieved by surrounding the metal center by layers of material that are sterically bulky, such as polymers or surfactants. These large adsorbates provide a steric barrier, which prevents close contact of the metal particles centers (Fig. 1b).

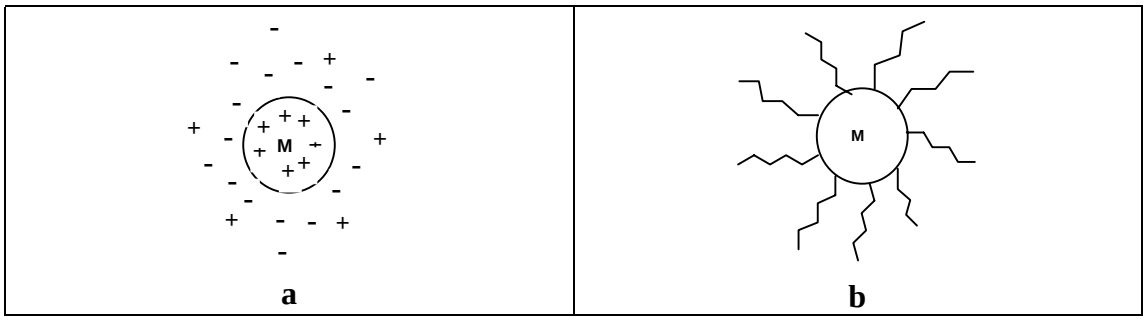


Figure 1. *A schematic illustration for (a) an electrostatically stabilized metal (M) particle and (b) a sterically stabilized metal particle.*

Metal clusters are constructed by successively packing layers- or shells- of metal atoms around a single metal atom. Metal clusters that have a complete, regular outer geometry are designated full-shell or "magic number" clusters. The total number of metal atoms, ***y***, per ***n*th** shell is given by the equation $\boldsymbol{y = 10n^2+2}$ (n = 1, 2, 3, …) (Fig. 2.)

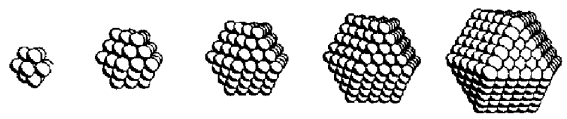
Full-Shell or "Magic Number" Clusters					
Number of Shells	1	2	3	4	5

Figure 2. *Idealized representation of hexagonal close-packed full-shell "magic number" clusters. Each metal atom has the maximum number of nearest neighbors, which impart some degree of extra stability to full-shell clusters.*

The most widely used technique for characterizing nanoclusters is transmission electron microscopy (TEM) or high resolution TEM (HR-TEM), techniques which provide direct visual information on the size, shape, dispersity, structure and morphology of nanoclusters.

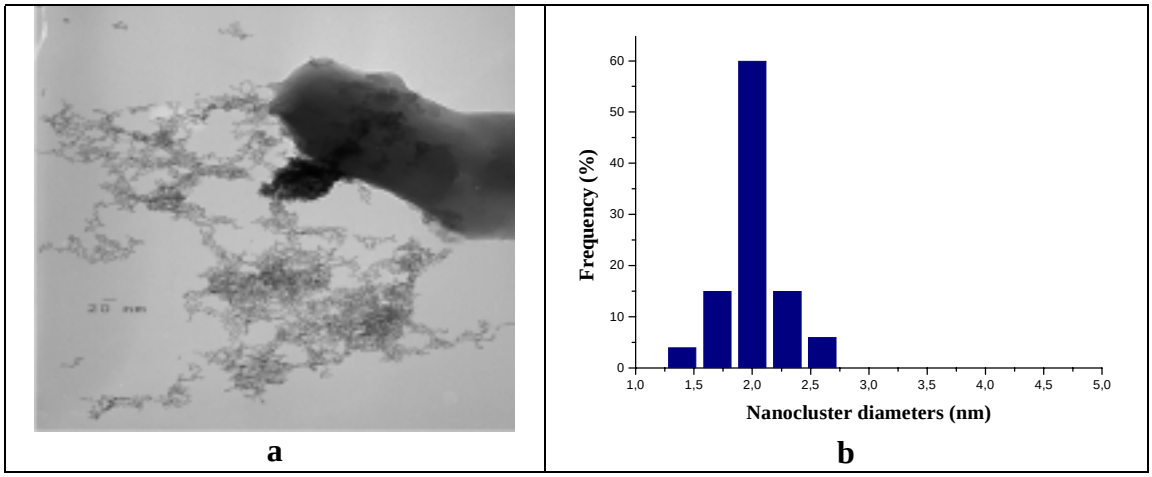


Figure 3. ***(a)*** *Transmission electron microscopy image of Pd(0) nanoclusters stabilized by a polymer.* ***(b)*** *Histogram of the Pd(0) nanocluster diameters.*

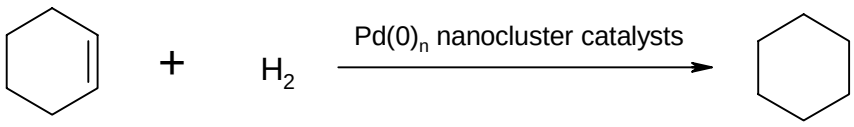
1 By direct reaction of Pd(II)-polymer complex (1 mM in water solution) with gas H_2, Pd(0) nanoclusters are prepared, as following:

$$nPd(II) + nH_2 \rightarrow Pd(0)_n + 2nH^+$$

A transmission electron micrograph of the isolated $Pd(0)_n$ nanoclusters shows spherical Pd(0) nanoclusters, protected by the polymer, with an average diameter of 2.05 nm.

Calculate the number (***N***) of Pd atoms per cluster. Are these nanoclusters full-shell nanoclusters? Calculate the number of shells (***n***) in the above Pd(0) nanoclusters. Density of Pd, ρ = 12.02 g/cm^3.

2 The catalytic activity of the polymer stabilized $Pd(0)_n$ nanoclusters is detected by a catalytic olefin hydrogenation reaction, such as the cyclohexene plus H_2 reaction:



In a 400 cm^{-3} high pressure reactor, an amount of the above polymer-protected $Pd(0)_n$ nanoclusters containing a total of 50 μmol of Pd(0) was dissolved in 50 cm^{-3} of acetone, followed by the addition of 5 cm^{-3} of cyclohexene. The reactor was then sealed, purged several times with prepurified H_2 (dry and O_2 free) and the H_2 pressure was set to the desired value, approximately 4 atm. The solution was stirred continuously during the reaction and the temperature was kept constant at 30°C. H_2 pressure vs. time until the end of the reaction is presented in Fig. 4.

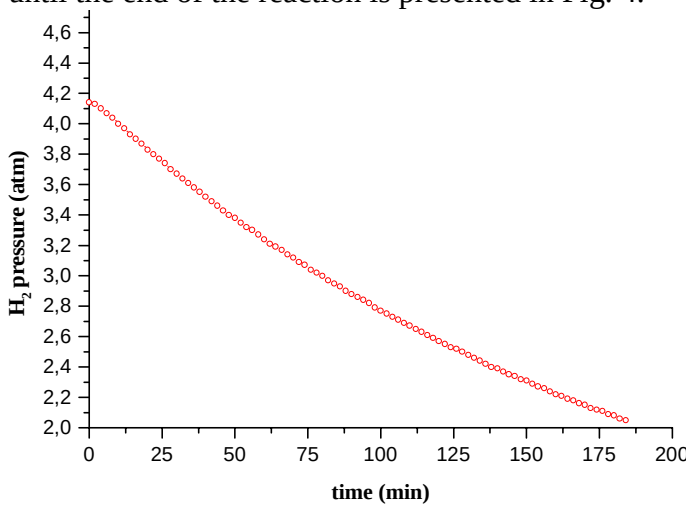


Figure 4. *Hydrogen uptake curve. Temperature 30°C, 0.5 μmol of Pd(0), 5 cm^{-3} of cyclohexene.*

(i) Calculate the % conversion of the cyclohexene.

(ii) Taking under consideration that only the surface Pd(0) atoms of the nanoclusters are catalytically active, calculate the turnover number, TON, where *TON = moles H_2 consumed / moles of catalytically active Pd(0)* and the turnover frequency, TOF, where *TOF = moles H_2 consumed / moles of catalytically active Pd(0)/ time (min) of the consumption*. Density of cyclohexene, ρ = 0.81 g cm^{-3}.

3 The polymer-protected $Pd(0)_n$ nanocluster catalyst are also used for the catalytic hydrogenation of hex-1-ene by H_2. The experiment was performed under the conditions cited above, exept that the solvent was chloroform. It was found that $Pd(0)_n$ nanoclusters are an efficient catalyst for the hydrogenation of hex-1-ene.

$$\underset{\text{hex-1-ene}}{CH_3(CH_2)_2CH_2CH{=}CH_2} + H_2 \xrightarrow{Pd(0)_n \text{ nanocluster catalysts}} \underset{\text{hexane}}{CH_3(CH_2)_4CH_3}$$

The ^{1}H-NMR spectra of the hex-1-ene and the reaction mixture after 30 min of reaction and after the removal of the catalyst are shown in the Fig. 5.

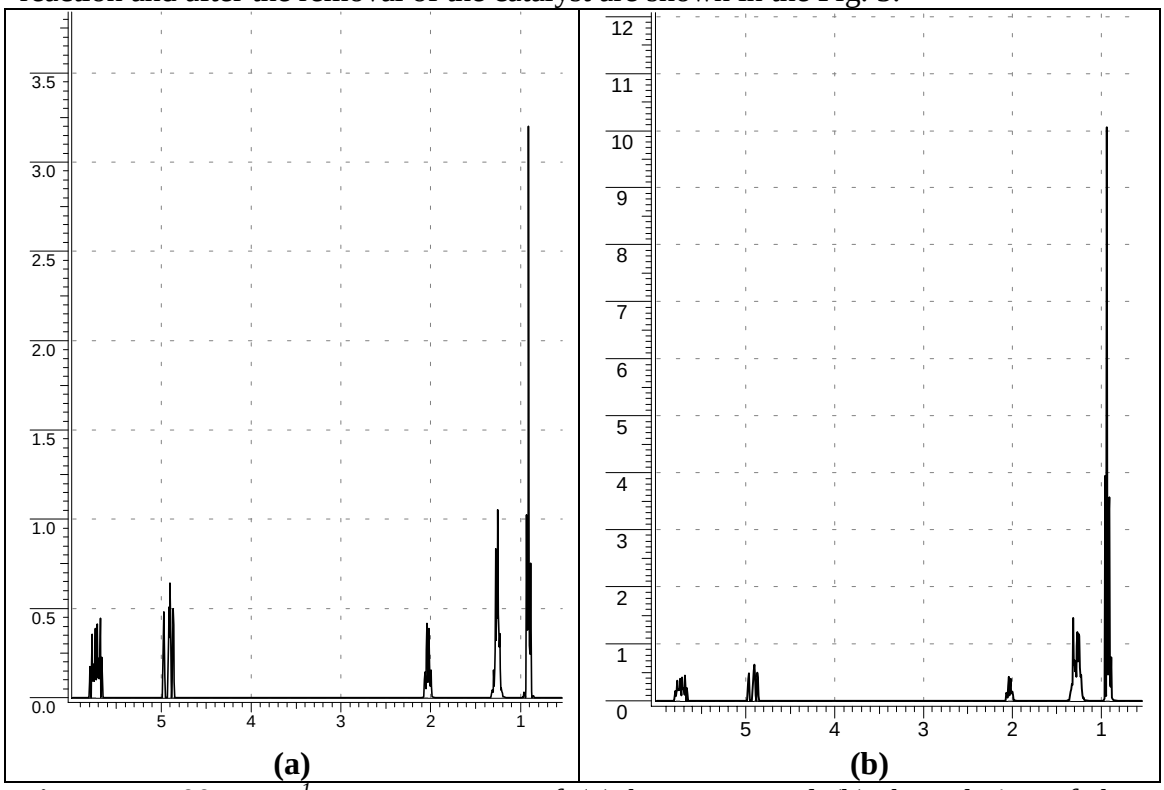


Figure 5. *300 MHz ^{1}H-NMR spectra of (a) hex-1-ene and (b) the solution of the reaction after 30 min of reaction and after the elimination of the catalyst and the solvent.*

The relative integrals of the ^{1}H-NMR spectra are given in the table below:

	δ / ppm	relative integral
Hex-1-ene (Fig. 5a)	0.88-0.96	3
	1.15-1.32	4
	1.99-2.08	2
	4.85-4.98	2
	5.65-5.79	1
Solution of the reaction (Fig. 5b)	0,88-0.96	9
	1.12-1.37	12
	1.99-2.08	2
	4.85-4.98	2
	5.65-5.79	1

Calculate the % conversion of hex-1-ene to hexane after 30 min.

Problem 20: Drug kinetics

The absorption of a drug by an organism often follows simple kinetics though the mechanism is very complicated. Consider a drug delivered orally in a common capsule. Let $[A]_s$ be its concentration in the stomach and assume that the rate of its introduction into the blood stream is first order with respect to this $[A]_s$. Also assume that the rate by which the drug is metabolized or removed from the blood stream is proportional to its concentration in the blood, $[A]_b$. Give the plot of $[A]_s$ as a function

of time and write the equation representing $d[A]_b/dt$. After one hour 75% of $[A]_s$ have been removed from the stomach. What percentage of the initial $[A]_s$ will remain in the stomach two hours after taking the drug?

Problem 21: $Br_2 + CH_4$ reaction mechanism

The reaction of bromine with methane is represented by the following chemical equation:

$$Br_2 + CH_4 \rightarrow CH_3Br + HBr$$

The proposed mechanism for this reaction is as follows:

$Br_2 + M \xrightarrow{k_1} 2Br + M$		(1) initiation
$Br + CH_4 \xrightarrow{k_2} CH_3 + HBr$		(2) propagation
$Br_2 + CH_3 \xrightarrow{k_3} CH_3Br + Br$		(3) propagation
$HBr + CH_3 \xrightarrow{k_4} CH_4 + Br$		(4) propagation
$2Br + M \xrightarrow{k_5} Br_2$		(5) termination

M stands for some molecular species. k_3 and k_4 are of the same order of magnitude.

1. In the proposed mechanism of this reaction some very unstable species are involved, such as the radicals CH_3 and Br. These very active species react as soon as they are formed, so their concentrations are very small compared to the other species. Shortly after the beginning of the reaction their concentrations remain approximately constant, so: $\frac{d[CH_3]}{dt} = 0$ and $\frac{d[Br]}{dt} = 0$. This is called the "steady state" condition or approximation for the CH_3 and Br radicals. Find the expression for the rate of formation of CH_3Br as a function of the concentration of the stable species that are involved in the reaction and the reaction rate constants, k_1, k_2, k_3, k_4, and k_5.

2. The rate law you found may be simplified when we consider the reaction progress. The three expressions below refer to the form of the rate law at the start, the steady state condition of the CH_3 and Br radicals and near the end of the reaction:

$v = \frac{k_1^{1/2} k_2}{k_5^{1/2}} \cdot \frac{[Br_2]^{1/2}[CH_4]}{\frac{k_4[HBr]}{k_3[Br_2]} + 1}$	**(I)**
$v' = \frac{k_1^{1/2} k_2}{k_5^{1/2}} \cdot [Br_2]^{1/2}[CH_4]$	**(II)**
$v'' = \frac{k_1^{1/2} k_2 k_3}{k_5^{1/2} k_4} \cdot \frac{[Br_2]^{3/2}[CH_4]}{[HBr]}$	**(III)**

Enter a numeral (I, II, III) next to each stage of the reaction to indicate which expression corresponds to which stage.

Start of the reaction	
Steady state condition	
Near the end of the reaction	

3. State the assumptions you need to make at each stage in order to simplify the rate law.